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Cheese — Cosmology

Cheese

A food product selectively concentrated from major milk components. It is generally rich in flavor and contains high-quality nutrients. There are many varieties of cheese, all produced in the following general manner: Raw or pasteurized milk is clotted by acid, rennet, or both. The curd is cut and shaped into the special form of the cheese with or without pressing. Salt is added, or the cheese is brined after pressing.

Acid is produced during manufacture of cheese by fermentation of the milk sugar, lactose. This fermentation is initiated by the addition of a culture of specially selected acid bacteria (starter culture) to the milk. Acid production in cheese curd retards growth of bacteria that cause undesirable fermentations in cheese. Moreover, it favors the expulsion of the whey and the fusion of the curd particles. Fresh cheese (cottage or cream cheese) does not require any ripening, and it is sold soon after it is made. Other varieties of cheese are cured or ripened to obtain the desirable consistency, flavor, and aroma. The flavor and aroma of cheese are obtained by a partial breakdown of milk proteins and fat by the action of microbial, milk, and rennet enzymes. In hard varieties (Cheddar, Gouda, Edam, Emmentaler or Swiss, and provolone) this is done by the microorganisms in the interior of cheese; in semisoft or soft types (Limburger, Camembert, and Roquefort) by the organisms on, or in contact with, the surface of cheese. *See* MILK.

Cheese Microbiology

Microorganisms are essential to the manufacture of cheese, imparting distinctive flavor, aroma, consistency, and appearance.

Starter cultures. Lactic acid starter cultures are important in making cheese. Different types of lactic acid bacteria (*Lactococcus lactis, L. lactis cremoris, Streptoccus thermophilus*, and homofermentative lactobacilli) are used, depending upon the kind of cheese desired. The starter (both single and mixed strains of bacteria are used) must convert all milk sugar left in the curd into lactic acid within a reasonable time. Several factors may prevent this: the occurrence of natural inhibitors in milk, antibiotics, and bacteriophages.

Some antibiotics (such as nisin) which affect the activity of the starter may be produced by microbes in the milk. Others may be excreted into the milk by cows treated for a particular disease; this happens if penicillin is used to treat mastitis. *See* ANTIBIOTIC.

Bacteriophages, or phages, are viruses which lyse sensitive bacterial cells (**Fig. 1**) and produce new phage particles. Phage particles may get into the milk with infected starter cultures or through contamination with phage-carrying dust particles. Phage

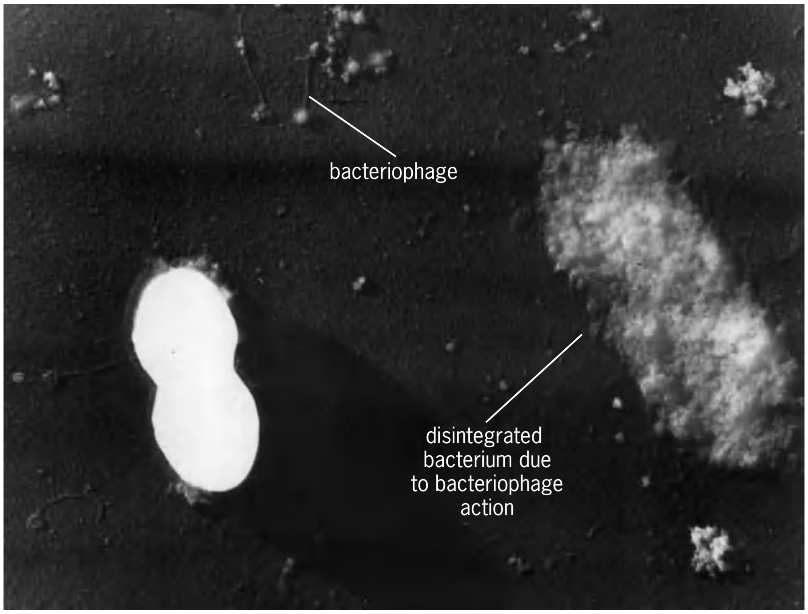

Fig. 1. Electron photomicrograph of *Lactococcus lactis* attacked by phages.

particles slow down or totally inhibit the activity of the starter culture, causing insufficient souring and spoilage of cheese. Phage multiplication is influenced by temperature, pH, and calcium content of the medium. Phage outbreaks cause serious economic losses. They can be controlled by rigorous hygienic handling of starters, by culture rotation, or by culturing starters in calcium-free media. Attempts to isolate phage-resistant strains have not met with success. *See* BACTERIOPHAGE; STREPTOCOCCUS.

Flora of cheese. Cheeses of the hard type contain lactic acid lactococci and other bacteria present in the starter. Moreover, they contain all the microorganisms originally present in the raw milk or pasteurized milk. The types of bacteria most important for ripening are the lactococci, lactobacilli, micrococci, and propionic acid bacteria. They, together with the enzymes of rennet and milk, break down the proteins to peptides and amino acids, hydrolyze the milk fat to fatty acids, and frequently produce carbon dioxide gas which causes the holes in cheese (**Fig. 2**). The structure of cheese is greatly changed during ripening.

In semisoft and soft cheeses the lactic acid originally produced by the starter is broken down afterward by molds, yeasts, and bacteria on the surface. The same flora decomposes the protein and the fat to a much greater extent than in hard cheeses. As a result, strong flavors are produced and the structure of the cheese becomes much softer. For the production of blue-veined cheese, needles are pushed into the interior to bring *Penicillium roqueforti* or the other molds, added during the manufacturing of the cheese, into contact with air they need for growth. The blue color is the color of the mold spores. The red color on the surface of some soft cheeses is caused by *Brevibacterium* (*Bacterium*) *linens* and micrococci. For good surface growth, soft cheeses must be cured in high-humidity air (caves or air-conditioned rooms).

Fig. 2. Swiss cheese with normal eye formation.

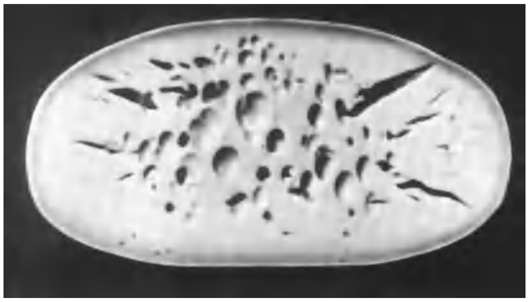

Fig. 3. Late blowing in Gouda cheese.

Fig. 4. Evidence of late gas production during the cheese ripening process.

Defects of cheese. In hard cheeses an abnormal gas formation is a problem. It can occur at almost any stage of manufacture or ripening. Early gas production can be caused by coliform bacteria or heterofermentative lactic bacteria. Gas production during cheese ripening (late gas, as in **Figs. 3** and **4**) may be caused by certain sporeforming bacteria, propionic acid bacteria, *Leuconostoc* species, and *Lactococcus lactis lactis* (biovar *diacetylactis*). The use of *L. lactis lactis* (biovar *diacetylactis*) and *L. lactis* as lactic starter cultures can cause fruity flavors, as well as gas formation, in Cheddar cheese. Other defects of hard cheese include insufficient or excessive acidity, various off flavors, and discoloration. Soft cheeses may be spoiled by gas production, excessive acidity, improper development of surface flora, and contamination with atypical molds.

Cheese blending. Cheeses of different ages are blended. The mixture, melted with the aid of emulsifying salts (citrates and phosphates), is packed in sealed containers (tins, paperboard, foil, or plastic). Few bacteria other than sporeformers survive the heat treatment. No substantial growth of the flora takes place in well-preserved processed cheese, but spoilage by anaerobic sporeformers may occur.

Clostridium sporogenes causes putrefaction and slit openness and *C. tyrobutyricum* causes blowing of tins and packages. Acidity, salt content, and temperature of storage are important in controlling spoilage. *See* INDUSTRIAL MICROBIOLOGY. Norman Olson

Cheese Manufacture

More than 150 countries make cheese, but 34 countries produce the major commercial quantities. Primitive cheesemaking exists in much of Africa, Latin America, and southwestern Asia, but advanced techniques are also found in these regions. Cheese manufacturing in developed world areas may be simple too, including that for the sheep-milk Broccio of Corsica, the mountain cheese of the Alps, the queso blanco of Venezuela, and the Pennsylvania pot cheese of the United States, but generally it is highly mechanized. Whether the method is primitive or sophisticated, the quality of the resulting cheese is usually excellent.

The primary objective of cheesemaking is to form a smooth acid curd, to reduce the size of the curd block and remove the whey, with or without prior cooking, and to salt and shape the curds. A different type of cheese emerges when the intensity of approximately eight steps is stressed or minimized as required; when special applications, usually microbial, are introduced; and when the environment is transformed to fit the optimum needs of a specific cheese type.

Materials. Key materials for cheesemaking include fresh or precultured milk, cultures, milk-coagulating enzyme preparations, special microorganisms, salt, and beta carotene or annatto color. The amounts used and the manner in which these materials are applied strongly influence the cheese character. Cheese may be made from the milk of the cow, sheep, goat, water buffalo, and other mammals, but the milk of the cow is most widely used despite some limitations. Sheep milk and water buffalo milk generally give more flavor to the cheeses, and the color is uniformly white because of a lack of carotene in such mammalian milks, but they are more expensive to make into cheese.

Major classes of cheeses. Two major classes of cheeses exist, fresh and ripened. Fresh cheeses are simpler to make than ripened, are more perishable, and do not develop as intense flavors, but give a mild acid, slightly aromatic flavor and soft, smooth texture.

Fresh cheeses. Three basic groups characterize fresh cheese types: group I—ricotta and Broccio; group II—cottage, Neufchâtel, and cream; and group III—mozzarella. Curd formation for these fresh cheese groups results from a combination of acid (pH 6.0) and heat (176°F or 80°C), as in group I; from acid alone to give a pH 4.6, as in group II; or from rennet (an enzyme preparation) at pH 6.3, as in group III. Essentially a dehydration of protein occurs, along with a partial or complete reduction of the negative electrical charges which surround the surfaces of the milk proteins. At a critical point, precipitation occurs, leading to a smooth gelatinous curd of varying strength. The curd may be scooped directly into cloth bags or perforated containers for immediate draining and eventual packaging, or the curd is cut and cooked, followed by drainage of whey, salting, and creaming.

Ricotta. Ricotta, or recooked cheese, in its most acceptable form is made from acidified whole milk heated to 176°F (80°C). By introducing large amounts of lactic starter culture, acid whey powder, food-grade acetic or citric acids, and small amounts of salt to cold milk and heating to the above temperatures in a kettle, smooth white particles appear which rise to the top and collect as a curd bed, which is left undisturbed. In about 30 min the hot curd is scooped into perforated containers for drainage and cooled. Later it is removed and consumer-packaged. The product is utilized directly or in a variety of Italian dishes.

Cottage. Cottage cheese is made from pasteurized skim milk, and in uniform discrete particles classified as small or large curd. A curd forms when the increasing lactic acid of milk during fermentation attains the isoelectric point of casein at pH 4.6. This soft curd additionally contains lactose, salt, and water. Later the curd matrix is cut and cooked to about 126°F (52°C). Separation of whey from the curd is rapid, and is followed by two or three water washings at warm to chill temperatures. Washing removes whey residues and acts as a cooling medium. After drainage of the last wash water, the chilled curd is blended with a viscous, salted creaming dressing to give 4.2% fat and 1% salt, and is packaged. One unsalted, uncreamed, nonfat form of cottage cheese has less flavor, calories, and sodium than standard cottage cheese. Another form is creamed to 9–11% fat and pressed as farmer's pressed cheese. *See* ISOELECTRIC POINT.

Cream and Neufchâtel. Cream and Neufchâtel cheeses resemble cottage cheese in manufacture, but they are made from high-fat mixes instead of skim milk, and no effort is undertaken to attain discrete particles. The minimum fat content of Neufchâtel cheese is 20%, and of cream cheese 33%. The cloth bags traditionally used to separate the whey from the curd have been replaced by centrifugal curd concentrators, which separate the stirred curds and whey at 165°F (74°C). The curd thereafter is pasteurized, treated with stabilizer or gums to prevent water leakage, and salted and homogenized hot. This hot mass is packaged and sealed directly, and tempered at room temperature for a number of hours. The products are used as spreads, in salads, and in cheesecake.

Cottage cheese keeps well at refrigerated temperatures for at least several weeks, but hot-pack cream and Neufchâtel cheeses, because of earlier exposure to high temperature and sealing hot in packages, maintain freshness for up to 2 months or more. Common microbial spoilage agents are molds and yeasts and frequently *Pseudomonas* bacteria which grow at low temperatures.

Mozzarella. Natural mozzarella cheese is normally made from pasteurized whole milk, but milks of 1 or 2% fat may be used if the cheeses are properly labeled. The warm cheese milk is incubated with lactic acid bacteria (*Lactococcus lactis*, *Streptococcus thermophilus*, or *Lactobacillus delbreuckii bulgaricus*), or may be directly acidified by the addition of food-grade acids such as acetic or citric. Added rennet coagulates the milk to a smooth curd, which is cut with wire knives. The curds, without cooking, may be drained of whey shortly after cutting or, depending upon the type of bacteria, may be cooked to 117°F (47°C) before whey removal. The blocks or patties of curd which result from this action are retained until a pH 5.2–5.5 is achieved, and then are milled into small cubes, placed in hot water, and stretched and molded until smooth. The resulting rectangular blocks are cooled and brined for 2–8 h, depending upon size, and dried and vacuum-packaged.

Acceptable natural mozzarella cheese has a bland, slightly acid flavor. It melts uniformly and smoothly when exposed to hot oven temperatures of 428°F (220°C) for a few minutes and, depending upon type, maintains its quality from several weeks to several months. Natural mozzarella cheese is used in a wide assortment of Italian dishes. Imitations containing vegetable fats, artificial flavors, and a variety of additives are made mainly for institutional and food supplementation use.

Ripened cheese. Ripened cheese is exposed to an optimum environment of temperature and moisture for a period of time to attain characteristic flavor, texture, and appearance. It may be made from raw, heat-treated, or pasteurized milk that is coagulated with a rennet preparation to form a smooth curd. After cutting and cooking to 95–131°F (35–55°C), the curds are salted, before or after pressing, and shaped. The pressed curds, usually salted, may be given a special microbial application, and then are usually held at 41–59°F (5–15°C) in rooms under controlled humidity (85–95%) to develop the desired traits. All standard ripened cheeses are salted, and the milks from which they are made are always coagulated with rennet, usually in the presence of small amounts of lactic acid and sometimes added calcium chloride.

Rennet milk coagulation occurs when rennin, a protease from rennet, hydrolyzes or splits kappa casein from casein into a whey-soluble component, glycomacropeptide. The cleavage of kappa casein by rennin destabilizes the casein molecule, permitting its dominant alpha and beta casein components in micelle form to precipitate. Such coagulated proteins are filamentous and, through strand overlapping under quiescent conditions, appear as a smooth, homogeneous, sweet (pH 6.3) gel or curd. This curd is cut and cooked, leading to a contraction which expresses whey. The dry curds thereafter are salted, pressed, and ripened. *See* MICELLE; RENNIN.

During ripening, many flavor compounds arise in the cheese. They include free fatty acids, amino acids, ketones, diacetyl, and alcohols. Their amounts in a balanced ratio, along with major components of the cheese, largely determine the characteristic flavor. Agents involved through proteolytic, lipolytic, decarboxylation, and deamination reactions include rennin, natural bacteria of milk, added microorganisms, natural milk enzymes, microbial enzymes, and added food-grade enzyme preparations. The microbial enzymes evolve from millions of microbial cells present in cheese; the sources of the added food-grade enzyme preparations usually are fungal.

Most ripened cheeses are contained in one of six basic groups. The characteristic cheeses in each group include: group I—Cheddar and Monterey; group II—Swiss (Emmentaler) and Gruyère; group III—Edam and Gouda; group IV—Muenster, brick, and Limburger; group V—provolone; and group VI—Camembert, Brie, and blue.

Cheddar and Monterey. For these cheeses the curds are formed at 88°F (31°C) by 0.2 qt (200 ml) of rennet in 2200 lb (1000 kg) of underheated whole milk previously inoculated with 1–2% lactic-type starter for 15–30 min. The curds are cut with wire knives, and cooked to 99°F (37°C) for 30–60 min. Then the whey is run off, and the curd bed is cut into rectangular blocks weighing approximately 11 lb (5 kg). These blocks usually are turned over every 15 min for 2 h in a step known as cheddaring, and the stringy nature of the curd evolves as sufficient lactic acid develops to give a pH of 5.3. The blocks, now flatter than at the start, are milled to small cubes, and dry-salted at the rate of 5 lb (2.3 kg) of salt per 220 lb (100 kg) of curd. These salted curds are pressed in single-service paper or cloth-lined stainless steel boxes. The standard 44- to 66-lb (20- to 30-kg) forms which result are removed, and repressed in plastic films of low oxygen permeability. The film-wrapped Cheddar cheese is ripened up to 1 year at 41–50°F (5–10°C). It is generally manufactured into various-size forms prior to reduction into consumer packages.

In modern industrial cheesemaking, another form of Cheddar cheese, known as barrel, is made by the stirred-curd step in contrast to the cheddaring. This avoids the more lengthy period required for the latter. In the stirred-curd step, individual small cut curd particles, after cooking and whey separation, are stirred for about 30 min, salted, and packed into large film-lined metal or fiber barrels of 640-lb (290-kg) capacity. Here, after excess whey is removed, the curds are pressed and the containers sealed and placed in ripening rooms. Later, the cheese is removed and used largely for making processed cheese. Ripening cheese in large blocks appears to improve typical flavor quality, so that some cheese that is cheddared and destined for long ripening, too, may be held in 640-lb (290-kg) capacity film-lined, sealed boxes.

Monterey cheese resembles Cheddar, but has a higher moisture level and ripens more rapidly. Its curds are washed with water in the vat and not cheddared, but are stirred prior to salting and then added to lined standard stainless steel forms for pressing and eventual ripening.

Swiss (Emmentaler) and Gruyère. Swiss and Emmentaler cheeses are the same, but in the United States the term Swiss is widely used, whereas in Europe and elsewhere the name is Emmentaler. The cheeses are made in block or round forms, but in the United States the former shape dominates because it is easier to slice for sandwiches. Also, economics of production are enhanced.

Underheated milk (158°F or 70°C for 16 s), standardized or partly skimmed, is set with rennet to form a curd, accompanied by three special bacterial cultures, *Streptococcus thermophilus, Lactobacillus delbrueckii bulgaricus*, and *Propionibacterium shermanii*. These cultures influence the acid, eye, flavor, and texture development of the cheese. *Propionibacterium shermanii* is mainly responsible for eye and typical flavor formation.

Renneting requires about 30 min by using 0.2 qt (180 ml) of rennet per 2200 lb (1000 kg) of warm (88°F or 31°C) milk. The size of the curds after cutting is very small, about like peas. These are cooked to about 126°F (52°C) in 60 min, and stirred until the pH decreases to 6.3.

To make block Swiss cheese, these stirred, cooked curds and considerable whey are pumped into cloth-lined, perforated stainless steel chambers. Here a large block is formed under the warm whey, the whey is removed, and the bed of curd remaining is cut into about 100-lb (45-kg) sections. These are immersed in cool brine for up to several days. After removal and drying, the blocks are sealed with plastic or rubberized film, placed in wooden boxes, with room for expansion, and covered by lids. Exposure to warm temperature, about 73°F (23°C) for 2–3 weeks, produces the typical eyes and sweet, hazelnut flavor. Further ripening continues at 41°F (5°C) for 4–12 months before the cheese is ready for market.

Gruyère cheese shows eyes like Swiss or Emmental, but they are usually smaller. This 125-lb (57-kg) round wheel cheese is made mostly in France, Switzerland, and Finland. The surfaces of Gruyère cheese, unlike the larger 224-lb (102-kg) round wheel Emmentals, are not washed daily or wiped with cloths. This leads to a special microbial growth on the surface which imparts to the cheese more flavor of a unique nature best typified by the Comté Gruyère of the French Jura area.

Edam and Gouda. Both of these cheese types may contain eyes, but these are small and lack uniform distribution. Edam cheese is produced in its normal size as 5-lb (2.3-kg) round balls waxed in red. Gouda cheese, softer in body because whole milk is invariably used, appears as orange- or yellow-waxed, medium-sized flat wheels of about 11–22 lb (5–11 kg). Manufacturing is essentially similar for both.

Pasteurized milk is set with lactic culture and rennet, but acid development is constrained usually by removing some of the whey and replacing it with water. Before the cheese is pressed, the pH is usually 5.4. This higher pH gives a sweeter flavor to the cheese and permits other species of bacteria to function. In Europe, where most of this cheese is made, sodium nitrate may be added to the cheese milk to suppress spoilage bacteria, but the practice is diminishing, and instead a continuous bacterial spore centrifugal removal process is substituted. Where nitrates are used, only small amounts are introduced, most of which disappear during ripening.

Unique metal forms shape the cheese after light pressing. The cheeses are brined and waxed. Ripening occurs at 50°F (10°C) for 2–3 months.

Muenster, brick, and Limburger. Good-quality pasteurized milk is required for these cheeses. At times, as for brick cheese, the renneted curd may be washed with water to reduce the acidity and to increase moisture. A reddish bacterium, *Bacterium linens*, along with yeasts, grows on the cheese surfaces at 59°F (15°C) in a highly moist room for 11 days. The surfaces take on the brick-reddish color of the bacterium. The three cheeses are differentiated by the intensity of their flavor, softness of body, and sizes and shapes. Muenster has least intensity of flavor, followed by brick cheese.

Provolone. Originating in Italy, provolone cheese also is manufactured in large quantities in Argentina and the United States. It is a pasta filàta, or pulled-curd ripened cheese, and is generally smoked. The texture is smooth and flaky and the flavor highly aromatic or piquante. Initially, the cheese is made almost exactly like that of a fresh, low-moisture mozzarella using *Lactobacillus delbrueckii bulgaricus* as the starter. Following proper acid development in the vat, the curd is stretched and formed into various shapes: cylindrical, pear, or ball. Thereafter, it is bound with ropes or twine and hung in hickory smoke–filled rooms for 3 weeks or exposed to smoke compounds. Ripening occurs at about 44°F (7°C) for up to 12 months, and cheese sizes range from 3 to 500 lb (1.4 to 227 kg). A related Italian type is caciocovàllo, literally meaning horse cheese.

Camembert, Brie, and blue. These are all rennet cheeses, and Camembert and Brie are made with pasteurized milk cultured to about 0.2% titratable acidity. The curds are not cooked and, following whey drainage and hooping in round forms, they are modified by the special application of white or blue-green mold spores. Introduction of the spores to the cheese may result from inoculating the milk, brine, or curds, or inoculating all three media.

Camembert and Brie are white mold cheeses about 1 in. (2.5 cm) thick whose manufacture is similar except that the diameter of the latter is larger. The characteristic feature of these cheeses is the appearance of a snow-white mat of *Penicillium caseicolum* or *P. camemberti* mold on the surfaces. These molds grow well only in an excessive air environment, and hence their appearance on the surface. They ripen the cheese from outside into the center through release of their many active enzymes, which transform the curds to a smooth, soft state. The cheeses are ready for consumption in 12–14 days at 50°F (10°C) and 95% relative humidity. Held thereafter in a refrigerated state for 40 days in supermarkets, the cheeses eventually become overripe. Ammoniacal flavor with the white surfaces becoming brown and the inner sections becoming light tan confirm an overripe state.

Blue cheese requires spores of *Penicillium roqueforti* or *P. glaucum*. These spores, appearing as a black powder, are present throughout the wheel of pressed, highly salted curd, and grow as filamentous blue-green mycelia when minimum air is supplied. In practice, the mold-inoculated wheels of cheese, from 5 to 12 lb (2.3 to 5.4 kg), are penetrated by a mechanical head containing 50 needles which create the long air channels. The mold grows along these air channels, and moves farther into the cheese if natural openings exist. Here the many lipolytic and proteolytic enzymes originating from the mold mycelia attack the cheese to give characteristic flavor. Molding occurs in 30 days after air channel formation at 50°F (10°C) and 95% relative humidity. Then the cheese is held at 41°F (5°C) during 2–6 months for more complete ripening.

The most famous blue cheese is Roquefort, made in southern France from sheep milk. Other widely known related cheeses are Stilton, Gorgonzola, Danish blue, and American blue.

Processed cheese. Processed cheese is made from natural types. Nearly any natural cheese can be processed, except that for blue cheese technical difficulties cause blackening of the blue mold due to the high heat.

Processed cheese is produced by grinding selected lots of natural cheese and adding cream, color, salt, and emulsifying agents. The mixture is blended and sent to cookers which heat the mass to 165–185°F (74–85°C). During the cooking, fat normally separates from the protein and water, but this is corrected by adding anhydrous citrate and phosphate salts, usually at 3% levels. The salts raise the cheese pH to about 5.6–5.8, making the protein more soluble. Under these circumstances a stable emulsion of protein, fat, and water occurs to give a smooth homogeneous mass. The hot mass is packaged directly. Processed cheese foods and spreads are made similarly, but include more water and less protein, fat, and other solids.

Sliced processed cheese is attained by spreading the hot process cheese mass emerging from the cookers over moving cold steel rolls. The chilled cheese in thin, wide sheets passes over rotary knives and cutting bars to give squares lying on top of each other, which are packaged in film wrappers.

Production developments. The cheese industries of the world have become rapid-growth industries with high consumer acceptance of their product. Cheese-manufacturing plants may be very large, utilizing more than 2.2×10^6 lb (10^6 kg) of cheese milk daily. In the operational areas, cheese vats of 5500-lb (2500-kg) capacity are common, as are giant presses.

Mechanization of cheesemaking too has advanced through the introduction of ingenious cheddaring towers, block formers, and moving web belts. This has led to significantly higher rates of production, with less manual labor, while maintaining quality. True continuous making methods of natural cheese have yet to be realized. However, a unique process incorporating ultrafiltration membrane technology has potential for continuous manufacture of certain cheeses.

Membrane separation is an application of biotechnology to cheesemaking. In this process, skim or whole milk is pumped at low pressure, 48 lb/in.^{2} (3.4 kg/cm^2), through tubes or plates containing many small pores, with a molecular-weight cutoff of 20,000. The milk passes across the membranes, usually at 126–129°F (52–54°C). Much of its water, lactose, soluble salts, and nonprotein nitrogen pass through the pores as permeate. Retained are all the fat, protein, insoluble salts, and some serum, which contains water, lactose, soluble salts, and nonprotein nitrogen. This retentate increases in concentration with time, so that its fat and protein may be five times greater than that of the starting milk. Emerging from the ultrafiltration unit in its final concentrated form as a plastic fluid, this retentate has the same composition as some cheeses. Cheesemaking is completed without vats, as there is no whey to separate. Simple mechanical injection of culture, rennet, salt, color, and fungal spores into the plastic fluid concentrate may follow. A curd develops within 5–10 min, and is placed directly in a ripening room. This is a French process, known as MMV after the names of the inventors, Maubois, Mocquot, and Vassal. Its major advantages are much greater cheese yields due to complete retention of whey protein in the cheese, lower requirements for rennet, a high potential for continuous-process application, and production of a neutral-pH permeate with a reduced biochemical oxygen demand (BOD) value. Much cheese in Europe is made in this manner, particularly fresh, soft acid cheeses—Feta, Camembert, and St. Paulin.

Other variations of ultrafiltration retentate application to cheesemaking include milk retentate supplementation and direct ultrafiltration of cheese milks, but only up to 2:1 protein concentration. The advantages of this alternative ultrafiltration process include improved cheesemaking efficiency, energy savings, and higher quality of marginal cheeses. Use of milk retentates in cheesemaking in this manner has led to the production of natural Cheddar cheese of good quality with significantly reduced sodium levels, 0.015 oz/3.5 oz cheese (420 mg/100 g) or less, compared with approximately 0.02 oz (700 mg) for commercial Cheddar cheeses.

Ultrafiltration has led to whey protein concentrates of 90–95% protein. This nonfat product can be modified to give a texture similar to cheese and is used as a food ingredient to replace butterfat by up to 50% for the making of commercial low-fat cheese. Another technology for the fluid milk and cheese industries is microfiltration. This system follows the same principles as those for ultrafiltration except for membrane pore size. Ultrafiltration retains fat, casein, bacteria, and insoluble salts. Passage through a micromembrane retains fat, bacteria, and insoluble solids, but no protein, making the resulting permeate an almost sterile skim milk. The creamlike retentate obtained is heated to 302°F (150°C) for 2 s, and then it is blended with the almost-sterile skim milk, pasteurized, and cooled to proper temperatures for use in milk and cheese processing. Results from Europe, where much research has been conducted on this subject, indicate an almost 99.5% reduction in total bacteria. Also, quality cheese without gas defects or loss of flavor was produced. *See* ULTRAFILTRATION.

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Cheilostomata

An order of ectoproct bryozoans (in which the anus opens outside the ring of tentacles) in the class Gymnolaemata. Cheilostomes possess delicate colonies composed of loosely grouped, highly complex, short, uncurved, box- or vase-shaped zooecia (chamber in which the animal lives), with solid, porous, chitinous, or calcareous walls, and with apertures closed by lidlike opercula. *See* BRYOZOA; GYMNOLAEMATA.

Morphology. Cheilostome colonies (**Fig. 1***a*–*e*) may be encrusting threadlike networks (*Pyripora*); thin encrusting sheets (*Membranipora*, *Steginoporella*); tabular, nodular, or globular masses (*Schizoporella*, *Celleporaria*); free-living (unattached) domes (*Cupuladria*); or erect tuftlike (*Bugula*, *Scrupocellaria*), twiglike (*Vincularia*), frondlike (*Coscinopleura*, *Flustra*), or trellislike (*Retepora*, *Sertella*) growths. These colonies are not divisible into distinct endozone (thin-walled, fragile, inner or lower portion of colony) and exozone (thick-walled, sturdy, outer or upper portion of colony) regions. All cheilostome colonies lack stolons (elongated projections of the body wall from which buds are formed, giving rise to new zooids) and monticules (or maculae; raised formations of zooids on the colony surface that control incurrent and excurrent flow). Some have rhizoids (individual rootlike outgrowths that reinforce the colony's attachment to a substrate) or small coelomic chambers, and most cheilostome colonies bear ovicells (or ooecia; brood chambers that protect developing embryonic larvae) developed at the distal ends of the normal autozooecia (feeding zooids; **Fig. 2**). Autozooecia possess several tentacles arranged in a circle (lophophore) around the mouth and held out to form a bell or funnel when protruded for feeding. Many cheilostome colonies are polymorphic, that is, they possess either one or both of two types of specialized zooids (heterozooids): avicularia, which are bird-head-like or mouse-trap-like heterozooids with a movable mandible that can be snapped at small animals attempting to settle on the colony, and vibracula, heterozooids with a bristlelike seta that sweeps animals and debris from the colony surface.

The walls of adjacent zooecia within a cheilostome colony are distinctly separate rather than fused together, and may be perforated by small openings filled with soft tissue. The zooecial walls may be thin chitinous membranes, moderately thick and firm chitinous walls, or thin to thick calcareous walls (in most species, they are made of calcite), displaying a great variety of pores, pits, granules, spines, and lacy fretwork (especially the frontal walls, which form the external surface of the colony). Zooecia lack internal transverse partitions (diaphragms). Round to

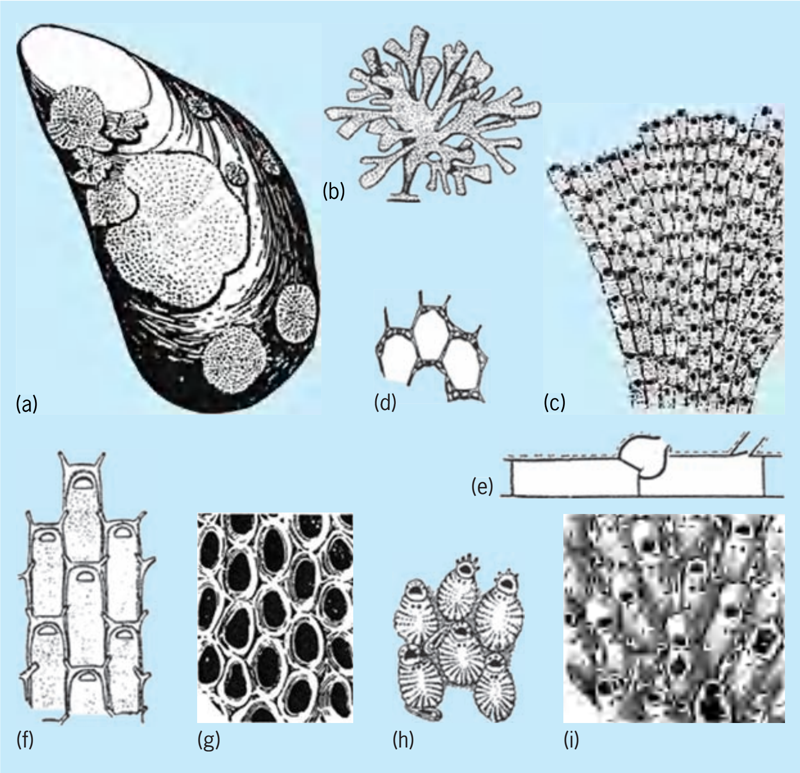

Fig. 1. Cheilostome colonies and zooecia (scale of colonies, ×1). (*a*) Encrusting sheets of *Membranipora* and *Electra* on bivalve shell. (*b*) Erect, flat branches of *Chartella*. (*c*) Upper (frontal) surface section (scale, ×8) of encrusting sheet of *Schizoporella*. (*d*) Tangential section (scale, ×20) of *Escharoides*. (*e*) Longitudinal section (scale, ×25) of an unnamed cheilostome. (*f*) Soft membranous frontal wall of *Membranipora* (scale, ×35). (*g*) Large open opesium of *Conopeum* (scale, ×25). (*h*) Cribrimorph frontal wall of *Cribrilaria* (scale, ×25). (*i*) Bulbous ovicells of *Diplotresis* (scale, ×25). (***Parts a*, *c*, *and f reprinted with permission from R. J. Cuffey and J. E. Utgaard, Bryozoans, in R. Singer, ed., Encyclopedia of Paleontology, Fitzroy Dearborn, 1999; all other images reprinted with permission from R. S. Bassler, Treatise on Invertebrate Paleontology, © 1953 Geological Society of America and University of Kansas Press***)

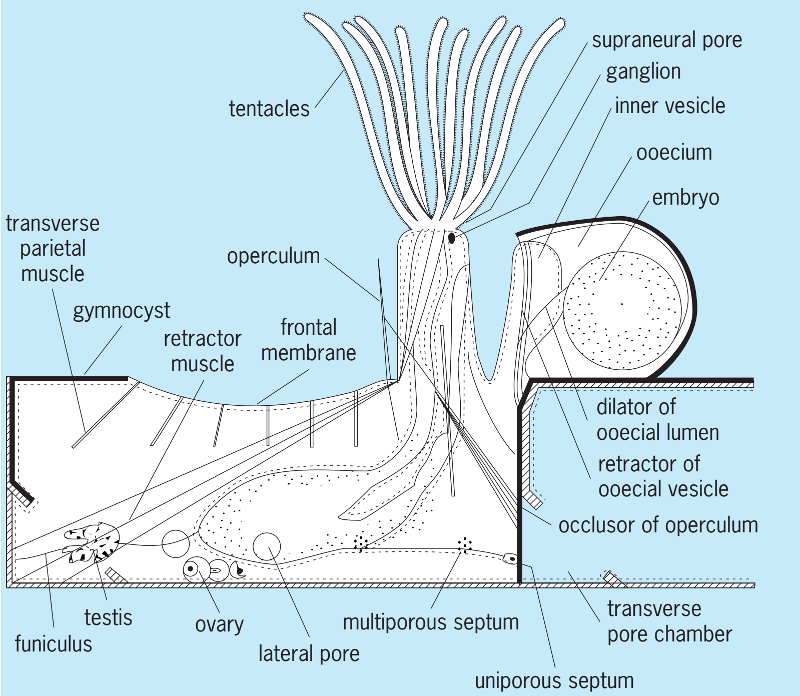

Fig. 2. Anascan cheilostome zooid, showing soft parts and zooecium, with tentacles extended. (***Reprinted with permission from R. J. Cuffey and J. E. Utgaard, Bryozoans, in R. Singer, ed., Encyclopedia of Paleontology, Fitzroy Dearborn, 1999***)

highly complicated in outline, and noticeably smaller in transverse diameter than the zooecium itself, the aperture is closed by a membranous or chitinous lid (operculum) hinged to the proximal edge of, and fitting snugly over, the aperture. The aperture may be flush with the colony surface or surrounded by spines or an elevated rim (peristome).

Life cycle. Usually sheltered in various ways by the parent (female) zooid, each cheilostome zygote develops into one larva. The larva in most species swims freely for less than a day, feeding on its own yolk (that is, it is lecithotrophic), and then attaches to a substrate and metamorphoses (with complete degeneration of its larval organs) into a primary zooid (ancestrula). In a few species, the zygote is shed directly into the water and develops there into a larva (cyphonautes) that swims freely for up to several weeks before settling. Afterward, repeated asexual budding from the ancestrula produces the rest of the cheilostome colony.

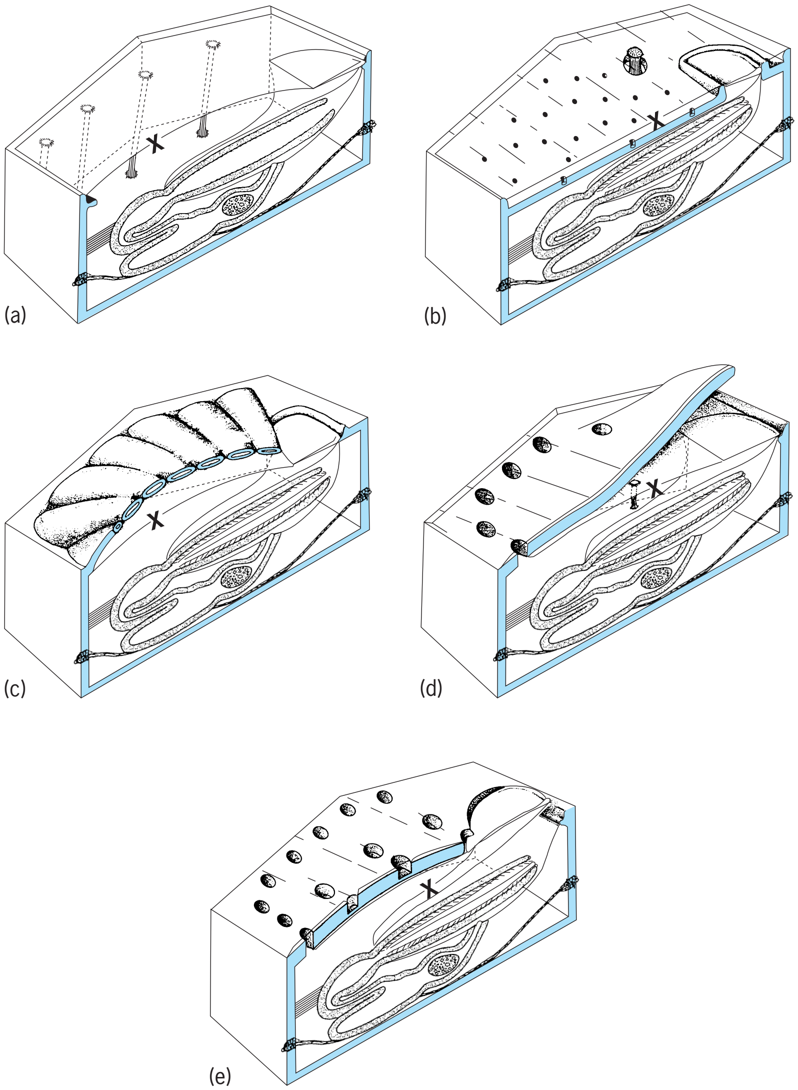

Fig. 3. Arrangements of frontal walls in Cheilostomata. The X indicates the membrane that can be pulled by muscles in order to displace fluid/liquid that pushes the polypide (shaded) out so that the tentacles can feed in the space above the skeleton. (*a*) Anascan with noncalcified frontal wall and retracted polypide unprotected by shield. (*b*) Anascan with perforated skeletal shelf (cryptocyst) below the outer, depressible cuticle. (*c*) Cribrimorph with shield of fused spines arched above the depressible cuticle. (*d*) “Umbonuloid” ascophoran with the frontal cuticle folded back on itself and the upper surface of the middle sheet of the frontal cuticle calcified, above the portion that is depressible. (*e*) Ascophoran as traditionally understood, with a small inflatable sac (ascus) formed by extension of the frontal cuticle lying immediately below the solid frontal wall/skeleton. (*After F. K. McKinney and J. B. C. Jackson, Bryozoan Evolution, Unwin Hyman, Boston, 1989*)

History and classification. Cheilostomes apparently evolved from ctenostomes as a single clade (monophyletic). First appearing in the latest Jurassic, the cheilostomes rapidly expanded during the Cretaceous to become the dominant bryozoan group throughout the Cenozoic, a position which they still maintain today. *See* CTENOSTOMATA.

Although cheilostomes are predominantly marine (ranging from intertidal to abyssal depths), some range into brackish waters, but none are found in freshwater. The oldest cheilostomes occupied near-shore habitats, but they soon invaded deep-water marine environments before the end of the Cretaceous. Maximum taxonomic, life-habit, and growth-form diversities are found near the shelf-slope break. In addition to being abundant in level-bottom communities, cheilostomes extensively but inconspicuously encrust the framework of many Cenozoic and modern coral reefs.

The cheilostomes have diversified into three major groups (anascans, cribrimorphs, and ascophorans) that appeared consecutively in geologic time and can be distinguished on the basis of differences in the frontal or upper wall (Fig. 1*f–i*). They are often classified as suborders, but may be considered as morphological grades of increasing complexity with time.

Anascan cheilostomes, the earliest, have a flexible, membranous, chitinous frontal wall that is completely open to the surrounding water (Fig. 1*f–g*; Fig. 2). Upon fossilization, the cuticle decays, leaving a top opening (opesium) that is much larger than the aperture would have been. Anascans protrude their tentacles via muscles that pull down on the membranous frontal wall, thereby squeezing the liquid body contents out through the aperture or orifice (**Fig. 3*a***). In some anascans, a porous calcareous plate (cryptocyst) may be secreted below, but detached from, the frontal membrane or cuticle (Fig. 3*b*). The primary radiation of anascans occurred in the Late Cretaceous, but they have maintained their high diversity to the present.

Cribrimorph cheilostomes (Fig. 1*h*) possess similar flexible frontal walls but are partially protected externally by overarching, partly fused, calcareous spines that meet above the midline of the zooid or zoeecium; they extend their tentacles in basically the same manner as anascans (Fig. 3*c*). Water passes in and out through the spaces between the spines as the underlying cuticle is flexed to displace polypides (internal contents of the zooid) out or to accommodate displaced fluid as polypides are retracted. The cribrimorphs had evolved by the early Late Cretaceous, reached a moderate diversity during the Late Cretaceous, and then persisted at a reduced or low diversity until the present.

Ascophoran cheilostomes (Fig. 1*i*), the most highly evolved, appeared by the mid-Late

Cretaceous, and display solid, shieldlike, calcareous frontal walls, below which is a special flexible sac (an ascus or compensatrix) used hydrostatically to protrude and retract the lophophore. The ascophoran condition, or grade, evolved several times and involved various ways of maintaining an inflatable structure below the rigid calcified frontal wall. In some (the umbonuloids), the frontal cuticle is deeply folded just behind the orifice (Fig. 3*d*). The reflected portion of the cuticle is calcified on its upper surface, while other portions remain uncalcified. Muscles pull the inner portion of the frontal membrane inward to protrude the polypide. Other ascophorans have developed a calcified plate under the frontal cuticle, and a balloonlike cuticular sac extends down through a pore in the calcified plate just behind or along the proximal edge of the operculum (Fig. 3*e*). By the end of the Cretaceous, ascophorans were diversifying rapidly, and have continued to diversify throughout the Cenozoic.

Many morphological and ecological innovations in cheilostomes originated in the mid-Cretaceous during a period of rapid diversification. Articulated spines, frontal budding, brood chambers, erect rigid and articulated colonies, free-living colonies, avicularia, and cribrimorph and ascophoran conditions originated between the late Early Cretaceous and mid-Late Cretaceous. Another (later) Early Cenozoic phase of rapid diversification primarily involved ascophorans and was accompanied by increased prevalence of frontal budding and more colonially integrated types of zooidal budding along the colony margins. Roger J. Cuffey; Frank K. McKinney

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Chelation

A chemical reaction or process involving chelate ring formation and characterized by multiple coordinate bonding between two or more of the electron-pair-donor groups of a multidentate ligand and an electron-pair-acceptor metal ion. The multidentate ligand is usually called a chelating agent, and the product is known as a metal chelate compound or metal chelate complex. Metal chelate chemistry is a subdivision of coordination chemistry and is characterized by the special properties resulting from the utilization of ligands possessing bridged donor groups, two or more of which coordinate simultaneously to a metal ion. *See* COORDINATION CHEMISTRY.

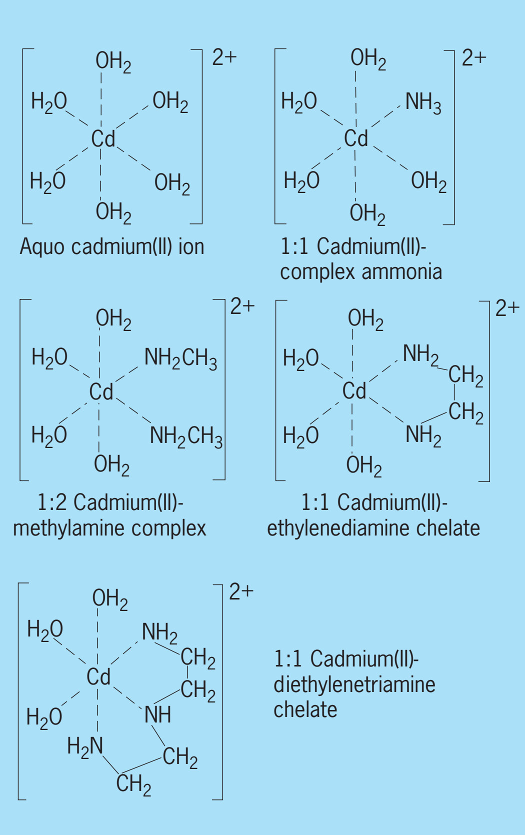


Fig. 1. Formulas of hydrated cadmium(II) ion, two cadmium(II) complexes, and two cadmium(II) chelates.

Ethylenediamine, $H_2NCH_2CH_2NH_2$, is a good example of a bidentate chelating agent consisting of two amino donor groups joined to each other by a two-carbon bridge. The coordination of both nitrogen atoms to the same metal ion would result in the formation of a five-membered chelate ring. If a chelating agent has three groups capable of attaching to a metal ion, as in diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$, it is tridentate (terdentate); if four, tetradentate (quadridentate); five, pentadentate (quinquidentate); six, hexadentate (sexadentate); and so on. In general, these chelating agents may be designated as multidentate or polydentate ligands. All chelating agents must be at least bidentate; tridentate agents give fused rings. An example of a nonchelated complex and two chelated complexes of the Cd(II) ion are illustrated in **Fig. 1**. In aqueous solution, metal ions are completely solvated, or hydrated, to give an aquo complex, as indicated for the Cd(II) ion in Fig. 1. Thus formation of a complex of a unidentate ligand involves the replacement of a water molecule by the unidentate donor group. Two water molecules are replaced by a single molecule of a bidentate ligand; three water molecules are replaced by a molecule of a terdentate ligand, and so on.

Many of the functional groups of both synthetic and naturally occurring organic compounds can form coordinate bonds to metal ions, producing metal-organic complexes or chelates, many of which

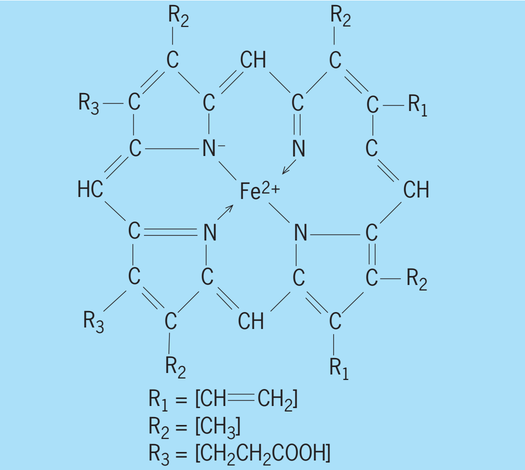


Fig. 2. Heme, a tetradentate chelate of iron(II).

are biologically active. Thus chelate compounds are frequently found in an interdisciplinary field of science called bioinorganic chemistry. The biological significance of chelates can be readily recognized if one notes that a large number of biologically important compounds are either metal chelates or chelating agents. This list includes the alpha amino acids, peptides, proteins, enzymes, porphyrins (such as hemoglobin), corrins (such as vitamin B_{12}), catechols, hydroxypolycarboxylic acids (such as citric acid), ascorbic acid (vitamin C), polyphosphates, nucleosides and other genetic compounds, pyridoxal phosphate (vitamin B_6), and sugars. The ubiquitous green plant pigment, chlorophyll, is a magnesium chelate of a tetradentate ligand formed from a modified porphin compound, and similarly the oxygen transport heme of red blood cells contains an Fe(II) chelate of the type illustrated in **Fig. 2**. *See* BIOINORGANIC CHEMISTRY; ORGANOMETALLIC COMPOUND.

A rapidly growing body of experimental evidence indicates that chelation may be important in the pharmacological action of many drugs. The use of chelating agents to remove certain toxic cations such as lead and plutonium from the body is now widely recognized in medical practice. Intensive research has been undertaken to either develop or discover an effective synthetic or natural chelating agent for the removal of iron deposits in the body that result from certain hereditary metabolic disorders.

Applications. The ability of chelating agents to reduce the chemical activity of metal ions has found extensive application in many areas of science and industry. Ethylenediaminetetraacetic acid (EDTA), a hexadentate chelating agent (**Fig. 3**), has been employed commercially for water softening, boiler scale removal, industrial cleaning, soil metal micronutrient transport, and food preservation. Nitrilotriacetic acid (NTA) is a tetradentate chelating agent (**Fig. 4**) which, because of lower cost, has taken over some of the commercial applications of EDTA. Chelating agents of related type have been used in biological systems to produce metal-ion buffers. By selection of the appropriate chelating agent, the free metal-ion concentration can be maintained at a very low and constant concentration level, just as a relatively constant pH can be maintained through the use of a conventional hydrogen-ion buffer system. Furthermore, the colors of certain chelating agents are sensitive to metal-ion concentration in a manner completely analogous to the pH-dependent color changes observed with acid-base indicators; such chelating agents serve as metal-ion indicators in analytical chemistry. The solubility of many chelating agents and metal chelates in organic solvents permits their use in solvent extraction of aqueous solutions for the separation or analysis of metal ions.

Many commercially important dyes and pigments, such as copper phthalocyanines, are chelate compounds. Humic and fulvic acids are plant degradation products in lake and seawater sediments that have been suggested as important chelating agents which regulate metal-ion balance in natural waters. By virtue of its abundance, low toxicity, low cost, and good chelating tendencies for metal ions that produce water hardness, the tripolyphosphate ion (as its sodium salt) is used in large quantities as a builder in synthetic detergents. Both synthetic ion exchangers and the mineral zeolites are chelating ion-exchange resins which are used in analytical and water-softening applications. As final examples, less conventional chelating agents are the multidentate, cyclic ligands, termed collectively crown ethers, which are particularly suited for the complexation of the alkali and alkaline-earth metals.

Stabilities of metal chelates in solution. One of the most striking properties of chelate ring compounds is their unusual thermodynamic and thermal stability. In this respect, they resemble the aromatic rings of organic chemistry. For example, in reaction (1),

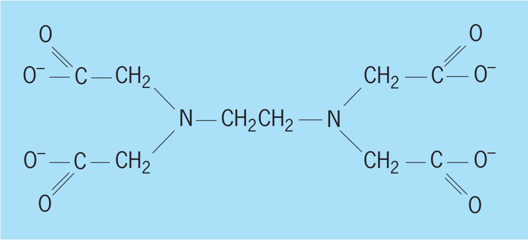


Fig. 3. Structural formula of anion of EDTA, a sexadentate ligand.

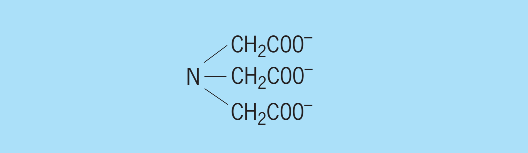
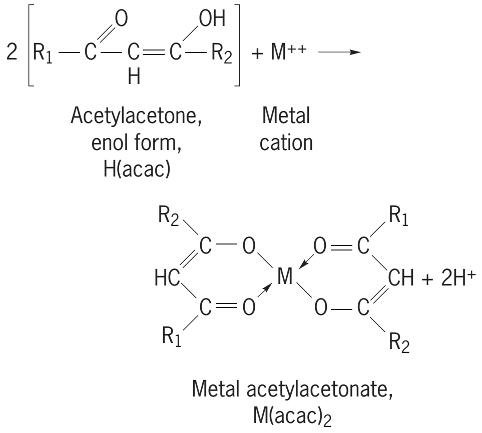


Fig. 4. Structural formula of NTA anion, a quadridentate ligand.



(1)

β-diketones in the enol form can lose a hydrogen ion and coordinate with a metal cation to give a six-membered ring of unusual thermal stability.

Beryllium acetylacetonate boils without decomposition at 270°C (518°F), and G. T. Morgan reported that scandium acetylacetonate, Sc(acac)$_3$, shows very little decomposition at 370°C (698°F). This remarkable stability contrasts sharply with the very low stability of coordination compounds containing simpler monodentate ketones, such as acetone.

Because of enhanced thermodynamic stability in solution, chelating agents may greatly alter the behavior of metal ions. The very insoluble compound, ferric hydroxide, will dissolve in a strongly alkaline solution of triethanol amine, $N(CH_2CH_2OH)_3$. Alternatively, the concentration of the ferric ion can be made vanishingly small at pH 2 by the addition of an equimolar amount of bis(orthohydroxybenzyl)-ethylenediamine-*N,N′*-diacetic acid (HBED; **Fig. 5**).

Since about 1940, both theoretical and practical considerations have focused attention on the factors which contribute to chelate stability. It is convenient to list such factors under three headings: (1) the nature of the metal cation, (2) the nature of the ligand, and (3) the formation of the chelate ring. It should be emphasized that these factors operate together, and their separation is somewhat artificial, but helpful for discussion purposes.

Role of metal in chelate stability. Since nitrogen, oxygen, and sulfur serve as the electron donor atoms in a majority of chelating agents, it is of interest to seek a relationship between the donor atom and the type of metal acceptor atom with which it combines. A large majority of the chelates of Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Si^{4+}, Ge^{4+}, and Sn^{4+} contain oxygen as at least one of the donor atoms. It may be furnished as an acid, alcohol, ether, ketone, or other group. These ions coordinate less frequently through two nitrogen or sulfur atoms. Cations of other metals such as vanadium, niobium, tantalum, molybdenum, and uranium, and the cations Be^{2+}, Al^{3+}, and Fe^{3+} show a preference for oxygen as the donor atom, but they may coordinate through nitrogen, sulfur, or phosphorus under special conditions. Cr^{3+}, Fe^{2+}, and the platinum metals show increasing preference for coordination through nitrogen as opposed to oxygen, while Cu$^+$, Zn^{2+}, Ag$^+$, Au$^+$, Cu^{2+}, Cd^{2+}, Hg^{2+}, V^{3+}, Co^{3+}, and Ni^{2+} show a marked preference for nitrogen and sulfur as the donor atoms. The ions of the last group retain the ability to coordinate with oxygen in even greater degree than do the ions of the first group, but their tendency to form bonds through nitrogen is so great that it exceeds their oxygen-binding tendency.

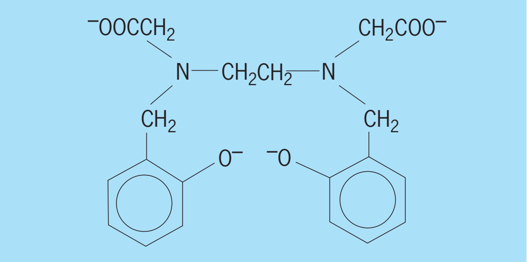


Fig. 5. Structural formula of anion of HBED, a sexadentate ligand.

It must be recognized that broad generalizations such as these have many exceptions, particularly in intermediate regions. On the other hand, such generalizations indicate clearly that attempts to arrange elements in the order of their chelating ability can be of significance only when cations of comparable type are selected. Thus, the stabilities of the alkali-metal, the alkaline-earth, and the rare-earth chelates decrease as the charge on the cation decreases or as the size of the cation increases. For example, the chelates of the alkaline-earth metal ions become less stable as the metal ion becomes larger (if the number of chelate rings remains the same), in the order Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}. The relationship between ion size and chelate stability is of major importance in the separation of the rare-earth and transuranium elements by ion-exchange processes. The selectivity of the ion-exchange column is increased by the use of appropriate chelating agents in the eluting solution.

Stability sequences established for other metal ions are somewhat less satisfactory. Metal chelates of several substituted β-diketones decrease in stability in the order: $Hg^{2+} > (Cu^{2+}, Be^{2+}) > Ni^{2+} > Co^{2+} > Zn^{2+} > Pb^{2+} > Mn^{2+} > Cd^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. If one restricts stability comparisons to bivalent metals of the first transition series, the following order is obtained: $Zn^{2+} < Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$. This latter listing of stabilities appears to be valid for a large variety of chelating ligands.

Lower valence states such as Ir(I) and Rh(I) are effectively coordinated by chelating ligands containing trivalent phosphorus or trivalent arsenic donor groups. For example, recently synthetic coordination chemists have synthesized a series of unusual chelating agents containing trivalent phosphorus, analogous to polyamines, an example of which is illustrated in **Fig. 6**.

General principles of selective coordination of metal ions by various types of donor atoms have now been worked out, and are described through concepts such as the principles of hard and soft acids

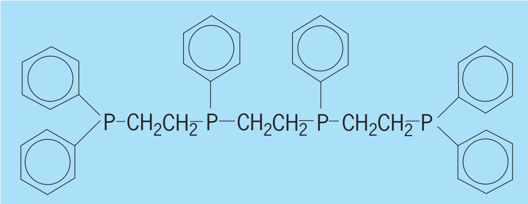
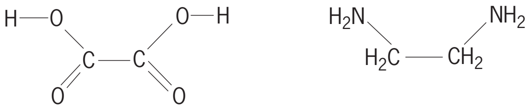
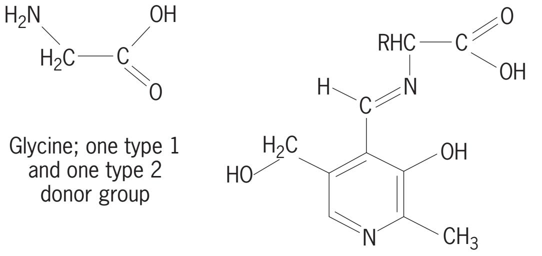


Fig. 6. "Tetraphos," a quadridentate ligand.



Oxalic acid; two type 1 (negative carboxylate) donor groups

Ethylenediamine; two type 2 (neutral amino) donor groups



Glycine; one type 1 and one type 2 donor group

Amino acid Schiff base of pyridoxal (vitamin B_6); two type 1 (carboxylate and phenolate) and one type 2 (azomethine nitrogen) donor group

Fig. 7. Chelating ligands indicating the types of donor groups available for coordination.

and bases, and type A and B character of metal ions. These qualitative principles are based on well-known laws of ionic attraction and polarizabilities of atoms, ions, or molecular groups, as well as on general principles of molecular orbital theory.

Role of ligand in chelate stability. Two general types of groups give rise to coordinate bonds between ligands and metal. These are (1) primary acid groups in which the metal ion can replace hydrogen ions and (2) neutral groups which contain an atom with a free electron pair suitable for bond formation. If two groups from either class 1 or 2, or from both classes, are present in the same molecule in such positions that both groups can form bonds with the same metal ion, a chelate ring may be formed. For example, as shown in **Fig. 7**, in oxalic acid two groups of type 1 are present; in ethylenediamine two groups of type 2 are present; glycine possesses one of each type; and pyridoxylidine-glycine (the Schiff base of glycine and vitamin B_6) possesses a carboxylate (type 1), an aromatic phenolate (type 1), and an imino group (type 2) available for chelate formation around a metal ion.

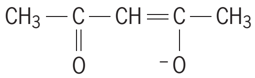
In general, anything which increases the localization of negative charge on the donor atom increases its ability to coordinate to a metal atom. Since a hydrogen ion is bound to a ligand by an electron pair in groups of type 1, an increase in electron density on the donor atom will increase the ability of the donor to bind either hydrogen ion or metal cation. The ability of a ligand to bind hydrogen ion is frequently referred to as its basic strength. It is surprising then that, for ligands of rather similar type, an increase in ligand basic strength implies an increase in its metal-chelating ability. A number of researchers have indicated this relationship by plotting the log of the equilibrium constant for the process represented by Eq. (2) against the log of the equilibrium con-

$$H^+ + L^- \rightleftharpoons HL \qquad K_1 = \frac{[HL]}{[H^+][L^-]} \qquad (2)$$

stant for the process of chelate dissociation shown by Eq. (3).

$$M^{n+} + L^- \rightleftharpoons M^{(n-1)+} \qquad K_2 = \frac{[ML^{(n-1)+}]}{[M^{n+}][L^-]} \qquad (3)$$

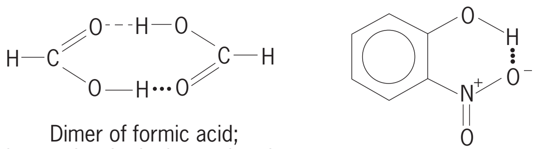
L^- is the chelating anion, such as the acetylacetonate anion,



$$CH_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{^-O}{|}}{C}-CH_3$$

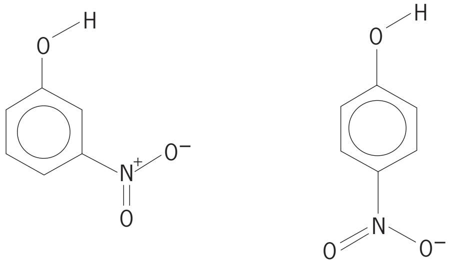
The constant K_1 is the protonation constant (its reciprocal is the acid dissociation constant), and K_2 is designated the stability constant of the metal chelate.

For the organic chemist, the analogy between the hydrogen cation and the metal cation is even more clearly drawn. Rings formed by hydrogen bonding are referred to as chelates; thus, formic acid dimerizes through hydrogen-bond chelation as shown in **Fig. 8**. The high volatility of *o*-nitrophenol compared with the much lower volatility of its meta or para isomers (Fig. 8) can only be explained in terms of



Dimer of formic acid; intermolecular hydrogen bonds

o-Nitrophenol; strong intramolecular hydrogen bond, relatively volatile



m-Nitrophenol; low volatility

p-Nitrophenol; low volatility

Fig. 8. Compounds forming intramolecular and intermolecular hydrogen bonds.

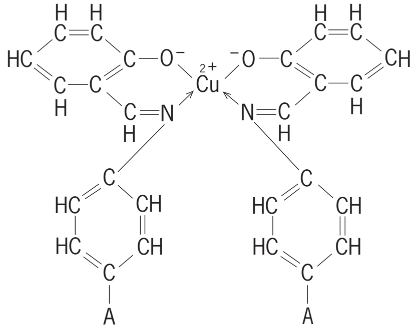
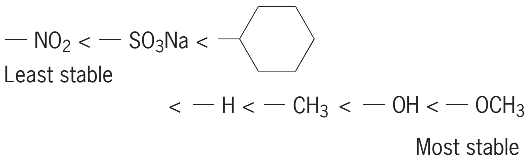


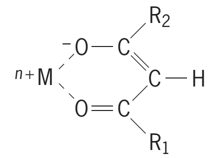
Fig. 9. Structure of a chelated copper compound.

intramolecular versus intermolecular hydrogen bonding. The properties of salicylaldehyde, enhanced enolization in acetoacetic ester, and many other organic compounds are altered by internal chelate-ring formation involving hydrogen bonds. *See* HYDROGEN BOND.

The role of ligand structure on chelate stability is illustrated by studies which have been conducted on compounds of the type shown by **Fig. 9**, where A represents an electron-attracting group. In general, it was found that with an increase in the electron-attracting power of group A, electrons were pulled away from the nitrogen atom, resulting in both lower base strength and lower chelating ability for the ligand. As A is changed successively through the groups shown below, chelate stability increases in the order:

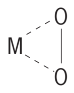


Similar studies on substitute *β*-diketone chelates of the type



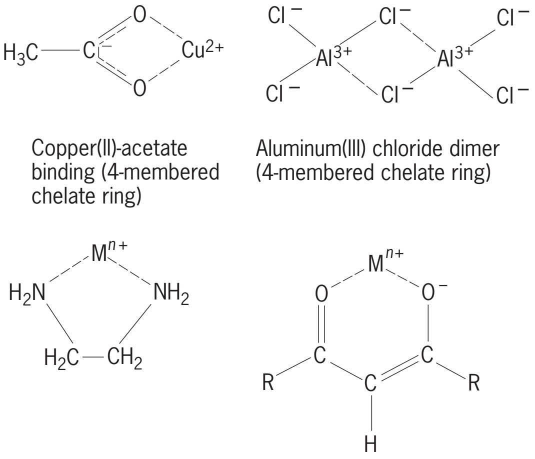
showed that, if R_1 were changed from a methyl group to an electron-withdrawing trifluoromethyl group, the stability of the resulting chelate is greatly decreased. In general, all molecular charge effects which can be invoked to shift charge in an organic molecule, such as inductive and resonance effects, will influence chelate stability. Thus the principles governing charge distribution and bond hybridization in organic chemistry are useful in working out the relationships between ligand structure and chelate stability.

Role of ring closure in chelate stability. The stability factors discussed above are applicable to coordination compounds generally, not to chelates alone. On the other hand, a number of stability factors may be considered to apply uniquely to chelates because of their ring structure. The most obvious variable in this category is ring size, a factor which is uniquely determined by the position of the donor atoms in the chelating ligand. When the groups are present in such a position as to form a five or six-membered ring, the resulting complex is the most stable although four-, seven-, eight-membered, and even larger rings are known. Examples of these would be found among biological ligands as well as in ion exchange resins. The existence of three-membered rings has not been established. Hydrazine, H_2NNH_2, which might in theory form a three-membered chelate ring, appears to be monodentate. There is some evidence for intermediate structures of metal-oxygen complexes



which may be considered three-membered chelate rings. Such compounds may be important reaction intermediates but are generally unstable and present in relatively low concentrations. The four-membered chelate rings are frequently strained. Examples of four-membered chelate rings are copper(II)-carboxylate complexes, and the aluminum chloride dimer (**Fig. 10**). While five-membered rings are very common and are formed preferentially by saturated organic ligands, ligands containing two double bonds tend to form six-membered structures. If only one double bond is present, five- or six-membered rings may form; five-membered saturated rings are illustrated in Fig. 10 by ethylene-diamine-metal chelates, and the conjugated six-membered rings by the metal acetylacetonates.

Rings of seven or more members are comparatively uncommon, but their existence is well established. As the length of the chain between the two donor atoms increases, so does the tendency of the ligand to form polymetallic complexes. Under such circumstances, the two donor atoms on the same chelate molecule coordinate with different



Copper(II)-acetate binding (4-membered chelate ring)

Aluminum(III) chloride dimer (4-membered chelate ring)

Fig. 10. Metal chelates containing four-, five-, and six-membered rings.

metal atoms rather than with one; thus, a polymeric chain, $M^+—NH_2CH_2CH_2CH_2CH_2NH_2—M^+$, may result instead of a ring structure.

The fact that chelate complexes are usually more stable than comparable nonchelate structures has been called the chelate effect. This effect is partly attributable to the fact that simultaneous rupture of both bonds holding the ligand to the metal is highly improbable, and if only one bond breaks there is a high probability that the broken bond will reform before the second bond is ruptured. As the chain length between the two donor atoms increases, the chance for reformation of the broken bond declines; thus, large rings usually show a decrease in stability. On the other hand, in fused ring systems, formed by polydentate ligands such as ethylenediaminetetraacetic acid, the probability that at least one bond will reform before all bonds are ruptured results in increased complex stability. When the bonding atoms are rigidly positioned around the metal by the organic framework, as in the porphins, the resulting increase in stability is extremely high. It has been reported that the copper phthalocyanine complex, with a completely interlocked ring system, is stable in the vapor phase near 500°C (930°F).

Chelate compounds are differentiated from their nonchelate analogs by several properties besides high stability. Although not all chelates are volatile, the existence of low-boiling metal acetylacetonates and related structures is noteworthy. If the coordination number of the metal cation for the oxygen atoms of the acetylacetone (that is, the number of nearest oxygens around the cation) is equal to twice the ionic charge of the cation, the resulting acetylacetonate is volatile; thus, beryllium with a charge of 2 and a coordination number of 4 forms an acetylacetonate which boils at 270°C (518°F); aluminum with a charge of 3 and a coordination number of 6 forms an acetylacetonate which boils at 314°C (597°F). If the coordination number of the central cation is less than twice the ionic charge, less volatile saltlike complexes are formed.

Isomerism of all types, so important in organic chemistry, is of major concern in chelation, particularly to the biochemist, since desired biological properties are frequently restricted to a particular chelate isomer. Ring formation may result in optical activity where analogous nonchelate structures are inactive. Thus, the ethylenediamine chelate structures shown in **Fig. 11** are optical isomers, whereas the analogous methylamine complexes represented in **Fig. 12** are optically inactive. *See* CHEMICAL BONDING; CHEMICAL EQUILIBRIUM; COORDINATION COMPLEXES; STEREOCHEMISTRY; STERIC EFFECT (CHEMISTRY).

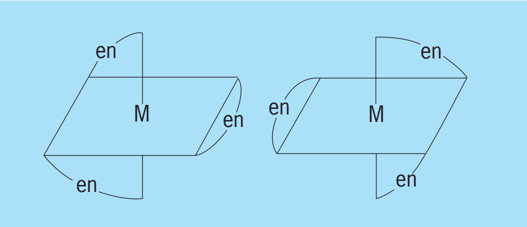


Fig. 11. Optical isomers of chelate complexes.

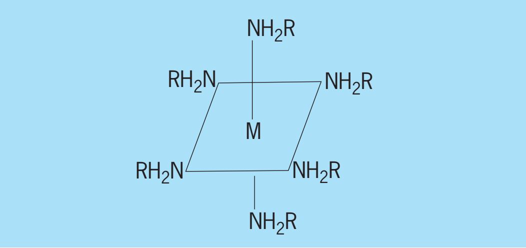


Fig. 12. Formula for an optically inactive nonchelate.

A. E. Martell; R. J. Motekaitis

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Chelicerata

A subphylum of the phylum Arthropoda. The Chelicerata can be defined as those arthropods with the anteriormost appendages as a pair of small pincers (chelicerae) followed usually by pedipalps and four pairs of walking legs, and with the body divided into two parts: the prosoma (corresponding approximately to the cephalothorax of many crustaceans) and the opisthosoma (or abdomen). There are never antennae or mandibles (lateral jaws). The Chelicerata comprise three classes: the enormous group Arachnida (spiders, ticks, mites, scorpions, and related forms); the Pycnogonida (sea spiders or nobodycrabs); and the Merostomata (including the extant Xiphosurida or horseshoe crabs). *See* ARACHNIDA; MEROSTOMATA; PYCNOGONIDA; XIPHOSURIDA.

With a few exceptions, the distinctive body and limb pattern of chelicerates is diagnostic. The Acarina (mites) have the prosoma and opisthosoma fused in a single armored globe. The segments of the prosoma are always fused (except in the minor order Solfugae or sun spiders), and the opisthosoma never bears locomotor appendages (although in the xiphosurids there are paired gills on six segments of the opisthosoma). Chelicerae are always present, but the form of the pedipalps varies greatly from tiny sensory appendages to enormous crablike chelae (in scorpions and certain minor orders). Four pairs of locomotor appendages follow the chelicerae and pedipalp on the prosoma; only in a few species of pycnogonids are there five or six pairs of walking legs. *See* ACARI.

Both Merostomata and Pycnogonida are marine, but the enormous numbers and varied forms of the

Arachnida are almost entirely terrestrial. The respiratory structures of chelicerates include gills, booklungs, and tracheae. Sexes are normally separate, with genital openings at the anterior end of the opisthosoma. Some mites and other small chelicerates are omnivorous scavengers, but the majority of species of larger chelicerates are predaceous carnivores at relatively high trophic levels in their particular ecotopes. *See* ARTHROPODA. W. D. Russell-Hunter

Chelonia

An order of the Reptilia, subclass Anapsida, including the turtles, terrapins, and tortoises. This order is also known as the Testudines. The group first appeared in the Triassic, and its representatives are among the commonest fossils from that time on. Members of the order are most frequently found in freshwater streams, lakes, and ponds or in marshy areas. However, a number of strictly terrestrial species are known, and several are marine. Turtles occur on all the major continents and continental islands in tropic and temperature regions. The marine forms are basically tropic in distribution, but some individuals stray into temperate waters. *See* ANAPSIDA.

The largest carapace length attained by living forms is around 8 ft (2.4 m) in the marine leatherback turtle (*Dermochelys*), which weighs 1500 lb (675 kg). Members of the large land tortoise group (*Geochelone*) reach lengths of 4 ft (1.2 m) and weights of about 560 lb (250 kg). The smallest living species is probably the stinkpot (*Kinosternon odoratus*) of eastern North America, which attains a maximum length of about $4^{1}/_{2}$ in. (11 cm). The longevity of turtles is well known, with many captive tortoises having lived 50–60 years and others estimated to be as old as 150 years.

Taxonomy. The living turtles are usually divided into two major groups, the suborders Pleurodira and Cryptodira, based upon the structures of the head and neck. Both lines are thought to be evolved from primitive forms placed in the suborder Amphichelydia (Triassic to Eocene). This latter group differs most markedly from recent species in having elongate neural spines on the neck vertebrae so that the neck is not retractible into the shell (**Fig. 1**). Correlated with the lack of retractibility, the skull is not emarginated to make room for attachment of muscle from the cervical region. The pleurodires, on the other hand, have spines on only the most posterior cervicals and the head is retractile laterally. The skull is emarginate. In the cryptodires the cervical spines are uniformly reduced, the skull is usually emarginate, and the head is folded directly back to within the shell. In several cryptodires, notably in the marine turtles, the neck is secondarily nonretractible because of a reduction in the shell, and the skull is nonmarginate. The **table** shows the principal groups and distribution of the approximately 225 living species of the order.

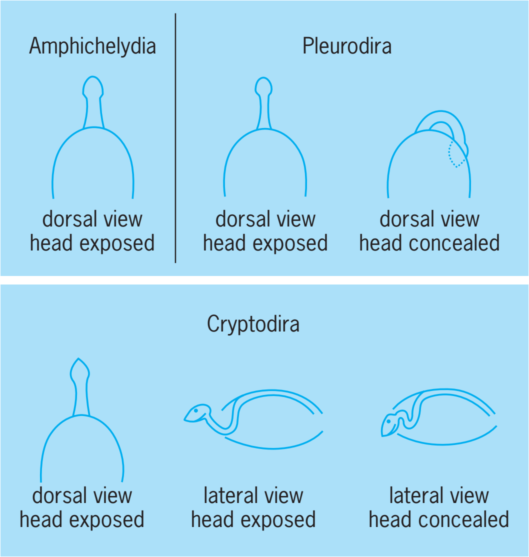

Fig. 1. Characteristics of turtle suborders, showing head in exposed and concealed positions.

Morphology. The Chelonia differ from most other vertebrates in possessing a hard bony shell which encompasses and protects the body (**Fig. 2**). The shell is made up of a dorsal portion, the carapace, and a ventral segment, the plastron, connected by soft ligamentous tissue or a bony bridge. The carapace is composed of the greatly expanded ribs and dorsal vertebrae overlain by a series of enlarged dermal ossifications and an outer covering of tough skin or horny scales. The plastron is similarly arranged

Families of the Chelonia

Group	Common name	Number of species	Distribution
Suborder Pleurodira			
Family Pelomedusidae	Side-necked turtles	14	Southern Africa, Madagascar, South America
Family Chelidae	Side-necked turtles	32	Australia, New Guinea, South America
Suborder Cryptodira			
Family Kinosternidae	Mud and musk turtles	22	North, Middle, and South America
Family Chelydridae	Snapping turtles	3	Middle and northern South America
Family Emydidae	Pond turtles and allies	102	All continents except Australia; only one or two South American species
Family Testudinidae	Tortoises	30	All continents except Australia; two South American species
Family Cheloniidae	Hawksbill, loggerhead, and green sea turtles	6	Tropical and subtropical seas
Family Dermocheylidae	Leatherback turtle	1	Tropical and subtropical seas
Family Trionychidae	Soft-shelled turtles	14	North America, Asia, central and southern Africa
Family Carretochelyidae	Fly River turtle	1	New Guinea

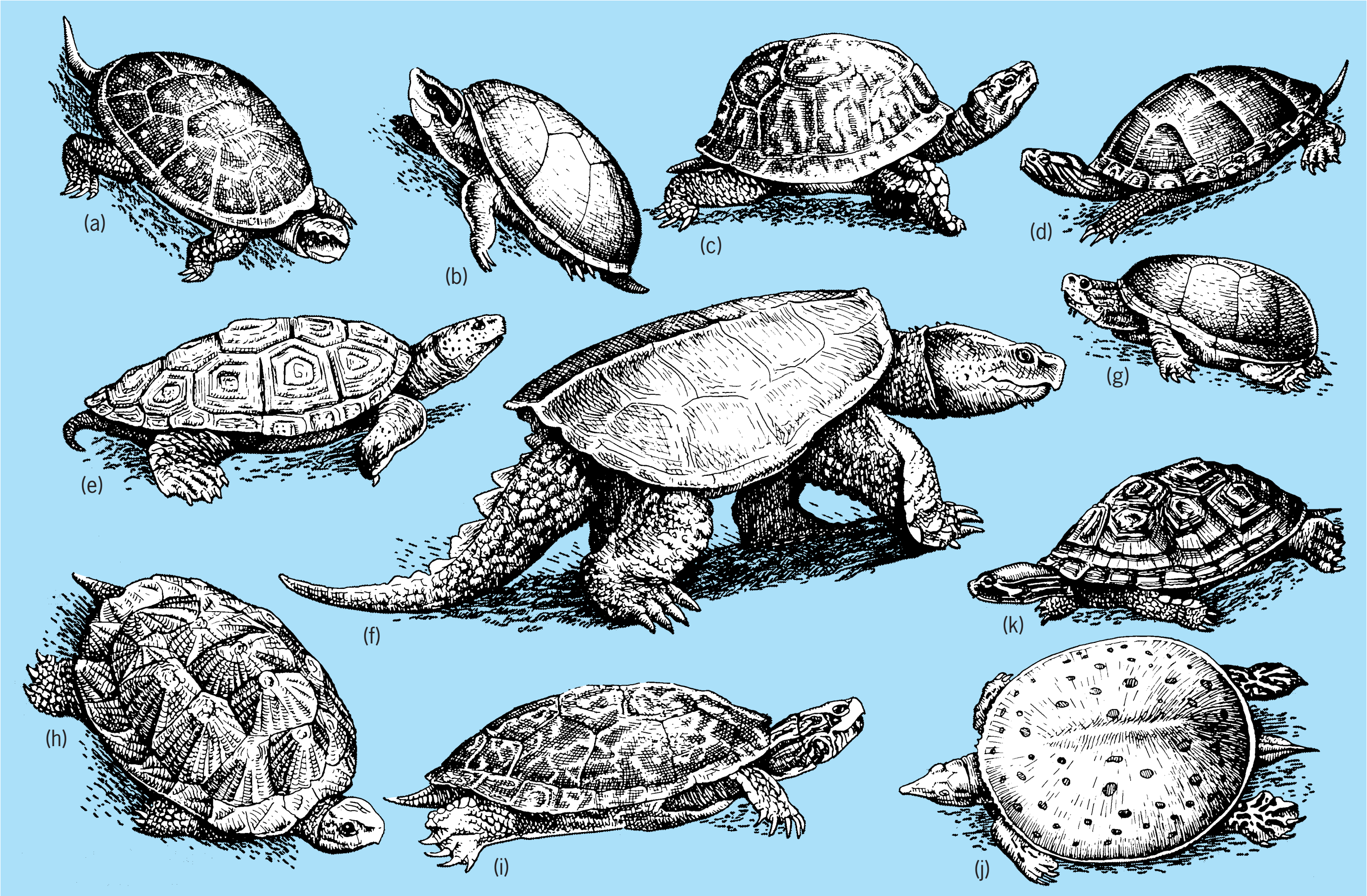

Fig. 2. Common United States turtles. (*a*) Spotted turtle, *Clemmys guttata*. (*b*) Stinkpot, *Kinosternon odoratus*, (*c*) Box turtle, *Terrapene carolina*. (*d*) Painted turtle, *Chrysemys picta*. (*e*) Diamondback terrapin, *Malaclemys terrapin*. (*f*) Common snapping turtle, *Chelydra serpentina*. (*g*) Mud turtle, *Kinosternon subrubrum*. (*h*) Wood turtle, *Clemmys insculpta*. (*i*) Map turtle, *Graptemys geographica*. (*j*) Spiny soft-shelled turtle, *Trionyx spiniferus*. (*k*) River terrapin, *Chrysemys floridana*. (*After J. J. Shomon*, *ed*., *Virginia Wildlife*, *15*(*6*):*27*, *1954*)

with remnants of the interclavicle, clavicles, and gastralia fused with dermal ossifications and covered by skin or scales. Other peculiarities associated with the shell include the fusion of the ribs to the vertebrae and the reduction of trunk muscles, the presence of the pectoral girdle completely inside the ribs (found in no other animal), the highly modified short, thick humerus and femur, and the lungs attached dorsally to the shell. In addition, living turtles differ from the tuatara, snakes, lizards, and crocodilians in having an anapsid skull, no true teeth but horny beaks on the jaws, an immovable quadrate, and a single median penis in males. Teeth are present in ancient primitive turtles.

The rigid bony shell of turtles imposes a basic body plan subject to relatively little variation. Turtles are always recognizable as such, and the principal obvious differences between them are in the shell shape, limbs, head, and neck. The general outline of the shell is variable, but in most forms the shell is moderately high-arched and covered with epidermal scales. In some of the tortoises, such as *Geochelone*, the shell is very high, equaling the breadth. In the soft-shelled turtles, Trionychidae, and the saxicolous African tortoise (*Malacochersus*), the shell is greatly depressed to a thin, almost platelike form. No scales are present on the shells of the families Dermochelyidae, Carrettochelyidae, and Trionychidae, which are covered by thick skin.

The majority of turtles have limbs more or less adapted to aquatic or semiaquatic life with moderate to well-developed palmate webbed feet. However, in strictly terrestrial forms such as the tortoises, the limbs are elephantine with the weight of the body being borne on the flattened sole of the feet. The marine turtles and the river turtle (*Carrettochelys*) of southern New Guinea have the anterior limbs modified into paddlelike flippers, used to propel them through the water rapidly.

Physiology. Associated with the tendency of most turtles toward a life in or near water is the auditory apparatus. Even though an eardrum is present, hearing is adapted to picking up sounds transmitted through the water or substratum. However, there is evidence that airborne sound can be heard. Vision is also important, and turtles have color vision. Sounds are produced by many species through expulsion of air through the glottis. Respiration is by means of the rather rigid lungs, which are inflated and deflated by a series of special muscles. Several species with aquatic habits have special vacularized areas in the mouth or cloaca which act as auxiliary respiratory devices and make possible gaseous exchanges when the turtle is submerged in water. Most forms emit highly pungent oily substances from specialized cloacal glands, and these secretions probably are useful as recognition cues in the water. Most of the species are gregarious and diurnal, and territoriality is unknown in the order.

Reproduction. The courtship patterns of various turtles are distinctive. In general, aquatic forms mate in the water, but tortoises breed on land. The male mounts the female from above, and fertilization is internal. Sperm may be stored in the cloacal region of the female for extended periods before fertilization. Because of the presence of the large median penis in males, the sexes of many species can be distinguished by the longer and broader tail of the male. In addition, in many forms the plastron of the male is concave while in the female it is moderately to strongly convex. No doubt this characteristic of the female is associated with the spatial requirements for egg production and storage. All turtles lay shelled eggs which are buried in sand or soil in areas where females congregate. The shell is calcareous in most forms, but the marine turtles have leathery shells. Eggs are rather numerous, as many as 200 being laid by a single individual in some species, and are highly valued as human food. Incubation takes 60–90 days,

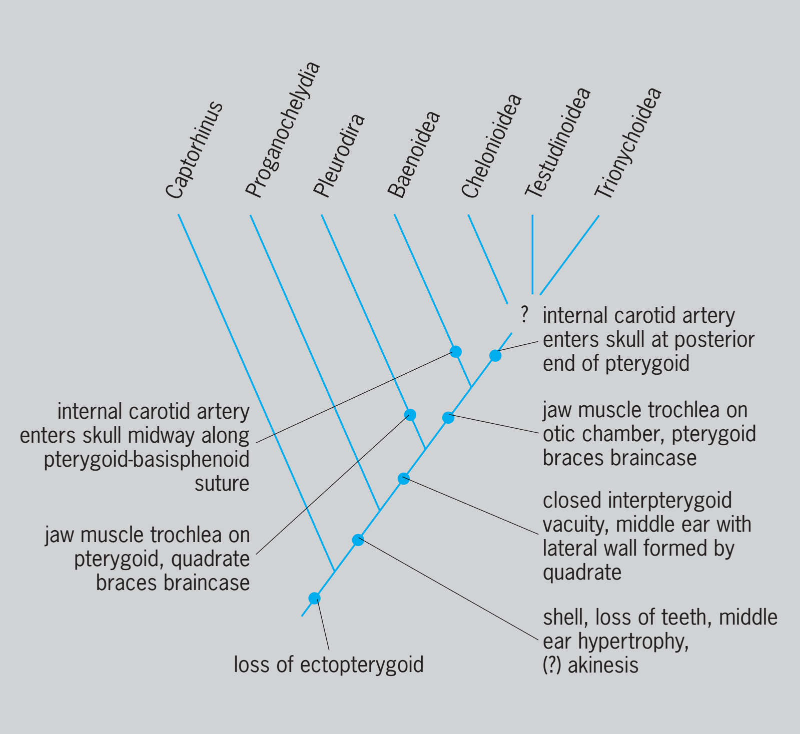

Fig. 3. Relationships of Chelonia derived from analysis of cranial features.

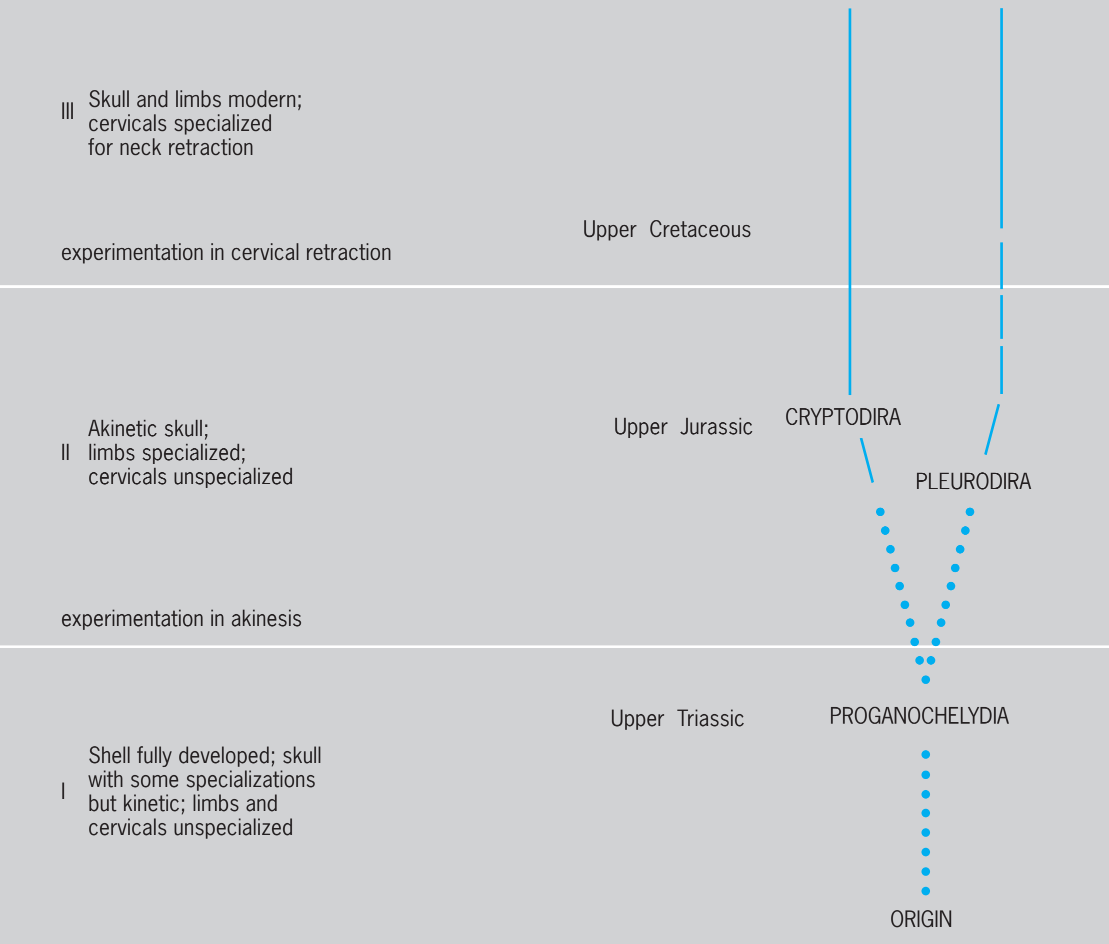

Fig. 4. Levels of organization in the order Chelonia.

and the little turtle cuts its way out of the shell with a small horny egg caruncle at the end of the snout.

Nutrition. Turtles feed on all types of organisms. Aquatic species may eat algae, higher plants, mollusks, crustaceans, insects, or fishes; terrestrial forms are similarly catholic in tastes. Most species are omnivores, but some have very specialized diets. The edges and internal surfaces of the horny beaks of these reptiles are frequently denticulate and modified to form specialized mechanisms adapted to handle particular food items. Jay M. Savage

Phylogeny. Turtles have long been considered a "primitive" or relict reptile group that has maintained a consistent morphologic structure since its origin. Phylogenetic and functional work on the skulls of fossil and modern turtles suggest that this approach is incorrect. The Cryptodira and the Pleurodira probably represent a very early dichotomy which took place soon after the origin of the turtles. These two groups passed through similar stages during their phylogeny and repeatedly evolved parallel adaptations.

The basicranium of turtles has rarely been used in a comparative sense, and the morphology of this region is still poorly known in many families of turtles. Nonetheless, the basicranium is one of the most useful regions for phylogenetic work because of its extreme complexity and relative conservativism compared with other areas. The main arterial and venous circulation of the head, the cranial nerves, the brain, and the neck and jaw musculature are all related to features in the basicranium. Changes in any of these systems can usually be seen in the basicranium. Although turtle skulls are rare compared to shells, the fossil record contains a good series with basicrania dating from the Upper Triassic to the Recent.

Previous phylogenies, however, have been based primarily on shell criteria and vertebral characters. Two major living groups are usually distinguished: the Cryptodira, with vertical neck retraction, and the Pleurodira, with horizontal neck retraction. A few of the shell characters also distinguish the living forms: pelvis sutured to carapace and plastron in pleurodires, pelvis free in cryptodires. These features rather clearly separate living turtles into two groups, but when fossils are examined it becomes difficult to distinguish pleurodires and cryptodires. The neck retractile mechanisms had not evolved until the end of the Mesozoic; thus the earlier phylogeny of the two groups is difficult to determine by neck characters.

Work on the skulls of fossil and recent turtles, however, has resulted in the development of a new hypothesis of chelonian relationships. The use of cranial features in a shared-derived character analysis is expressed in **Fig. 3**. Arterial characters provide the basis for relating the major groups of cryptodires, whereas jaw mechanics and middle ear morphology are used in comparing Proganochelydia, Pleurodira, and Cryptodira. By using these characters, pleurodires and cryptodires can be recognized well into the Mesozoic as distinct lineages, and the divergence of the two groups from a common ancestor probably took place before the Jurassic.

The new phylogenetic information has enabled functional interpretations to be made concerning the biologic significance of the differences between cryptodires and pleurodires. These interpretations show that the two lineages have developed similar structures in parallel during their evolution (**Fig. 4**). A similar but nonhomologous jaw mechanism involving a trochlea to compensate for the expanded otic chamber (**Fig. 5**) and a method of bracing the palatoquadrate against the braincase are complex features evolved independently in both groups. Later in their evolution the neck retractile mechanisms evolved, but by this time the two groups had been separate for many millions of years.

Origin. The origin of turtles is more in doubt than ever. Previous workers have emphasized the peculiar adaptations of a Permian reptile from South Africa, *Eunotosaurus*. This animal, represented by postcranial remains but very little skull material, was suggested as an ancestor for turtles on the basis of its expanded ribs, which form a rudimentary shell. However, T. S. Parsons and E. E. Williams in 1961 and, in particular, C. B. Cox in 1969 showed that *Eunotosaurus* is not related to turtles. Cox stated that *Eunotosaurus* is a captorhinomorph and that its Chelonia-like features are due to structural convergence with turtles. *Eunotosaurus* lacks separate ribs on its last dorsal vertebra, and Cox held that this feature prevents *Eunotosaurus* from being a chelonian ancestor. No reptile known to science

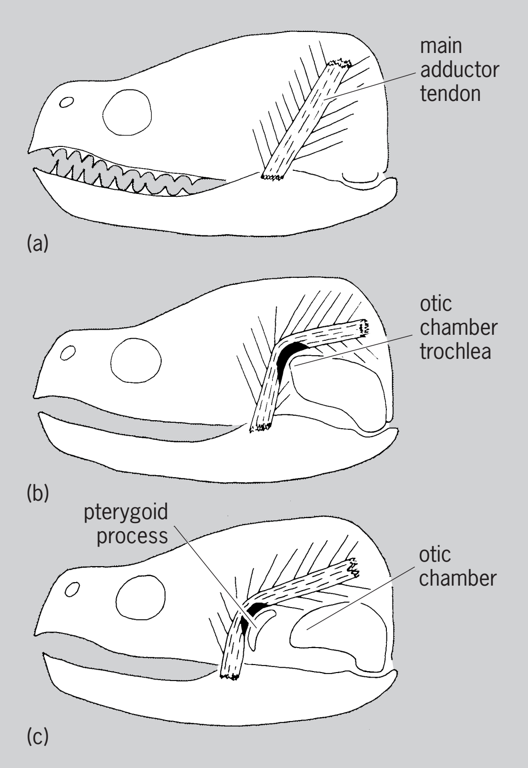

Fig. 5. Position of main jaw muscle tendon in (*a*) early reptiles, (*b*) cryptodires, and (*c*) pleurodires. The trochlea or pulley formed in turtles to get around the expanded otic chamber is independently derived in pleurodires and cryptodires.

definitely possesses specialized characters in common with turtles that would allow it to be a close relative or ancestor of that order. Presumably the stem reptile group Captorhinomorpha includes the eventual forebears of turtles since captorhinomorphs probably were ancestral to all reptiles, but the intermediate forms are unknown. *See* REPTILIA.

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Chemical bonding

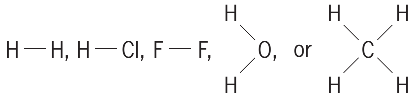
The force that holds atoms together in molecules and solids. Chemical bonds are very strong. To break one bond in each molecule in a mole of material typically requires an energy of many tens of kilocalories.

It is convenient to classify chemical bonding into several types, although all real cases are mixtures of these idealized cases. The theory of the various bond types has been well developed and tested by theoretical chemists. *See* COMPUTATIONAL CHEMISTRY; MOLECULAR ORBITAL THEORY; QUANTUM CHEMISTRY.

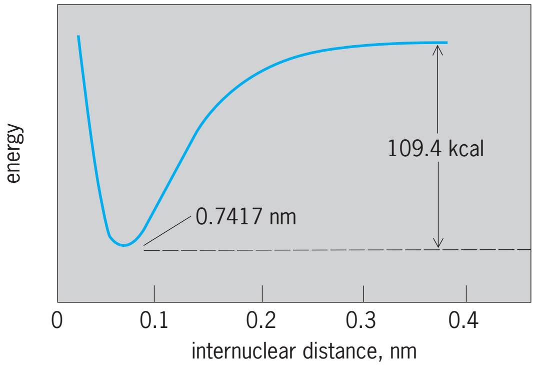
The simplest chemical bonds to describe are those resulting from direct coulombic attractions between ions of opposite charge, as in most crystalline salts. These are termed ionic bonds. *See* COULOMB'S LAW; IONIC CRYSTALS; STRUCTURAL CHEMISTRY.

Other chemical bonds include a wide variety of types, ranging from the very weak van der Waals attractions, which bind neon atoms together in solid neon, to metallic bonds or metallike bonds, in which very many electrons are spread over a lattice of positively charged atom cores and give rise to a stable configuration for those cores. *See* CRYSTAL STRUCTURE; INTERMOLECULAR FORCES.

Covalent bond. But it is the normal covalent bond, in which two electrons bind two atoms together, as in



that is the most characteristic link in chemistry. The theory that accounts for it is a cornerstone of chemical science. The physical and chemical properties of any molecule are direct consequences of its particular detailed electronic structure. Yet the theory of any one covalent chemical bond, for example, the H—H bond in the hydrogen molecule, has much in common with the theory of any other covalent bond, for example, the O—H bond in the water molecule. The current theory of covalent bonds both treats their qualitative features and quantitatively accounts for the molecular properties which are a consequence of those features. The theory is a branch of quantum theory. *See* NONRELATIVISTIC QUANTUM THEORY; QUANTUM CHEMISTRY.



Potential energy of the hydrogen molecule.

Hydrogen molecule. A brief outline of the application of quantum theory to the bond in the hydrogen molecule H—H follows. Here two electrons, each of charge $-e$, bind together two protons, each of charge $+e$, with the electrons much lighter than the protons. What must be explained, above all else, is that these particles form an entity with the protons 0.074 nanometer apart, more stable by $D = 109$ kcal (456 kilojoules) per mole than two separate hydrogen atoms, where D is the binding energy. In more detail, a molecular energy is involved (ignoring nuclear kinetic energy) that depends on internuclear distance, as shown in the **illustration**. This curve can be determined experimentally, and it can be used to interpret the characteristic spectroscopic properties of hydrogen gas. *See* MOLECULAR STRUCTURE AND SPECTRA.

The quantum theory accounts for the properties of isolated atoms by assigning atomic orbitals for individual electrons to move in, not more than two electrons at a time. For the hydrogen atom, the orbitals are labeled $1s$, $2s$., $2p_x$, $2p_y$, $2p_z$, and so on, with $1s$ the one having the lowest energy. For the molecule H_2 one electron, say electron 1, might be assigned to a $1s$ orbital on proton A, with $1s_A(1)$ written to signify this; similarly electron 2 might be assigned to the same kind of orbital on proton B, written as $1s_B(2)$. Since independent probabilities multiply and orbitals represent probability amplitudes, the description for the combined system shown in Eq. (1) is arrived

$$\phi(1, 2) = 1s_A(1)1s_B(2) \qquad (1)$$

at. Unfortunately, this fails to account for the bond properties; it gives a binding energy of only 10 kcal (41.9 kJ) per mole. *See* ATOMIC STRUCTURE AND SPECTRA; EXCLUSION PRINCIPLE.

An essential defect of Eq. (1) is the numbering of the electrons; it puts electron 1 on proton A, electron 2 on proton B. Electrons cannot be distinguished experimentally, so they should not be given unique numbers; the function $1s_A(2)1s_B(1)$ would be just as good as the foregoing. It is necessary to use a description that is not affected by interchange of electron labels, as in the additive combination of Eq. (2).

$$\phi(1,2) = 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1) \qquad (2)$$

(The difference combination also is an acceptable description, but it represents an excited state of the molecule.)

Any complete molecular electronic wave function should include electron spin. Symmetric space wave functions like Eq. (2) must be multiplied by antisymmetric spin wave functions to give total wave functions that are antisymmetrical with respect to interchange of electrons. For the ground state of hydrogen, and for the normal covalent bond elsewhere, this requirement means that the electron spins must be paired to give a total electron spin of zero.

The simple relationship described by Eq. (2) qualitatively accounts for the existence of the covalent bond; the predicted binding energy is $D = 74$ kcal (310 kJ) per mole; and the shape of the curve, with the minimum appearing at 0.080 nm, is right.

The description of Eq. (2) can be systematically improved. The charge acting on the electron may be changed from $+1e$ to the larger value, $+Ze$, which is more realistic for the actual molecule. With $Z = 1.17$ this gives $D = 87$ kcal (364 kJ) per mole. Polarization effects may be introduced by taking Eq. (3), where

$$\phi(1,2) = 1\sigma_A(1)1\sigma_B(2) + 1\sigma_A(2)1\sigma_B(1) \qquad (3)$$

$1\sigma_A = 1s_A + \lambda 2pz_A$ and $1\sigma_B = 1s_B + \lambda 2pz_B$. This gives $D = 93$ kcal (389 kJ). Ionic terms may be introduced, acknowledging the possibility that both electrons may be on one atom, by taking Eq. (4) where C

$$\phi(1,2) = C_1[1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)] + C_2[1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)] \qquad (4)$$

represents a constant. This also gives (with $Z = 1.19$) $D = 93$ kcal (389 kJ). Another possible approach is to include both ionic terms and polarization effects, and other terms involving $2s$, $3d$, $4f$, and other orbitals. If this is done, eventually one obtains the observed D value and a potential curve that is in complete agreement with experiment.

The linear mixing of terms such as $1s_A(1)1s_B(2)$ is called resonance; the method of mixing covalent and ionic structures is called the valence bond (VB) method. The particular mixing coefficients can be found by the variational principle: The best values for such parameters are those that make the total energy of the molecule, properly computed from quantum mechanics, a minimum. The energy expression contains only terms that have a direct classical interpretation: the kinetic energy of the electrons, their energy of repulsion for one another, their energy of attraction for the nuclei, and the nuclear-nuclear repulsion energy. *See* RESONANCE (MOLECULAR STRUCTURE).

Alternative descriptions of H_2 are possible, of which the most important is provided by the molecular orbital (MO) method. Here electrons are put one at a time into orbitals which are spread over the whole molecule, usually approximating these orbitals by linear combinations of atomic orbitals (LCAO). For H_2 the lowest molecular orbital is $\phi_1 \approx 1s_A + 1s_B$, the next $\phi_2 \approx 1s_A - 1s_B$. The simplest molecular orbital description is displayed in Eq. (5),

$$\phi(1,2) = \phi_1(1)\phi_2(2) \qquad (5)$$

which represents an equal weighting of covalent and ionic structures; it gives $D = 61$ kcal (255 kJ) for $Z = 1.00$ and $D = 80$ kcal (335 kJ) for $Z = 1.20$. More suitable is a mixture of this function with the function obtained by promoting both electrons from ϕ_1 to ϕ_2. The result of this configuration interaction process has the form of Eq. (6), and it is identical with the va-

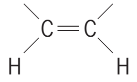
$$\phi(1,2) = D_1\phi_1(2) + D_2\phi_2(1)\phi_2(2) \qquad (6)$$

lence bond function of Eq. (4). In this manner more terms can be added, using more orbitals, until, again, the accurate potential energy curve is obtained.

The most accurate description known for the chemical bond in H_2 is a very complicated electronic wave function. The calculated and observed values of D and other properties agree absolutely.

Complex molecules. The problem of the proper description of chemical bonds in molecules that are more complicated than H_2 has many inherent difficulties. The qualitative theory of chemical bonding in complex molecules preserves the use of many chemical concepts that predate quantum chemistry itself; among these are electrostatic and steric factors, tautomerism, and electronegativity. The quantitative theory is highly computational in nature and involves extensive use of computers and supercomputers.

The number of covalent bonds which an atom can form is called the covalence and is determined by the detailed electron configuration of the atom. An extremely important case is that of carbon. In most of its compounds, carbon forms four bonds. When these connect it to four other atoms, the directions of the bonds to these other atoms normally make angles of about 109° to one another, unless the attached atoms are crowded or constrained by other bonds. That is, covalent bonds have preferred directions. However, in accord with the idea that carbon forms four bonds, it is necessary to introduce the notion of double and triple bonds. Thus in the structural formula of ethylene, C_2H_4 (**1**), all lines denote covalent bonds, the double line connecting the carbon atoms being a double bond. Such double bonds are distinctly shorter, almost twice as stiff, and require considerably more energy to break completely than do single bonds. However, they do not require twice as much energy to break as a single bond. Similarly,



(**1**)

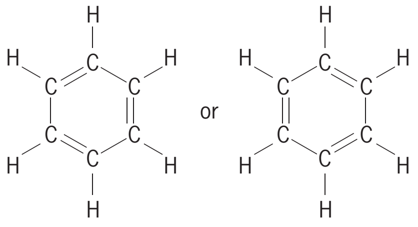
acetylene (**2**) is written with a triple bond, which

$$H{-}C{\equiv}C{-}H$$

(**2**)

is still shorter than a double bond. A carbon-carbon single bond has a length close to 1.54×10^{-8} cm, whereas the triple bond is about 1.21×10^{-8} cm long. *See* BOND ANGLE AND DISTANCE; VALENCE.

In many compounds the rules for writing bond formulas are not unique. For example, benzene, C_6H_6 (**3**), can be written in two forms. Evidence proves that all six C-C bonds are equivalent, so neither formula can be correct. The correct picture is a blend of the two, in which the bonds have many properties intermediate between those of double and single bonds but in which the whole molecule displays an additional stability. This resonance occurs whenever the structure is such that two or more different bond formulas can legitimately be drawn for the same geometry. *See* BENZENE; ELECTRON CONFIGURATION.



(**3**)

Many substances have some bonds which are covalent and others which are ionic. Thus in crystalline ammonium chloride, NH_4Cl, the hydrogens are bound to nitrogen by electron pairs, but the NH_4 group is a positive ion and the chlorine is a negative ion.

Both electrons of a covalent bond may come from one of the atoms. Such a bond is called a coordinate or dative covalent bond or semipolar double bond, and is one example of the combination of ionic and covalent bonding.

The hydrogen bond is a special bond in which a hydrogen atom links a pair of other atoms. The linked atoms are normally oxygen, fluorine, chlorine, or nitrogen. These four elements are all quite electronegative, a fact which favors a partially ionic interpretation of this kind of bonding. *See* ELECTRONEGATIVITY; HYDROGEN BOND.

To illustrate the level of accuracy of contemporary quantum-chemical calculations, the **table** gives observed and calculated values for certain spectroscopic properties of the H_2O molecule.

Spectroscopic properties of H_2O[*]

Property	Observed value	Calculated value
r_{OH} (Å[†])	0.957	0.962
∠(HOH) (degrees)	104.5	104.6
Harmonic vibrational frequencies (cm^{-1})	3832 1649 3943	3912 1683 4041

[*] After B. H. Besler et al., *J. Chem. Phys.*, 89:360, 1988.
[†] 1 Å = 10^{-10} m.

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Chemical conversion

A chemical manufacturing process in which chemical transformation takes place, that is, the product differs chemically from the starting materials. Most chemical manufacturing processes consist of a sequence of steps, each of which involves making some sort of change in either chemical makeup, concentration, phase state, energy level, or a combination of these, in the materials passing through the particular step. If the changes are of a strictly physical nature (for example, mixing, distillation, drying, filtration, adsorption, condensation), the step is referred to as a unit operation. If the changes are of a chemical nature, where conversion from one chemical species to another takes place (for example, combustion, polymerization, chlorination, fermentation, reduction, hydrolysis), the step is called a unit process. Some steps involve both, for example, gas absorption with an accompanying chemical reaction in the liquid phase. The term chemical conversion is used not only in describing overall processes involving chemical transformation, but in certain contexts as a synonym for the term unit process. The chemical process industry as a whole has tended to favor the former usage, while the petroleum industry has favored the latter. *See* CHEMICAL PROCESS INDUSTRY; UNIT PROCESSES.

Another usage of the term chemical conversion is to define the percentage of reactants converted to products inside a chemical reactor or unit process. This quantitative usage is expressed as percent conversion per pass, in the case of reactors where unconverted reactants are recovered from the product stream and recycled to the reactor inlet. *See* CHEMICAL ENGINEERING.

William F. Furter

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Chemical dynamics

That branch of physical chemistry which seeks to explain time-dependent phenomena, such as energy transfer and chemical reaction, in terms of the detailed motion of the nuclei and electrons which constitute the system.

Molecular Dynamics

In principle, it is possible to prepare two reagents in specific quantum states and to determine the quantum-state distribution of the products. In practice, this is very difficult, and experiments have mostly been limited to preparing one reagent or to determining some aspect of the product distribution. This approach yields data concerning the detailed aspects of the dynamics.

Bimolecular reactions. Molecular-beam and luminescence techniques have played a major role in the development of chemical dynamics. Since these techniques largely complement each other, they are illustrated by discussing the results of a single reaction, the formation of deuterium chloride (DCl) from atomic deuterium (D) and molecular chlorine (Cl_2), reaction (1).

$$D + Cl_2 \rightarrow DCl + Cl \qquad (1)$$

Chemiluminescence. Reaction (1) is 46 kilocalories per mole (192 kilojoules per mole) exoergic. If all of the exoergicity were to go into vibration of the newly formed DCl molecule, enough energy would be available to populate the $v' = 9$ vibrational level. In a gas-phase reaction at high pressure, much of this energy would be dissipated as heat at the walls of the container; but at very low pressures, where the frequency of collisions is small, DCl molecules in excited vibrational states, DCl^*, will emit infrared emission prior to undergoing a collision.

An apparatus to study this infrared chemiluminescence is shown in **Fig. 1**. Deuterium atoms are made by dissociating D_2 gas in an electrical discharge, and together with Cl_2 are injected into the observation cell at the top. The reagents mix and react inside a vessel with walls maintained at 77 K (−320°F), which freeze out species hitting the wall. The pressure is kept low to minimize vibrationally deactivating collisions. Infrared emission from the products is gathered by mirrors at the end, taken out through the sapphire window, and analyzed with an infrared spectrometer. By analyzing the spectrum, it is possible to determine which vibration-rotation states are emitting and, as a consequence, which vibration-rotation states are formed in the reaction. **Figure 2** shows the relative distribution of vibrational states from the reaction, and also shows, for comparison, the relative distribution of vibrational states calculated from the Boltzmann equation for hot DCl (6000 K or 10,800°F). Thermal distributions at any other temperatures would still show a monotonic decline. (The population for $v' = 0$ is not determined by the chemiluminescence experiments, because that state does not emit.) The DCl formed in the reaction clearly has different properties than hot DCl: the vibrational population displays an inversion, and this system (the hydrogen isotope) was the active medium for the first chemically pumped laser. *See* CHEMILUMINESCENCE.

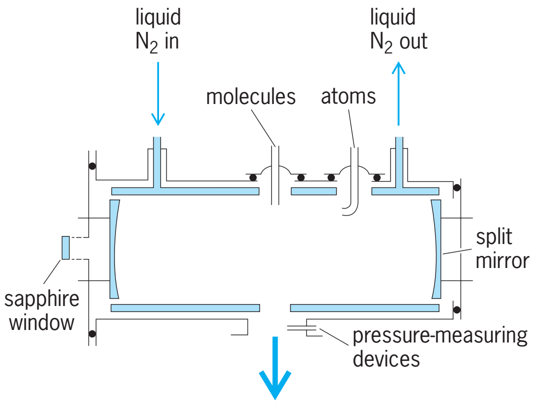

Fig. 1. Reaction vessel for studying infrared chemiluminescence between atoms and molecules at low pressure. (*After D. H. Maylotte, J. C. Polanyi, and K. B. Woodall, J. Chem. Phys., 57:1547–1561, 1972*)

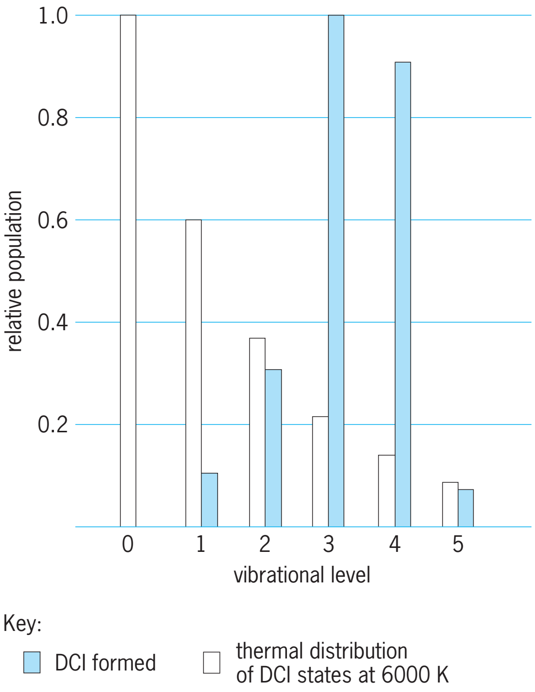

Fig. 2. Relative populations of DCl molecules in different vibrational states formed in the reaction $D + Cl_2 \rightarrow DCl + Cl$. 6000 K = 10,800°F.

Molecular-beam experiments. Molecules can be isolated in molecular beams, and collisions between these isolated molecules can be observed by crossing two tenuous molecular beams in a region of otherwise high vacuum. **Figure 3** shows such an experiment. Gaseous atoms or molecules emerge from the ovens, and collimating slits select the particles which are all going in the same direction. The molecular beams cross at the center of rotation of a large platform which can be rotated under vacuum relative to the two beams. Large vacuum pumps maintain a high vacuum, which ensures that collisions take place only at the intersection of the two beams. Product molecules are ionized by electron bombardment, and detected with a quadrupole mass spectrometer housed within a region of ultrahigh vacuum.

Measurements are made of the scattered product intensity and speed at various scattering angles. For ease of interpretation, these data are transformed into the center-of-mass system in which the two reagents approach each other with equal and opposite momenta. **Figure 4** shows a contour map of the DCl intensity in the center-of-mass coordinate system

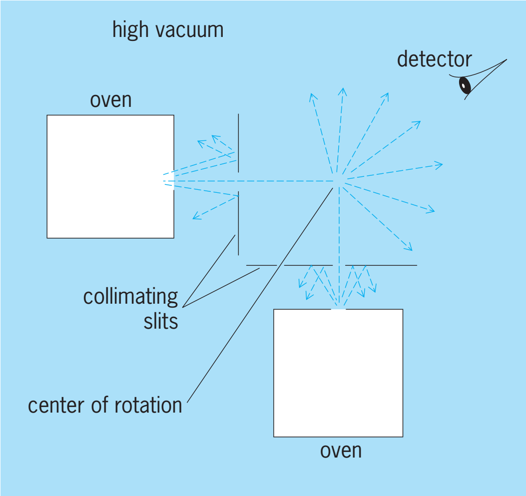

Fig. 3. Schematic of a molecular beam experiment; entire apparatus is under high vacuum.

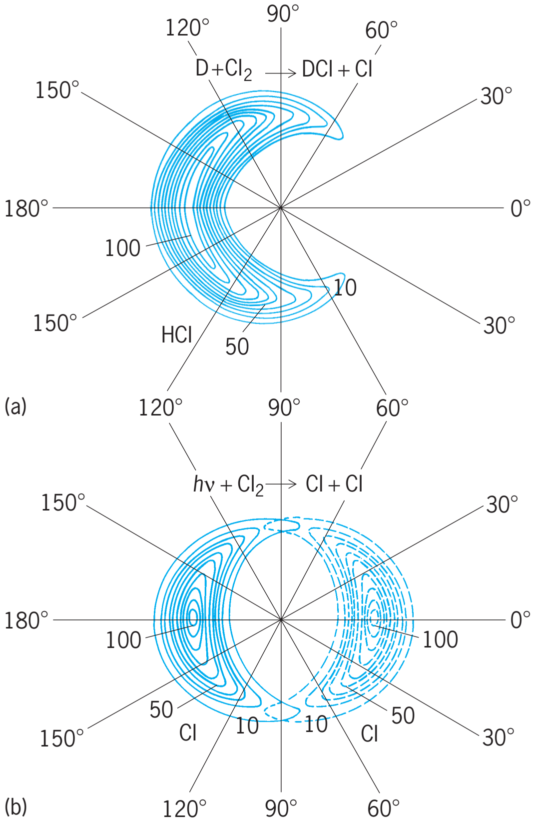

Fig. 4. Contour map of the DCl intensity. (*a*) Center-of-mass angular distribution of DCl from the reaction D + Cl_2. (*b*) Angular distribution of Cl atoms from photodissociation of Cl_2 molecules. Broken lines correspond to the second Cl atom. (*After D. R. Herschbach, Molecular dynamics of chemical reactions, Pure Appl. Chem., 47:61–73, 1976*)

in which the D atom is incident from the left and the Cl_2 molecule is incident from the right. The product DCl recoils backward (in the direction from which the D came) in a broad but nonetheless anisotropic distribution. The speed of the product is high, and corresponds to about half of the reaction exoergicity appearing in translation recoil of the products, with the balance appearing in vibration and rotation of the DCl; this is consistent with the chemiluminescence results. *See* MOLECULAR BEAMS.

The anisotropic product distribution shows that reaction occurs in a time of less than a molecular rotation, about 1 picosecond. The partitioning of energy roughly equally between vibration and translation suggests that the major amount of energy is released in repulsion between the DCl and Cl. This repulsion is similar to that experienced by a Cl_2 molecule in photodissociation, also shown in Fig. 4. Because the deuterium atom is so light, the direction in which the product is expelled is a measure of the orientation of the Cl_2 molecule during reaction. For this reaction the collinear arrangement D-Cl-Cl is preferred, whereas bent arrangements are preferred for D + I_2.

Other investigations. Molecular-beam machines (and to some extent chemiluminescence machines) have been modified in various ways to explore even finer details of specific reactions. For example, electric and magnetic fields have been used to prepare reagents in various orientations or to determine the magnitude and polarization of the product rotational angular momentum; lasers have been used to prepare reagents in initial vibrational states and to determine the final vibration-rotation state of products by inducing fluorescence from the products; and reactions may be conducted at hyperthermal energies to produce dissociation or even ionization.

Advances in subnanosecond laser technology have made it possible to study a few bulk phase reactions under nearly collision-free circumstances. For example, H atoms can be formed by dissociating a hydrogen halide (HX) with a fast laser pulse, and reaction of the H can be monitored by a second pulse delayed enough to probe reaction products after only a few collisions. *See* ULTRAFAST MOLECULAR PROCESSES.

Information about chemical reactions has so far come from observations made on the disappearance of reagents or appearance of products. However, several experiments on systems such as H + H_2, K + NaCl, and ICN (iodine cyanide) have shown that it is possible to use lasers to probe the chemical system during the very short time in which the chemical bonds are rearranging. This forms the basis of a new spectroscopy of the transition region. *See* LASER PHOTOCHEMISTRY.

Unimolecular reactions. Unimolecular reactions are possible when the energy of an isolated molecule lies above the energy of the asymptotically separated products. Molecules were traditionally energized by collisions, and unimolecular reactions have been studied by using collisional excitation in both crossbeam and chemiluminescence experiments. Several laser methods—multiphoton excitation, stimulated emission pumping, and overtone excitation—can also be used to populate a very narrow range of energy levels in isolated molecules to study unimolecular reactions as well as the related process of photodissociation.

Considerable insight into unimolecular processes has been obtained. Energy initially deposited locally is distributed on a picosecond time scale, and most processes seem to be described by a statistical model. Furthermore, bond-selective photochemistry (in which different reactions would occur for excitation of different molecular vibrations) seems unlikely, because reaction is usually slow compared to the energy redistribution process. *See* PHOTOCHEMISTRY.

Philip R. Brooks

Theoretical Methods

The goal of chemical dynamics is to understand kinetic phenomena from the basic laws of molecular mechanics, and it is thus a field which sees close interplay between experimental and theoretical research.

Energy distribution. An important question regarding the dynamics of chemical reactions has to do with the product energy distribution in exothermic reactions. For example, because the hydrogen fluoride (HF) molecule is more strongly bound than the H_2 molecule, reaction (2) releases a considerable amount of energy (more than 30 kcal/mol or 126 kJ/mol). The two possible paths for this energy release to follow are into translations, that is, with HF and H speeding away from each other, or into vibrational motion of HF.

$$\mathrm{F} + \mathrm{H_2} \longrightarrow \mathrm{HF} + \mathrm{H} \qquad (2)$$

In this case it is vibration, and this has rather dramatic consequences; the reaction creates a population inversion among the vibrational energy levels of HF—that is, the higher vibrational levels have more population than the lower levels—and the emission of infrared light from these excited vibrational levels can be made to form a chemical laser. A number of other reactions such as reaction (1) also give a population inversion among the vibrational energy levels, and can thus be used to make lasers.

Most effective energy. The rates of most chemical reactions are increased if they are given more energy. In macroscopic kinetics this corresponds to increasing the temperature, and most reactions are faster at higher temperatures. It seems reasonable, though, that some types of energy will be more effective in accelerating the reaction than others. For example, in reaction (3), where potassium (K) reacts with hydrogen chloride (HCl) to form potassium chloride (KCl), studies in a molecular beam have shown that if HCl is vibrationally excited (by using a laser), this reaction is found to proceed approximately 100 times faster, while the same amount of energy in translational kinetic energy has a smaller effect. Here, therefore, vibrational energy is much more effective than translational energy in accelerating the reaction.

$$\mathrm{K} + \mathrm{HCl} \longrightarrow \mathrm{KCl} + \mathrm{H} \qquad (3)$$

For reaction (2), however, translational energy is more effective than vibrational energy in accelerating the reaction. The general rule of thumb is that vibrational energy is more effective for endothermic reactions (those for which the new molecule is less stable than the original molecule), while translational energy is most effective for exothermic reactions.

Lasers. As seen from the above, lasers are also an important supplement to molecular-beam techniques for probing the dynamics of chemical reactions. Because they are light sources with a very narrow wavelength, they are able to excite molecules to specific quantum states (and also to detect what states molecules are in), an example of which is reaction (3). For polyatomic molecules—that is, those with more than two atoms—there is the even more interesting question of how the rate of reaction depends on which vibration is excited.

For example, when the molecule allyl isocyanide, $CH_2{=}CH{-}CH_2{-}NC$, is given sufficient vibrational energy, the isocyanide part (—NC) will rearrange to the cyanide (—CN) configuration. A laser can be used to excite a C-H bond vibrationally. An interesting question is whether the rate of the rearrangement process depends on which C-H bond is excited. Only with a laser is it possible to excite different C-H bonds and begin to answer such questions. This question of mode-specific chemistry, that is, the question of whether excitation of specific modes of a molecule causes specific chemistry to result, has been a subject of great interest. (For the example above, the reaction is fastest if the C-H bond closest to the NC group is excited.) Mode-specific chemistry would allow much greater control over the course of chemical reactions, and it would be possible to accelerate the rate of some reactions (or reactions at one part of a molecule) and not others. *See* LASER.

Models and methods. Many different theoretical models and methods have been useful in understanding and analyzing all of the phenomena described above. Probably the single most useful approach has been the calculation of classical trajectories. Assuming that the potential energy function or a reasonable approximation is known for the three atoms in reaction (2), for example, it is possible by use of electronic computers to calculate the classical motion of the three atoms. It is thus an easy matter to give the initial molecule more or less vibrational or translational energy, and then compute the probability of reaction. Similarly, the final molecule and atom can be studied to see where the energy appears, that is, as translation or as vibration.

It is thus a relatively straightforward matter theoretically to answer the questions and to see whether or not mode-specific excitation leads to significantly different chemistry than simply increasing the temperature under bulk conditions.

The most crucial step in carrying out these calculations is obtaining the potential energy surface—that is, the potential energy as a function of the positions of the atoms—for the system. **Figure 5** shows a plot of the contours of the potential energy surface for reaction (2). Even without carrying out classical trajectory calculations, it is possible to deduce some of the dynamical features of this reaction; for example, the motion of the system first surmounts a small potential barrier, and then it slides down a steep hill,

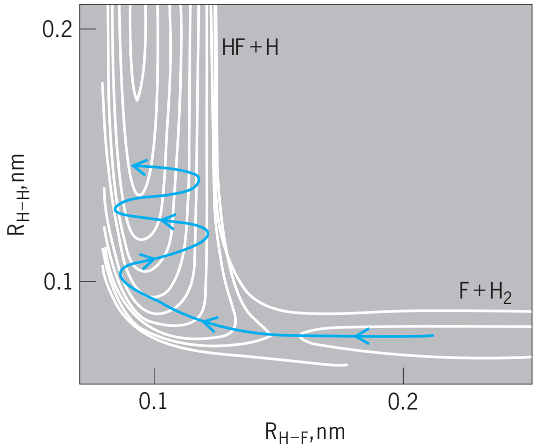

Fig. 5. Contour plot of the potential energy surface for the reaction $F + H_2 = HF + H$, with a typical reactive trajectory indicated.

turning the corner at the bottom of the hill. It is evident that such motion will cause much of the energy released in going down the hill to appear in vibrational motion of HF.

This and other theoretical methods have interacted strongly with experimental research in helping to understand the dynamics of chemical reactions. *See* CHEMICAL KINETICS; INORGANIC PHOTOCHEMISTRY.

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Chemical ecology

The study of ecological interactions mediated by the chemicals that organisms produce. These substances, known as allelochemicals, serve a variety of functions, the growing list of which reflects the rapid discoveries made in this discipline. These compounds influence or regulate interspecific and intraspecific interactions of microorganisms, plants, and animals, and operate within and between all trophic levels—producers, consumers, and decomposers—and in terrestrial, fresh-water, and marine ecosystems.

Function is an important criterion for the classification of allelochemicals. Allelochemicals beneficial to the emitter are called allomones; those beneficial to the recipient are called kairomones. An allomone to one organism can be a kairomone to another. For example, floral scents benefit the plant (allomones) by encouraging pollinators, but also benefit the insect (kairomones) by providing a cue for the location of nectar.

The chemicals involved are diverse in structure and are often of low molecular weight (<10,000). They may be volatile (for example, monoterpene essential oils from peppermint, cyanide from trefoil, musks of mammals, mustard oils from cabbage, aldehyde pheromones in insects) or nonvolatile (such as nicotine alkaloids in tobacco, flavonoids in most plants), and water-soluble (phenols in many insect defenses) or fat-soluble (leaf waxes). Proteins, polypeptides, and amino acids are also found to play an important role.

Plant allelochemicals are often called secondary compounds or metabolites to distinguish them from those chemicals involved in primary metabolism, although this distinction is not always clear. The functions of secondary chemicals were a mystery until 1959, when G. Fraenkel emphasized their potential importance in the interactions of plants and animals. The role of chemicals in the ecology of microorganisms and of animals was recognized earlier: since the discovery of penicillin, scientists have known that fungi can produce substances that destroy bacteria, and the odors of such animals as stink bugs and skunks serve an obvious function.

Chemical defense in plants. Perhaps to compensate for their immobility, plants have made wide use of chemicals for protection against competitors, pathogens, herbivores, and abiotic stresses.

Production of defenses by plants is not cost-free; it requires energy that could be used for other purposes. Although the actual cost is usually not known, many plants do concentrate defensive compounds in those tissues that contain the highest energy reserves or growth potential, such as new leaves or seeds. Some plants may also change the amount of resources used for defense, in response to changes in their environment, and the availability of the raw materials for making defenses, for example, carbon from photosynthesis and nitrogen from soil.

Allelopathy. A chemically mediated competitive interaction between higher plants is referred to as allelopathy. This is one of the few examples in plants where the effects of chemicals can be obvious: observations that areas around the bases of walnut trees are free of plant growth led to the first description of allelopathy. In walnuts, the mechanism involves leaching of the chemical juglone (5-hydroxy napthoquinone) from the leaves to the ground, and this inhibits growth and germination of a variety of plants. Allelopathy appears to occur in many plants, may involve phenolics or terpenoids that are modified in the soil by microorganisms, and is at least partly responsible for the organization of some plant communities. *See* ALLELOPATHY.

Active and passive defenses. Chemicals that are mobilized in response to stress or attack are referred to as active or inducible chemicals, while those that are always present in the plant are referred to as passive or constitutive. In many plants, fungus attack induces the production of defensive compounds called phytoalexins, a diverse chemical group that includes isoflavonoids, terpenoids, polyacetylenes, and furanocoumarins. The phytoalexin is produced in the area immediately surrounding the fungus and probably acts by interfering with the nutrition or membrane permeability of the fungal cells. Plant susceptibility to fungus attack is partly related to the speed of production of phytoalexins. *See* PHYTOALEXINS.

Defensive chemicals can be induced by herbivore attack. For example, when snowshoe hares feed on paper birch there is an increase in the levels of phenolic resins in new growth. These levels decrease with time, and the activity of these induced chemicals is thought to cause population cycles of hares. There has been increasing evidence that inducible defenses, such as phenolics, are important in plant–insect interactions.

Constitutive defenses include the chemical hydrogen cyanide. Trefoil, clover, and ferns have been found to exist in two genetically different forms, one containing cyanide (cyanogenic) and one lacking it (acyanogenic); acyanogenic forms are often preferred by several herbivores. Acacia trees also have these two forms; the acyanogenic forms are protected from herbivores by ants that live in the tree and feed on special food bodies on the leaves. Other constitutive chemicals include some phenolic acids, flavonoids, pyrethrins, and alkaloids. *See* ALKALOID; FLAVONOID; PHENOL.

Diversity of activities. Chemical defenses frequently occur together with certain structures which act as physical defenses, such as spines and hairs. In tomatoes, glandular trichomes (hairlike structures) on the leaf surface contain the toxic chemical 2-tridecanone that is active against many insects, while other glands contain phenolics that polymerize like fast-setting glue.

While many chemicals protect plants by deterring herbivore feeding or by direct toxic effects, other defenses may act more indirectly. Chemicals that mimic juvenile hormones, the antijuvenile hormone substances found in some plants, either arrest development or cause premature development in certain susceptible insect species.

Plant chemicals potentially affect not only the herbivores that feed directly on the plant, but also the microorganisms, predators, or parasites of the herbivore. For example, the tomato plant contains an alkaloid, tomatine, that is effective against certain insect herbivores. The tomato hornworm, however, is capable of detoxifying this alkaloid and can thus use the plant successfully—but a wasp parasite of the hornworm cannot detoxify tomatine, and its effectiveness in parasitizing the hornworm is reduced. Therefore, one indirect effect of the chemical in the plant may be to reduce the effectiveness of natural enemies of the plant pest, thereby actually working to the disadvantage of the plant.

Types of plant defenses. Most plant chemicals can affect a wide variety of herbivores and microorganisms, because the modes of action of the chemicals they manufacture are based on a similarity of biochemical reaction in most target organisms (for example, cyanide is toxic to most organisms). In addition, many plant chemicals may serve multiple roles: resins in the creosote bush serve to defend against herbivores and pathogens, conserve water, and protect against ultraviolet radiation.

It is argued that there are two different types of defensive chemicals in plants. The first type occurs in relatively small amounts, is often toxic in small doses, and poisons the herbivore. These compounds, for example, some phenolic acids, alkaloids, and monoterpenes, may also change in concentration in response to plant damage; that is, they are inducible. These kinds of qualitative defensive compounds are the most common in short-lived or weedy species that are often referred to as unapparent. They are also characteristic of fast-growing species with short-lived leaves. In contrast, the second type of defensive chemicals often occurs in high concentrations, is not very toxic, but may inhibit digestion by herbivores and is not very inducible. These quantitative defenses, such as tannins, are most common in long-lived, so-called apparent plants such as trees that have slow growth rates and long-lived leaves. Some plants may use both types of defenses.

Aquatic habitats. There is accumulating evidence that marine plants may be protected against grazing by similar classes of chemicals to those found in terrestrial plants. In algae, for example, phenols appear to be an important defense against limpets. One interesting difference in the marine environment is the large number of halogenated organic compounds that are rare in terrestrial and fresh-water systems.

Evolution of defenses and adaptation. Through evolution, as plants accumulate defenses, herbivores that are able to bypass the defense in some way are selected for and leave more offspring than others. This in turn selects for new defenses on the part of the plant in a continuing process called coevolution.

Animals that can exploit many plant taxa are called generalists, while those that are restricted to one or a few taxa are called specialists. Specialists often have particular detoxification mechanisms to deal with specific defenses. For example, certain bruchid beetles that feed on seeds containing the toxic nonprotein amino acid canavanine possess enzyme systems that recognize this "false" amino acid and avoid incorporating it into proteins. In addition, they are able to convert the amino acid to ammonia via urea and generate energy in the process. Some generalists possess powerful, inducible detoxification enzymes, while others exhibit morphological adaptations of the gut which prevent absorption of compounds such as tannins, or provide reservoirs for microorganisms that accomplish the detoxification. Animals may avoid eating plants, or parts of plants, with toxins. For instance, monkeys choose low-toxin, high-nutrient plant tissues and are capable of learning which plants to avoid.

Some herbivores that have completely surmounted the plant toxin barrier use the toxin itself as a cue to aid in locating plants. The common white butterfly, *Pieris rapae*, for example, uses mustard oil glycosides, which are a deterrent and toxic to many organisms, to find its mustard family hosts. The monarch butterfly and other insects have gone so far as to store plant defensive chemicals in their bodies as protection against predators.

Chemical defense in animals. Many animals make their own defensive chemicals—such as all of the venoms produced by social insects (bees, wasps, ants), as well as snakes and mites. These venoms are usually proteins, acids or bases, alkaloids, or combinations of chemicals. They are generally injected by biting or stinging, while other defenses are produced as sprays, froths, or droplets from glands. For instance, the bombardier beetle expels hot quinones as a spray from its posterior. A response of one predatory mouse to this action is to bury the beetle's dangerous posterior into the sand before biting the head. There are also darkling beetles that mimic the bombardier's actions but do not have a defensive spray. While insects provide the best examples of chemical defense in animals, such defenses are also found in other groups, such as in stinging cells of jellyfish and in poisonous spurs on the duckbill platypus.

Animals frequently make the same types of toxins as plants, presumably because their function as protective agents is similar. Examples include the production of cyanide by millipedes and bracken fern, phenols in the secretions of grasshoppers and in most plant leaves, alkaloids in ant venoms and pepper plants, and cardiac glycosides in milkweed plants and beetles.

Other organisms, particularly insects, use plant chemicals to defend themselves. For example, the monarch butterfly sequesters or stores cardenolides from the milkweed plant, and the lubber grasshopper can sequester a variety of plant chemicals into its defensive secretion by feeding exclusively on certain plants. Sequestration may be a low-cost defense mechanism and probably arises when insects specialize on particular plants.

Microbial defenses. Competitive microbial interactions are regulated by many chemical exchanges involving toxins. They include compounds such as aflatoxin, botulinus toxin, odors of rotting food, hallucinogens, and a variety of antibiotics. *See* ANTIBIOTIC; TOXIN.

Microorganisms also play a role in chemical interaction with plants and animals that range from the production of toxins that kill insects, such as those produced by the common biological pest control agent *Bacillus thuringiensis*, to cooperative biochemical detoxification of plant toxins by animal symbionts.

Information exchange. A large area of chemical ecology concerns the isolation and identification of chemicals used for communication.

Insects. Pheromones, substances produced by an organism that induce a behavioral or physiological response in an individual of the same species, have been studied particularly well in insects. These signals are compounds that are mutually beneficial to the emitter and sender, such as sex attractants, trail markers, and alarm and aggregation signals.

Sex pheromones are volatile substances, usually produced by the female to attract males. Each species has a characteristic compound that may differ from that of other species by as little as a few atoms. For example, the pheromone of the cabbage looper moth is *cis*-7-dodecenyl acetate; the oriental fruit fly's is *cis*-8-dodecenyl acetate. The activity of these compounds can be destroyed by minor changes in their structure. In addition, sex pheromones generally are active at extremely low concentrations—a few molecules impinging on a moth's antenna may be sufficient to stimulate a response. The pheromone blend released by a female moth may be dominated by one or two components but also contains many trace components. The dominant compounds may attract males, but the full repertoire of male behavior that results in successful mating also involves the trace components.

Pheromones are typically synthesized directly by the animal and are usually derived from fatty acids. In a few cases the pheromone or its immediate precursors may be derived from plants, as in danaid butterflies. Male danaids visit certain nonhost plants solely to obtain pyrrolizidine alkaloids, which are used to make pheromones used in courtship.

Trail pheromones are used by social insects and some lepidopterans to recruit others of its species to a food source. These are synthesized by the animal as well as acquired from hosts, and are diverse in structure. The honeybee uses geraniol, which it acquires from nectar. Methyl 4-methylpyrrole 2-carboxylate, the trail pheromone of the leaf-cutting ant, may be synthesized in the gut by bacteria. The ideal trail pheromone loses its potency over time unless reinforced, and is therefore relatively unstable and difficult to analyze chemically. *See* PHEROMONE.

Vertebrates. Very little work has been done in identifying specific pheromones in vertebrates, particularly mammals. It is known, however, that they are important in marking territory, in individual recognition, and in mating and warning signals. Frequently these signals involve sebaceous oils from the skin, urine, or feces. Some mammals have a very complex series of glands; it is possible that microorganisms on these glands convert urine compounds to components of the signal chemical. The complexity of this chemical mix, and the complexity of the animal, means that the strong positive or negative response to single compounds that is found in some insects is not found as often in mammalian systems. In female primates of several species, mixtures of short-chain organic acids, such as acetic and butanoic, lead to sexual excitation in the male. These same chemicals have been found in human females, but in different concentrations. *See* REPRODUCTIVE BEHAVIOR; SCENT GLAND; TERRITORIALITY.

Plants and microorganisms. Chemical communication may also occur among plants and microorganisms, although it is rarer and less obvious than in animals. The release of ethylene by ripening fruit stimulates the ripening of nearby fruit, thus ensuring simultaneous presentation of an attractive mass for potential dispersers. Certain plants produce high concentrations of volatile isoprenes. The concentrations and composition of these compounds change under stress, but it is not known whether this signal, if it is one, is recognized by other plants.

Bacterial contact and recognition is accomplished by cell wall proteins and by secretions. This type of communication is important in strain recognition, and also takes place in fungi such as *Mucor* prior to mating. Here chemical communication is at the cellular level.

Value. The chemicals involved in chemical interactions between organisms are important in the pharmaceutical, perfume, and many other chemical industries. These substances, together with many antibiotics and pesticides, are based on compounds found in plants. However, information about chemical ecology is only just beginning to be exploited, particularly in the field of plant protection. For example, pheromones which are highly specific and nontoxic are used to trap insect pests for a variety of purposes, including monitoring and population reduction. As the mechanisms of pathogen resistance are understood, the proper chemical attributes may be bred or genetically engineered into plants. For example, the genes for production of a legume seed protein toxin have been transferred to tobacco leaves. The genes were expressed and the leaves became protected from insect attack. The potential for exploiting naturally occurring defenses may thus reduce reliance on costly, potentially hazardous synthetic chemicals. *See* ECOLOGY; GENETIC ENGINEERING; INSECT CONTROL, BIOLOGICAL; INSECTICIDE. Clive G. Jones; Alcinda C. Lewis

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Chemical energy

A useful but obsolescent term for the energy available from elements and compounds when they react, as in a combustion reaction. In precise terminology, there is no such thing as chemical energy, since all energy is stored in matter as either kinetic energy or potential energy. *See* COMBUSTION; ENERGY.

When a chemical reaction takes place, the atoms of the reactants change their bonding pattern and become products. The breaking of bonds in the reactants requires energy, and the formation of bonds in the products releases energy. The net change in energy is commonly referred to as chemical energy. To be more precise, when a reaction takes place, there is an overall change in the enthalpy H of the system as bonds are broken and new bonds are formed. This change in enthalpy is denoted ΔH. Under standard conditions [a pressure of 1 bar (100 kilopascals) and all substances pure], the change is noted ΔH° and called the standard enthalpy of reaction. Provided the pressure is constant, the standard enthalpy can be identified with the energy released as heat (when $\Delta H^\circ < 0$) or gained as heat ($\Delta H^\circ > 0$) when the reaction takes place. Reactions for which $\Delta H^\circ < 0$ are classified as exothermic; those for which $\Delta H^\circ > 0$ are classified as endothermic. All combustions are exothermic, the released heat being used either to provide warmth or to raise the temperature of a working fluid in an engine of some kind. There are very few common endothermic reactions; one example is the dissolution of ammonium nitrate in water (a process utilized in medical cold packs). *See* CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; ENTHALPY; THERMOCHEMISTRY.

The "chemical energy" available from a typical fuel (that is, the enthalpy change accompanying the combustion of the fuel, when carbon-hydrogen bonds are replaced by stronger carbon-oxygen and hydrogen-oxygen bonds) is commonly reported as either the specific enthalpy or the enthalpy density. The specific enthalpy is the standard enthalpy of combustion divided by the mass of the reactant. The enthalpy density is the standard enthalpy of combustion divided by the volume of the reactant. The former is of primary concern when mass is an important consideration, as in raising a rocket into orbit. The latter is of primary concern when storage space is a limitation. The specific enthalpy of hydrogen gas is relatively high (142 kilojoules/g), but its enthalpy density is low (13 kJ/L). The values for octane, a compound representative of gasoline, are 48 kJ/g and 38 MJ/L, respectively (note the change in units). The high enthalpy density of octane means that a gasoline tank need not be large to store a lot of "chemical energy." *See* AIRCRAFT FUEL; ENERGY SOURCES; GASOLINE; ROCKET PROPULSION. Peter W. Atkins

Chemical engineering

The branch of engineering involved in the research, design, improvement, operation, and commercialization of plants, processes, and products for the chemical industry and related fields, such as biotechnology, energy, and materials. The work of chemical engineers has evolved continuously with the changing needs of society. Chemical engineering arose from attempts at inventing ways to make products such as gunpowder and wine. Early on (in the nineteenth century), the large-scale and efficient manufacturing of inorganic chemicals, such as salt, soda ash, sulfuric acid, and nitrogen fixation, were the main occupation of American chemical engineers. However, for the small-scale dyestuff and drug industries in Europe, chemical engineers were less involved. In the twentieth century, large-scale petroleum refining, petrochemicals, and polymers were the dominant industrial problems. In the twenty-first century, the focus has shifted to smaller-scale processes across many disciplines of science and technology, such as molecular biology, genetics, information technology, and nanotechnology. *See* GENETICS; INFORMATION TECHNOLOGY; INORGANIC CHEMISTRY; NANOTECHNOLOGY; PETROCHEMICAL; POLYMER; PROCESS ENGINEERING.

Professional work and achievements. Chemical engineers work in the development, manufacturing, and service sectors. They are engaged in the design, construction, and operation of equipment and plants. Increasingly, chemical engineers are involved in product engineering, which is the design of new products and the improvement of existing products such as controlled drug-delivery devices, biodegradable polymers, and fuel cells. In addition, chemical engineers play an important role in the commercialization of novel medicines, materials, and environmental remediation and recycling technology. *See* DRUG DELIVERY SYSTEMS; FUEL CELL; RECYCLING TECHNOLOGY.

Chemical engineers often play leading roles in the manufacturing industries of basic chemicals and petroleum refining. They work in pharmaceutical, biochemical, biomedical, food, agricultural chemicals, plastics, rubber, textile fibers, paper, ink, soap and cosmetics, and water purification industries. In the electronics industry, the manufacture of integrated circuits and other microelectronic devices involves chemical processing. Chemical engineers also are employed in services, such as education, government, business and professional services, and, increasingly, health care. *See* BIOCHEMICAL ENGINEERING; BIOMEDICAL CHEMICAL ENGINEERING; CHEMICAL PROCESS INDUSTRY; FOOD ENGINEERING; INK; MANUFACTURED FIBER; MICROLITHOGRAPHY; PAPER; PHARMACEUTICAL CHEMISTRY; RUBBER; TEXTILE.

Some characteristic operations in chemical engineering involve the conversion of raw materials (such as petroleum) into useful products (such as gasoline, jet fuel, and asphalt), as well as the conversion and recycling of environmental pollutants (such as municipal waste). Other conversions involve chemical reactions such as the fixation of nitrogen from air into fertilizers for agriculture, physical modifications such as blowing polymers into films and extruding polymers into fibers, and biochemical reactions such as the fermentation of sugar into alcohol. These conversions also involve separations, such as making freshwater out of seawater, recovering penicillin from very dilute solutions in fermentation tanks, and extracting water and waste products from blood in artificial kidneys. *See* CHEMICAL CONVERSION; CHEMICAL SEPARATION; FERMENTATION; NITROGEN FIXATION; PETROLEUM PROCESSING AND REFINING; PLASTICS PROCESSING; WATER DESALINATION.

Education and professional training. Chemical engineers require knowledge in chemistry, biology, mathematics, physics, and machinery. The education and training of chemical engineers includes a rigorous curriculum of courses, laboratories, design projects, and quite often periods of industrial practice or internships. In common with other engineers, mathematics and physics form the core curriculum. The major distinction of chemical engineers is their understanding of chemistry, and increasingly of molecular and cell biology and materials science. *See* CELL BIOLOGY; MATERIALS SCIENCE; MATHEMATICS; MOLECULAR BIOLOGY; PHYSICS.

The earliest engineering education program began in France, where mathematics played a decisive role. The modern chemical engineering curriculum evolved from a program in 1888 at the Massachusetts Institute of Technology by L. M. Norton, which was centered on the study of the applied chemistry of specific inorganic chemicals. The first paradigm, or systemic knowledge, that could be applied to many problems was the concept of unit operations, introduced in 1923 in the *Principles of Chemical Engineering* by W. H. Walker, W. K. Lewis, and W. H. McAdams. The concept of unit operations became the standard taught everywhere and provided the effective tools for the graduates to engineer new chemical industries. Thermodynamics and chemical reaction engineering were added later, and the accreditation of chemical engineering degrees was based on the mastery of these subjects. *See* CHEMICAL REACTOR; CHEMICAL THERMODYNAMICS; UNIT OPERATIONS.

After World War II, during which scientists with no engineering background made the atomic bomb, engineering educators turned toward science for inspiration. Transport phenomena began as the second paradigm of chemical engineering, with the publication (1960) of *Transport Phenomena* by R. B. Bird, W. E. Stewart, and E. N. Lightfoot. The transport of momentum, heat, and mass is fundamental to the unit operations and chemical reactors. Applied mathematics and computation formed the basis for the rational modeling and design of chemical machinery and operations, as well as the systematic optimization of entire chemical plants. *See* TRANSPORT PROCESSES.

In the United States, the American Institute of Chemical Engineers, founded in 1908, is the principal professional society. Chemical engineering became a worldwide force with the founding of the Institution of Chemical Engineers in 1953 and the World Chemical Engineering Council in 2001.

James Wei

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Chemical equilibrium

In a dynamic or kinetic sense, chemical equilibrium is a condition in which a chemical reaction is occurring at equal rates in its forward and reverse directions, so that the concentrations of the reactant and product substances do not change with time. In a thermodynamic sense, it is the condition in which there is no tendency for the composition of the system to change. From the viewpoint of statistical mechanics, the equilibrium state places the system in a condition of maximum freedom (or minimum restraint) compatible with the energy, volume, and composition of the system. The statistical approach has been merged with thermodynamics into a field called statistical thermodynamics; this merger has been of immense value for its intellectual stimulus, as well as for its practical contributions to the study of equilibria. *See* CHEMICAL THERMODYNAMICS; STATISTICAL MECHANICS.

Because thermodynamics is concerned with relationships among observable properties, such as temperature, pressure, concentration, heat, and work, the relationships possess general validity, independent of theories of molecular behavior. Because of the simplicity of the concepts involved, this article utilizes the thermodynamic approach.

Chemical potential. Thermodynamics attributes to each chemical substance a property called the chemical potential, which may be thought of as the tendency of the substance to enter into chemical (or physical) change. Although the absolute chemical potential of a substance cannot be measured directly, differences in chemical potential are measurable. The units of chemical potential are joules per mole.

The importance of the chemical potential lies in its relation to the affinity or driving force of a chemical reaction. It is useful to consider the general reaction (1), and let μ_A be the chemical potential of substance A, μ_B be the chemical potential of B, and so on. Then, according to one of the fundamental principles of thermodynamics (the second law), the reaction will be spontaneous (left to right) when the total chemical potential of the reactants is greater than that of the products. Thus, for spontaneous change (naturally occurring processes), notation (2) applies.

$$aA + bB \rightleftharpoons gG + hH \tag{1}$$

$$[g\mu_G + h\mu_H] - [a\mu_A + b\mu_B] < 0 \tag{2}$$

When equilibrium is reached, the total chemical potentials of products and reactants become equal; thus Eq. (3) holds at equilibrium. The difference in chemical potentials in Eqs. (2) and (3) is called the driving force or affinity of the process or reaction; the affinity is zero when the chemical system is in chemical equilibrium.

$$[g\mu_G + h\mu_H] - [a\mu_A + b\mu_B] = 0 \tag{3}$$

For reactions at constant temperature and pressure (the usual restraints in a chemical laboratory), the difference in chemical potentials becomes equal to the Gibbs energy change $\Delta_r G$ for the process in Eq. (4). The decrease in Gibbs energy represents the maximum net work obtainable from the process. When no more work is obtainable, then the system is at equilibrium. Conversely, if the value of $\Delta_r G$ for a process is positive, some useful work will have to be expended upon the process, or reaction, in order to make it proceed from left to right; the process cannot proceed naturally or spontaneously. The term "spontaneously" as used here implies only that a process can occur. It does not imply that the reaction will actually occur. Thus, the reaction between hydrogen and oxygen is a spontaneous process in the sense of the term as used here, even though a mixture of hydrogen and oxygen can remain unchanged for years unless ignited or exposed to a catalyst.

$$\Delta_r G = [g\mu_G + h\mu_H] - [a\mu_A + b\mu_B] \tag{4}$$

Because, by definition, a catalyst does not undergo a net chemical change during the reaction, its chemical potential does not appear in Eqs. (2), (3), and (4). A catalyst, therefore, can contribute nothing to the driving force of a reaction, nor can it, in consequence, alter the position of the chemical equilibrium in a system. *See* CATALYSIS.

In addition to furnishing a criterion for the equilibrium state of a chemical system, the thermodynamic method goes much further. In many cases, it yields a relation between the change in chemical potentials (or change in Gibbs energy) and the equilibrium concentrations of the substances involved in the reaction. To do this, the chemical potential must be expressed as a function of concentration and possibly other properties of the substance.

The chemical potential μ is usually represented by Eq. (5), where R is the gas constant, T is the absolute temperature, x is the concentration of the substance, γ is the activity coefficient of the substance, and μ^0 is the chemical potential of the substance in its standard state. *See* CONCENTRATION SCALES.

$$\mu = \mu^0 + RT \ln x + RT \ln \gamma \tag{5}$$

For substances obeying the laws of ideal solutions (or ideal gases), the last term, $RT\ln\gamma$, is zero ($\gamma = 1$), because it is a measure of the deviation from ideal behavior caused by intermolecular or inter-ionic forces. An ideal solution would then be a solution for which $RT\ln\gamma$ is zero ($\gamma = 1$) over the whole concentration range. For real solutions, the state standard (where γ is unity) is generally chosen as the pure substance [mole fraction = 1 at 1 bar (100 kilopascals) and the temperature of interest] for solids and solvents, and as the hypothetical ideal gas or the unit concentration solute in solution at 1 bar and the temperature of interest. Although the activity coefficient γ is dimensionless, its numerical values depend upon the particular concentration scale x with which it is associated.

Although the choice of concentration scales is a matter of convenience, the following are conventionally used: $x = p$ = partial pressure, for gases; $x = c$

(or m) = molar (or molal) concentrations, respectively, for solutes in electrolytic solutions; x = mole fraction, for solids and solvents. When the choice is not established by convention, the mole fraction scale is preferred.

Activity and standard states. It is often convenient to utilize the product, γx, called the activity of the substance and defined by $a = \gamma x$. The activity may be looked upon as an effective concentration of the substance, measured in the same units as the concentration x with which it is associated. The standard state of the substance is then defined as the state of unit activity (where $a = x = 1$) at 1 bar and the temperature of interest and is characterized by the standard chemical potential μ^0. Clearly, the terms μ^0, γ, and x are not independent; the choice of the activity scale serves to fix the standard state. For example, for hydrochloric acid, the standard state for the solute (HCl) would be an (hypothetical) ideal 1 molar (or 1 molal) solution, and for the solvent (H_2O) the standard state would be pure water (mole fraction = 1), both at 1 bar and the temperature of interest. The reference state would be an infinitely dilute solution; here the activity coefficients would be unity for both solute and solvent. For the vapor of HCl above the solution, the standard state would be the hypothetical gaseous state at 1 bar partial pressure. For gases, the term "fugacity" is often used instead of "activity." *See* FUGACITY.

Equilibrium constant. If the general reaction in Eq. (1) occurs at constant temperature T and pressure P when all of the substances involved are in their standard states of unit activity, Eq. (4) would become Eq. (6). The quantity $\Delta_r G^0$ is known as the standard

$$\Delta_r G^0 = \left[g\mu^0_{\mathrm{G}} + h\mu^0_{\mathrm{H}}\right] - \left[a\mu^0_{\mathrm{A}} + b\mu^0_{\mathrm{B}}\right] \qquad (6)$$

Gibbs energy change for the reaction at the temperature and pressure for the chosen standard states. (Standard state properties are commonly designated by a superscript zero, as in $\Delta_r G^0$, μ^0.) Since each of the standard chemical potentials (μ^0_i) is a unique property determined by the temperature, pressure, standard state, and chemical identity of the substance concerned, the standard free energy change ΔG^0 is a constant characteristic of the particular reaction for the chosen temperature, pressure, and standard states.

If, for Eq. (1), at constant temperature and pressure, the chemical potential of each substance is expressed in terms of Eq. (5), then the Gibbs energy change for the reaction, from Eq. (4), becomes Eq. (7) in terms of the activities and the standard

$$\Delta_r G = \Delta_r G^0 + RT \ln \frac{a^g_{\mathrm{G}} a^h_{\mathrm{H}}}{a^a_{\mathrm{A}} a^b_{\mathrm{B}}} \qquad (7)$$

Gibbs energy change, Eq. (6). Equation (7) is often written in the form of Eq. (8), where Q is the ratio

$$\Delta_r G = \Delta_r G^0 + RT \ln Q \qquad (8)$$

of the activities of products to the activities of reactants, each activity bearing as an exponent the corresponding coefficient in the balanced equation for the reaction [as in Eq. (7)]. The standard Gibbs energy change $\Delta_r G^0$ serves as a reference point from which the actual Gibbs energy change $\Delta_r G$ can be calculated in terms of the activities of the reacting substances.

When the system has come to chemical equilibrium at constant temperature and pressure, $\Delta_r G = 0$, from Eq. (3). Equation (7) then leads to the very important relation shown in Eq. (9), where the value of K is shown as Eq. (10), and the activities are

$$\Delta_r G^0 = -RT \ln K \qquad (9)$$

$$K = \left[\frac{a^g_{\mathrm{G}} a^h_{\mathrm{H}}}{a^a_{\mathrm{A}} a^b_{\mathrm{B}}}\right] \qquad (10)$$

the equilibrium values. The quantity K is called the equilibrium constant for the reaction. The equilibrium constant is a characteristic property of the reaction system, because it is determined uniquely at a given temperature in terms of the standard Gibbs energy change. The term $-\Delta_r G^0$ represents the maximum net work that the reaction could make available when carried out at constant temperature and pressure with the substances in their standard states. It should be clear from Eq. (6) that the magnitude of $\Delta_r G^0$ is directly proportional to the amount of material represented in the reaction in Eq. (1). Likewise, Eqs. (7) through (10) denote this same proportionality through the exponents a, b, g, and h in the terms K and Q. Naturally, the value of $\Delta_r G^0$, as well as K and Q, will depend upon the particular concentration scales and standard states selected for the system. Therefore it is essential that sufficient information be stated about a system to fully describe the chosen standard states.

Equations (8) and (10) can be combined in the form of Eq. (11), sometimes denoted as the Lewis

$$\Delta_r G = RT \ln \frac{Q}{K} \qquad (11)$$

equation after G. N. Lewis, who was the first to formulate this equation. When Q for a specified set of conditions is larger than K (so that $\Delta_r G$ is positive), the proposed reaction cannot occur left to right. On the other hand, when Q is less than K, then the proposed process or reaction can occur. The equilibrium constant thus serves as a measure of the position of chemical equilibrium for a system. For a proposed process for which Q is greater than K, the reaction system would have to move away from its equilibrium state (impossible of its own accord) to proceed from left to right, and for a proposed process for which Q is less than K, the process would bring the system closer to its equilibrium state (as in all naturally occurring processes).

Instead of activities, values of concentrations and activity coefficients at equilibrium may be used to express the form of the equilibrium constant K in Eq. (12). This gives the equilibrium constant as a

$$K = \left[\frac{x^g_{\mathrm{G}} x^h_{\mathrm{H}}}{x^a_{\mathrm{A}} x^b_{\mathrm{B}}}\right] \cdot \left[\frac{\gamma^g_{\mathrm{G}} \gamma^h_{\mathrm{H}}}{\gamma^a_{\mathrm{A}} \gamma^b_{\mathrm{B}}}\right] \qquad (12)$$

product of two terms. The first term, involving concentrations, is directly measurable if the system can be analyzed at equilibrium. On the other hand, the activity coefficient term, as seen in Eq. (13), is frequently difficult to evaluate.

$$K_\gamma = \frac{\gamma_G^g \gamma_H^b}{\gamma_A^a \gamma_B^b} \tag{13}$$

Intensive studies of activity coefficients made upon a wide variety of chemical systems led to a number of simplifying principles and some useful theoretical treatments of the subject. For gases, the activity coefficients differ only slightly from unity for pressures up to a few atmospheres and often can be evaluated from equation-of-state data. For mixtures of nonelectrolytes, the values also are not far from unity in many cases. For solutions of electrolytes, the activity coefficients vary greatly with concentration, and in many cases approach unity only below a useful or even attainable concentration. The theoretical treatments of P. Debye, E. Hückel, and others have systematized the patterns of electrolyte behavior, making possible a reasonable estimate of the activity coefficients of electrolytes in many cases. *See* ACTIVITY (THERMODYNAMICS); SOLUTION.

In general, the function K_γ, Eq. (13), approaches unity as the composition of the system approaches ideal behavior, so in practice most equilibrium constants K are evaluated through some suitable extrapolation procedure involving Eq. (12). See the discussion following Eq. (5).

For many approximate calculations or when data for K_γ are scarce, it is common to express the equilibrium constant as the concentration term only; that is, Eq. (14) is applied.

$$K_{\text{app}} = \frac{x_G^g x_H^b}{x_A^a x_B^b} \approx K \tag{14}$$

Unless K_γ is a rather insensitive function of concentration, the so-called constants (K_{app} denotes an apparent or approximate value of K), obtained in this manner are not constant as the composition is varied, and even though approximately constant, may vary considerably from the true value of K. Although the practice of assigning K_γ a value of unity will often give useful results and is frequently the only expedient available, the results must be used with caution.

The kinetic concept of chemical equilibrium introduced by C. M. Guldberg and P. Waage (1864) led to the formulation of the equilibrium constant in terms of concentrations. Although the concept is correct in terms of the dynamic picture of opposing reactions occurring at equal speeds, it was not successful in coping with the problems of activity coefficients and cannot lead to the useful relations, Eqs. (4) and (11), in terms of an energetic criterion for the position of equilibrium. Conversely, the thermodynamic approach yields no relationship between the driving force at the reaction and the rate of approach to equilibrium. *See* CHEMICAL DYNAMICS.

The influence of temperature upon the chemical potentials, and hence upon the equilibrium constant, is given by the Gibbs-Helmholtz equation (15).

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^0}{RT^2} \tag{15}$$

The derivative on the left represents the slope of the curve obtained when values of ln K for a reaction, obtained at different temperatures, are plotted against temperature. The standard enthalpy of reaction $\Delta_r H^0$ for the temperature T at which the slope is measured, is the heat effect which could also be observed by carrying out the reaction involving the standard states in a calorimeter at the corresponding temperature and 1 bar.

For endothermic reactions, which absorb heat ($\Delta_r H^0$ positive), K increases with increasing temperature. For exothermic reactions, which evolve heat ($\Delta_r H^0$ negative), K decreases with increasing temperature and the yield of products is reduced. A more useful arrangement of Eq. (15) is shown in Eq. (16).

$$\frac{d \ln K}{d(1/T)} = \frac{-\Delta_r H^0}{R} \tag{16}$$

Plots of ln K against $1/T$ are nearly linear for reactions where the value of $\Delta_r H^0$ changes slowly with temperature. Hence, over small temperature ranges, Eq. (16) becomes, in integrated form, Eq. (17).

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^0}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \tag{17}$$

This relation is much used for calculating heats of reaction from two equilibrium measurements or for determining an equilibrium constant K_2 at temperature T_2 from values of K_1, and $\Delta_r H^0$.

For accurate work, or for extending the calculations over a wide range of temperature, $\Delta_r H^0$ must be known as a function of temperature before Eq. (15) or (16) can be integrated. When sufficient heat capacity data are available, Kirchhoff's equation, involving the difference in heat capacities between the products and reactants, Eq. (18), may be combined with Eq. (15) to yield Eq. (19).

$$\Delta_r H^0 = \Delta_r H_0^0 + \alpha T + \frac{\beta T^2}{2} + \frac{\delta T^3}{3} \tag{18}$$

$$R \ln K = -\frac{\Delta_r H_0^0}{T} + \alpha \ln T + \frac{\beta T}{2} + \frac{\delta T^2}{6} + I \tag{19}$$

In these equations, the coefficients α, β, and δ are determined from heat capacity data; the constants $\Delta_r H_0^0$ and I require knowledge of one value of $\Delta_r H^0$ and one value of K, or values of K at two temperatures. *See* HEAT CAPACITY; THERMOCHEMISTRY.

Homogeneous equilibria. These equilibria involve single-phase systems: gaseous, liquid, or solid solutions.

A representative gas-phase equilibrium is the ammonia synthesis shown in Eq. (20), where (g) denotes a gas-phase species.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{20}$$

The most natural concentration measures are mole fraction or partial pressure. The partial pressures p_i are defined in terms of mole fractions x_i, and the total pressure P by $p_i = x_i P$. For low pressures, where activity coefficients are practically unity, Eq. (21) holds. Equation (21) is a special case of Eq. (22), where Δn is the change in

$$K_p = \frac{p^2_{\mathrm{NH_3}}}{p_{\mathrm{N_2}} p^3_{\mathrm{H_2}}} = \frac{x^2_{\mathrm{NH_3}}}{x_{\mathrm{N_2}} x^3_{\mathrm{H_2}}} P^{-2} \qquad (21)$$

$$K_p = K_x P^{\Delta n} \qquad (22)$$

the number of moles of gases [$\Delta r = -2$ for Eq. (20)]. The mole fraction equilibrium constant K_x is pressure dependent, but K_p is independent of pressure. Consequently, an increase in total pressure P must lead to an increase in K_x in this case. If the increase in total pressure is due to a decrease in volume of the system, then the result will be an increased yield of products (NH_3). An increase in pressure brought about by injection of an inert gas into a constant volume system would not affect the partial pressures of the reacting gases nor the ultimate yield of products. The value of K_x, and thus that of $\Delta_r G_x$, will be affected by a change in total pressure owing to a change in the net work of mixing and unmixing the gases. The reaction described by Eq. (20) is exothermic, so better yields will be obtained at lower temperatures. However, the rate of attainment of equilibrium in this case is very slow at low temperatures [Eq. (15)].

A typical liquid-phase equilibrium is the deprotonation of acetic acid in water, reaction (23) and Eq. (24), where (aq) denotes an aqueous-phase

$$\mathrm{HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)} \qquad (23)$$

$$\frac{K}{K_\gamma} = \frac{(m_{\mathrm{H_3O^+}})(m_{\mathrm{C_2H_3O_2^-}})}{m_{\mathrm{HC_2H_3O_2}} a_{\mathrm{H_2O}}} \qquad (24)$$

species and (l) denotes a liquid-phase solvent. In this particular case, the activity coefficient ratio K_γ is less than unity in dilute solutions. The activity of water $a_{\mathrm{H_2}}\mathrm{O} \simeq x_{\mathrm{H_2}}\mathrm{O}$ at low molalities (≤ 1 *m*) is close to unity. For this reason, $a_{\mathrm{H_2}}\mathrm{O}$ is commonly omitted in the formulation of the equilibrium constant expressions of this type, because $a_{\mathrm{H_2}}\mathrm{O} \simeq 1$. *See* IONIC EQUILIBRIUM.

Heterogeneous equilibria. These are usually studied at constant pressure, because at least one of the phases will be a solid or a liquid. The imposed pressure may be that of an equilibrium gaseous phase, or it may be an externally controlled pressure.

In describing such systems, as for all reaction systems, the nature of each phase must be specified. In the examples to follow, s, l, g, aq, and soln identify solid, liquid, gaseous, aqueous, and nonaqueous phases, respectively. For solutions or mixtures, the composition is needed, in addition to the temperature and pressure, to complete the specification of the system; the nature of any solvent also must be specified.

In the equilibrium shown as (25), the relationship of Eq. (26) holds. Here $K \approx p/x$, the ratio of

$$\mathrm{H_2O(l) \rightleftharpoons H_2O(g)} \qquad (25)$$

$$\Delta_r G^0 = \mu_g^0 - \mu_l^0 = -RT \ln \frac{p}{x} \qquad (26)$$

the vapor pressure p to the liquid mole fraction x. For pure water, the equilibrium constant is approximately equal to the vapor pressure of water at least at low pressures. When a small amount of solute is added, thereby decreasing the mole fraction of solvent, the vapor pressure p must be lowered to maintain equilibrium (Raoult's law). The effect of the total applied pressure P upon the vapor pressure p of the liquid is given by the Gibbs-Poynting equation (27). Here V_l and V_g are the molar volumes

$$\left[\frac{dp}{dP}\right]_T = \frac{V_l}{V_g} \qquad (27)$$

of liquid and vapor, respectively. The equilibrium vapor pressure will increase as the total pressure is increased (both V_l and V_g are positive and the activity of the liquid increases with pressure). If the external pressure is applied to a solution by a semipermeable membrane, then an applied pressure can be found which will restore the vapor pressure (or activity) of the solvent to its standard state value. *See* OSMOSIS.

For a solid, such as barium sulfate, $BaSO_4$, which dissolves in water as shown in Eq. (28), the equilibrium relationship is shown in Eq. (29). When the

$$\mathrm{BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)} \qquad (28)$$

$$K^0 = \frac{a_{\mathrm{Ba^{2+}}} + a_{\mathrm{SO_4{}^{2-}}}}{a_{\mathrm{BaSO_4(s)}}} \qquad (29)$$

solid state is pure, its activity is unity at 1 bar. If the solid is extremely finely divided, then its activity is greater than unity; with this increase in the activity of the solid state, the solubility must increase to maintain equilibrium. On the other hand, inclusion of foreign ions in the crystal lattice (solid solution formation) lowers the activity of the solid state.

When a gas, such as CO_2, is dissolved in a liquid, its equilibrium with the gas phase is as shown in Eq. (30). Equation (31), Henry's law, represents the

$$\mathrm{CO_2(soln) \rightleftharpoons CO_2(g)} \qquad (30)$$

$$K = \frac{a_{\mathrm{CO_2(g)}}}{a_{\mathrm{CO_2(soln)}}} \approx \frac{P_{\mathrm{CO_2}}}{m_{\mathrm{CO_2}}} \qquad (31)$$

equilibrium constant for this equation, where *m* is the molality of dissolved CO_2. When the gas dissociates in the liquid, as in reaction (32), Eq. (33) may

$$\mathrm{H^+(aq) + Cl^-(aq) \rightleftharpoons HCl(g)} \qquad (32)$$

$$K = \frac{p}{m^2_{\mathrm{HCl}}} \cdot K_\gamma \qquad (33)$$

be utilized. Here *m* is the molality of dissolved HCl.

Similarly, when a solute distributes itself between two immiscible phases, that is, $nA(\text{soln } 1) \rightleftharpoons A_n(\text{soln } 2)$, the equilibrium constant takes the form of Eq. (34). The equilibrium concentrations c_i in

$$K = \frac{c_{A_n}}{c_A^n} \cdot K_\gamma \qquad (34)$$

Eq. (34) reflect the relative solubilities of the solute in the two phases; since solubilities may vary widely, solvent extraction may provide an effective means for concentrating a widely dispersed solute. *See* EXTRACTION.

When components form immiscible phases at equilibrium, each condensed phase will be a saturated solution; complete immiscibility is impossible in principle, because the chemical potential of any component must be the same in all phases. The separation of a liquid system into two liquid phases is a manifestation of the nonideality of the solutions. For practical purposes, however, many solids may be regarded as immiscible because of the stringent requirements associated with formation of solid solutions.

In reactions involving condensed and immiscible phases, for example, reaction (35), there can be no

$$\mathrm{Pb(s)} + 2\mathrm{AgCl(s)} \rightleftharpoons \mathrm{PbCl_2(s)} + 2\mathrm{Ag(s)} \qquad (35)$$

change in concentration of any phase during the reaction. In such a case the Q term in Eq. (10) will be constant, and $\Delta_r G$ is fixed at a given pressure and temperature. Although a reaction is possible, there is at most one pressure at each temperature for which $\Delta_r G$ could be zero. Such is the case in transition phenomena, or melting-freezing phenomena. From the phase-rule viewpoint, the system in reaction (35) has only one degree of freedom if reaction is possible, so once a value of P or T is chosen, the remaining variable (T or P) is fixed by nature at equilibrium. *See* PHASE RULE.

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Chemical fuel

The principal fuels used in internal combustion engines (automobiles, diesel, and turbojet) and in the furnaces of stationary power plants are organic fossil fuels. These fuels, and others derived from them by various refining and separation processes, are found in the earth in the solid (coal), liquid (petroleum), and gas (natural gas) phases.

Special fuels to improve the performance of combustion engines are obtained by synthetic chemical procedures. These special fuels serve to increase the fuel specific impulse of the engine (specific impulse is the force produced by the engine multiplied by the time over which it is produced, divided by the mass of the fuel) or to increase the heat of combustion available to the engine per unit mass or per unit volume of the fuel. A special fuel which possesses a very high heat of combustion per unit mass is liquid hydrogen. It has been used along with liquid oxygen in rocket engines. Because of its low liquid density, liquid hydrogen is not too useful in systems requiring high heats of combustion per unit volume of fuel (“volume-limited” systems). In combination with liquid fluorine, liquid hydrogen produces extremely large specific impulses. *See* AIRCRAFT FUEL.

A special fuel which produces high flame temperatures of the order of 9000°F (5000°C) is gaseous cyanogen, C_2N_2. This is used with gaseous oxygen as the oxidizer. The liquid fuel hydrazine, N_2H_4, and other hydrazine-based fuels, with the liquid oxidizer nitrogen tetroxide, N_2O_4, are used in many space-oriented rocket engines. The boron hydrides, such as diborane, B_2H_6, and pentaborane, B_5H_9, are high-energy fuels which are being used in advanced rocket engines. *See* BORANE.

For air-breathing propulsion engines (turbojets and ramjets), hydrocarbon fuels are most often used. For some applications, metal alkyl fuels which are pyrophoric (that is, ignite spontaneously in the presence of air), and even liquid hydrogen, are being used.

A partial list of additional liquid fuels and their associated oxidizers is shown in the **table**.

Fuels which liberate heat in the absence of an oxidizer while decomposing either spontaneously or because of the presence of a catalyst are called monopropellants and have been used in rocket engines. Examples of these monopropellants are hydrogen peroxide, H_2O_2, and nitromethane, CH_3NO_2.

Liquid fuels and oxidizers are used in most large-thrust (large propulsive force) rocket engines. When thrust is not a consideration, solid-propellant fuels and oxidizers are frequently employed because of the lack of moving parts such as valves and pumps, and the consequent simplicity of this type of rocket engine. Solid fuels fall into two broad classes, double-base and composites. Double-base fuels are compounded of nitroglycerin (glycerol trinitrate) and nitrocellulose, with no separate oxidizer required. The nitroglycerin plasticizes and swells the nitrocellulose, leading to a propellant of relatively high strength and low elongation. The double-base propellant is generally formed in a mold into the desired shape (called a grain) required for the rocket case. Composite propellants are made of a fuel and

Liquid fuels and their associated oxidizers

Fuel	Oxidizer
Ammonia	Liquid oxygen
95% Ethyl alcohol	Liquid oxygen
Methyl alcohol	87% Hydrogen peroxide
Aniline	Red fuming nitric acid
Furfural alcohol	Red fuming nitric acid

an oxidizer. The latter could be an inorganic perchlorate such as ammonium perchlorate, NH_4ClO_4, or potassium perchlorate, $KClO_4$, or a nitrate such as ammonium nitrate, NH_4NO_3, potassium nitrate, KNO_3, or sodium nitrate, $NaNO_3$. Fuels for composite propellants are generally the asphalt-oil-type, thermosetting plastics (phenol formaldehyde and phenolfurfural resins have been used) or several types of synthetic rubber and gumlike substances. Recently, metal particles such as boron, aluminum, and beryllium have been added to solid propellants to increase their heats of combustion and to eliminate certain types of combustion instability. *See* HYDROGEN PEROXIDE; ROCKET PROPULSION. Wallace Chinitz

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Chemical kinetics

A branch of physical chemistry that seeks to measure the rates of chemical reactions, describe them in terms of elementary steps, and understand them in terms of the fundamental interactions between molecules.

Reaction Kinetics

Although the ultimate state of a chemical system is specified by thermodynamics, the time required to reach that equilibrium state is highly dependent upon the reaction. For example, diamonds are thermodynamically unstable with respect to graphite, but the rate of transformation of diamonds to graphite is negligible. As a consequence, determining the rate of chemical reactions has proved to be important for practical reasons. Rate studies have also yielded fundamental information about the details of the nuclear rearrangements which constitute the chemical reaction.

Traditional chemical kinetic investigations of the reaction between species X and Y to form Z and W, reaction (1), sought a rate of the form given in Eq. (2),

$$\mathrm{X + Y \rightarrow Z + W} \qquad (1)$$

$$d[\mathrm{Z}]/dt = kf([X], [Y], [Z], [W]) \qquad (2)$$

where $d[\mathrm{Z}]/dt$ is the rate of appearance of product Z, f is some function of concentrations of X, Y, Z, and W which are themselves functions of time, and k is the rate constant. Chemical reactions are incredibly diverse, and often the function f is quite complicated, even for seemingly simple reactions such as that in which hydrogen and bromine combine directly to form hydrogen bromide (HBr). This is an example of a complex reaction which proceeds through a sequence of simpler reactions, called elementary reactions. For reaction (3*d*), the sequence of elementary reactions is a chain mechanism known to involve a series of steps, reactions (3*a*)–(3*c*). This sequence of elementary reactions was formerly known

$$\mathrm{Br_2 \rightarrow 2Br} \qquad (3a)$$

$$\mathrm{Br + H_2 \rightarrow HBr + Br} \qquad (3b)$$

$$\mathrm{H + Br_2 \rightarrow HBr + Br} \qquad (3c)$$

$$\mathrm{H_2 + Br_2 \rightarrow 2HBr} \qquad (3d)$$

as the reaction mechanism, but in the chemical dynamical sense the word mechanism is reserved to mean the detailed motion of the nuclei during a collision.

Bimolecular processes. An elementary reaction is considered to occur exactly as written. Reaction (3*b*) is assumed to occur when a bromine atom hits a hydrogen molecule. The products of the collision are a hydrogen bromide molecule and a hydrogen atom. On the other hand, the overall reaction is a sequence of these elementary steps and on a molecular basis does not occur as reaction (3*d*) is written. With few exceptions, the rate law for an elementary reaction $\mathrm{A + B \rightarrow C + D}$ is given by $d[\mathrm{C}]/dt = k[\mathrm{A}][\mathrm{B}]$. The order (sum of the exponents of the concentrations) is two, which is expected if the reaction is bimolecular (requires only species A to collide with species B). The rate constant k for such a reaction depends very strongly on temperature, and is usually expressed as $k = Z_{\mathrm{AB}}\rho \exp(-E_a/RT)$. Z_{AB} is the frequency of collision between A and B calculated from molecular diameters and temperature; ρ is an empirically determined steric factor which arises because only collisions with the proper orientation of reagents will be effective; and E_a, the experimentally determined activation energy, apparently reflects the need to overcome repulsive forces before the reagents can get close enough to react.

Unimolecular processes. In some instances, especially for decompositions, $\mathrm{AB \rightarrow A + B}$, the elementary reaction step is first-order, Eq. (4), which

$$d[\mathrm{A}]/dt = d[\mathrm{B}]/dt = k[\mathrm{AB}] \qquad (4)$$

means that the reaction is unimolecular. The species AB does not spontaneously dissociate; it must first be given some critical amount of energy, usually through collisions, to form an excited species AB^*. It is the species AB^* which decomposes unimolecularly. Philip R. Brooks

Relaxation Methods

Considerable use has been made of perturbation techniques to measure rates and determine mechanisms of rapid chemical reactions. These methods provide measurements of chemical reaction rates by displacing equilibria. In situations where the reaction of interest occurs in a system at equilibrium, perturbation techniques called relaxation methods have been found most effective for determining reaction rate constants.

A chemical system at equilibrium is one in which the rate of a forward reaction is exactly balanced by the rate of the corresponding back reaction. Examples are chemical reactions occurring in liquid solutions, such as the familiar equilibrium in pure water, shown in reaction (5). The molar equilibrium constant at 25°C (77°F) is given by Eq. (6), where

$$\mathrm{H_2O} \underset{k_b}{\rightleftharpoons} \mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \tag{5}$$

$$K_{\mathrm{eq}} = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]} = \frac{10^{-14}}{55.5} = 1.8 \times 10^{-16} \tag{6}$$

bracketed quantities indicate molar concentrations. It arises naturally from the equality of forward and backward reaction rates, Eq. (7). Here k_f and k_b are

$$k_f[\mathrm{H_2O}] = k_b[\mathrm{H^+}][\mathrm{OH^-}] \tag{7}$$

the respective rate constants that depend on temperature but not concentrations. Furthermore, the combination of Eqs. (6) and (7) gives rise to Eq. (8).

$$K_{\mathrm{eq}} = k_f/k_b = 1.8 \times 10^{-16} \tag{8}$$

Thus a reasonable question might be what the numerical values of k_f in units of $\mathrm{s^{-1}}$ and k_b in units of $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ must be to satisfy Eqs. (6) through (8) in water at room temperature. Stated another way, when a liter of 1 *M* hydrochloric acid is poured into a liter of 1 *M* sodium hydroxide (with considerable hazardous sputtering), how rapidly do the hydronium ions, $\mathrm{H^+}(aq)$, react with hydroxide ions, $\mathrm{OH^-}(aq)$, to produce a warm 0.5 *M* aqueous solution of sodium chloride? In the early 1950s it was asserted that such a reaction is instantaneous. Turbulent mixing techniques were (and still are) insufficiently fast (mixing time of the order of 1 ms) for this particular reaction to occur outside the mixing chamber. The relaxation techniques were conceived by M. Eigen, who accepted the implied challenge of measuring the rates of seemingly immeasurably fast reactions. *See* ULTRAFAST MOLECULAR PROCESSES.

The essence of any of the relaxation methods is the perturbation of a chemical equilibrium (by a small change in temperature, pressure, electric-field intensity, or solvent composition) in so sudden a fashion that the chemical system, in seeking to reachieve equilibrium, is forced by the comparative slowness of the chemical reactions to lag behind the perturbation (**Fig. 1**).

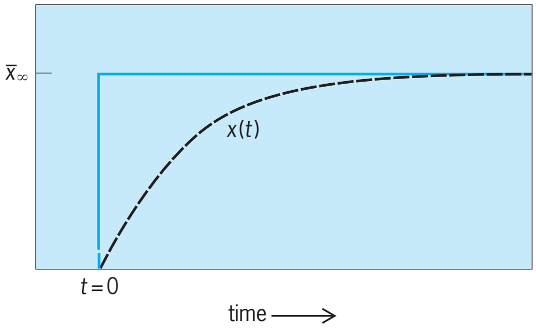

Fig. 1. Relaxational response to a rectangular step function in an external parameter such as temperature or pressure. The broken line represents the time course of the adjustment (relaxation) of the chemical equilibrium to the new temperature or pressure. (*After C. Bernasconi, Relaxation Kinetics, Academic Press, 1976*)

Temperature jump. Reaction (5) has a nonzero standard enthalpy change, ΔH°, associated with it, so that a small increase in the temperature of the water ($\mathrm{H_2O}$) requires the concentrations of hydrogen ions $[\mathrm{H^+}]$ and hydroxide ions $[\mathrm{OH^-}]$ to increase slightly, and $[\mathrm{H_2O}]$ to decrease correspondingly, for chemical equilibrium to be restored at the new higher temperature. Thus a small sample cell containing a very pure sample of water may be made one arm of a Wheatstone conductance bridge, and further configured so that a pulse of energy from a microwave source (or infrared laser of appropriate wavelength) is dissipated in the sample liquid. The resulting rise in temperature of about 2°C (3.6°F) will produce a small increase in conductance that will have an exponential shape and a time constant or relaxation time $\tau \simeq 27$ microseconds; τ is the time required for the signal amplitude to drop to $1/e = 1/2.718$ of its initial value, where e is the base of natural logarithms.

In pure water at 25°C (77°F), $[\mathrm{H^+}] = [\mathrm{OH^-}] = 10^{-7}$ *M*, and for small perturbations, the value for τ is given by Eq. (9), from which it follows that $k_b \simeq 1.8 \times 10^{11}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$. This is an exceptionally large rate constant for a bimolecular reaction between oppositely charged ions in aqueous solution and is, in fact, larger than that for any other diffusive encounter between ions in water. Eigen and L. DeMaeyer, who first determined this rate constant (using another relaxation method called the electric-field jump method), attributed the great speed of the back reaction of the equilibrium, reaction (5), to the exceptionally rapid motion of a proton through water, accomplished by the successive rotations of a long string of neighboring water molecules (Grotthuss mechanism). Since sample solutions can be heated by a mode-locked laser on a picosecond time scale or by a bunsen burner on a time scale of minutes, the temperature jump (T-jump) relaxation method just described is very versatile. The choice of the particular means of effecting the temperature perturbation is dictated only by the requirement that the temperature rise somewhat more rapidly than the time constant of the chemical reaction to be explored, so that a tedious deconvolution can be avoided. The discharge of a high-voltage (15–30-kV) capacitor through the sample liquid containing sufficient inert electrolyte to make it a good electrical conductor is the now classic Joule heating T-jump method used by Eigen and coworkers in their pioneering studies. A schematic of such an apparatus is shown in **Fig. 2**. The 30-kV voltage generator charges the 0.1-microfarad condenser to the voltage at which the spark gap breaks down. The condenser then discharges across the spark gap and through the sample cell, containing

$$\begin{aligned} \tau^{-1} &= k_b([\mathrm{H^+}] + [\mathrm{OH^-}]) + k_f \\ &= k_b([\mathrm{H^+}] + [\mathrm{OH^-}] + K_{\mathrm{eq}}) \end{aligned} \tag{9}$$

an aqueous 0.1 *M* ionic strength solution, to ground. The sample cell is an approximately 50 ml (3.05 in.^3) Plexiglas cell containing two platinum electrodes spaced 1 cm (0.4 in.) apart and immersed in an aqueous 0.1 *M* ionic strength solution. The surge of current raises the temperature of the 1-ml (0.061-in.^3) volume of solution between the electrodes by 10°C (18°F) in a few microseconds.

Electric-field jump. In a situation, such as reaction (8), in which electrically neutral reactant species dissociate into oppositely charged ions, an especially sensitive tool for measuring rate constants of forward and backward reactions is the electric-field jump (E-jump) technique with conductometric detection. In a strong electric field (of the order of 4×10^6 V m^{-1}), a weak acid in solution is caused to dissociate to a greater degree than it would in the absence of the electric field. For weak electrolytes, such as aqueous acetic acid or ammonia, the effect is the order of 10% or less of the total normal dissociation, even at very high electric-field strengths. However, with a sensitive, high-voltage, Wheatstone bridge, the exponential increase with time in the concentration of ions following a precipitous increase in electric-field strength is readily detected. The measured relaxation time (τ) is clearly that corresponding to the high-electric-field environment, but since the rate constants for these reactions differ little in and out of the electric field, no serious problem is posed.

A more serious concern is that the sample solution may have a very high electrical resistance, so that the supposedly square step function in the electric-field strength is distorted by a significant voltage drop with concomitant heating of the sample liquid. Problems of working with high voltages, balancing capacitive and inductive effects in a very sensitive conductance bridge (now often circumvented by spectrophotometric detection), and the comparative difficulty of evaluating amplitudes of relaxations (as opposed to their readily determined time constants) are all factors that have worked against the wide use of the E-jump technique. There are many more ways of achieving a T-jump than an E-jump, and ΔH° values for chemical equilibria are readily available in the thermodynamic literature, whereas the extent to which a chemical equilibrium is displaced by an electric-field increment is rarely already known and is difficult to determine. Thus the commercialization of the T-jump method and the comparative neglect of the E-jump relaxation technique are readily understood.

Notwithstanding these difficulties, the E-jump technique is without peer for the investigation of the kinetics of solvent autoionization or for the exploration of the properties of weak electrolyte solutes in exotic solvents such as acetonitrile or xenon (the latter liquefied under a pressure of about 50 atm or 5 megapascals), so long as the relaxation time to be measured lies in the range 30 nanoseconds $< \tau < 100\ \mu\text{s}$.

Ultrasonic absorption. Two other relaxation methods more widely used than the E-jump technique are pressure jump (P-jump) and ultrasonic absorption. Each relies for its effectiveness on a volume change, ΔV°, occurring in an aqueous sample equilibrium undergoing kinetic investigation. (In a nonaqueous solvent it will frequently be more important that ΔH° be large than that ΔV° be so for the equilibrium to be susceptible to study by these two relaxation techniques.) As electrically neutral, weak electrolyte solute species dissociate into ions in aqueous solution, there is an increase in the number of solvent molecules drawn into a highly ordered solvation sheath. The higher the charge density of the ion, the more water molecule dipoles are bound and the greater the change in V° as reactants become products. Thus the dissociation of an aqueous neodymium(III) sulfate complex is particularly susceptible to study by one or more of the four or five ultrasonic absorption methods that cover the $f \simeq$ 100 kHz–1 GHz sound frequency range. Unlike the T-jump and E-jump relaxation methods, which usually employ step function perturbations, the ultrasonic absorption techniques are continuous-wave experiments in which the sample chemical equilibrium absorbs a measurable amount of the sound wave's energy when the frequency of the sound wave (f) and the relaxation time of the chemical equilibrium bear the relation to one another given by Eq. (10).

$$\tau^{-1} = 2\pi f \qquad (10)$$

A particularly easy ultrasonic absorption experiment to understand and perform is the laser Debye-Sears technique. A continuously variable frequency sound wave is introduced by a quartz piezoelectric transducer into a 30-ml (1.83-in.^3) sample cell that has entrance and exit windows for a visible laser light beam that passes through the cell at about 90° to the direction of travel of the planar sound wave. The regions of compression and rarefaction in the sound wave act as a diffraction grating for the laser light beam. If a chemical equilibrium in the sample strongly absorbs a particular frequency of sound (f), the definition of the "diffraction grating" will deteriorate and the measured intensity of the first-order diffracted laser light will diminish. The frequency of minimum diffracted light intensity will be that of Eq. (10). **Figure 3** shows a diagram of the

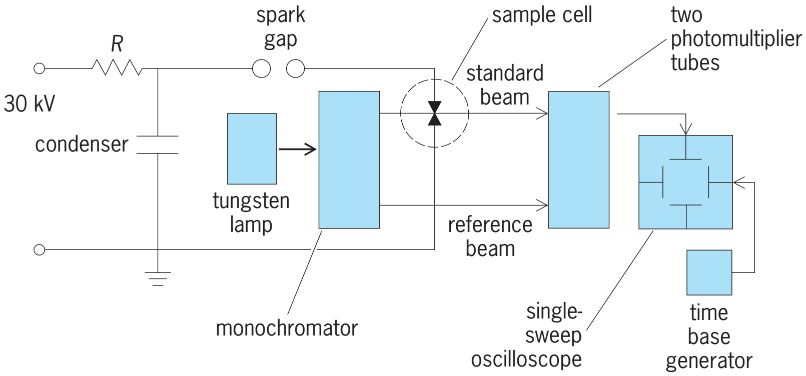

Fig. 2. Schematic of a Joule heating temperature-jump apparatus. (*After H. Eyring and E. M. Eyring, Modern Chemical Kinetics, Reinhold, 1963*)

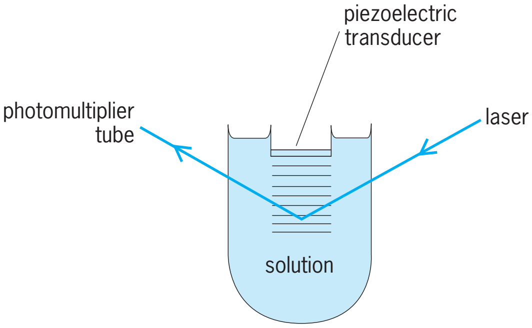

Fig. 3. Schematic of laser Debye-Sears apparatus for measuring ultrasonic absorption (about 15–300 MHz) in a sample liquid. (*After W. J. Gettins and E. Wyn-Jones, Techniques and Applications of Fast Reactions in Solution, D. Reidel, 1979*)

apparatus. The piezoelectric (quartz) tranducer cemented to the bottom of a plastic rod that is driven up and down by a stepping motor is controlled by a mini computer. The angle of diffraction of the laser beam by the alternating regions of compression and rarefaction in the liquid (suggested by the horizontal lines) is exaggerated in the diagram.

Ultrasonic absorption techniques have been used in kinetic investigations of complicated biophysical systems such as the order-disorder transitions that occur in liquid crystalline phospholipid membranes. While the ultrasonic techniques look through a conveniently broad time window at kinetic processes in solution, this picture window is difficult to "see through" in that many equilibrium processes in solution can absorb sound energy and the responsible process is not instantly identified by a characteristic absorption of electromagnetic radiation as in a spectrophotometric T-jump or E-jump experiment. A further disadvantage arises from the great breadth of the ultrasonic absorption "peaks" in a plot of normalized sound absorption versus sound frequency. Unless multiple relaxation times in a chemical system are quite widely separated in time, they are difficult to resolve in an ultrasonic absorption spectrum. *See* ULTRASONICS.

Pressure jump. The typical pressure-jump (P-jump) experiment is one in which a liquid sample under about 200 atm (20 MPa) pressure is suddenly brought to atmospheric pressure by the bursting of a metal membrane in the sample cell autoclave. Relaxation times measured spectrophotometrically or conductometrically are thus accessible if $\tau > 100\ \mu s$. This technique has proven particularly useful in the elucidation of micellar systems of great interest for catalysis and for petroleum recovery from apparently depleted oil fields.

The continuous- and stopped-flow techniques antedate somewhat the relaxation techniques described above, and have the sometimes important advantage of permitting kinetic measurements in chemical systems far from equilibrium. The stopped-flow experiment is one in which two different liquids in separate syringes are mixed rapidly in a tangential jet mixing chamber and then the rapid flow of mixed reactants is almost immediately brought to a halt in a spectrophotometric, conductometric, or calorimetric observation chamber. Reaction half-lives exceeding 2 ms are easily accessible. *See* SHOCK TUBE.

Other relaxation methods. Stopped-flow equipment has been used in concentration-jump and solvent-jump relaxation kinetic studies. An example of an application of the solvent-jump technique to a system insensitive to concentration-jump is a kinetic study of reaction (11) in mixed CCl_4-acetic acid solvents

$$\mathrm{NOCl} + n\mathrm{BuOH} \rightarrow n\mathrm{BuONO} + \mathrm{HCl} \qquad (11)$$

of varying composition (Bu = butyl). The thermodynamic treatment of the solvent jump is just about the only aspect of the presently known relaxation techniques that was not described in exhaustive detail by the earliest publications of Eigen and DeMaeyer. *See* CHEMICAL THERMODYNAMICS. Edward M. Eyring

Gas-Phase Reactions

The rates of thermal gas-phase chemical reactions are important in understanding processes such as combustion and atmospheric chemistry.

Elementary reactions, mechanisms, and rates. Chemical conversion of one stable, gas-phase molecule into another is an apparently simple process; yet it is highly unlikely to occur in just a single step, but as a web of sequential and parallel reactions involving many species. The oxidation of methane (CH_4) to carbon dioxide (CO_2) and water provides an excellent example. It occurs in combustion (for example, in burning natural gas, which is mostly methane) as well as in the atmosphere. In both cases, the net process may be written down as single reaction (12).

$$\mathrm{CH_4 + 2O_2 \rightarrow 2H_2O + CO_2} \qquad (12)$$

The reaction does not, however, result from collision of two oxygen (O_2) molecules with one methane molecule. Rather, it involves many separate steps. A simplified list of the steps involved in reaction (12) for both combustion and for the atmosphere is given below.

Combustion:

$$\begin{aligned}
\mathrm{CH_4 + OH} &\rightarrow \mathrm{CH_3 + H_2O}\\
\mathrm{CH_4 + M} &\rightarrow \mathrm{CH_3 + H + M}\\
\mathrm{CH_4 + H} &\rightarrow \mathrm{H_2 + CH_3}\\
\mathrm{CH_4 + O} &\rightarrow \mathrm{CH_3 + OH}\\
\mathrm{CH_4 + CH_2} &\rightarrow \mathrm{2CH_3}\\
\mathrm{CH_3 + M} &\rightarrow \mathrm{CH_2 + H + M}\\
\mathrm{CH_3 + H} &\rightarrow \mathrm{CH_2 + H_2}\\
\mathrm{CH_3 + O} &\rightarrow \mathrm{CH_2O + H}\\
\mathrm{CH_3 + OH} &\rightarrow \mathrm{CH_2 + H_2O}\\
\mathrm{CH_3 + O_2} &\rightarrow \mathrm{CH_2O + OH}\\
\mathrm{CH_3 + O_2} &\rightarrow \mathrm{CH_3O + O}\\
\mathrm{CH_3O + M} &\rightarrow \mathrm{CH_2O + H + M}\\
\mathrm{CH_3O + H} &\rightarrow \mathrm{CH_2O + H_2}\\
\mathrm{CH_3O + O} &\rightarrow \mathrm{CH_2O + OH}\\
\mathrm{CH_3O + OH} &\rightarrow \mathrm{CH_2O + H_2O}
\end{aligned}$$

$$\begin{aligned} \mathrm{CH_3O + O_2} &\rightarrow \mathrm{CH_2O + HO_2} \\ \mathrm{CH_2O + M} &\rightarrow \mathrm{HCO + H + M} \\ \mathrm{CH_2O + H} &\rightarrow \mathrm{HCO + H_2} \\ \mathrm{CH_2O + O} &\rightarrow \mathrm{HCO + OH} \\ \mathrm{HCO + O_2} &\rightarrow \mathrm{CO + HO_2} \\ \mathrm{CO + OH} &\rightarrow \mathrm{CO_2 + H} \end{aligned}$$

Atmospheric oxidation:

$$\begin{aligned} \mathrm{CH_4 + OH} &\rightarrow \mathrm{CH_3 + H_2O} \\ \mathrm{CH_3 + O_2 + M} &\rightarrow \mathrm{CH_3O_2 + M} \\ \mathrm{CH_3O_2 + NO} &\rightarrow \mathrm{CH_3 + NO_2} \\ \mathrm{CH_3O + O_2} &\rightarrow \mathrm{CH_2O + HO_2} \\ \mathrm{CH_2O} + h\nu &\rightarrow \mathrm{CHO + H} \\ \mathrm{CH_2O} + h\nu &\rightarrow \mathrm{CO + H_2} \\ \mathrm{CHO + O_2} &\rightarrow \mathrm{CO + HO_2} \\ \mathrm{CO + OH} &\rightarrow \mathrm{CO_2 + H} \end{aligned}$$

Even though the overall reaction is the same in both environments, the steps are quite different, as are the rates, temperature dependences, and byproducts. Each is called an elementary reaction, and the sum of the steps that makes up the overall reaction is called the mechanism. Currently, the major thrust of chemical kinetics is to elucidate such mechanisms and to measure (or calculate) the rates of the elementary reactions.

All elementary reactions fundamentally require a collision between two molecules. Even in the case of a unimolecular reaction, in which a single molecule breaks apart or isomerizes to another form, the energy required for the process comes from collision with other molecules. The species involved in many gas-phase elementary reactions are free radicals, molecules that have one or more unpaired electrons. Such species tend to be highly reactive, and they are responsible for carrying out most gas-phase chemistry.

A reaction rate is the rate at which the concentration of one of the reactants or products changes with time. The objective of a kinetics experiment is not to measure the reaction rate itself but to measure the rate coefficient, an intrinsic property of the reaction that relates the reactant concentrations to their time rates of change. For example, the mathematical expression for the rate of a biomolecular reaction, $\mathrm{A + B} \rightarrow$ products, is differential equation (13). The

$$-d[\mathrm{A}]/dt = -d[\mathrm{B}]/dt = k[\mathrm{A}][\mathrm{B}] \qquad (13)$$

square brackets denote the concentrations of A and B, and k is the rate coefficient described above. The dependence of the rate expression on reactant concentrations is determined experimentally, and it also arises from a fundamental tenet of chemistry known as the law of mass action. Once the rate constant is known, the rate of a reaction can be computed for any given set of concentrations.

Rate constants usually change with temperature because of the change in the mean energy of colliding molecules. The temperature dependence often follows an Arrhenius expression, $k = A \exp(-E_A/RT)$, where A is a preexponential factor that is related to the gas-phase collision rate, R is the universal gas constant, and T is the absolute temperature (in kelvins). The key quantity is the activation energy, E_A, the amount of energy required to induce a reaction. Pressure dependences are usually important only for association reactions, $\mathrm{A + B} \rightarrow \mathrm{AB}$, since collision of A with B will form an energized complex, AB^*, that will simply redissociate unless a subsequent collision carries away enough energy to stabilize the AB product. The probability of a stabilizing collision increases with the collision frequency and thus the total pressure.

In the simple case of a unimolecular reaction, $\mathrm{A} \rightarrow \mathrm{P}$, the rate expression is Eq. (14). Equation (14)

$$-d[\mathrm{A}]/dt = d[\mathrm{P}]/dt = k[\mathrm{A}] \qquad (14)$$

is first-order since the rate is proportional to the reactant concentration to the first power, and it leads to an expression for the change in the concentration of A or P with time (called an integrated rate expression), as in Eqs. (15). The subscripts denote

$$[\mathrm{A}]_t = [\mathrm{A}]_0 \exp(-kt) \qquad (15a)$$

$$[\mathrm{P}]_t = [\mathrm{A}]_0\{1 - \exp(-kt)\} \qquad (15b)$$

the concentrations at zero time (initial concentration) and an arbitrary time t. The concentration of A decreases (because it is reacting away) as a function of time, while the concentration of P increases with time such that the sum of the concentrations of A and P is always constant and equal to the initial concentration of A (**Fig. 4**). Because first-order reactions are mathematically simple, kineticists try to reduce all studied reactions (if at all possible) to this form. A second-order reaction, for example $\mathrm{A + B} \rightarrow$ products, has the rate expression given in Eq. (13). To reduce the second-order expression to the first-order expression, Eq. (14), one chooses one of the concentrations to be in large excess, for example $[\mathrm{B}] >> [\mathrm{A}]$. The concentration of B is then approximately constant during the course of the reaction, and it may be combined with the rate constant

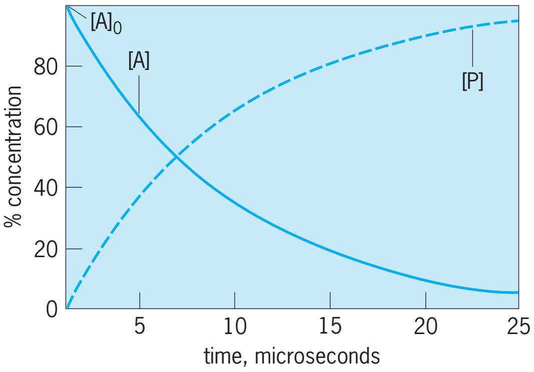

Fig. 4. Concentration of reactant (A) decreases while product (P) increases with time (arbitrarily shown in microseconds).

to give an expression identical to Eq. (14) that depends on the concentration of A alone.

Experimental methods. The experimental challenges to rate constant measurements include generation of reactive species of interest, the measurement of their concentration on a time scale fast enough to follow the course of the reaction, and the measurement of the reaction time itself. The capability for measurement of small concentrations (down to a few molecules in a milliliter) and short times (down to femtoseconds; 1 fs $= 10^{-15}$ s) has improved dramatically since the early 1980s and has enabled kineticists to study extremely fast gas-phase reactions. The following examples illustrate how rate constants are measured.

The rate constant for the bimolecular reaction of OH with methane is very important. **Figure 5*a*** illustrates its measurement via the commonly used pulsed photolysis–laser induced fluorescence (PP–LIF) technique. A pulse of short-wavelength ultraviolet light from a laser irradiates a gas mixture containing a precursor molecule, such as hydrogen peroxide (H_2O_2) or nitric acid (HNO_3), that absorbs the light and fragments instantaneously to produce OH. A second laser produces a pulse of light that is tuned to a color (wavelength) absorbed by the OH radicals, which in turn emit light (fluoresce) in all directions. The fluorescence intensity falling on a detector is proportional to the OH concentration. Both laser pulses have very short duration (typically $<2 \times 10^{-8}$ s or 20 nanoseconds) on the time scale of the reaction. The first pulse creates the OH radicals and defines zero time, and variation of the time delay between the two lasers varies the reaction time. Methane is present in large excess over OH, and thus its concentration, as measured by its pressure, is essentially constant during the course of the reaction. *See* LASER; LASER PHOTOCHEMISTRY.

The same rate coefficient may also be measured using the apparatus shown in Fig. 5*b*. In this case, a flow of gas containing hydrogen (H_2) passes through a microwave discharge, where H_2 breaks down to H atoms. Then it reacts with nitrogen dioxide (NO_2) to make OH and nitric oxide (NO). The NO is unreactive with methane and does not interfere with the OH reaction. Methane flows through a movable injector at the center of a flow tube. The two gas flows mix at the injector and initiate reaction between OH and methane. A laser-induced fluorescence detector, similar to the one described above, at the end of the tube measures the amount of OH present at that point. (Other detectors, such as a mass spectrometer, also can be used.) Since the gas flow velocity down the tube is constant, the distance from the injector to the mass spectrometer can be converted to a reaction time, and movement of the injector to different positions in the tube varies the reaction time. As above, its pressure in the flow tube gives the approximately constant methane concentration.

Both of the above examples are direct methods in which the time rate of concentration change is directly observed. Relative rate constant measurements can be done for the determination of the rate constant for reaction of OH with hydrofluorocarbon 134a (HFC-134a). This compound is used as an automobile refrigerant in place of the banned CFCs

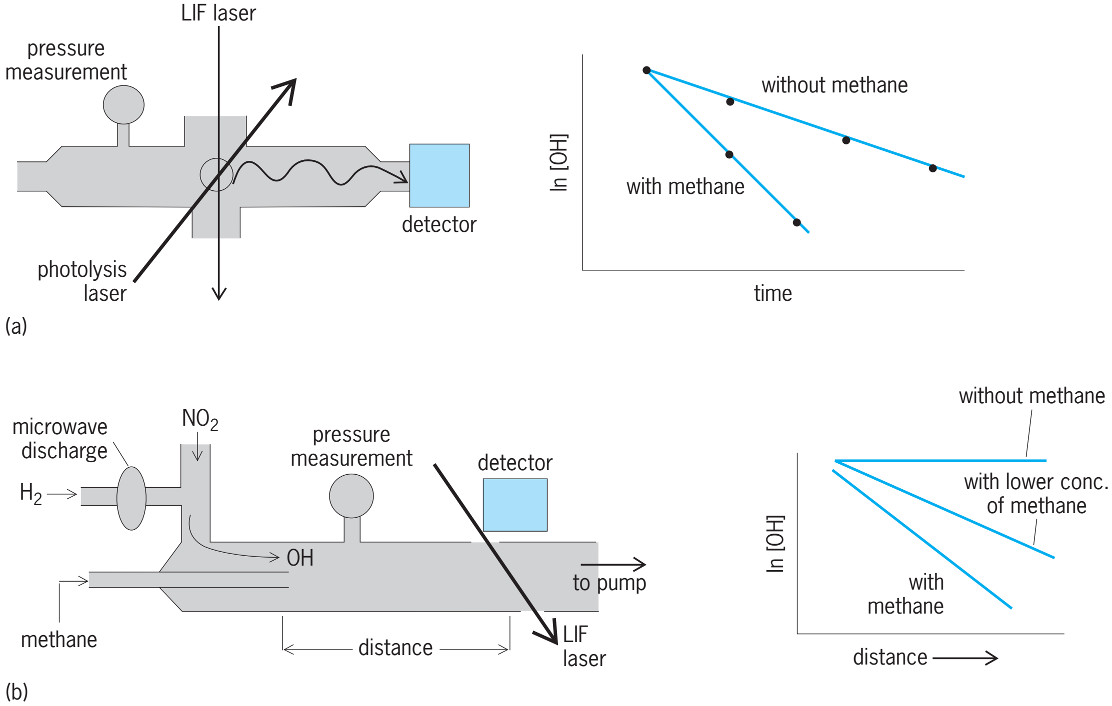

Fig. 5. Measurement of the rate constant for the bimolecular reaction of OH with methane. (*a*) Pulsed photolysis. OH concentrations are measured with methane and without methane. (*b*) Discharge flow. OH concentrations are detected at various distances from a detector. The plot shows OH concentrates measured with methane, with a lower concentration of methane, and without methane.

(chlorofluorocarbons), and, similar to methane, its reaction with OH determines its degradation rate in the atmosphere. The OH radicals are continuously produced in a mixture containing both methane and HFC-134a, and the depletion of methane and HFC-134a is measured. The ratio of the depletions is then proportional to the rate constants for reaction of OH with each compound. Since the rate constant for reaction of OH with methane is known, the measurement provides the previously unknown rate constant for reaction of OH with HFC-134a.

There are many other techniques for measurement of reactant or product concentrations, including ultraviolet, visible, and infrared light absorption, gas chromatography, and a host of additional fluorescence and mass spectrometric methods.

Outlook. Complex gas-phase chemical reactions may be broken down into elementary steps that describe reactions at the level of collisions between individual molecules. The rate constants for such elementary steps allow calculation of the reaction rates from reactant concentrations as well as kinetic modeling of larger chemical processes. Determination of elementary rate constants involves measurement of reactant or product concentrations on the time scale of the reaction. Rate constants may also be made in a relative fashion in cases where two reactions share a common reactant and one rate constant is known. A. R. Ravishankara; S. S. Brown

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Chemical microscopy

A scientific discipline in which microscopes are used to solve chemical problems. The unique ability to form a visual image of a specimen, to select a small volume of the specimen, and to perform a chemical or structural analysis on the material in the selected volume makes chemical microscopy indispensable to modern chemical analysis. *See* MICROSCOPE.

Microscopes are instruments which form images of objects too small to be seen with the unaided eye. Microscopes can also be combined with most analytical instruments. For example, a light microscope can be combined with a spectroscope, making it possible to determine the molecular composition of microscopic objects or structures. Similarly, an x-ray spectrometer can be combined with an electron microscope to determine the elemental composition of small objects. *See* ELECTRON MICROSCOPE; SPECTROSCOPY; X-RAY SPECTROMETRY.

Phase analyses can also be made microscopically. The boundaries of amorphous phases can usually be distinguished in the microscope, and an elemental or physical analysis can be used to identify the phase. An example of a physical analysis is the measurement of refractive index. Crystalline phases are even more amenable to microscopical analysis. For example, a polarizing microscope can be used to measure the optical properties of a crystalline phase and thus identify it. Or a transmission electron microscope can be used to select a tiny area of a crystalline phase and identify the crystal structure by means of electron diffraction. *See* ELECTRON DIFFRACTION.

While the idea of selecting a small volume for analysis is straightforward, the minimum volume that can be analyzed varies widely with the instrument used. Light microscopes can be used to identify particles as small as 1 micrometer in diameter and weighing about 1 picogram. A field ion microscope has been combined with a mass spectrometer and used to identify single atoms extracted from the surface of a specimen. *See* FIELD-EMISSION MICROSCOPY; MASS SPECTROMETRY; OPTICAL MICROSCOPE.

After a portion of a specimen has been selected microscopically, it can be analyzed in many ways. An experienced microscopist may learn to recognize various structures by studying known materials, using published atlases, or an atlas that the individual microscopist has constructed. Analyses done in this fashion can be fast and simple. If the object or structure cannot be recognized, many means of analysis are available. For example, a polarizing microscope may be employed to identify the object by using optical crystallographic methods. Other light microscopes useful for chemical analysis include phasecontrast and interference-contrast microscopes, microspectrophotometers, the confocal scanning laser microscope, and the laser Raman microscope. Physicochemical methods may be used to measure melting points, or mixed-melt phenomena and dispersion staining may also be used. *See* INTERFERENCE MICROSCOPE; LASER SPECTROSCOPY; PHASE-CONTRAST MICROSCOPE; RAMAN EFFECT.

Microscopes using other types of image-forming beams serve for chemical analysis. Scanning or transmission electron microscopes are powerful tools for chemical microscopy. Scanning electron microscopes are often fitted with x-ray spectrometers which are capable of both qualitative and quantitative analysis for most of the elements. Other electron microscopes capable of chemical analysis are the Auger electron microscope, field electron microscope, scanning tunneling microscope, and cathodoluminescence microscope. Microscopes which use ion beams, neutron beams, and x-ray beams also have analytical capabilities. *See* AUGER EFFECT; NEUTRON SPECTROMETRY; SCANNING ELECTRON MICROSCOPE; X-RAY MICROSCOPE.

A specific example of a chemical microscopical analysis involves portland cement which is formulated for use in geothermal-energy extraction wells (see **illustration**). In this micrograph, two types of crystals can be recognized by their morphology.

Micrograph of a portland cement formulation cured at 390–450°F (200–230°C) for 72 h; gypsum and xonotlite crystals are growing into a cavity.

If the microscopist does not recognize the crystals from their morphology, the crystals must be analyzed. This can be done in a number of ways. With a light microscope, it is possible to identify the crystals by scraping them from the sample and determining their optical properties through a variety of standard techniques. Another method is to examine each of the crystals by using x-ray or electron diffraction techniques. A third option is to perform an elemental analysis with an electron microscope fitted with an x-ray spectrometer. From the elemental analysis, it should be possible to identify the chemical compound that makes up the crystal. There should be no confusion resulting from the fact that the sample consists of more than one crystalline compound, because with the electron microscope a single crystal or a small portion of a crystal can be analyzed. Each crystal that appears different from the other can be analyzed quantitatively for its elemental composition. Knowledge of the combination of elemental composition and diffraction data nearly always leads to the identification of the crystals in the sample. This does require that the diffraction pattern for the crystals has been published and is accessible to the microscopist. If this information is not available, the microscopist can usually construct a list of data for the materials considered, so that in future work the individual crystals or amorphous materials can be recognized when they are encountered again.

In the example illustrated, only the commonly available microscopes, that is, the polarizing microscope, the scanning electron microscope, and the transmission electron microscope, were considered. Less commonly available microscopes, such as the Auger microscope, the laser Raman microscope, and the microspectrophotometer, can be used to identify crystalline and amorphous phases. *See* ANALYTICAL CHEMISTRY. George Cocks

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Chemical process industry

An industry, abbreviated CPI, in which the raw materials undergo chemical conversion during their processing into finished products, as well as (or instead of) the physical conversions common to industry in general. In the chemical process industry the products differ chemically from the raw materials as a result of undergoing one or more chemical reactions during the manufacturing process. The chemical process industries broadly include the traditional chemical industries, both organic and inorganic; the petroleum industry; the petrochemical industry, which produces the majority of plastics, synthetic fibers, and synthetic rubber from petroleum and natural-gas raw materials; and a series of allied industries in which chemical processing plays a substantial part. While the chemical process industries are primarily the realm of the chemical engineer and the chemist, they also involve a wide range of other scientific, engineering, and economic specialists.

For a discussion of the more prominent chemical process industries *see* ADHESIVE; BIOCHEMICAL ENGINEERING; BIOMEDICAL CHEMICAL ENGINEERING; CEMENT; CERAMICS; COAL CHEMICALS; COAL GASIFICATION; COAL LIQUEFACTION; DISTILLED SPIRITS; DYEING; ELECTROCHEMICAL PROCESS; EXPLOSIVE; FAT AND OIL; FERMENTATION; FERTILIZER; FOOD MANUFACTURING; FUEL GAS; GLASS; GRAPHITE; HYDROCRACKING; INSECTICIDE; LIME (INDUSTRY); MANUFACTURED FIBER; NUCLEAR CHEMICAL ENGINEERING; NUCLEAR FUELS; PAPER; PETROCHEMICAL; PETROLEUM PROCESSING AND REFINING; PETROLEUM PRODUCTS; PLASTICS PROCESSING; POLYMER; RADIOACTIVE WASTE MANAGEMENT; RUBBER; WATER SOFTENING. William F. Furter

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Chemical reactor

A vessel in which chemical reactions take place. A combination of vessels is known as a chemical reactor network. Chemical reactors have diverse sizes, shapes, and modes and conditions of operation based on the nature of the reaction system and its behavior as a function of temperature, pressure, catalyst properties, and other factors.

Laboratory chemical reactors are used to obtain reaction characteristics. Therefore, the shape and mode of operation of a reactor on this scale differ markedly from that of the large-scale industrial reactor, which is designed for efficient production rather than for gathering information. Laboratory reactors are best designed to achieve well-defined conditions of concentrations and temperature so that a reaction model can be developed which will prove useful in the design of a large-scale reactor model.

Chemical reactions may occur in the presence of a single phase (liquid or gas), in which case they are called homogeneous, or they may occur in the presence of more than one phase and are referred to as heterogeneous. In addition, chemical reactions may be catalyzed. Examples of homogeneous reactions are gaseous fuel combustion (gas phase) and acid-base neutralization (liquid phase). Examples of heterogeneous systems are carbon dioxide absorption into alkali (gas-liquid); coal combustion and automobile exhaust purification (gas-solid); water softening (liquid-solid); coal liquefaction and oil hydrogenation (gas-liquid-solid); and coke reduction of iron ore (solid-solid).

Modes of operation. Chemical reactors may be operated in batch, semibatch, or continuous modes.

Batch. When a reactor is operated in a batch mode, the reactants are charged, and the vessel is closed and brought to the desired temperature and pressure. These conditions are maintained for the time needed to achieve the desired conversion and selectivity, that is, the required quantity and quality of product. At the end of the reaction cycle, the entire mass is discharged and another cycle is begun. The complete cycle includes charging, heat-up, reaction (cook) time, cool-down, and discharge. Batch operation is labor-intensive and therefore is commonly used only in industries involved in limited production of fine chemicals, such as pharmaceuticals. *See* AUTOCLAVE.

Semibatch. In this type of reactor operation, one or more reactants are in the batch mode, while the coreactant is fed and withdrawn continuously. For example, a batch of liquid is exposed to a continuously fed and withdrawn gas phase, as in the hydrogenation of unsaturated oils catalyzed by a solid Raney nickel catalyst (a gas-liquid-solid system).

Continuous. In a chemical reactor designed for continuous operation, there is continuous addition to, and withdrawal of reactants and products from, the reactor system. The reaction time is the actual residence time of the molecules within the reactor. There are two extremes of residence or exposure time. If all molecules have the same reaction exposure time, the reactor is a plug- or piston-flow reactor (PFR); that is, reactant-product species move through the reactor as would a piston or plug, with no (zero) mixing in the direction of flow. If, however, the mixing is perfect (infinite) in the direction of flow, the reactor is a continuously fed stirred-tank reactor (CSTR). For this type of reactor, concentrations and temperature are uniform throughout the vessel due to vigor of agitation, and the residence times are distributed around the mean value. In contrast, in the piston-flow reactor, concentrations and temperature are distributed nonuniformly between reactor inlet and outlet, and residence time is unique.

Selection of reactor. The choice between a continuously fed stirred-tank reactor and a piston-flow reactor for continuous operation is determined by reaction characteristics. The reactor environment with respect to temperature is likewise determined, and may be isothermal (heat removal or addition matching heat generation or extraction), adiabatic (no heat removal or addition in the reaction zone), or the intermediate case (partial heat removal or addition).

An example is the sequence of reactions shown below, where k_1 and k_2 represent rate coefficients.

$$\text{Ethylene} \xrightarrow{k_1} \text{ethylene oxide} \xrightarrow{k_2} \text{carbon dioxide} + \text{water}$$

This reaction is exothermic (heat is released), and the rate coefficient k_1 increases with increase in temperature more slowly than does k_2. A decision must be made as to what reactor type, mode of operation, and environment should be employed. If large quantities of ethylene are to be treated annually, the continuous mode is economically justified. The desired product will determine the choice between a continuously stirred tank reactor and a piston-flow reactor.

The adiabatic environment is readily achieved in large-scale industrial reactors by the denial of heat exchange. Such an adiabatic reactor consists of a large-diameter tube packed with catalyst. The adiabatic temperature rise (in exothermic reactions) may require limitation due to safety and equilibrium factors in addition to integrity of the catalyst and reactor materials. These considerations led to the development of the staged adiabatic fixed-bed reactor system for sulfur dioxide oxidation and hydrocracking. In each case, interstage cooling is effected either by means of indirect heat exchange to generate steam or preheat reactants or by means of direct cooling by the addition of "cold" coreactant (cold-shot addition). The adiabatic reactor is the least expensive, since it does not require a costly heat-transfer surface area.

Gas-solid reactors. There are a number of different types of reactors designed for gas-solid heterogeneous reactions. These include fixed beds, tubular catalytic wall reactors, and fluid beds.

The design of these components involves consideration of the properties of solid catalysts. Catalytic agents (for example, platinum, palladium, vanadium pentoxide among other zeolites, metal oxides, sulfides) are usually supported upon porous solids, such as aluminum oxide and silicon dioxide. Thus the components are, typically, support, catalyst, and promoter. Characterization of these components is imperative, since deactivation over time periods of minutes (catalytic cracking), months (reforming), and years (ammonia synthesis) plagues all catalysts. The actual catalytic sites exposed to reactants may be partially inaccessible because of the diffusional limitations of the reactants and the nature of the sites dictated by the fluid-phase environment (oxidizing, reducing). Furthermore, the reactivity and yield selectivity per exposed catalyst site may change with catalyst crystallite size (dispersion), a phenomenon known as fractal behavior. Since the reactions and associated enthalpy changes are forcing functions that affect reactor performance, consideration of the complexities of heterogeneous catalytic phenomena is necessary both in reaction modeling and in reactor modeling. *See* HETEROGENEOUS CATALYSIS.

Fixed bed. A common catalytic reactor that consists of a tube or parallel array of tubes filled with solid catalyst particles is the fixed-bed reactor. It is commonly employed in processes such as partial oxidation, ammonia synthesis, and reforming.

Minimization of tube surface area (large tube diameter) invites adiabaticity. In the general case (nonisothermal or nonadiabatic), temperature varies in axial and radial directions and radial heat-transfer limitations can cause "hot" or "quench" spots with consequent threats to safety and product quality. Radial temperature gradients can be minimized by use of small tube diameter; however, there will be consequent increase in heat-transfer surface and reactor cost. Usually a piston-flow reactor is used. When catalyst decay is rapid (as in catalytic cracking), fresh catalyst is added and spent solid removed continuously. This arrangement is known as a moving bed. *See* CRACKING.

Tubular catalytic wall reactor. Resistance to radial heat transfer can be vastly reduced by using this type of reactor, in which all the catalyst is impregnated upon the alumina wash-coated wall. This is the monolith tubular reactor used in auto-exhaust fume abatement. Catalyst replacement is obviously more difficult in this instance than in the conventional fixed bed; the tubular catalytic wall reactor cannot host catalysts of short life.

Fluid bed. When a fluid is passed upward through an unretained bed of fine solid particles, a velocity can be induced so that the bed moves, with bubbles of gas passing through the agitated solids. The bed behaves as a boiling fluid. Intensity of gas dispersion in the usually baffled bed induces rapid motion and circulation of the solid. Reaction heat is thus nearly uniformly dispersed and, unlike the fixed bed, the fluid bed approaches isothermality. Fine particles can be used with increase in surface area and reaction efficiency. Since the fluid bed is a multiphase system (gas-and-solids emulsion phases), bypassing or short-circuiting of unreacted species can occur, which reduces reactor efficiency. Staging or horizontal baffling can minimize bypassing and deleterious bubble growth.

The fluid bed can be operated in batch or continuous fashion with respect to the solids phase, while the fluiding (gas or liquid) phase is continuous. If catalyst life is short (seconds or minutes) or noncatalytic solid coreactant is converted, the continuous fluid bed must be employed. Residence time is complex.

A variation of the fluidized bed is the spouted-bed reactor, in which a jet of gas is injected at one or more points to disperse even rather large-sized particles with which the gas interacts (for example, drying of wheat, gas-solid reaction, or solid-catalyzed reaction). Solids may be batch or continuous.

At sufficiently high fluid velocities, the fluidized bed becomes entrained; that is, solids are carried out of the bed when fluid velocity exceeds particle terminal velocity. In a transport line or riser reactor, fresh solids are continuously fed at the reactor bottom with the entraining fluid. This is an ideal unit for rapidly decaying catalyst or solid noncatalytic coreactants. Modern catalytic cracking of oils to produce gasoline is largely done in the transport line reactor. Residence time approaches the piston-flow reactor limit as opposed to more complex residence time behavior of the continuous fluidized bed. Reactant exposure times are of the order of seconds, during which deactivating coke is laid down upon the catalyst. Coked catalyst is separated from the product vapors at the top of the reactor and is then sent to a regenerator, where oxygen-bearing gas is contacted with the coked catalyst to burn off the coke. The product of this gas-solid reaction, the regenerated cracking catalyst, is returned to the inlet of the transport line cracker. *See* FLUIDIZATION; FLUIDIZED-BED COMBUSTION.

Gas-liquid-solid reactors. Many different types have been developed for specific reaction conditions. The trickle-bed reactor employs a fixed bed of solid catalyst over which a liquid phase trickles downward in the presence of a cocurrent gas phase. This three-phase reactor, commonly employed for the removal of sulfur or nitrogen from high-boiling oil feedstocks, can pose problems of catalyst wetting, gas-liquid-solid transport, and liquid-phase bypassing. Reasonable catalyst life is required in trickle-bed operation.

An alternative is the slurry reactor, a vessel within which coreactant gas is dispersed into a liquid phase bearing suspended catalyst or coreactant solid particles. Unlike the trickle bed, liquid-solid wetting is complete. With short catalyst life or solid consumption, continuous feed and withdrawal of the liquid-solid phase is feasible, but with attendant problems of solid-liquid separation. Slurry reactors are usually of the continuously stirred tank type.

At high ratios of reactor length to diameter, the gas-liquid-solid reactor is often termed an ebullating-bed (high solids concentration) or bubble column reactor (low solids concentration). A trickle bed operating at high liquid holdup and countercurrent (upward) flow of gas becomes an ebullating bed.

Gas-liquid reactors assume a form virtually identical to the absorbers utilized in physical absorption processes. *See* ADSORPTION OPERATIONS.

Solid-solid reactions are often conducted in rotary kilns which provide the necessary intimacy of contact between the solid coreactants. *See* KILN.

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Chemical senses

In vertebrates, the senses of smell (olfaction) and taste (gustation) plus the so-called common chemical sense constitute the external chemical senses, as contrasted with such internal chemoreceptors as the carotid sinus detectors of carbon dioxide in blood, glucose receptors of brain and certain visceral organs, and so on. The olfactory cells of vertebrates, usually located in the olfactory mucosa of the upper nasal passages, are specialized neural elements that are responsive to chemicals in the vapor phase. The floral fragrance of roses and the putrid smell of hydrogen sulfide are two examples of human olfactory sensations. Taste buds of the oral cavity, especially the tongue, are composed of modified epithelial cells responsive to chemicals in solution. Sweet, salty, sour, and bitter are the basic taste qualities experienced by humans. In certain fish (for example, catfish), taste buds occur over the body surface and barbels. The common chemical senses are composed of free nerve endings in the mucous membrane of the eye, nose, mouth, and digestive tract and are responsive to irritants or other chemicals in either the vapor or liquid phase. *See* CAROTID BODY; CHEMORECEPTION.

Chemical sensitivity occurs in single-cell and other lower organisms. Among invertebrates, sense organs occur as specialized hairs and sensilla, or minute cones supplied with sensory nerves and nerve cells. Characteristic of male moths, for example, are their distinctive bushy antennae, by which they detect and locate females by sex pheromones. Rodents, ungulates, carnivores, and other mammals also show sexual attraction to female odors produced by specialized glands. Whether humans in general are susceptible to pheromonal influences from other humans is highly debatable. *See* CHEMICAL ECOLOGY; PHEROMONE.

Taste plays an important role in selection and acceptance of food. Although the "sweet tooth" is widespread throughout the animal kingdom as well as humans, there are great species differences in sweet sensitivity, especially for artificial sweetners. Besides the protective, inborn aversion to bitter (many poisons, but not all, are bitter), a single experience with the particular taste of a toxic substance which caused illness may establish a strong and persistent learned taste aversion. By contrast, a compensatory salt hunger may occur in persons or animals suffering salt deficiency. The intake of salt in civilized people, however, may be determined not only by physiological need but by social custom and habit, and excess intake with high incidences of hypertension has been reported in some groups. *See* HYPERTENSION; SALT (FOOD).

The limbic system of the brain, which modulates appetitive and emotional behavior and hedonic (pleasant vs. unpleasant) experiences, has both taste and olfactory neural pathways to it, providing the neural substrate for the pleasure or displeasure of sensations. *See* NEUROBIOLOGY; OLFACTION; SENSATION; TASTE.

Carl Pfaffmann

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Chemical separation (chemical engineering)

A process used to purify substances or to isolate them from other substances. In industrial applications, the ultimate goal is the isolation of a product of given purity. Most industrial chemical processes involve a separation stage. This may involve a preliminary purification stage before the reaction process, or a final stage involving the separation of the desired product. Two well-known processes are distillation and crystallization.

Distillation and crystallization. The distillation process is based on the relative volatilities (that is, vapor pressures) of the components. It involves the heating of the feed material (which is to be separated) in a boiler. The heated vapors enter a column and partially condense on the many plates or trays. These plates have a large surface area to facilitate the equilibrium between the vapor and the liquid. The vapor in the column is richer in the more volatile (lighter) component. As the vapor travels up the column, this process of enrichment is enhanced. The final stage of the distillation process is the complete condensation of this vapor as it leaves the column. This is done by cooling the vapor to a temperature well below its boiling point. The result is a separation of a light component or components (the condensate) from heavy components left in the boiler. The overall separation achieved depends not only on the relative vapor pressures of the components but also on the number of trays in the column. In spite of the high energy demands of the distillation process, 90% of all separation processes in the chemical and petrochemical industries worldwide are distillation processes. *See* DISTILLATION; VAPOR PRESSURE.

In the crystallization process, separation is based on the relative solubilities of the components. The separation of sea salt from water is usually done by crystallization through the evaporation of the water either by heating or by using solar energy. *See* CRYSTALLIZATION.

Thermodynamics offers a proper understanding of all separation processes. Not only is it useful in quantifying the separation of components, but thermodynamic relationships are also vital in the design of industrial separation plants.

Basic theory. When an equilibrium exists between phases (solids, liquids, or gases), the chemical potential, μ_i, for species *i* in each phase may be expressed by Eq. (1). For a vapor-liquid equilibrium process (distillation) this equality results in Eq. (2), the relationship between the vapor composition (y_i) and the liquid composition (x_i) at a temperature T.

$$\mu_i(\text{solid}) = \mu_i(\text{liquid}) = \mu_i(\text{gas}) \qquad (1)$$

$$y_i/x_i = \gamma_i P_i^0/P_{(\text{total})} \qquad (2)$$

Here, γ_i is the activity coefficient of species *i*, P_i^0 is the vapor pressure of pure *i* at T, and $P_{(\text{total})}$ is the total vapor pressure of the system. It is this ratio that defines the separating efficiency and is known as the distribution coefficient. Other relationships can be derived for other phase separation processes (such as crystallization), and in every case the results will be based on Eq. (1). *See* CHEMICAL EQUILIBRIUM.

Separation processes. Industrial separation processes involve all the possible phase pairs apart from solid-solid, which is kinetically too slow for useful applications (**Table 1**). *See* ADSORPTION OPERATIONS.

TABLE 1. Some important separation processes

Phase pair	Process	Industrial separation
Gas-liquid	Distillation	(i) Gasoline, paraffin and diesel fuel separated from oil (ii) Acetic acid from water
	Gas adsorption	Ammonia gas and air separated by passing the gas mixture through water
	Gas desorption	Ammonia and water mixture separated by passing air through the solution
	Pervaporation	Alcohols removed from esters and aroma compounds in aroma production
Gas-gas	Membrane	Methane gas or hydrogen gas separated from carbon dioxide
Gas-solid	Sublimation	Removal of water from heat-sensitive foodstuff by freeze drying; the food is cooled below 0°C and vacuum is applied, resulting in the sublimation of water
	Desorption	Drying of clay or wood by exposure to air
	Adsorption	Drying of wet air by passing over silica gel
Liquid-liquid	Solvent extraction	A mixture of acetone and water can be separated by adding carbon tetrachloride (CCl_4); phase separation takes place and the acetone is found in the CCl_4-rich layer
	Reverse osmosis	Seawater and brackish water purified by removal of salts
Liquid-solid	Supercritical fluid extraction	Separation of caffeine from coffee; the caffeine in the ground coffee beans readily dissolves in supercritical carbon dioxide
	Zone refining	Purification of benzene or metals to produce ultrapure compounds
	Fractional crystallization	Salts from seawater are usually separated on a basis of solubility

Supercritical fluid extraction. The process of supercritical fluid extraction is a relatively new separation technique. Interest in it is based on the high solubility of some solids in the supercritical solvent, the high degree of selectivity, the ease of separating the required product, and the ease with which the solvent can be recovered. To understand the process requires an understanding of the critical point. *See* SUPERCRITICAL FLUIDS.

The liquid-vapor phase line (as opposed to the solid-vapor and solid-liquid phase lines) for pressure and temperature discontinues at a certain point (**Fig. 1**), known as the critical point. At temperatures above the critical temperature (T_c), it is not possible to liquefy the gas by pressure alone. In other words, it is impossible to produce a liquid meniscus from the gas phase by pressure alone. At conditions above the critical temperature and pressure (P_c), the gas is known as a supercritical fluid (Fig. 1).

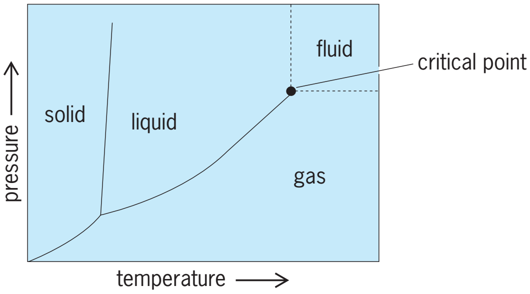

Fig. 1. Typical pressure-temperature (*P-T*) phase diagram showing the critical point discontinuity.

For an understanding of the general process, it is best to look at the most important supercritical fluid extraction process, the decaffeination of coffee using carbon dioxide. Carbon dioxide fluid, at a pressure of 200 atm (20 megapascals) and a temperature of 50°C (122°F) [in excess of $P_c\,(CO_2) = 73$ atm and $T_c\,(CO_2) = 31°C$ (88°F)], is pumped through the extraction cell containing the ground coffee in a mesh basket. The supercritical carbon dioxide has the unique capacity for dissolving only the caffeine and not the compounds that give coffee its taste and flavor. The carbon dioxide fluid, now containing dissolved caffeine, leaves the cell, and its pressure is reduced to below its critical value. As a result, the fluid vaporizes to a gas and the solid caffeine precipitates as it is not soluble in gaseous carbon dioxide. The coffee without caffeine is recovered and the carbon dioxide compressed and recycled. Apart from the simplicity of the process and the fact that it is done at a low temperature (it apparently does not affect the coffee taste or flavor), its main advantage is that the solvent is a natural substance and if any residue is left in the coffee it will be harmless. This is not true for some other decaffeination processes which use organic solvents such as methylene chloride.

TABLE 2. Examples of separations based on membrane processes

Membrane	Mixture	Preferentially selective for	Process
		Gas separation	
Polyimide	O_2/N_2	O_2	Oxygen enrichment
Polyethersulfone	CH_4/CO_2	CO_2	CO_2 recovery
Cellulose acetate	H_2/CO_2 or H_2/N_2	H_2	Hydrogen recovery
		Reverse osmosis	
Cellulose acetate, aromatic polyamides	Seawater	Water	Desalination
	Sugar solutions	Water	Concentration of food ingredients
	Fruit juices	Water	Concentration of food ingredients
		Pervaporation	
Poly(vinyl alcohol)	Water+alcohol	Water	Dehydration
Polyoctylmethylsiloxanes	Water+alcohol	Alcohol	Dealcoholization
Polyoctylmethylsiloxanes	Aroma compounds in water	Aroma compounds	Aroma production

Carbon dioxide is the most popular solvent used in supercritical fluid extraction. This is largely due to its relatively low critical pressure and temperature, and the ease with which the supercritical state can be achieved. It is extensively used in the perfume industry, where high temperatures would destroy the chemicals. It is used, for example, in separating oxygenated compounds (such as geranyl acetate), valuable as perfumes, from lemon oil, which consists largely of terpenes of low value, such as limonene.

Water has received much attention as a possible solvent for supercritical fluid extraction. Its critical properties are, however, too high for convenience [$P_c = 218$ atm (22.1 MPa) and $T_c = 374°C$ (705°F)], but it does have the interesting property of dissolving nonpolar liquids such as hexane. This is not possible at ambient temperature and pressure.

Membrane separation processes. An important new technology uses membranes to effect separation. The membrane is usually a thin plastic film (0.1–5 micrometers) on a thick porous and inert support layer (100–500 μm) [**Fig. 2**]. The driving force pushing the permeate across the membrane is invariably a pressure difference between the feed mixture and the permeate. The membranes are made of synthetic polymers such as poly(vinyl alcohol), for separating water and alcohol liquids; polyurethane, for separating aromatic liquids from cycloalkane liquids; polyimides, for separating gases such as oxygen and nitrogen; and cellulose acetate, for separating pure water from seawater. *See* MEMBRANE SEPARATIONS.

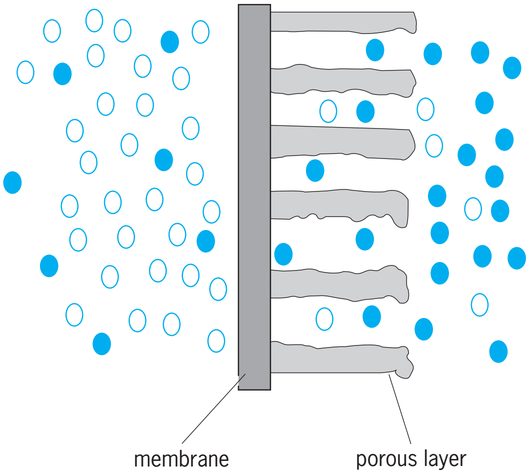

Fig. 2. General description of the membrane separation process. Molecules A (white) and B (black) are separated by a membrane supported on a porous layer and driven by a flux, which is usually pressure.

When the feed and the permeate are both gases, the process is known as gas separation. The pressure difference is usually between 10 and 100 atm (1 and 10 MPa), with the pressure of the permeate being about 1 atm (0.1 MPa). When the feed and permeate are liquids, the process is reverse osmosis, and it is best known for desalination of dilute aqueous solutions such as seawater, brackish water, and industrial wastewater. The pressure applied on the feed side is usually 80–100 atm (8–10 MPa), while the permeate is kept at ambient pressure. If the feed is a liquid under its own saturation pressure and the permeate is a gas or vapor kept at a low pressure ($5–20 \times 10^{-3}$ atm or 0.5–2 kPa) by a suitable vacuum pump, the process is known as pervaporation. The permeate is recovered in a cooling trap. *See* WASTEWATER REUSE; WATER DESALINATION.

Perhaps the main advantage of the membrane technique is that it is possible to tailor-make a membrane for a particular separation. Its limitations include chemical breakdown of the membrane with time and its slowness. The mechanism of the process is complex and involves properties such as the relative solubilities and relative diffusion coefficients of the feed chemicals in the membrane (**Table 2**).

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Chemical separation techniques

A method used in chemistry to purify substances or to isolate them from other substances, for either preparative or analytical purposes. In industrial applications the ultimate goal is the isolation of a product of given purity, whereas in analysis the primary goal is the determination of the amount or concentration of that substance in a sample. In principle it is always more convenient to carry out quantitative determinations directly on portions of the original sample. In cases where the analytical methods available are not sufficiently selective to permit this direct approach, it is necessary to employ preliminary separations to reduce the concentration of, or to remove completely, those substances which interfere in the final estimation.

Although special considerations arise in a comparison of separation methods for engineering or laboratory analytical purposes because of differences in the scales of operations, the various separation processes are based on the same principles. There are three factors of importance to be considered in all separations: (1) the completeness of recovery of the substance being isolated, (2) the extent of separation from associated substances, and (3) the efficiency of the separation. The recovery factor or yield R_A of a separation of substance A is defined as Eq. (1) where

$$R_A = \frac{Q_A}{(Q_A)_0} \qquad (1)$$

Q_A and $(Q_A)_0$ are the amount of A after and before the separation.

The degree of separation $S_{B/A}$ of two substances A and B is given by the separation factor R_B for B with respect to A, and is defined as Eq. (2). Although

$$S_{B/A} = \frac{(Q_A)_0 Q_B}{(Q_B)_0 Q_A} \cong \frac{Q_B}{(Q_B)_0} \cong R_B \qquad (2)$$

complete separations are usually preferred, they are not always necessary in analytical applications. The degree of purity will depend upon the choice of the method of final estimation. Sometimes merely a reduction in the quantity of foreign substance present is enough to simplify the subsequent analytical task.

The third factor, efficiency, is a measure of the amount of work required to obtain a given amount of product with a prescribed purity. This consideration is of much greater consequence in industrial separations in which both the scale and the cost of the operation are important.

There are many types of separations based on a variety of properties of materials. Among the most commonly used properties are those involving solubility, volatility, adsorption, and electrical and magnetic effects, although others have been used to advantage. The most efficient separation will obviously be obtained under conditions for which the differences in properties between two substances undergoing separation are at a maximum.

The common aspect of all separation methods is the need for two phases. The desired substance will partition or distribute between the two phases in a definite manner, and the separation is completed by physically separating the two phases. The ratio of the concentrations of a substance in the two phases is called its partition or distribution coefficient.

In analytical work the original phase is usually a liquid, that is, a solution of the sample, and the separation is brought about through the addition or formation of a solid, a liquid, or a gaseous second phase. Although the actual separation of the phases may be physical in nature, chemical reactions are usually required to convert or modify the substance to a form which permits the formation of the new phase or the partition of the substance to the second phase. In some separation methods this step may also be accomplished by physical means.

If two substances have very similar distribution coefficients, many successive steps may be required for a separation. The resulting process is called a fractionation.

Based on the nature of the second phase, the more commonly used methods of separation are classified as follows: (1) Methods involving a solid second phase include precipitation, electrodeposition, chromatography (adsorption), ion exchange, and crystallization. These methods involve a solid second phase either through the formation of a slightly soluble product, deposition as a metal on the surface of an electrode, or by physical or chemical adsorption on a suitable solid material. (2) The outstanding method involving a liquid second phase is solvent extraction, in which the original solution is placed in contact with another liquid phase immiscible with the first. Separations are achieved as a result of differences in the distribution of solutes between the two phases. Solid materials may also be separated by extraction with organic solvents. (3) Methods involving a gaseous second phase include gas evolution, distillation, sublimation, and gas chromatography. Mixtures of volatile substances can often be separated by fractional distillation. *See* CHROMATOGRAPHY; EXTRACTION.

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Chemical symbols and formulas

A system of symbols and notation for the chemical elements and the combinations of these elements which form numerous chemical compounds. This system of symbols, devised since about 1800 by chemists, consists of letters, numerals, and marks that are designed to denote the chemical element, formula, or structure of the molecule or compound. These symbols give a concise and instantly recognizable description of the element or compound. In many cases, through the efforts of international conferences, the symbols are recognized throughout the scientific world, and they greatly simplify the universal languge of chemistry.

Elements. Of the 115 elements known as of mid-2000, 109 have been given symbols, usually derived from the name of the element. Examples of names and symbols are chlorine, Cl; fluorine, F; beryllium, Be; aluminum, Al; oxygen, O; and carbon, C. However, symbols for some elements are derived from Latin or other names for the element. Examples are Au, gold (from *aurum*); Fe, iron (from *ferrum*); Pb, lead (from *plumbum*); Na, sodium (from *natrium*); and K, potassium (from *kalium*). The symbols consist of one or, more commonly, two letters. The first letter is always a capital letter and is followed by a lowercase second letter.

Inorganic molecules and compounds. Simple diatomic molecules of a single element are designated by the symbol for the element with a subscript 2, indicating that it contains two atoms. Thus the hydrogen molecule is H_2; the nitrogen molecule, N_2; and the oxygen molecule, O_2. Polyatomic molecules of a single element are designated by the symbol for the element with a numerical subscript corresponding to the number of atoms in the molecule. Examples are the phosphorus molecule, P_4; the sulfur molecule, S_8; and the arsenic molecule, As_4.

Diatomic covalent molecules containing unlike elements are given a similar designation. The formula for hydrogen chloride is HCl; for iodine monochloride, ICl; and for hydrogen iodide, HI. The more electropositive element is always designated first in the formula.

For polyatomic covalent molecules containing unlike elements, numerical subscripts are used to designate the number of atoms of each element that are present in the molecule. Examples are phosphorus(III) chloride, PCl_3; arsine, AsH_3; ammonia, NH_3; and water, H_2O. Again, as in diatomic molecules, the more electropositive element is placed first in the formula.

Ionic inorganic compounds are designated by a similar notation. The positive ion is given first in the formula, followed by the negative ion; subscripts are again used to denote the number of ions of each element present in the compound. The formulas for several common compounds are sodium chloride, NaCl; ammonium nitrate, NH_4NO_3; aluminum sulfate, $Al_2(SO_4)_3$; and iron(III) oxide, Fe_2O_3.

More complex inorganic compounds are designated in a manner similar to that above. The positive ion is given first, but may contain attached or coordinated groups, and this is followed by the negative ion. Examples are hexammine-cobalt(III) chloride, $[Co(NH_3)_6]Cl_3$; dichlorobis(ethylenediamine)chromium(III) nitrate, $[Cr(en)_2Cl_2](NO_3)_3$, where en is the abbreviation for ethylenediamine; and potassium trioxalatoferrate(III), $K_3[Fe(C_2O_4)_3]$. Hydrates of inorganic compounds, such as copper(II) sulfate pentahydrate, are designated by the formula of the compound followed by the formula for water, the number of water molecules being designated by a numerical prefix. Thus the symbol for the above compound is $CuSO_4 \cdot 5H_2O$.

Organic compounds. Because there are many more organic than inorganic compounds, the designation or notation for the first group becomes exceedingly complex. Many different types of organic compounds are known; in the case of hydrocarbons, there are aromatic and aliphatic, saturated and unsaturated, cyclic and polycyclic, and so on. The system of notation used must distinguish between the various hydrocarbons themselves as well as setting this group of compounds apart from others such as alcohols, ethers, amines, esters, and phenols. *See* CHEMISTRY; COORDINATION COMPLEXES; INORGANIC CHEMISTRY; ORGANIC CHEMISTRY. Wesley Wendlandt

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Chemical thermodynamics

The application of thermodynamic principles to systems involving physical and chemical transformations is carried out in order to (1) develop quantitative relationships among the identifiable forms of energy and their conjugate variables, (2) establish the criteria for spontaneous change, for equilibrium, and for thermodynamic stability, and (3) provide the macroscopic base for the statistical-mechanical bridge to atomic and molecular properties. The thermodynamic principles applied are the conservation of energy as embodied in the first law of thermodynamics, the principle of entropy production as embodied in the second law, and the principle of absolute entropy and its statistical thermodynamic formulation as embodied in the third law of thermodynamics.

Basic concepts. The basic goal of thermodynamics is to provide a description of a system of interest in order to investigate the nature and extent of changes in the state of that system as it undergoes spontaneous change toward equilibrium and interacts with its surroundings. This goal implicitly carries with it the concept that there are measurable properties of the system which can be used to describe adequately the state of the system, and that the system is enclosed by a boundary or wall which separates the system and its surroundings. Properties that define the state of the system can be classified as extensive and intensive. Extensive properties are proportional to the total mass of the system, whereas intensive properties are not. Typical extensive properties are the energy, volume, and numbers of moles of each component in the system, while typical intensive properties are temperature, pressure, density, and the mole fractions or concentrations of the components.

Extensive properties can be expressed as functions of other extensive properties, for instance, as in Eq. (1), where the volume V of the system is expressed in terms of the internal energy U, the entropy S, and $\{n_i\}$, the set of numbers of moles of the various components labeled by the index i. A suitable transformation procedure can be used to replace extensive variables by conjugate intensive variables. For example, the volume can be expressed as in Eq. (2*a*) or (2*b*).

$$V = V(U, S, \{n_i\}) \qquad (1)$$

$$V = V(P, S, \{n_i\}) \qquad (2a)$$

$$V = V(P, T, \{n_i\}) \qquad (2b)$$

Because temperature T and pressure P are particularly convenient variables to control and measure in chemical systems, the form of Eq. (2*b*) is of great utility. All extensive thermodynamic properties X can be rewritten in this form, as Eq. (3). Because all such properties are linear homogeneous functions of the mass, it can be shown that at a given temperature and pressure Eq. (4) holds, where $\bar{X}_i$ is the partial molar value of the extensive property for the ith component. The value of $\bar{X}_i$ is given by Eq. (5), where the notation $\{n_i\}'$ means that all amounts are constant, except the ith one involved in the derivative. The variable $\bar{X}_i$ is itself intensive.

$$X = X(T, P, \{n_i\}) \qquad (3)$$

$$X = \sum_i n_i \bar{X}_i \qquad (4)$$

$$\bar{X}_i = (\partial X/\partial n_i)_{T,P,\{n_i\}'} \qquad (5)$$

Specification of boundaries. The concept of a boundary enclosing the system and separating it from the surroundings requires specification of the nature of the boundary and of any constraints that the boundary places upon the interaction of the system and its surroundings. Boundaries that restrain a system to a particular value of an extensive property are said to be restrictive with respect to that property. A boundary which restrains the system to a given volume V is a fixed, rigid wall. A boundary which is restrictive to one component of a system but not to the other components is called a semipermeable wall or membrane. A system whose boundaries are restrictive to energy and to mass of components is said to be an isolated system. A system whose boundaries are restrictive only to mass of components is called a closed system, whereas an open system has nonrestrictive walls and hence can exchange energy, volume, and mass with its surroundings. Boundaries can be restrictive with respect to specific forms of energy. Two important types are those restrictive to thermal energy but not work (adiabatic walls), and those restrictive to work but not thermal energy (diathermic walls).

First law of thermodynamics. Thermodynamics concerns the conversion of energy. The laws of thermodynamics differ from other scientific laws in that they are stated in terms of the impossibility of achieving certain types of energy transfers. The laws are usually stated in terms of the primary thermodynamic variables of temperature, energy, heat, work, and entropy.

Stated in terms of the primary thermodynamic functions of temperature, energy, and entropy, the laws of thermodynamics for any actual (that is, nonhypothetical) process are the first law: the total energy is conserved (that is, remains unchanged); the second law: the total entropy increases in any real process; and the third law: the absolute zero of temperature always cannot be reached in any real process.

Temperature. A device designed to measure temperature is called a thermometer. Familiar examples are the liquid-in-glass capillary, thermocouples, and resistance thermometers. All these devices have a property that varies monotonically with temperature. The fundamental thermometer is the constant-volume–ideal-gas thermometer, which is based on the fact that gases for which the constituent molecules do not combine or disassociate (that is, $A + A \rightleftharpoons A_2$ or $A_2 \rightleftharpoons 2A$) obey the ideal-gas equation (6) in the limit as $P \to 0$, where P is the pressure of the gas, V is the volume, n is the number of moles of the gas, and R is the gas constant. With a constant-volume gas thermometer, the temperature of a fixed reference point, such as the melting point of lead metal, is measured using Eq. (7).

$$PV = nRT \qquad (6)$$

$$T = (273.16\ \mathrm{K}) \lim_{P_{273.16\ \mathrm{K}} \to 0} \left[\frac{P_T}{P_{273.16\ \mathrm{K}}} \right] \qquad (7)$$

The pressure, P_T, of the fixed mass of the gas at temperature T is measured for progressively smaller values of the mass of the gas. The resulting calculated values of temperature are extrapolated to zero pressure to obtain the thermodynamic temperature. The value of $P_{273.16\ \mathrm{K}}$ is the corresponding measured pressure of the gas when the thermometer bulb is in contact with water at its triple point. The triple point of water is the single most important reference point in thermometry. It is arbitrarily assigned a temperature of exactly 273.16 K simply in order to preserve a close numerical agreement with older temperature scales, such as the Celsius scale. *See* TRIPLE POINT.

The temperature scale defined by Eq. (7) is an absolute scale. Zero is the lowest possible temperature, and all measurable temperatures on this scale are positive. This temperature scale is called the absolute Kelvin temperature scale, and temperatures are expressed as kelvins. Celsius temperatures are related to Kelvin temperatures via Eq. (8). The temperatures of fixed reference points obtained in the manner

$$t(^\circ\mathrm{C}) = T(\mathrm{K}) - 273.15 \qquad (8)$$

outlined above are, in turn, used to calibrate other, more convenient thermometers. *See* ABSOLUTE ZERO; GAS THERMOMETRY; TEMPERATURE; THERMOMETER.

Energy, work, and heat. Energy is an abstract mathematical concept that is characterized by an energy function, U. Some other thermodynamic functions also are called energy functions (Gibbs energy, Helmholtz energy) and are chosen specifically as state functions that yield exact differentials in terms of experimentally convenient variables such as temperature and pressure. Energy is not a thing. There are no meters capable of the direct measurement of energy, yet there are instruments that measure electric current, gas flow, volume, mass, pressure, length, time, and temperature. These measurable properties are used to calculate energy changes. Determination of the amount of energy transferred from one system to another always involves measurements of the appropriate physical parameters, followed by calculations involving the appropriate energy formulas. *See* ENERGY.

The principle of energy conservation amounts to the statement that, for any real process, the total energy of the system remains unchanged during the process. Energy can be transferred and transformed, but it cannot be created or destroyed. Work and heat are the two modes of energy transfer between systems. The transfer of energy as work requires the existence of an unbalanced force between a system and its surroundings. The transfer of energy as heat requires the existence of a temperature difference between the system and its surroundings. When a force F acts on a system and displaces the system by a differential amount dx, then the work done on the system is given by Eq. (9).

$$\delta w = -F\,dx \tag{9}$$

See CONSERVATION OF ENERGY.

The work w done on a system depends on the path along which the process is carried out, which must be specified before w can be calculated. When the path must be specified before the integral in Eq. (9) can be evaluated, then the integral is called a line integral. If the work done is independent of the path, then the force F is said to be conservative. A conservative force can always be expressed as the negative derivative of a potential energy, ϕ, with respect to the displacement, as in Eq. (10). Thus, for a conservative force, Eq. (11) holds for the process.

$$F = -\frac{d\phi}{dx} \tag{10}$$

$$w = -\int F\,dx = \int_1^2 \frac{d\phi}{dx}\,dx = \int_1^2 d\phi = \phi_2 - \phi_1 \tag{11}$$

Equation (11) shows that, if the force is conservative, then the work done depends only on the end states (1 and 2) and is thus path-independent. *See* WORK.

If at any stage in the process energy is transferred as heat, then the forces acting on the system cannot be conservative, the value of w depends on the path, and the discipline that describes the process moves from classical mechanics to thermodynamics. For a general process involving both work and heat transfers, the first law of thermodynamics is given by Eq. (12). *See* HEAT.

$$dU = \delta q + \delta w \tag{12}$$

The energy function, U, is called the internal energy, and it is a thermodynamic state function. The differential of a thermodynamic state function is said to be exact because the value of $\Delta U = U_2 - U_1$ for the process is path-independent, even if energy is transferred as heat and work in the process, as in Eq. (13).

$$\begin{aligned}\int_1^2 dU &= U_2 - U_1 = \Delta U\\ &= \int_1^2 \delta q + \int_1^2 \delta w = q + w\end{aligned} \tag{13}$$

See DIFFERENTIAL EQUATION; INTERNAL ENERGY.

A key point is that for a given change in state (that is, $1 \rightarrow 2$) the value of $U_2 - U_1$ is independent of path, whereas the values of both q and w depend on the path. It is only the sum $q + w$ that is independent of path. This statement constitutes the essence of the first law of thermodynamics. The following special cases are notable. If the process is adiabatic (that is, $\delta q = 0$), then δw is exact, because $w = \Delta U$. If no work is done (that is, $\delta w = 0$), then δq is exact (pure heat transfer), because $q = \Delta U$. *See* ADIABATIC PROCESS.

Reversible and irreversible processes. Changes in the state of the system can result from processes taking place within the system and from processes involving exchanges of mass or energy with the surroundings. After a process is carried out, if it is possible to restore both the system and the surroundings completely to their original states, then the process is said to be reversible; otherwise the process is irreversible. All naturally occurring spontaneous processes are more or less irreversible.

The internal energy of the system is given by the fundamental equation of state (14). Processes which

$$U = U(S, V, \{n_i\}, \{X_j\}) \tag{14}$$

give rise to a change in U are then limited to those for which Eq. (15) holds. Because all the extensive

$$\begin{aligned}dU = {} & (\partial U/\partial S)_{V,\{n_i\},\{X_j\}}\,dS + (\partial U/\partial V)_{S,\{n_i\},\{X_j\}}\,dV\\ & + \sum_i (\partial U/\partial n_i)_{S,V,\{n_i\}',\{X_j\}}\,dn_i\\ & + \sum_j (\partial U/\partial X_j)_{X,V,\{n_i\},\{X_j\}'}\,dX_j\end{aligned} \tag{15}$$

state properties are linear homogeneous functions, the coefficients of the differential terms are themselves intensive functions and correspond in each case to the conjugate variable of the respective extensive variable. Their product is thus the differential work associated with the appropriate form of energy transfer. The **table** lists several forms of internal energy transfer, their conjugate pair of variables, and their corresponding work terms.

Internal energy and generalized work

Type of energy	Intensive factor	Extensive factor	Element of work
Mechanical			
Expansion	Pressure (P)	Volume (V)	$-PdV$
Stretching	Surface tension (γ)	Area (A)	γdA
Extension	Tensile stretch (F)	Length (l)	Fdl
Thermal	Temperature (T)	Entropy (S)	TdS
Chemical	Chemical potential (μ)	Amount (n)	μdn
Electrical	Electric potential (E)	Charge (Q)	EdQ
Gravitational	Gravitational field strength (mg)	Height (h)	$mgdh$
Polarization			
Electrostatic	Electric field strength ($\mathcal{E}$)	Total electric polarization (dP)	$\mathcal{E}dP$
Magnetic	Magnetic field strength ($\mathcal{H}$)	Total magnetic polarization (M)	$\mathcal{H}dM$

Equation (15) can be rewritten as Eq. (16), where

$$dU = T\,dS - p\,dV + \sum_i \mu_i\,dn_i + \sum_j I_j\,dX_j \tag{16}$$

μ_i is the chemical potential of the ith component and I_j is the conjugate potential for X_j. The internal energy change given by Eq. (16) is dependent only upon the state properties of the system, and hence is independent of the process causing the change.

Enthalpy and heat capacity. A process involving only pressure-volume work may be described by Eq. (17).

$$\delta w = -F\,dx = -(F/A)A\,dx = -P_{\text{ext}}\,dV \tag{17}$$

Here, P_{ext} denotes the externally applied pressure, the definition of pressure $P = F/A$ = force/area is employed, and the volume element dV = (area of the base) × (vertical displacement) = $A\,dx$. Combination of Eqs. (12) and (17) yields Eq. (18).

$$dU = \delta q - P_{\text{ext}}\,dV \tag{18}$$

The enthalpy H, a thermodynamic state function, is defined by Eq. (19), and differentiation of this equation yields Eq. (20).

$$H = U + PV \tag{19}$$

$$dH = dU + P\,dV + V\,dP \tag{20}$$

Combination of Eqs. (18) and (20) yields Eq. (21), and, at constant pressure ($dP = 0$), Eq. (22) holds.

$$dH = \delta q + V\,dP \tag{21}$$

$$dH = \delta q_p \tag{22}$$

From this equation it follows that the addition or removal of energy as heat from a system at constant pressure is equal to the change in enthalpy of the system ($\Delta H = q_p$). *See* ENTHALPY.

The heat capacity of a system is a quantitative measure of the capacity of a system to take up or supply energy as heat. The greater the heat capacity of a system, the smaller the change in temperature produced by the input of energy as heat. The heat capacity is necessarily positive. The heat capacity C_x of a system at constant x (where x is a thermodynamic state function, such as pressure) is defined by Eq. (23), where $C_x(x, T)$ denotes that C_x is a function of both x and T.

$$C_x = \lim_{\Delta T \to 0}\left(\frac{q_x}{\Delta T}\right) = C_x(x, T) \tag{23}$$

For a constant-pressure process, it follows from Eqs. (22) and (23) that Eq. (24) holds.

$$C_p = \lim_{\Delta T \to 0}\left(\frac{q_p}{\Delta T}\right) = \lim_{\Delta T \to 0}\left(\frac{\Delta H}{\Delta T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{24}$$

Also, from Eqs. (24) and (22), it follows that Eq. (25) is valid.

$$q_p = \int_1^2 C_p\,dT \tag{25}$$

A large heat capacity indicates that the system can take up substantial amounts of energy as heat, owing to storage of the energy in the internal modes (translation, rotation, vibration, molecular dissociation) of the constituent particles. For example, the molar heat capacities of solid (s), liquid (l), and gaseous (g) water over the temperature range 250 to 500 K (−23 to 227°C or −10 to 440°F) are as follows:

$$\text{H}_2\text{O(s)}: C_p = 37.66\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\text{H}_2\text{O(l)}: C_p = 75.32\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\text{H}_2\text{O(g)}: C_p = 30.54\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + (1.03 \times 10^{-2}\ \text{T})\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The roughly twofold greater heat capacity of liquid water relative to solid or gaseous water results from the fact that a substantial (roughly half) part of the heat input to liquid water is absorbed in breaking the hydrogen bonds between water molecules in liquid water (about 20 kJ/mol). Ice absorbs energy as heat below its melting point without breaking any hydrogen bonds and thus has a lower value of C_p than liquid water, whereas there are no hydrogen bonds in gaseous water and thus this mode of energy uptake is absent for the gas. *See* HEAT CAPACITY.

Second law of thermodynamics. Most naturally occurring processes involve the transfer of energy as heat. The first law of thermodynamics places no restrictions on energy transfers other than that of conservation of energy. There are, however, other restrictions on energy transfer, namely:

1. Heat always flows spontaneously from higher- to lower-temperature systems.

2. Heat can be induced to flow from a lower- to a higher-temperature system only through the use of energy as work to drive the transfer.

3. When a system undergoes a change in thermodynamic state, then the system and its surroundings cannot both be restored exactly to their original states. All naturally occurring processes are in this sense irreversible.

A mathematical statement of the second law of thermodynamics is that the change in entropy of the system, dS_{sys}, obeys inequality (26), where T is the

$$dS_{\mathrm{sys}} \geq \frac{\delta q_{\mathrm{sys}}}{T} \qquad (26)$$

absolute thermodynamic temperature [measured in kelvins (K)]. The equality sign holds if the process is reversible, and the inequality sign holds if the process is irreversible. The entropy S is a thermodynamic state function, and it is expressed in units of joules per kelvin (J/K).

It is useful to consider a system and its surroundings between which energy can be transferred. If the system undergoes a change in state, then the total entropy change is given by Eq. (27). If the process is

$$dS_{\mathrm{tot}} = dS_{\mathrm{sys}} + dS_{\mathrm{sur}} \qquad (27)$$

adiabatic, then $\delta q_{\mathrm{sys}} = \delta q_{\mathrm{sur}} = 0$ and from Eq. (26) $dS_{\mathrm{sur}} \geq 0$ and $dS_{\mathrm{sys}} \geq 0$. Thus $dS_{\mathrm{tot}} \geq 0$, or $\Delta S_{\mathrm{tot}} \geq 0$.

If the system undergoes an isothermal process, then $T = T_{\mathrm{sys}} = T_{\mathrm{sur}}$. From the second law, it follows that the system and the surroundings obey inequalities (28), but $q_{\mathrm{sys}} = -q_{\mathrm{sur}}$ and thus $\Delta S_{\mathrm{tot}} \geq 0$. Note

$$dS_{\mathrm{sys}} \geq \frac{\delta q_{\mathrm{sys}}}{T} \quad \text{and} \quad dS_{\mathrm{sur}} \geq \frac{\delta q_{\mathrm{sur}}}{T} \qquad (28)$$

that in both cases there is a net entropy production if the process is irreversible, but the total entropy remains unchanged if the process is reversible.

All real processes involve some degree of irreversibility and thus lead to an increase in the total entropy. Entropy is not conserved, except in the hypothetical limiting case of a reversible process.

A thermodynamic system is said to be in an equilibrium state when it can no longer undergo any spontaneous (entropy-producing) processes. The increase in total entropy that occurs in an irreversible process is a consequence of the failure to fully exploit the potential of the system for performing work. When less than the maximum possible work is performed in a process, then net entropy production inevitably results. The total entropy can never decrease and, for a given energy and volume for a closed system, a maximum in entropy indicates the most stable configuration of the system, that is, equilibrium.

Because entropy is a state function, Eq. (29) is

$$\int_1^2 dS = S_2 - S_1 = \Delta S \qquad (29)$$

satisfied. For a given change in state (1 → 2) the change in entropy of the system (but not the total entropy change, $\Delta S_{\mathrm{tot}} = \Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{sur}}$) is independent of the path that the system takes from state 1 to state 2.

There are no entropy meters. Rather, entropy changes are calculated from measurable quantities, such as temperature, pressure, volume, and heat capacity. The total entropy of a system is a measure of the spatial and energy disorder (randomness) in a system.

Compared at the same pressure and temperature, liquids are more disordered than solids and gases are more disordered than liquids. This results follows from the fact that the molecules of a gas have more freedom to move around than the molecules of a liquid. The same holds true for the molecules or ions of a liquid as compared to those of a solid. The melting of a solid involves an entropy increase in the range 8–40 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The temperature dependence of the entropy is found from Eqs. (26) and (24). From Eq. (26) it follows that $q_p = T\Delta S$ for an isothermal pure heat transfer (that is, $\delta w = 0$) at constant pressure. Substitution of this result into Eq. (24) yields Eq. (30). Thus, Eqs. (31) and (32) are valid.

$$\begin{aligned} C_p &= \lim_{\Delta T \to 0} \left(\frac{q_p}{\Delta T} \right) \\ &= T \lim_{\Delta T \to 0} \left(\frac{\Delta S}{\Delta T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \qquad (30) \end{aligned}$$

$$\left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \qquad (31)$$

$$\Delta S = \int_1^2 \frac{C_p}{T}\, dT \quad (\text{constant } P) \qquad (32)$$

Because C_p is greater than 0, the entropy of a substance always increases with increasing temperature at constant pressure. The increase in the entropy of a substance that undergoes an increase in temperature at fixed pressure is a consequence of the increased thermal randomness of the molecules at the higher temperature. A greater amount of energy is more randomly distributed over the same number of particles. *See* ENTROPY.

Gibbs energy and Maxwell relations. Combination of the first law, Eq. (12), with the second law, Eq. (26), yields Eq. (33). If a process involves only pressure-volume work and occurs reversibly, then, applying Eq. (17), Eq. (33) becomes Eq. (34). Because U and

$$dU \geq T\, dS + \delta w \qquad (33)$$

$$dU = T\, dS - P\, dV \qquad (34)$$

S are state functions, the values of ΔU and ΔS can be computed along a reversible path between the given initial and final states of the actual process, and the results for ΔU and ΔS for the system can be equated to those for the actual irreversible process. The values of q and w differ for the two paths, but not the values of ΔU_{sys} or ΔS_{sys}.

Equation (34) is the differential equation used to calculate ΔU. It expresses the change in the dependent variable in terms of changes in the independent variables S and V; that is, $U = U(S, V)$. The variables S and V are not convenient independent variables because they are very difficult to control in the laboratory. More convenient independent variables for experimental work are pressure and temperature. Equation (34) can be transformed into a differential equation with P and T as independent variables through Eqs. (35).

$$dU - T\,dS + P\,dV = 0 \tag{35a}$$

$$dU - T\,dS + P\,dV - S\,dT + V\,dP = -S\,dT + V\,dP \tag{35b}$$

$$d(U - TS + PV) = -S\,dT + V\,dP \tag{35c}$$

For compactness, the thermodynamic energy state function G is defined by Eq. (36). It can be used as a

$$G = U + PV - TS = H - TS \tag{36}$$

criterion for system equilibrium in terms of the more convenient variables, T and P. Here, H is defined by Eq. (19).

The function G is called the Gibbs energy after its creator, J. W. Gibbs; it plays a central role in chemical thermodynamics. From Eqs. (34) and (36), it obeys Eq. (37), which gives the differential equation for

$$dG = -S\,dT + V\,dP \tag{37}$$

dG, where $G = G(T, P)$. Because dG is an exact differential, G is a state function, and from mathematics Eq. (38) holds. Comparison of Eqs. (38) and (37) leads to Eqs. (39) and (40). Equation (39) shows that

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial P}\right)_T dP \tag{38}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{39}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{40}$$

the temperature dependence of the Gibbs energy at constant pressure is determined by the entropy, and Eq. (40) shows that the pressure dependence of the Gibbs energy at constant temperature is determined by the volume.

Because dG is an exact differential, it follows directly that the second cross partial derivatives of Eq. (37) are equal, as given by Eq. (41). This prop-

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P \tag{41}$$

erty is characteristic of an exact differential. Thus, from Eqs. (39), (40), and (41), the Maxwell relation, Eq. (42), is obtained. This relation tells how the

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{42}$$

entropy changes with pressure at constant temperature.

Affinity and chemical equilibrium. Many chemical systems can be considered closed systems in which a single parameter ξ can be defined as a measure of the extent of the reaction or the degree of advancement of a process. If the reaction proceeds or the process advances spontaneously, then entropy must be produced according to the second law, and the uncompensated heat, defined by Eq. (43), must

$$\delta a = T\,dS + \delta w - dU \tag{43}$$

be positive. In terms of the advancement parameter ξ, the uncompensated heat δa is given by Eq. (44),

$$\delta a = \mathcal{A}\,d\xi = T\,d_iS \tag{44}$$

where $\mathcal{A}$ is the affinity of the process or reaction. The affinity is related to internal entropy production d_iS by Eq. (45).

$$\mathcal{A} = T\,d_iS/d\xi \geq 0 \tag{45}$$

The condition that the entropy production is zero represents equilibrium, and hence $\mathcal{A} = 0$ is an equivalent condition for equilibrium in a closed system. For spontaneous processes, because the signs of $\mathcal{A}$ and $d\xi$ must be the same, for positive $\mathcal{A}$ the process must advance or go in a forward direction in the usual sense of chemical reactions or physical processes, while for negative $\mathcal{A}$ the process must proceed in the reverse direction.

For a process that involves only pressure-volume work, Eqs. (17), (36), (43), and (44) can be combined to give Eqs. (46). These equations indicate that the affinity is a state function, given by Eq. (47).

$$dG = -S\,dT + V\,dP - \delta a \tag{46a}$$

$$= -S\,dT + V\,dP - \mathcal{A}\,d\xi \tag{46b}$$

$$\mathcal{A} = -(\partial G/\partial \xi)_{P,T} = \mathcal{A}(T, P, \xi) \tag{47}$$

It is useful to consider a closed system in which a chemical reaction can be characterized by the stoichiometry of reaction (48). This stoichiometry re-

$$\alpha\mathrm{A} + \beta\mathrm{B} \rightarrow \gamma\mathrm{C} + \delta\mathrm{D} \tag{48}$$

quires that at each time element t in the reaction the number of moles of the ith component n_i be given by Eq. (49), where n_i^0 is the number of moles of i

$$n_i = n_i^0 + \upsilon_i\xi \tag{49}$$

in the initial or original state ($t = 0$). The quantity υ_i is the stoichiometric coefficient for the ith component as given in the balanced equation (the convention is that υ_i is positive for products and negative for reactants), and ξ is the degree-of-advancement parameter, whose range is zero to unity. In terms of differential changes in advancement, Eq. (50) holds.

$$dn_i = \upsilon_i\,d\xi \tag{50}$$

For closed systems (constant temperature and pressure) in which only thermal, expansion, and chemical work terms are included, Eqs. (51) and (52)

$$dG = \sum_i \mu_i \, dn_i = -\delta a \qquad (51a)$$

$$= \left(\sum_i \upsilon_i \mu_i \right) d\xi = -\mathcal{A} \, d\xi \qquad (51b)$$

$$\mathcal{A}(T, P, \xi) = -\sum_i \upsilon_i \mu_i \qquad (52)$$

hold. The condition for equilibrium is $\mathcal{A} = 0$, and thus for a chemical reaction, equilibrium is achieved when Eq. (53) holds. If electrical work is included in Eq. (51), Eqs. (54) and (55) hold, where z is the number of units of charge and F is the Faraday constant (the magnitude of the charge per mole of electrons); $F = eN_A$, where e is the electron charge and N_A is Avogadro's number. Because $\mathcal{A} = 0$ is the equilibrium condition, equilibrium in an electrochemical system is given by Eq. (56).

$$\sum_i \upsilon_i \mu_i = 0 \qquad (53)$$

$$dG = \sum_i \mu_i \, dn_i + E \, dQ = -\delta a \qquad (54a)$$

$$= \left(\sum_i \upsilon_i \mu_i + zFE \right) d\xi = -\mathcal{A} \, d\xi \qquad (54b)$$

$$\mathcal{A}(T, P, E, \xi) = -\sum_i \upsilon_i \mu_i - zFE \qquad (55)$$

$$\sum_i \upsilon_i \mu_i = -zFE \qquad (56)$$

More than one reaction can take place in a chemical system, each characterized by a degree-of-advancement parameter ξ_r, and thus for r independent reactions, Eqs. (57) and (58) hold, where the equilibrium condition is Eq. (59). At equilibrium, each of the affinities $\mathcal{A}_r$ must be zero; but for the spontaneous condition, inequality (60) holds. In a two-reaction system inequality (61) holds, but now $\mathcal{A}_1$ and $d\xi_1$ do not necessarily have the same sign. If their signs are different, then the first reaction can be driven in the nonspontaneous direction by the second reaction. The reactions are then said to be coupled; reaction coupling is a common situation in biological systems. *See* CHEMICAL EQUILIBRIUM.

$$dG = \sum_i \mu_i \, dn_i = -\delta a \qquad (57a)$$

$$= -\sum_r \mathcal{A}_r \, \delta\xi_r \qquad (57b)$$

$$= \sum_r \left(\sum_i \upsilon_{ir} \mu_i \, \delta\xi_r \right) \qquad (57c)$$

$$\mathcal{A}_r(T, P, \{\xi_r\}) = -\sum_i \upsilon_{ir} \mu_i \qquad (58)$$

$$\sum_r \mathcal{A}_r \, d\xi_r = 0 \qquad (59)$$

$$\sum_r \mathcal{A}_r \, d\xi_r > 0 \qquad (60)$$

$$\mathcal{A}_1 \, d\xi_1 + \mathcal{A}_2 \, d\xi_2 > 0 \qquad (61)$$

Third law of thermodynamics. Although implicit in the concept of the existence of the fundamental equations of state for U or S is an absolute value of these functions, and therefore an extensive quantity which could be calculated on the basis of molecular properties from quantum mechanics and statistical mechanics, neither the first nor second law considers anything but differences in these state functions. The second law does suggest the existence of an absolute zero for an intensive variable, the temperature, but this is not sufficient to bridge the areas of classical and statistical thermodynamics. *See* ABSOLUTE ZERO.

It is found experimentally, for many isothermal processes involving pure phases, that Eq. (62) applies. This equation includes phase transitions between different crystalline modifications, solid-state chemical reactions, and even the solid-liquid and liquid-liquid isotope transitions in helium. This equation along with Eq. (63), obtained from Eq. (31), implies that at zero absolute temperature the entropy of pure crystalline phases of the same substance or different substances are equal. If the entropies of pure phase are equal at $T = 0$, then it is reasonable to take the value of $S(0)$ to be zero. A statement of the third law then is that the entropy of all pure crystalline fully ordered phases at $T = 0$ is zero. This makes it possible, by using Eq. (63), to calculate the absolute or third-law entropy of a substance from experimental measurements of its heat capacities. Comparison of such experimental values with those calculated by statistical thermodynamic methods has provided evidence for the validity of the third law. In some cases, thorough investigation of apparent discrepancies from the third law has led to new conclusions concerning the molecular structure of the substances or new information on the energy level system for the molecules. Calculation of the thermodynamic properties for a gas from the spectroscopic properties of molecules is an important result stemming from the third law. An alternative statement of the third law is that the absolute zero of temperature is unattainable in any real process. *See* STATISTICAL MECHANICS.

$$\lim_{T \to 0} \Delta S = 0 \qquad (62)$$

$$S(T, P) - S(0, P) = \int_0^T (C_p/T) \, dT \qquad (63)$$

Thermodynamics of irreversible processes. From a mathematical standpoint, if the equations describing a time-dependent physical process change sign when the time variable t is changed to $-t$, then the process is said to be irreversible. If the substitution of t by $-t$ does not change the equations, then the process described is said to be reversible. An example of an irreversible thermodynamic process is the approach to thermal equilibrium, which is described by the Fourier equation (64), where T is the temperature, t

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \qquad (64)$$

is the time, and α is a parameter called the thermal diffusivity. The physicochemical processes of diffusion, heat and electrical conduction, and chemical reactions are irreversible processes. *See* CONDUCTION (ELECTRICITY); CONDUCTION (HEAT); DIFFUSION.

By utilizing Eqs. (44) and (26), the entropy production is found to be given by Eq. (65), where $\mathcal{A}$,

$$dS = \frac{\delta q}{T} + \frac{\mathcal{A}\,d\xi}{T} = d_eS + d_iS \qquad (65)$$

the affinity of the chemical reaction, is related to the chemical potentials by Eq. (52). The reaction rate v is defined by Eq. (66), and thus Eq. (67) holds. It is clear

$$v = \frac{d\xi}{dt} \qquad (66)$$

$$\frac{d_iS}{dt} = \frac{\mathcal{A}v}{T} > 0 \qquad (67)$$

that $\mathcal{A}$ and v always have the same sign and that the affinity $\mathcal{A}$ is directly related to entropy production.

If several reactions are involved simultaneously, then Eq. (68) holds, where the affinities are related

$$d_iS = \frac{1}{T}\sum_k \mathcal{A}_k\,d\xi_k > 0 \qquad (68)$$

to the chemical potentials by Eq. (58). At equilibrium all of the affinities are zero. The entropy production per unit time is given by Eq. (69).

$$\frac{d_iS}{dt} = \frac{1}{T}\sum_k \mathcal{A}_k v_k > 0 \qquad (69)$$

The net entropy production arising from the simultaneous reactions must be positive. However, it is possible to have the inequalities (70) in a two-reaction system, provided that inequality (71) is satisfied. As noted above, such reactions are said to be

$$\mathcal{A}_1 v_1 < 0, \qquad \mathcal{A}_2 v_2 > 0 \qquad (70)$$

$$\mathcal{A}_1 v_1 + \mathcal{A}_2 v_2 > 0 \qquad (71)$$

coupled in that a reaction can proceed in a direction opposed to its affinity, a phenomenon frequently encountered in biological systems. For example, matter may diffuse against its concentration gradient with negative entropy production driven by positive entropy production arising from heat flow.

Equation (69) can be rewritten as Eq. (72), where J_k and X_k are defined by Eqs. (73). The variable J_k

$$\frac{d_iS}{dt} = \sum_k J_k X_k > 0 \qquad (72)$$

$$J_k = v_k, \qquad X_k = \frac{\mathcal{A}_k}{T} \qquad (73)$$

is called a flux (rate) and the variable X_k is called a (generalized) force. At thermodynamic equilibrium Eqs. (74) are satisfied for all values of k.

$$J_k = 0, \qquad X_k = 0 \qquad (74)$$

Close to equilibrium, various empirical laws, such as Fourier's law for heat flow and Fick's law for diffusion, show a linear relation between the J_k and X_k values. Such linear laws are called phenomenological relations. Although such relations do not necessarily hold far from equilibrium, it will be assumed that they do hold close to equilibrium.

It is useful to consider the case of two simultaneous irreversible processes which, in general, satisfy Eqs. (75). The coefficients L_{ij} are called phenomenological coupling coefficients. For example,

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned} \qquad (75)$$

L_{11} and L_{22} may denote heat conductivity and diffusion, while L_{12} describes the interference between these two processes (that is, thermodiffusion). Thus the L_{ij} ($i \neq j$) are called interference coupling coefficients.

Substitution of Eq. (75) into Eq. (72) yields Eq. (76), where the equality sign prevails when

$$\frac{d_iS}{dt} = L_{11}X_1^2 + (L_{12} + L_{21})X_1X_2 + L_{22}X_2^2 \geq 0 \qquad (76)$$

$X_1 = X_2 = 0$. From algebra it follows that the L_{ij} values must satisfy inequalities (77) and (78). Thus

$$L_{11} > 0, \qquad L_{22} > 0 \qquad (77)$$

$$(L_{12} + L_{21})^2 < 4L_{11}L_{22} \qquad (78)$$

while L_{11} and L_{22} must be positive, L_{12} and L_{21} may be positive or negative.

Onsager's theorem states that the coupling coefficients satisfy Eq. (79), which is called the Onsager

$$L_{ij} = L_{ji} \qquad (79)$$

reciprocity relation after its derivation by Lars Onsager. These relations express the fact that if the flux J_i corresponding to the irreversible process i is coupled to the force X_j of the irreversible process j, then the flux J_j also is influenced by the force X_i through the same interference coefficient L_{ij}. *See* OPEN-SYSTEMS THERMODYNAMICS (BIOLOGY); OSMOREGULATORY MECHANISMS; THERMOELECTRICITY; THERMOMAGNETIC EFFECTS.

In the general case, Eq. (80) holds, and when

$$J_i = \sum_i L_{ij}X_j \qquad (80)$$

$L_{ij} \neq 0$ there is a coupling between the flux J_i and the force (gradient) X_j. The principle of microscopic reversibility implies that at least close to equilibrium $L_{ij} = L_{ji}$. Far from equilibrium the situation becomes much more complex, and a detailed molecular-level kinetic (as opposed to a phenomenological) approach is required in the analysis of such cases. *See* THERMODYNAMIC PRINCIPLES; THERMODYNAMIC PROCESSES. Peter A. Rock

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Chemical vapor deposition

The process of producing a microscopic solid-material structure through chemically reacting vapor- or gas-phase reactants on a heated surface. Many of today's most important and most common technologies make use of very thin films of electrically active materials. Chemical vapor deposition (CVD) is a widely used manufacturing technique for products such as electric circuits and processors. Development of novel CVD processes and of new materials for advanced electronics and sensors produced by CVD are active research areas at universities and laboratories around the world. *See* INTEGRATED CIRCUITS; MICROSENSOR.

Basic principle. The fundamental principle of the CVD process is that the chemical reactants, called precursors, are in the gas or vapor state when they arrive at the base material or substrate. A chemical reaction, which is usually activated by heat or some other energy source, occurs on the substrate surface. The products of the reaction are the desired solid-film material and a gaseous product. Layers of semiconductors, dielectrics, conductors, and insulators are built up on the substrate and further processed to produce electronic devices. Scientists study the way the chemistry, flow dynamics, and deposition rate affect the structure and composition of the films and their electrical properties. *See* DIELECTRIC MATERIALS; FILM (CHEMISTRY); SEMICONDUCTOR; SOLID-STATE CHEMISTRY.

Process sequence. The process is summarized in **Figs. 1** and **2.** Reactants and precursor chemicals either are gases or are vaporized from liquid and solid sources by spraying, bubbling, heating, or sublimation. The precursors are supplied as a gas or as vapors in a carrier gas to the reactor chamber. Once in the reactor, the vapors are transported by convection and gas dynamics to the substrate's surface, which is at the desired deposition temperature. Deposition of the thin film occurs on the substrate's surface through reaction of the vapors and gases, usually on a heated substrate. The exhaust products are removed from the reactor by vacuum and treated.

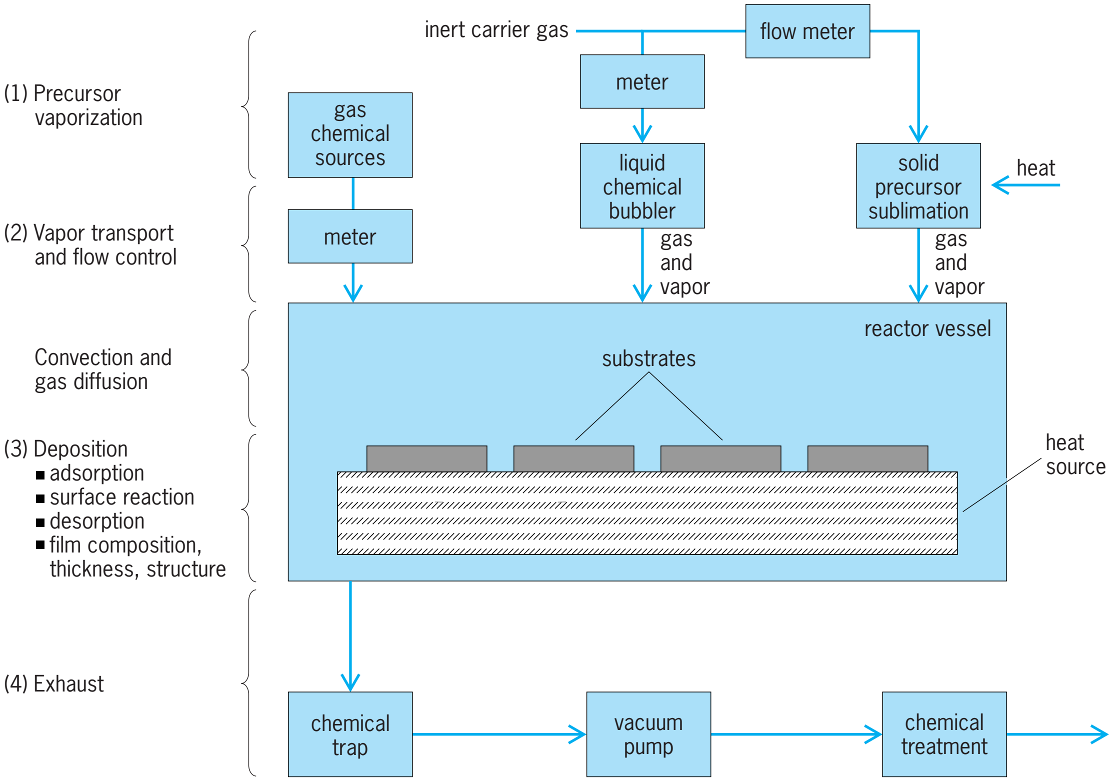

Fig. 1. The components of CVD manufacturing technology reflect the sequence of steps in the CVD process.

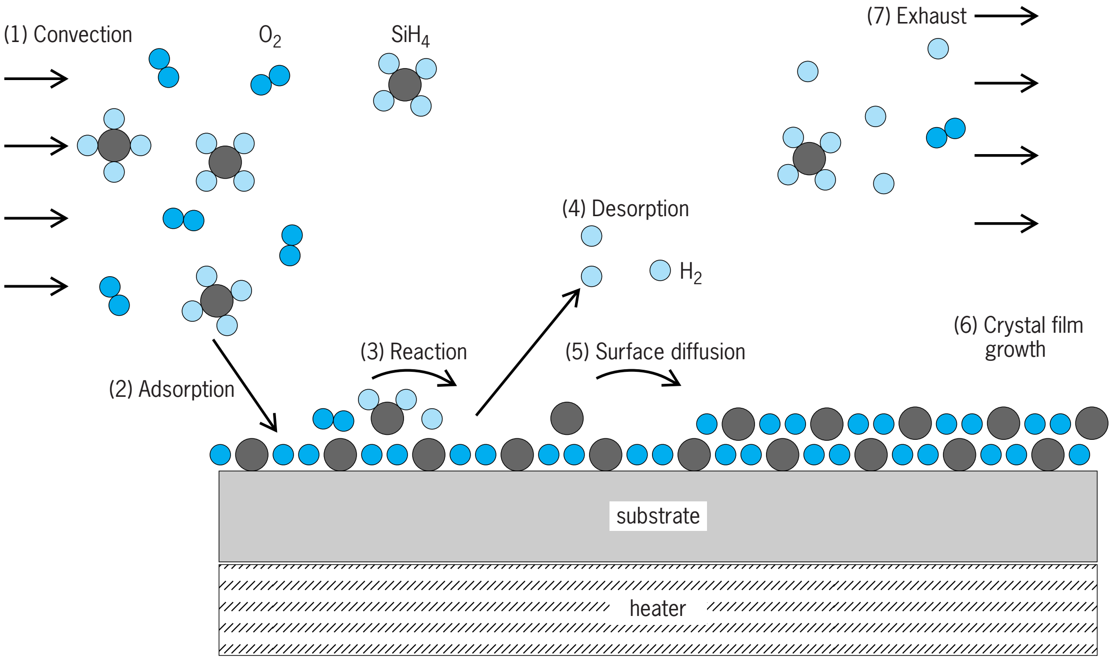

Fig. 2. Sequence of steps involved in the deposition and crystal growth of a solid material (SiO_2) from gas precursors ($SiH_4 + 2O_2$) on the surface of a heated substrate (Si).

Deposition rate. The quality and composition of the thin-film material depends directly on the rates of each step in the process sequence (Fig. 1). The evaporation rate of the precursors is controlled through the flow rate of carrier gases and the evaporation temperature. The feed rate of gas and vapors into the reactor and the pressure at which the reactor is maintained greatly affect the rate at which precursor molecules arrive at the substrate. In addition, the reaction rate at the surface is a strong function of the surface temperature and of the chemical thermodynamics and kinetics. *See* CHEMICAL KINETICS; CHEMICAL THERMODYNAMICS.

Thin-film applications. CVD manufacturing equipment is designed to control each step of the process in order to produce high-quality thin films with the desired properties. The chemistry involved can require the use of high-temperature and high-energy sources, such as plasma, and may require very high vacuum. However, many commercial CVD processes are done at atmospheric pressure, without extreme temperatures. Silicon dioxide (SiO_2) for solid-state electronic devices and optical fibers is produced in a relatively low-temperature (450°C or 840°F) process, using the chemical oxidation reaction of a common precursor, silane (SiH_4) with oxygen (Fig. 2). The CVD system to produce compound semiconductors for solar (photovoltaic) cells (for example, GaAs) must be capable of handling corrosive gases and temperatures over 600°C (1110°F). Batch reactors are used to modify the surface of steel drills and cutting tools by deposition of titanium nitride (TiN) from a precursor gas mixture of titanium tetrachloride ($TiCl_4$), nitrogen (N_2), and hydrogen (H_2) at 1000°C (1840°F). Self-cleaning glass with low reflectivity can be manufactured by deposition of an optically clear film of titanium dioxide (TiO_2) onto glass at less than 450°C (840°F) by using an organometallic precursor [$Ti(OC_3H_7)_4$]. While semiconductor CVD processes have been in practice for well over 20 years, the range of new materials, devices, and applications is expanding rapidly. *See* SEMICONDUCTOR HETEROSTRUCTURES; SOLAR CELL.

Process variations. There are two main categories for CVD processing: atmospheric pressure (APCVD) and low pressure (LPCVD). APCVD is often lower in cost, but it can be more difficult to control the vapor/gas transport processes. LPCVD is most common for electronics, as the low pressure helps ensure the purity necessary for electronically functional materials. When more energy is needed to activate the deposition reaction, plasma-enhanced (PECVD) and laser-enhanced (LECVD) processes are used. Relatively recent developments in a type of precursor chemicals called metal-organic compounds (MOCVD) has led to reduced toxic gas products and reduced processing temperatures.

Developments. CVD researchers investigate the properties of new materials, and the effects that different processing parameters have on these properties. Many scientists also work on reducing toxic-waste gas production through improving the conversion efficiency or through investigating new precursor chemicals. In an effort to reduce the cost of CVD equipment and to improve the control of the evaporation and transport steps in the process, several research groups have begun injecting liquid precursors directly into an evaporation chamber, sometimes using atomization to assist vaporization. For controlling structure, the rate of crystal growth has been found to be enhanced by pulsing, or turning on and off the precursor flow. This gives the crystal time to grow into more highly ordered structures with improved electrical and other properties. *See* CRYSTAL GROWTH; CRYSTAL STRUCTURE. Susan Krumdieck

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Chemiluminescence

The type of luminescence wherein a chemical reaction supplies the energy responsible for the emission of light (ultraviolet, visible, or infrared) in excess of that of a blackbody (thermal radiation) at the same temperature and within the same spectral range. Below 900°F (500°C), the emission of any light during a chemical reaction is a chemiluminescence. The blue inner cone of a bunsen burner or the Coleman gas lamp are examples. *See* BLACKBODY.

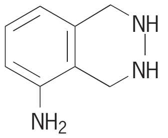
Reactions. Many chemical reactions generate energy. Usually this exothermicity appears as heat, that is, translational, rotational, and vibrational energy of the product molecules; whereas, for a visible chemiluminescence to occur, one of the reaction products must be generated in an excited electronic state (designated by an asterisk) from which it can undergo deactivation by emission of a photon. Hence a chemiluminescent reaction, as shown in reactions (1) and (2), can be regarded as the reverse of a photochemical reaction.

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}^* + \mathrm{D} \tag{1}$$

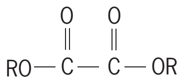
$$\mathrm{C}^* \rightarrow \mathrm{C} + h\nu \tag{2}$$

Energy. The energy of the light quantum $h\nu$ (where h is Planck's constant, and ν is the light frequency) depends on the separation between the ground and the first excited electronic state of C; and the spectrum of the chemiluminescence usually matches the fluorescence spectrum of the emitter. Occasionally, the reaction involves an additional step, the transfer of electronic energy from C* to another molecule, not necessarily otherwise involved in the reaction. Sometimes no discrete excited state can be specified, in which case the chemiluminescence spectrum is a structureless continuum associated with the formation of a molecule, as in the so-called air afterglow: $\mathrm{NO} + \mathrm{O} \rightarrow \mathrm{NO_2} + h\nu$ (green light). *See* HEAT RADIATION; LUMINESCENCE; PHOTOCHEMISTRY.

Efficiency. The efficiency of a chemiluminescence is expressed as its quantum yield ϕ, that is, the number of photons emitted per reacted molecule. Many reactions have quantum yields much lower (10^{-8} $h\nu$ per molecule) than the maximum of unity. Einsteins of visible light (1 einstein $= Nh\nu$, where N is Avogadro's number), with wavelengths from 400 to 700 nanometers, correspond to energies of about 70 to 40 kcal per mole (300 to 170 kilojoules per mole). Thus only very exothermic, or "exergonic," chemical processes can be expected to be chemiluminescent. Partly for this reason, most familiar examples of chemiluminescence involve oxygen and oxidation processes; the most efficient examples of these are the enzyme-mediated bioluminescences. The glow of phosphorus in air is a historically important case, although the mechanism of this complex reaction is not fully understood. The oxidation of many organic substances, such as aldehydes or alcohols, by oxygen, hydrogen peroxide, ozone, and so on, is chemiluminescent. The reaction of heated ether vapor with air results in a bluish "cold" flame, for example. The efficiency of some chemiluminescences in solution, such as the oxidation of luminol (**1**) and, especially, the reaction of some oxalate esters (**2**) with hydrogen peroxide, can be very high ($\phi = 30\%$).



(1)



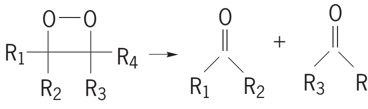
$$\mathrm{RO{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{\overset{\large O}{\|}}{C}{-}OR}$$

(2)

See BIOLUMINESCENCE.

Other aspects. It is believed that the requirements for chemiluminescence are not only that there be sufficient exothermicity and the presence of a suitable emitter, but also that the chemical process be very fast and involve few geometrical changes, in order to minimize energy dissipation through vibrations. For example, the transfer of one electron from a powerful oxidant to a reductant (often two radical ions of opposite charge generated electrochemically) is a type of process which can result, in some cases, in very effective generation of electronic excitation. An example, with 9,10-diphenylanthracene (DPA), is shown in reaction (3). The same is true of the decomposition of four-membered cyclic peroxides (**3**) into carbonyl products, as shown in reaction (4),

$$\mathrm{DPA}^{\overset{-}{\cdot}} + \mathrm{DPA}^{\overset{+}{\cdot}} \rightarrow \mathrm{DPA}^* + \mathrm{DPA} \tag{3}$$



(4)

(3)

which may be the prototype of many chemiluminescences. Therese Wilson

Electrogenerated chemiluminescence. Also known as electrochemiluminescence, this is a luminescent chemical reaction in which the reactants are formed electrochemically. Electrochemical reactions are electron-transfer reactions occurring in an electrochemical cell. In such a reaction, light emission may occur as with chemiluminescence; however, the excitation is from the application of a voltage to an electrode. In chemiluminescence, the luminophore is excited to a higher energetic state by means of a chemical reaction initiated by mixing of the reagents. In electrogenerated chemiluminescence, the emitting luminophore is excited to a higher energy state by reactions of species that are generated at an electrode surface by the passage of current through the working electrode. Upon decay to the electronic ground state, light emitted by the luminophore (fluorescent or phosphorescent) can be detected. The luminophore is typically a polycyclic hydrocarbon, an aromatic heterocycle, or certain transition-metal chelates. *See* ELECTRON-TRANSFER REACTION.

Reaction mechanism. There are many reactions which give rise to electrogenerated chemiluminescence. However, they all share some common features. A typical reaction scheme involves the oxidation of a luminophore (Z), as in reaction, and reduction of a second molecule of the luminophore, as in reaction (5), and reduction of a second molecule of the luminophore, as in reaction (6) where e^- is an electron.

$$\mathrm{Z} \longrightarrow \mathrm{Z}^+ + e^- \qquad (5)$$

$$\mathrm{Z} + e^- \longrightarrow \mathrm{Z}^- \qquad (6)$$

The excited state of the luminophore (Z^*) is formed by a homogeneous charge-transfer reaction (7), between the oxidized and reduced luminophore. The excited luminophore decays to the ground state and emits a photon at a wavelength characteristic of the luminophore, which is measured by means of a photomultiplier detector [(8)].

$$\mathrm{Z}^+ + \mathrm{Z}^- \longrightarrow \mathrm{Z}^* + \mathrm{Z} \qquad (7)$$

$$\mathrm{Z}^* \xrightarrow{h\nu} \mathrm{Z} \qquad (8)$$

An example is the oxidative-reduction reaction using ruthenium tris(2,2′-bipyridine) [$Ru(bpy)_3^{2+}$], and oxalate $C_2O_4^{2-}$. The luminophore $Ru(bpy)_3^{2+}$ and oxalate are oxidized by application of a positive voltage to the electrode [reactions (9) and (10)].

$$\mathrm{Ru(bpy)_3}^{2+} \longrightarrow \mathrm{Ru(bpy)_3}^{3+} + \mathrm{e}^- \qquad (9)$$

$$\mathrm{C_2O_4}^{2-} \longrightarrow \mathrm{C_2O_4}^{-}\cdot + \mathrm{e}^- \qquad (10)$$

In both reactions, one electron is removed for each molecule of starting material. The oxidized oxalate rapidly disassociates [reaction (11)]. The products formed are carbon dioxide and, importantly, a strong reducing agent, $CO_{2-}\cdot$ radical anion. The term oxidative-reduction is descriptive of the process of forming a strong reducing agent through an electrochemical oxidation reaction. An exothermic and energetic reaction between the reducing agent and the oxidized luminophore occurs. Provided the enthalpy of the reaction is greater than the excitation energy, the excited state of the luminophore results from reaction (12). After the emission reaction [(8)], the luminophore is returned to the initial state and is able to again participate in the reaction sequence, and thus it is able to emit many photons during each measurement cycle.

$$\mathrm{C_2O_4^-}\ \cdot \longrightarrow \mathrm{CO_2} + \mathrm{CO_2^-}\ \cdot \qquad (11)$$

$$\mathrm{Ru(bpy)_3}^{3+} + \mathrm{CO_2^-}\ \cdot \longrightarrow \mathrm{Ru(bpy)_3}^{2+*} + \mathrm{CO_2} \qquad (12)$$

Applications. Chief among the developments since the early research and discovery of electrogenerated chemiluminescence was the construction of instrumentation for detection of electrogenerated chemiluminescence. These instruments made it possible for the methodology to be used by practitioners other than electrochemists.

Measurement of the light intensity of electrogenerated chemiluminescence is very sensitive and is proportional to the luminophore concentration. Trace amounts of luminophore as low as 10^{-13} mol/liter can be detected, making electrogenerated chemiluminescence very useful in analytical and diagnostic applications.

A commercial application of the phenomenon forms the basis of a highly sensitive technique for detection of biological analytes such as deoxyribonucleic acid (DNA), ribonucleic acid (RNA), proteins, antibodies, haptens, and therapeutic drugs in the clinical laboratory. The technique combines a binding assay method and a system for detecting electrogenerated chemiluminescence. The reaction is an oxidative-reduction type of mechanism using tripropyl amine and $Ru(bpy)_3^{2+}$. The concentration of analyte from a blood or serum sample is proportional to the intensity of the light from the electrogenerated chemiluminescence reaction. The reaction is carried out with a luminophore that is specially bound to the analyte of interest. The process of specifically binding a label (that is, a luminophore) to an analyte and measuring the extent of binding to determine concentration is referred to as a binding assay. An immunoassay uses as the binding reaction an antibody-antigen reaction. By covalently bonding the luminophore to the antibody, an electrogenerated chemiluminescence–active label is produced. The binding reaction may be of many types; antibody-antigen, ligand-receptor, DNA hybridization, and others.

Relating the intensity of the electrogenerated chemiluminescence to concentration requires the integration of several types of systems: a biological binding reaction that is selective for the analyte and attaches the luminophore; an electrochemiluminescent reaction causing the luminophore to emit light;

and an instrument which integrates the electrochemical cell, light measurement system, and means for sample handling and preparation.

Separation scientists requiring more sensitive detection system capabilities for chromatography have used electrogenerated chemiluminescence as a substitute for more traditional methods of detection, such as fluorescence and spectrophotometry.

Jonathan K. Leland; Laurette Nacamulli; Hongjun Yang

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Chemiosmosis

The coupling of metabolic and light energy to the performance of transmembrane work through the intermediary of electroosmotic gradients. Processes include synthesis of adenosine triphosphate (ATP) by oxidative phosphorylation or by photosynthesis, production of heat, accumulation of small molecules by active transport, movement of bacterial flagella, uptake of deoxyribonucleic acid (DNA) during bacterial conjugation, genetic transformation and bacteriophage infection, and insertion or secretion of proteins into or through membranes.

Oxidative phosphorylation. During the 1940s and 1950s, mitochondria were shown to be the powerhouses of the eukaryotic cell and the site of synthesis of ATP by oxidative phosphorylation. In the oxidation portion of ATP synthesis, reductants, such as reduced nicotinamide adenine dinucleotide (NADH) and succinate, are generated during metabolism of carbohydrates, lipids, and protein. These compounds are oxidized through the series of redox reactions performed by membrane-bound complexes, called electron transport or respiratory chains. The respiratory chains have common features. All are found associated with the inner mitochondrial membrane, and each chain pumps protons from inside the mitochondrion to the cytosol. Each begins with a membrane-bound dehydrogenase enzyme which oxidizes the soluble reductant. The dehydrogenase complex transfers electrons to a lipid-soluble quinone coenzyme, such as ubiquinone, which in turn passes electrons to a series of cytochromes. Cytochromes are proteins which have a heme moiety. Unlike the oxygen-carrier protein hemoglobin, which maintains its heme iron in the reduced state, the irons of cytochromes undergo a cycle of oxidation-reduction, alternating between the ferrous and ferric states. During reduction a cytochrome accepts an electron from the reduced side of the chain and passes it to the cytochrome on the oxidized side of the chain. The terminal cytochrome interacts with molecular oxygen, forming water. The overall reaction for the mitochondrial NADH oxidase is expressed in (1). The reaction

$$\mathrm{NADH} + \mathrm{H}^+ + {}^1/{}_2\mathrm{O}_2 \longrightarrow \mathrm{NAD}^+ + \mathrm{H}_2\mathrm{O} \qquad (1)$$

is exergonic, with a standard free-energy change ($\Delta G^{\circ\prime}$) at pH 7 of −52.6 kcal/mol. *See* CYTOCHROME; HEMOGLOBIN; MITOCHONDRIA.

The phosphorylation half of oxidative phosphorylation is catalyzed by a specific H^+-translocating adenosine triphosphatase (ATPase) enzyme. The ATPase is also a membrane-bound enzyme located in the inner mitochrondrial membrane, catalyzing reaction (2), where ADP is adenosine diphosphate and P_i

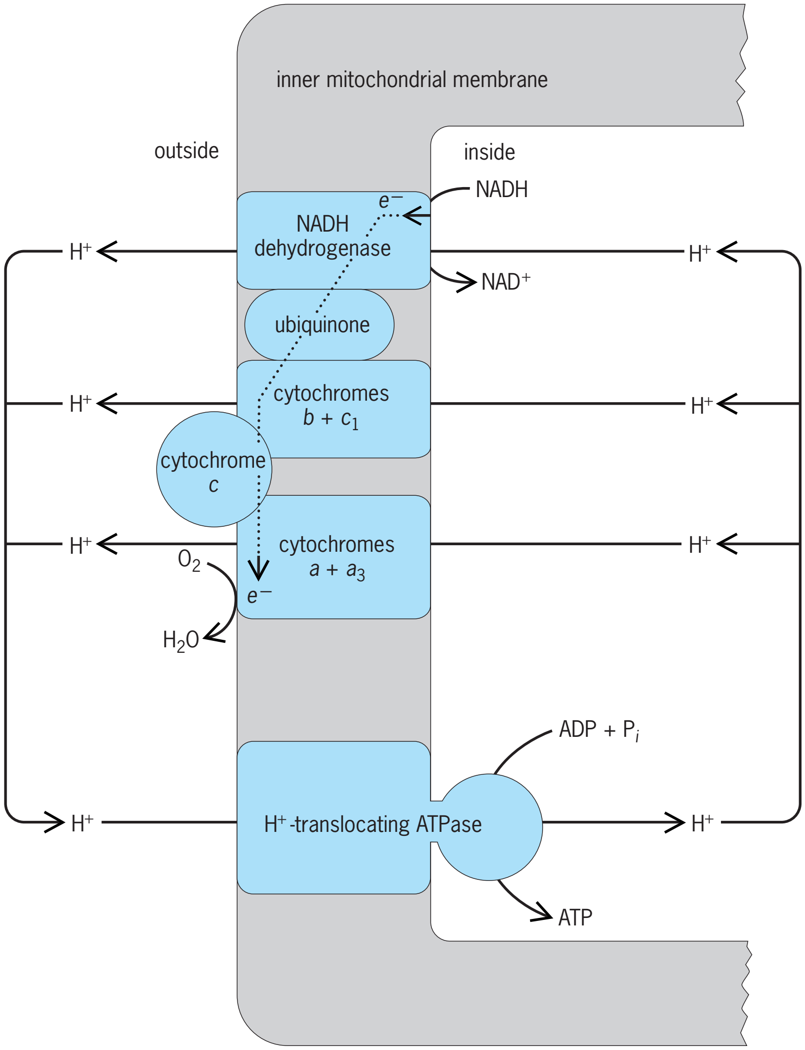
$$\mathrm{ADP} + \mathrm{P}_i + \mathrm{H}^+ \longrightarrow \mathrm{ATP} + \mathrm{H}_2\mathrm{O} \qquad (2)$$

is inorganic phosphate. The reaction occurs with a standard free-energy change, $\Delta G^{\circ\prime}$, of +7.3 kcal/mol. The two processes, oxidation and phosphorylation, are metabolically coupled, so that mitochondria continually synthesize ATP by using energy derived from the respiratory chain. In the case of NADH oxidase, the net reaction is shown as (3). In the overall biological reaction, three ATP's are synthesized for each NADH reduced, even though enough energy was available for six or seven ATP's. This assumes that the actual free-energy change, ΔG, is approximately the same as the standard free-energy change at pH 7, $\Delta G^{\circ\prime}$. Calculations suggest that the free energy of formation of ATP is probably greater than −7.3 kcal/mol, perhaps as much as −10 to −15 kcal/mol, but it is difficult to determine this parameter in a living system. The stoichiometry is a function of the molecular mechanism of coupling.

$$\begin{aligned}&\mathrm{NADH} + {}^1/{}_2\mathrm{O}_2 + 3\mathrm{ADP} + 3\mathrm{P}_i + 4\mathrm{H}^+ \longrightarrow \\ &\qquad\qquad \mathrm{NAD}^+ + 3\mathrm{ATP} + 4\mathrm{H}_2\mathrm{O} \quad (3)\end{aligned}$$

Most early postulates about the mechanism by which the redox energy of NADH is converted into the energy-rich phosphoric anhydride bond of ATP involved the formation of a high-energy chemical intermediate during the flow of electrons down the respiratory chain. This chemical intermediate could then interact with ADP, forming a high-energy nucleotide which could finally interact with P_i, producing ATP. For two decades this chemical intermediate proved elusive. The search culminated in the formulation of the chemiosmotic hypothesis by Peter Mitchell in 1961. For this contribution Mitchell was awarded the Nobel prize in medicine in 1978.

Mitchell postulated that chemical energy, that is, the energy of a chemical bond, can be reversibly converted into electroosmotic energy. The reactions are catalyzed by enzyme complexes which function as primary ion pumps. From the work of Mitchell and of others, the respiratory chain and the ATPase have both been shown to be proton pumps. The respiratory chain transports protons out of the mitochondrion into the cell cytosol, creating an electrochemical gradient of protons. When the ATPase hydrolyzes ATP, it also pumps protons out of the mitochondrion, hence the name H^+-translocating ATPase. Since the free energy produced by respiration is so



Mitochondrial oxidative phosphorylation. The chemiosmotic proton circuit of the inner mitochondrial membrane is depicted. NADH oxidase is composed of three proton-translocating units connected in series to form an electron transport chain. Electrons flow down a redox potential gradient from NADH to oxygen (broken line). Protons are pumped up an electrochemical gradient from inside to outside the mitochondrion, generating a proton motive force. Uptake of protons by the proton-translocating ATPase couples the phosphorylation of ADP to ATP.

much greater than that derived from ATP hydrolysis, proton translocation by the respiratory chain creates a force which drives the uptake of protons by the ATPase and consequently the synthesis of ATP. A diagram of the coupling of oxidation and phosphorylation is shown in the **illustration**.

Mitchell termed the force derived from proton translocation the proton motive force (pmf), by analogy with the electromotive force (emf) of electrochemical cells. Since the pmf is produced by pumping of H^+ ions across the mitochondrial membrane, it has both electrical and chemical components. The electrical or membrane potential ($\Delta\psi$) is due to the separation of positive and negative charges across the mitochondrial membrane. The chemical component results from the separation of H^+ and OH^-. Since $\text{pH} = -\log [H^+]$, $[H^+]$ being the concentration of H^+ ions, the chemical proton gradient is measured as a pH difference, ΔpH. Thus, $\text{pmf} = \Delta\psi - (2.3RT/F) \cdot \Delta\text{pH}$ and $\text{pmf} = \Delta G/F$, where R is the gas constant, T is the temperature, and F is the Faraday constant.

The concept of chemiosmosis is now well accepted, although some still question whether the pmf is the primary source of energy for phosphorylation. Most effort is concentrated on the molecular mechanisms of chemiosmotic coupling. It is clear that respiratory chains pump out protons, but questions such as which components directly transport protons, how many protons are translocated per pair of electrons, and what is the catalytic mechanism of proton translocation are still not adequately answered. It is clear that the ATPase transports protons outward during ATP hydrolysis and inward during synthesis, but the number of protons per ATP is controversial. The protons may directly interact with substrate within an active site, participating directly in catalysis. Conversely, binding of protons may change the shape or conformation of the ATPase enzyme in such a way as to alter its affinity for ATP. These are not trivial distinctions. How these macromolecular complexes work, how chemical energy is transformed into electrochemical and back into chemical energy, cannot be understood without the answers to the more basic questions. *See* ADENOSINE TRIPHOSPHATE (ATP); BIOLOGICAL OXIDATION.

Bacterial oxidative phosphorylation. Bacteria do not contain mitochondria, but many of the functions of the mitochondrial membrane are carried out by the bacterial cytoplasmic membrane. All bacteria contain a H^+-translocating ATPase in their cytoplasmic membrane. This enzyme is nearly identical to that of mitochondria. In fact, the genes for the bacterial and mitochondrial versions are clearly derived from a single evolutionary precursor. Many bacteria also use respiratory chains. Oxygen is not always the terminal electron acceptor of those chains. In some, nitrate or other oxidants can serve this role. But all of the chains are proton pumps. Thus, oxidative phosphorylation in bacteria is also chemiosmotic in nature. This resemblance to mitochondria is more than chance. The evidence, although mostly circumstantial, suggests that mitochondria, chloroplasts, and perhaps other eukaryotic organelles were originally free-living bacteria. These bacteria and larger protoeukaryotic cells became mutually symbiotic, so that neither was complete or viable without the other. The animal and plant kingdoms arose from these endosymbiotic events. *See* BACTERIAL PHYSIOLOGY AND METABOLISM.

Photosynthesis. Photosynthesis is the conversion of light energy into chemical energy. Overall photosynthetic bacteria and the chloroplasts of eukaryotic plants capture sunlight or other light and use that energy to generate both ATP and a reductant for use in biosynthesis. The mechanism of photophosphorylation, that is, the use of light energy to drive the phosphorylation of ADP to ATP, resembles that of oxidative phosphorylation. Chloroplasts use a H^+-translocating ATPase for phosphorylation. Again, the genes for the chloroplast ATPase are derived from the same evolutionary precursor as the mitochondrial and bacterial genes. Electron transport chains are also components of membranes found within chloroplasts. These chains have components similar to those of mitochondria, but the direction of electron flow is reversed. Water is oxidized to produce oxygen. Nicotinamide adenine dinucleotide phosphate ($NADP^+$) is reduced to NADPH, which is used for CO_2 fixation and the synthesis of carbohydrates. The energy to drive these endergonic reactions is derived from light through the absorption of photons by chlorophyll-containing photosystems. The chloroplast electron transport chain comprises a proton pump, generating a pmf which drives the phosphorylation of ADP to ATP by the ATPase. *See* PHOTOSYNTHESIS.

Thermogenesis. Not all of the energy of the proton motive force is coupled productively. It was noted above that enough chemiosmotic energy is generated by respiration to allow for phosphorylation of six or seven ATP. Yet, at best only three are produced. If not coupled to the performance of work, the excess energy may be lost as heat. In some cases, heat production or thermogenesis through the dissipation of the pmf is regulated. Some mammals, for example, cold-adapted animals, hibernating animals, and infants of hairless species (including humans), have a specialized form of adipose tissue called brown fat. The inner membrane of brown-fat mitochondria has unique proton channels which open or close depending on the need for heat. When open, the channels allow for the return of protons extruded by respiration. This cycling of protons uncouples the pmf from ATP synthesis. The energy from proton cycling becomes heat energy. By controlling the rate of the cycle, animals can regulate body temperature. *See* ADIPOSE TISSUE; THERMOREGULATION.

Other chemiosmotic systems. Oxidative phosphorylation and photophosphorylation are but specialized examples of chemiosmotic energy coupling. In the broader sense, the pmf is an ion current analogous to an electric current. Electric generators are machines which convert stored energy into a current of electrons. Among the forms of useful energy are chemical energy, such as that derived from fossil fuels, and light energy in the case of solar cells. Electricity is transmitted to motors, which couple electrical energy to the performance of work. Bacterial cells, mitochondria, and chloroplasts have protonic generators and protonic motors. Respiratory and photosynthetic electron transport chains are generators of proton currents pmf's, which then drive the various motors of the cell or organelle. When the H^+-translocating ATPase is "plugged in," the proton current drives phosphorylation. There are other motors present in the cell. Most membranes contain specific transport systems for small molecules, such as ions, sugars, and amino acids. Many of these transport systems are protonic; that is, they use the energy of the pmf to drive the accumulation or extrusion of their substrate. To give one example, in many bacteria the transport system for the sugar lactose consists of a single membrane protein which catalyzes the simultaneous co-transport of both lactose and a proton. Entry of protons through this carrier protein is driven by the pmf. Since a molecule of lactose enters the cell with each proton, entry and accumulation of lactose is thus coupled to the pmf. *See* BIOPOTENTIALS AND IONIC CURRENTS.

Other metabolic events have been found to use the pmf. Flagellar rotation in bacteria is coupled to the pmf. The flagellum is a motor which uses a flow of protons to do mechanical work, just as a paddle wheel uses a flow of water to turn it. Another example of a membrane event which uses the pmf is the uptake of DNA by bacterial cells. Foreign DNA can enter cells by sexual conjugation, by direct uptake (transformation), or by injection of viral DNA by bacteriophage. Similarly, some proteins destined to be secreted by cells require a pmf to be inserted into, or translocated through, the cytoplasmic membrane. Exactly how the pmf functions in the transport of DNA or protein is not clear. In conclusion, chemiosmosis is a universal phenomenon involved in many membrane and transmembrane events. *See* BACTERIAL GENETICS; BACTERIOPHAGE; CELL MEMBRANES.

Barry Rosen

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Chemistry

The science that embraces the properties, composition, and structure of matter, the changes in structure and composition that matter undergoes, and the accompanying energy changes. It is important to distinguish chemical change, implicit in this definition, and changes in physical form. An example of the latter is the conversion of liquid water to solid or gas by cooling or heating; the water substance is unchanged. In chemical change, such as the rusting of iron, the metal is consumed as it reacts with air in the presence of water to form the new substance, iron oxide.

Modern chemistry grew out of the alchemy of the Middle Ages, and the attempts to transmute base metals into gold. Seminal observations were made in the early eighteenth century on the changes in volume of air during combustion in a closed vessel, and the French chemist Antoine Lavoisier in the 1770s interpreted these phenomena in essentially modern terms.

Atoms and elements. Underlying all of chemistry is the concept of elementary units of matter which cannot be subdivided. This idea was adumbrated in classical Greek writings, and was clearly expressed by the Englishman John Dalton in 1803, who called these units atoms. Different kinds of atoms were recognized, each corresponding to one of the chemical elements such as oxygen, sulfur, tin, iron, and a few other metals. By the mid-nineteenth century, about 80 elements had been characterized, and these were organized on the basis of regularities in behavior and properties, into a periodic table. *See* ELEMENT (CHEMISTRY); PERIODIC TABLE.

In the early twentieth century, observations of radiation from various sources and its impact on solid targets led to the recognition of three fundamental particles that are common to all elements; the electron, with negative charge; the proton, with positive charge; and the neutron, with zero charge. An atom consists of a nucleus containing protons and neutrons, and a diffuse cloud of electrons, equal in number to the number of protons and arranged in orbitals of progressively higher energy levels as the distance from the nucleus increases. The atomic number of an element (Z) is defined as the number of protons in the nucleus; this is the sequence of ordering in the periodic table. The mass number corresponds to the total number of protons and neutrons. *See* ATOMIC NUMBER; ELECTRON; NEUTRON; PROTON.

Isotopes. Most elements exist as isotopes, which have differing numbers of neutrons. All isotopes of an element exhibit the same chemical behavior, although isotopes can be separated on the basis of differences in atomic mass. The known elements as of mid-2000 total 115; of these, 97 have been detected in one or more isotopic forms in the Earth's crust. The other elements, including all but one of those with atomic number above 92, are synthetic isotopes produced in nuclear reactions that take place in nuclear piles or particle accelerators. Most of the isotopes of these heavier elements and also some lighter ones are radioactive; that is, the nuclei are unstable and decay, resulting in the emission of radiation. *See* ISOTOPE; PARTICLE ACCELERATOR; RADIOACTIVITY.

Molecules and chemical reactions. Molecules are combinations of two or more atoms, bonded together in definite proportions and specific geometric arrangements. These entities are chemical compounds; a molecule is the smallest unit. The bonding of atoms in compounds involves the distribution of electrons, and is the central concern of chemistry.

Compounds result from chemical reactions of atoms or molecules. The process involves formation and breaking of bonds, and may be either exothermic, in which the net bond charges lead to a more stable (lower-energy) system and heat is evolved, or endothermic, in which energy must be added to overcome a net loss of bonding energy.

A simple case is the reaction of hydrogen and oxygen to give water, which can be expressed as reaction (1).

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (1)$$
$$\Delta H = 572 \text{ kilojoules}$$

The equation is balanced; no atoms are gained or lost in a chemical reaction. The symbols represent the nature of the initial and final materials and also the relative amounts. Thus H_2O represents a molecule of water or a mole, which is the quantity in grams (or other mass units) equivalent to the molecular weight. The symbol ΔH indicates the energy (enthalpy) change for the process. The reaction of hydrogen and oxygen is highly exothermic, and the sign of the energy charge is therefore negative since the system has lost heat to the surroundings. *See* ENTHALPY; MOLE (CHEMISTRY); STOICHIOMETRY.

Bonds. Bonds can be broadly classified as ionic or covalent. An ion is an atom or molecule which has an electric charge. Ionic compounds can be illustrated by salts such as sodium chloride, NaCl, in which a positive sodium ion, Na^+, and negative chloride ion, Cl^-, are associated by electrostatic attractions in regular locations of a crystal lattice. In solution the ions are solvated by water molecules and can conduct an electric current.

In covalent molecules, bonds are formed by the presence of pairs of electrons in overlapping orbitals between two atoms. Thus when two hydrogen atoms ($H\cdot$) come within bonding distance, a molecule of hydrogen is formed in an exothermic reaction, by formation of a covalent bond. In this case the heat of reaction represents the energy of the H-H bond [reaction (2)].

$$2H\cdot \rightarrow H\text{—}H \qquad (2)$$
$$\Delta H = -435 \text{ kilojoules}$$

See CHEMICAL BONDING.

Chemical compounds. A compound is specified by the elements it contains, the number of atoms of each element, the bonding arrangement, and the characteristic properties. The number of unique compounds that have been isolated from natural sources or prepared by synthesis is enormous; as of 2000, over 15 million substances were registered in the file maintained by Chemical Abstracts (American Chemical Society). Most of these are organic compounds, containing from a few to many hundred carbon atoms. The element carbon, unlike any others, can form long chains of covalently bonded atoms. Moreover, there can be many compounds, called isomers, with the same atomic composition. Thus a molecular formula such as $C_8H_{16}O$ can represent many thousand different compounds. *See* CARBON; MOLECULAR ISOMERISM.

Branches. Traditionally, five main subdivisions are designated for the activities, professional organizations, and literature of chemistry and chemists.

Analytical chemistry. This subdivision is an overarching discipline dealing with determination of the composition of matter and the amount of each component in mixtures of any kind. Analytical measurements are an integral and indispensable part of all chemical endeavor. Originally, analytical chemistry involved detection, separation, and weighing of the substances present in a mixture. Determination of the atomic ratio and thence the molecular formula of a compound is a prerequisite for any other investigation; the development of balances and techniques for doing this on milligram quantities of material had an enormous impact on organic chemistry. Advances since the 1950s have involved increasingly sophisticated instrumentation; mass spectrometers are a notable example. Other important methods include high-resolution chromatography and various applications of electrochemistry. A constant goal in analytical chemistry is the development of methods and instruments of greater sensitivity. It is now possible to detect trace compounds such as environmental pollutants at the picogram level. *See* ANALYTICAL CHEMISTRY.

Biochemistry. Biochemistry is the study of living systems from a chemical viewpoint; thus it is concerned with the compounds and reactions that occur in plant and animal cells. Most of the substances in living tissues, including carbohydrates, lipids, proteins, nucleic acids, and hormones, are well-defined organic substances. However, the metabolic and regulatory processes of these compounds and their biological function are the special province of biochemistry. One of the major areas is the characterization of enzymes and their cofactors, and the mechanism of enzyme catalysis. Other topics of interest include the transport of ions and molecules across cell membranes, and the target sites of neurotransmitters and other regulatory molecules. Biochemical methods and thinking have contributed extensively to the fields of endocrinology, genetics, immunology, and virology. *See* BIOCHEMISTRY.

Inorganic chemistry. This discipline is concerned with any material in which metals and metalloid elements are of primary interest. Inorganic chemistry is therefore concerned with the structure, synthesis, and bonding of a very diverse range of compounds. One of the early interests was the composition of minerals and the discovery of new elements; from this has grown the specialized area of geochemistry. Early synthetic work emphasized compounds of the main group elements, and particularly in this century, complex compounds of the transition metals. These studies have led to soluble transition-metal catalysts, and a greatly increased understanding of catalytic processes and the pivotal role of metal atoms in major biochemical processes, such as oxygen transport in blood, photosynthesis, and biological nitrogen fixation. Other contributions of inorganic chemistry are seen in advanced ceramics, high-performance composite materials, and the growing number of high-temperature superconductors. *See* CATALYSIS; CERAMICS; COMPOSITE MATERIAL; INORGANIC CHEMISTRY; PHOTOSYNTHESIS.

Organic chemistry. This subdivision is centered on compounds of carbon. Originally these were the compounds isolated from plant and animal sources, but the term was early broadened to include all compounds in which a linear or cyclic carbon chain is the main feature. Two of the major thrusts have been the elucidation of new structures and their preparation by synthesis; another long-standing interest has been study of the reaction mechanisms and rearrangments of organic compounds. Structure work on naturally occurring compounds progressed over a 150-year period from simple straight-chain compounds with 2–10 carbon atoms, hydrogen, and 1 or 2 oxygen atoms to antibiotics and toxins with many rings and as many as 100 carbon atoms. In modern work, nuclear magnetic resonance spectroscopy and x-ray diffraction have become indispensable tools. Paralleling structural studies has been the synthesis of increasingly complex target molecules. Synthetic work is directed also to the preparation of large numbers of compounds for screening as potential drugs and agricultural chemicals. Plastics, synthetic fibers, and other high polymers are other products of organic chemistry. *See* NUCLEAR MAGNETIC RESONANCE (NMR); ORGANIC CHEMISTRY; X-RAY DIFFRACTION.

Physical chemistry. This discipline deals with the interpretation of chemical phenomena and the underlying physical processes. One of the classical topics of physical chemistry involves the thermodynamic and kinetic principles that govern chemical reactions. Another is a description of the physical states of matter in molecular terms. Experimentation and theoretical analysis have been directed to the understanding of equilibria, solution behavior, electrolysis, and surface phenomena. One of the major contributions has been quantum chemistry, and the applications and insights that it has provided. The methods and instruments of physical chemistry, including such hardware as spectrometers and magnetic resonance and diffraction instruments, are an integral part of every other area. *See* CHEMICAL THERMODYNAMICS; PHYSICAL CHEMISTRY; QUANTUM CHEMISTRY.

Others. Each broad area of chemistry embraces many specialized topics. There are also a number of hybrid areas, such as bioorganic and bioinorganic chemistry, analytical biochemistry, and physical organic chemistry. Each of these areas has borrowed extensively from and contributed to every other one. It is better to view chemistry as a seamless web, rather than a series of compartments. *See* BIOINORGANIC CHEMISTRY.

James A. Moore

Chemometrics

A chemical discipline that uses mathematical and statistical methods to design or select optimal measurement procedures and experiments and to provide maximum chemical information by analyzing chemical data. Chemometrics is actually a collection of procedures, mathematics, and statistics that can help chemists perform well-designed experiments and proceed rapidly from data, to information, to knowledge of chemical systems and processes.

Medicinal chemists use chemometrics to relate measured or calculated properties of candidate drug molecules to their biological function; this subdiscipline is known as quantitative structure activity relations (QSAR). Environmental chemists use chemometrics to find pollution sources or understand the effect of point pollution sources on regional or global ecosystems by analyzing masses of environmental data. Forensic chemists analyze chemical measurements made on evidence (for example, gasoline in an arson case) or contraband to determine its source. Experimental physical chemists use chemometrics to unravel and identify physical or chemical states from spectral data acquired during the course of an experiment. *See* FORENSIC CHEMISTRY; PHYSICAL CHEMISTRY.

In analytical chemistry, chemometrics has seen rapid growth and widespread application, primarily due to the computerization of analytical instrumentation. Automation provides an opportunity to acquire enormous amounts of data on chemical systems. Virtually every branch of analytical chemistry has been impacted significantly by chemometrics; commercial software implementing chemometrics methods has become commonplace in analytical instruments. *See* ANALYTICAL CHEMISTRY.

Whether the analyst is concerned with a single sample or, as in process analytical chemistry, an entire chemical process (for example, the human body, a manufacturing process, or an ecosystem), chemometrics can assist in the experimental design, instrument response, optimization, standardization, and calibration as well as in the various steps involved in going from measurements (data), to chemical information, to knowledge of the chemical system under study.

Tensorial calibration. Chemical processes are usually controlled by acquiring information on physical properties (such as temperature, pressure, and flow rate) and chemical properties (composition) at one or more locations in a chemical reactor. These data are then fed to process control computers that open or close valves and provide heating or cooling of the process to optimize yield and quality of the product. Sensors that measure product in terms of intermediate or starting material composition are calibrated by using pure standards. One problem often encountered is that the sensor may be sensitive to an unsuspected interferent in the process, causing the reported composition data to be erroneous. Simple sensors generating only one measurement or datum can be classified as zero-order sensors and cannot separate the signal generated by the analyte from the interferent. This is a serious problem in process control.

First order. To solve the problem of separating the signals, chemists have turned to multivariate calibration using first-order instruments. These are instruments capable of producing a vector of measurements, a first-order tensor, per sample and include spectrometers and arrays of nonselective zero-order sensors. For the calibration of such instruments, methods such as classical multilinear regression (MLR), principal components regression (PCR), and partial least-squares regression (PLS) have become popular, especially in infrared and near-infrared spectrophotometry. Besides being able to analyze for multiple analytes in one sample while correcting for interferences, the methods have also been used to predict physical properties from spectral data. While these methods correct for interferences, the interferents must be included in the calibration step according to a good statistical experimental design. If an uncalibrated interferent is present in a sample to be analyzed, these methods can detect its presence but cannot, in general, correct for its effect, and therefore the results are biased.

First-order calibration is used in many areas of process control. The physical properties of polymers, such as tensile strength and the ability to incorporate dyes for color, can be predicted from on-line spectral data acquired during a polymerization process before the process is complete. Another important application involves the use of on-line fiber-optic-based near-infrared spectrometers to predict the octane number of gasoline at various stages of refining and blending. Accurate knowledge of fuel properties during production can save millions of dollars per year at a large refinery. A multivariate calibration method is used to relate the spectral data from calibration samples to one or more known performance properties. If the calibration model passes various statistical tests, it can be used in the refinery. *See* PROCESS CONTROL.

Second order. Quite often the relationship between the analytical measurements and the analyte concentration, or physical property, is nonlinear. Methods are available for calibration and analysis in these cases, for example locally weighted regression, nonlinear partial least squares, and neural networks. *See* LEAST-SQUARES METHOD; NEURAL NETWORK.

A common problem in environmental science is determining the concentrations of pollutants in very complex samples containing completely unknown components. For example, in order to determine the migration of toxic chemicals in the ground near a known or suspected dump site, environmental analytical chemists sample ground and subsurface water from monitoring wells located around the site. Environmental analyzers have been developed that can be lowered down the wells for in-place analysis in order to avoid the time, expense, and other problems associated with taking hundreds of samples to the laboratory. The in-place analyzers must be calibrated, and the calibration models must be capable of accurate determination of the toxic chemicals, even though what may be present in the wells is not fully known. When an unknown interferent is present, it must be physically separated from the analyte by chromatography; or the analyst can move up to second-order calibration using an instrument capable of acquiring a matrix of data, second-order tensor, per sample. These instruments involve all so-called hyphenated methods, for example, gas chromatography–mass spectrometry (GC/MS) and liquid chromatography–ultraviolet, and include as well tandem mass spectrometers (MS/MS), two-dimensional nuclear magnetic resonance spectrometers (2D-NMR), and emission-excitation fluorescence spectrometers. Methods to analyze these data include the generalized rank annihilation method (GRAM) and residual bilinearization; they come in a variety of algorithms according to the mathematical characteristics (for example, bilinearity) of the data. The most important benefit associated with second-order calibration (the second-order advantage) is the possibility to analyze for analytes in the presence of unknown interferents. Also, under certain conditions these methods yield qualitative information about sample components as well as quantitative information. This characteristic is particularly important for environmental or medical applications and assures the analyst that the analyzer is operational. *See* CALIBRATION; CHROMATOGRAPHY.

Standardization. The composition of many agricultural and food products is determined by spectrometers. For example, near-infrared reflectance (NIR) is commonly used to determine the moisture, protein, and fat concentration in wheat or other grains in farm fields. These data are useful for determining harvest time, irrigation, and fertilizer requirements and for setting the value of the product. Either the spectrometers must be calibrated individually or, more desirably, a reference instrument can be calibrated and the calibration model then used with several other similar instruments. Unfortunately, the latter is problematic since no two analytical instruments are exactly alike, even if they come from the same company and have the same model numbers. Also, a single instrument's response to a standard reference sample will change over time because of subtle changes in its components. To circumvent these and similar problems, chemometricians have developed the topic of instrument standardization. This is fundamentally different than calibration, which is used to relate instrument response to the property of interest. The goal of standardization is to correct the response of an instrument to be in accord with another instrument or with itself over the time it is in service.

Standardization can be as simple as using a stable wavelength reference such as a laser line to correct for shifts in wavelength that can invalidate calibration and produce incorrect analyses. There are multivariate instrument standardization methods that use multiple standardization or transfer samples to calculate the parameters of a model that can, for example, correct the response obtained from one instrument so that the response is like that obtained from another instrument. This approach can facilitate the use of a calibration model among several instruments. In process analytical chemistry, this is a major advantage, since a calibration model developed on one instrument, perhaps a high-quality laboratory spectrometer, can be transferred to several process analyzers; thus the need to calibrate each one is avoided, often a very costly process. Also, as the process analyzers change over time (for example, drift), they can be restandardized to generate the same response as when they were first put into service. *See* INSTRUMENT SCIENCE.

Curve resolution. Chromatography is widely used in product testing and quality control, especially in the pharmaceutical industry. As the components of a sample are separated in a chromatogram, it is imperative that the purity of each component be assured in order to avoid having a contaminant in the final product. To help solve this problem, chromatographers employ rapid scanning or diode array spectrometers as detectors so that the spectrum of each component eluting can be checked for purity.

When two analytes coelute near each other during a chromatographic separation of a mixture sample, a single peak in the chromatogram may result. If the analyst has previous knowledge of the shape of a pure analyte elution profile, it may be possible to resolve the mixture peak into the two pure analyte peaks by using, for example, Fourier deconvolution. Fourier deconvolution uses the fast Fourier transform algorithm to mathematically extract a curve with a known shape from a more complex mixture curve, itself composed of a number of curves.

If a spectrometer is used as the detector, multivariate curve resolution methods based on principal components analysis, factor analysis, or singular value decomposition can be used to resolve the mixtures into their component parts, thereby detecting the presence of a product contaminant. *See* CURVE FITTING; FACTOR ANALYSIS.

Pattern recognition. Perhaps the oldest activity in modern chemometrics is the application of data analysis methods developed in computer science and electrical engineering under the heading of pattern recognition to chemical data. As with most of the multivariate methods mentioned above, a pattern recognition application begins when a series of measurements is made on a collection of samples called the training set. For example, the concentrations of a number of trace elements may be measured on several quartzite samples acquired from three known quarries involved in an archeological study. One goal would be to determine if the pattern of trace-element concentrations can be used to distinguish the samples from a given quarry from all of the others. If this training step is successful, the rule or model can be used to classify samples taken from statues or monuments in order to determine their origin. Several studies of this type have been carried out in archeology, where trace-element patterns in antiquities (such as statues or arrowheads) have been traced back to their origins in order to study trade routes or cultural diversity.

Many similar studies have been conducted in forensic chemistry, drug design, screening, taxonomy, and product quality determination. In drug design, structural, chemical, or physical properties are used to classify previously untested drugs as active or inactive in a particular drug screening test. The chemometric methods used are called multivariate classification or supervised learning methods, and they are the same as those used in archeological studies. If the methods are successful, they can be used to predict the activity of untested candidate drug compounds and even to indicate which of the structural, chemical, or physical properties are the most related to biological activity, giving the medicinal chemist information useful for finding more potent drugs.

A medicinal chemist may want to subject a subset of a large set of chemical compounds to a biological screening test. The subset would be selected to represent the structural diversity of the full set as much as possible. Based on structural properties available for each compound, cluster analysis (a type of pattern recognition) might determine that the many compounds can be arranged in, say, 20 groups or clusters, with the compounds belonging to any one group being similar to its class members. The chemist need only test one compound per group, thereby saving considerable expense but getting a good coverage of available compounds.

Other areas. There are several other areas of chemometrics research. Experimental design is a well-developed topic in statistics that chemists use to get the maximum amount of pertinent information from the smallest investment of time, money, or effort. Using one of several multivariate optimization methods, computers can optimally tune complex instruments to get the best possible results. Wherever experiments generating data, particularly large quantities of data, are being conducted, modern chemometrics methods can be applied to make the best measurements possible and move quickly from data to information to knowledge. *See* STATISTICS.

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Chemoreception

The ability of organisms to detect changes in the chemical composition of their exterior or interior environment. It is a characteristic of every living cell, from the single-celled bacteria and protozoa to the most complex multicellular organisms. Chemoreception allows organisms to maintain homeostasis, react to stimuli, and communicate with one another. *See* HOMEOSTASIS.

At the single-cell level, bacteria orient toward or avoid certain chemical stimuli (chemotaxis); algal gametes release attractants which allow sperm to find oocytes in a dilute aqueous environment; and unicellular slime molds are drawn together to form colonial fruiting bodies by use of aggregation pheromones. *See* CELLULAR ADHESION; TAXIS.

In multicellular organisms, both single cells and complex multicellular sense organs are used to homeostatically maintain body fluids (interoreceptors) as well as to monitor the external environment (exteroreceptors). The best-studied interoreceptors are perhaps the carotid body chemoreceptors of higher vertebrates, which monitor the levels of oxygen, carbon dioxide, and hydrogen ions in arterial blood. The best-studied exteroreceptors are those associated with taste (gustation) and smell (olfaction). Such receptors may occur anywhere on the bodies of different organisms, from antennae and tongues to legs and fins, and range from single hair cells in some invertebrates to the complex nasal epithelia of higher vertebrates. Internal communication is also effected by chemical means in multicellular organisms. Thus both hormonal and neural control involve the perception, by cells, of control chemicals (hormones and neurotransmitters, respectively). *See* CAROTID BODY; CHEMICAL SENSES; OLFACTION; SENSE ORGAN; TASTE; TONGUE.

Basic mechanism of action. Although tremendous diversity can be seen in the evolution of complex chemosensory structures, chemoreception is ultimately a property of single cells. The basic mechanism underlying chemoreception is the interaction of a chemical stimulus with receptor molecules in the outer membrane of a cell. These molecules are believed to be proteins which, because of their three-dimensional shapes and chemical properties, will have the right spatial and binding "fit" for interaction with only a select group of chemicals (the same basic mechanism by which enzymes are specific for various substrates). The interaction between a chemical stimulus and a receptor molecule ultimately leads to structural changes in membrane channels by mechanisms that are not totally clear. In some instances, the chemical stimulus–receptor complex activates an enzyme (adenylate cyclase) that synthesizes cyclic adenosine monophosphate (cAMP), which acts as a second messenger interacting with membrane channels and changing their conductance. In other instances, the chemical stimulus interacts with the channel protein directly, altering its conductance. In either case, the net result is usually a change in membrane conductance (permeability) to specific ions which changes both the internal chemical composition of the cell and the charge distribution across the cell membrane. In single-celled organisms, this may be sufficient to establish a membrane current which may elicit responses such as an increase or decrease in ciliary movement. In multicellular organisms, it usually results in changes in the rate of release of hormones or the stimulation of neurons. *See* CELL MEMBRANES.

Characteristics of chemoreceptors. The basic characteristics of all chemoreceptors are specificity (the chemicals that they will respond to); sensitivity (the magnitude of the response for a given chemical stimulus); and range of perception (the smallest or largest level of stimulus that the receptor can discriminate). Specificity is a consequence of the types of proteins found in the membrane of a receptor cell. Each cell will have a mosaic of different receptor molecules, and each receptor molecule will show different combinations of excitatory or inhibitory responses to different molecules. In an excitatory response, there is a net flux of positive ions into the cell (depolarization); for an inhibitory response, there is a net flux of negative ions into the cell (hyperpolarization). In single cells, or in primary sensory neurons, the receptor current will spread along the membrane by passive electrotonic means. The stronger the stimulus—that is, the more of the chemical present—the more receptors affected, the greater the change in conductance, and the larger the membrane current.

In animals with nervous systems, these changes in conductance of primary sensory cells can lead to one of two events. In some receptors, if the current is excitatory and sufficient in magnitude (threshold), an action potential will be generated at a spike-initiating zone on the neuron. Other receptors are not able to generate action potentials but respond by releasing a neurotransmitter (the depolarizing current causes a change in membrane conductance of the transmitter substance) that acts on a second-order neuron which is excitable and therefore can generate action potentials. *See* BIOPOTENTIALS AND IONIC CURRENTS.

The sensitivity of a chemoreceptor reflects both the amount of chemical substance required to initiate a change in membrane potential or discharge of the receptor cell, and the change in potential or discharge for any given change in the level of the chemical stimulus. There are real limits as to the extent of change in membrane conductance or firing frequency. Thus, for more sensitive cells, there is a smaller range over which they can provide information about the change in concentration of any given chemical before it has reached its maximum conductance or discharge rate and has saturated.

In most chemoreceptors, this problem is reduced by a variety of mechanisms. To begin with, the relationship between stimulus intensity and neuronal discharge frequency is usually logarithmic. This means that the high-intensity end of the scale is compressed, greatly extending the range of discrimination of the receptor. Although this may seem to decrease the sensitivity of the receptor at higher stimulus intensities in absolute terms, the increment in discharge remains the same for any given percentage change in stimulus intensity. In other words, a doubling of the stimulus intensity will produce the same increase in receptor potential anywhere over the full range of sensitivity of the cell. Receptor adaptation, a decrease in receptor discharge despite a constant chemical stimulus, also extends the dynamic range over which receptors operate. Finally, in chemoreceptive organs of multicellular organisms, the interaction of chemoreceptors with different threshold levels (range fractionation) can also extend the dynamic range of sensory perception.

Chemosensory systems can be extremely sensitive. Humans can detect 1 molecule of mercaptan in 5×10^{10} molecules of air, while marine crabs have been shown to respond to as little as 10^{-17} lb (10^{-15} g) of prey tissue in 0.264 gal (1 liter) of seawater. Perhaps most impressive, however, is the ability of the antennal chemoreceptor cells of the male silkworm (*Bombyx mori*) to detect a single molecule of female pheromone. Only about 90 molecules per second impinging on a single receptor are required to alter the firing rate of a cell, and stimulation of only 40 chemoreceptors out of roughly 20,000 per antenna is sufficient to evoke a behavioral response (excited wing flapping). *See* PHEROMONE.

Chemoreceptor tuning. In animals, the responsiveness of some chemoreceptors can be either enhanced or attenuated by other neural input. These influences come in the form of efferent inputs from the central nervous system, from neighboring receptors, or even from recurrent branches of the chemoreceptor's own sensory axons. The net effect is either (1) to increase the acuity of the receptors (excitatory input brings the membrane potential of the receptor cell closer to threshold, requiring less chemical stimulus to elicit a response); or (2) to extend the range of responsiveness of the receptors (inhibitory input lowers the membrane potential of the receptor cell, requiring more chemical stimulus to bring the cell to threshold). For example, chemical sensitivity is greatly heightened in most animals when they are hungry.

Central integration of input. Any given chemoreceptor cell can have any combination of receptor proteins, each of which may respond to different chemical molecules with either an increase or a decrease in the membrane potential. Thus, chemoreceptor cells do not exhibit a unitary specificity to a single chemical substance, but rather an action spectrum to various groups of chemicals. The ability of animals to distinguish such a large number of different, complex, natural chemical stimuli resides in the ability of higher centers in the nervous system to "recognize" the pattern of discharge of large groups of cells. Sensory quality does not depend on the activation of a particular cell or group of cells but on the interaction of cells with overlapping response spectra.

Structural adaptations. Despite the common, basic mechanism underlying chemoreception in all organisms, there is a great diversity in the design of multicellular chemoreceptive organs, particularly in animals. The complex structures of most of these organs reflect adaptations that serve to filter and amplify chemical signals. Thus, the antennae in many insects, and the irrigated protective chambers, such as the olfactory bulb of fishes and nasal passages of mammals, increase the exposure of chemoreceptor cells to the environment. At the same time, they allow the diffusion distances between chemoreceptive cells and the environment to be reduced, thereby increasing acuity. In terms of filtering, they may serve to convert turbulent or dispersed stimuli into temporal patterns that can be more easily interpreted. The extent to which such structural adaptations are seen in various organisms tends to reflect the relative importance of chemoreception to the organism, which, to a large extend, reflects the habitat in which the organism lives. *See* CHEMICAL ECOLOGY.

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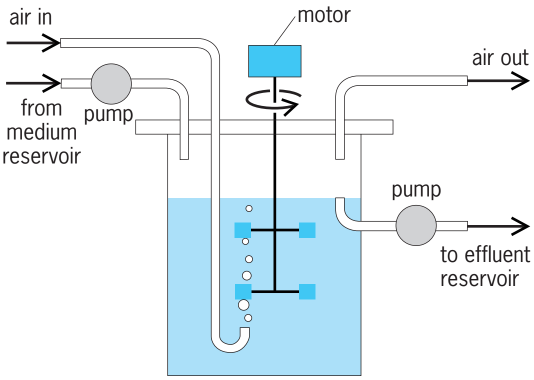
Chemostat

An apparatus (see **illus.**) for the continuous cultivation of microorganisms, such as bacteria, yeasts, molds, and algae, or for the cultivation of plant cells. The nutrients required for cell growth are supplied continuously to the culture vessel by a pump



Schematic representation of chemostat apparatus.

connected to a medium reservoir. The cells in the vessel grow continuously on these nutrients. Residual nutrients and cells are removed from the vessel (fermenter) at the same rate by an overflow, thus maintaining the culture in the fermenter at a constant volume.

Parameters. An important feature of chemostat cultivation is the dilution rate, defined as the volume of nutrient medium supplied per hour divided by the volume of the culture. During chemostat cultivation, an equilibrium is established (steady state) at which the growth rate of the cells equals the dilution rate. The higher the dilution rate, the faster the organisms are allowed to grow. Above a given dilution rate the cells will not be able to grow any faster, and the culture will be washed out of the fermenter. The chemostat thus offers the opportunity to study the properties of organisms at selected growth rates. This is particularly important because in their natural environment microorganisms seldom grow at their maximum rate. Under nutrient limitation, cells may display properties which also are of great importance in a number of applications, such as industrial fermentation and wastewater treatment. *See* FERMENTATION; WATER TREATMENT.

The nutrient medium which is fed to the fermenter contains an excess of all growth factors except one, the growth-limiting nutrient. The concentration of the cells (biomass) in the fermenter is dependent on the concentration of the growth-limiting nutrient in the medium feed. Upon entering the fermenter, the growth-limiting nutrient is consumed almost to completion, and only minute amounts of it may be found in the culture and the effluent. Initially, when few cells have been inoculated in the growth vessel, even the growth-limiting nutrient is in excess. Therefore, the microorganisms can grow at a rate exceeding their rate of removal. This growth of cells causes a fall in the level of the growth-limiting nutrient, gradually leading to a lower specific growth rate of the microorganisms. Once the specific rate of growth balances the removal of cells by dilution, a steady state is established in which both the cell density and the concentration of the growth-limiting nutrient remain constant. Thus the chemostat is a tool for the cultivation of microorganisms almost indefinitely in a constant physiological state.

To achieve a steady state, parameters other than the dilution rate and culture volume must be kept constant (for example, temperature and pH). The fermenter is stirred to provide a homogeneous suspension in which all individual cells in the culture come into contact with the growth-limiting nutrient immediately. Furthermore, stirring is also required to achieve optimal distribution of air (oxygen) in the fermenter when aerobic cultures are in use.

Laboratory chemostats usually contain 0.5 to 10.5 quarts (0.5 to 10 liters) of culture, but industrial chemostat cultivation can involve volumes up to 343,000 gal (1300 m^3) for the continuous production of microbial biomass.

Advantages. The chemostat offers a number of advantages for the cultivation of cells as compared with growth in a batch culture. In the latter, a closed system, organisms grow in excess nutrients at their maximum rate, and the nutrient concentration, products, and biomass change continuously. When a nutrient becomes depleted, a rapid fall in the growth rate takes place. This often leads to the death of cells. In the chemostat, however, the constancy of all parameters allows accurate and reproducible experiments. By varying the dilution rate, within limits, the rate of growth of the organisms can be changed at will. The density of cells in the cultures can be chosen by the appropriate concentration of the growth-limiting nutrient in the medium reservoir. Depending on the question to be answered, the type of growth-limiting nutrient can be selected. Of course, possible choices are limited by the nature and capabilities of the organisms studied.

The chemostat can be used to grow microorganisms on very toxic nutrients since, when kept growth-limiting, the nutrient concentration in the culture is very low. The chemostat can be used to select mutants with a higher affinity to the growth-limiting nutrient or, in the case of a mixed population, to select the species that are optimally adapted to the growth limitation and culture conditions. The chemostat is of great use in such fields of study as physiology, ecology, and genetics of microorganisms. *See* BACTERIAL GENETICS; BACTERIAL PHYSIOLOGY AND METABOLISM; MICROBIOLOGY.

Mathematical description. The operation of a chemostat can also be described in mathematical terms. Growth of a microorganism can be described by the empirical formula of J. Monod (1942) as a function of the growth-limiting substrate, Eq. (1), in

$$\mu = \mu_{\max} \frac{C_s}{K_s + C_s} \qquad (1)$$

which μ is the specific growth rate (h^{-1}), $\mu_{\max}$ is the maximum specific growth rate, C_s is the concentration of the growth-limiting substrate, and K_s is a Monod saturation constant, numerically equal to the substrate concentration at which $\mu = {}^1\!/_2\mu_{\max}$. The relationship between C_s and μ is a typical saturation curve. When an organism is grown in a closed system (batch culture) with, initially, excess substrate, it will grow at $\mu_{\max}$. During growth its environment will constantly change, but if the conditions remain favorable, growth will continue until the growth-limiting compound is depleted. Near the end of growth, μ will fall because of the factors described by Eq. (1), and will finally become zero.

The chemostat can be considered as an open culture system in which fresh (sterilized) medium is introduced at a constant flow rate ϕ, and from which the culture fluid emerges at the same flow rate. At a constant volume υ and an in-flow rate ϕ, the dilution rate D is defined by Eq. (2), in which the dilution rate is expressed in h^{-1}.

$$D = \frac{\phi}{V} \tag{2}$$

Monod demonstrated that over a large range of growth rates a fixed relationship exists between the amount of (growth-limiting) substrate consumed and the amount of biomass produced, Eq. (3), in which C_x

$$\frac{dC_x}{dt} = -Y''_{sx}\frac{dC_s}{dt} \tag{3}$$

is the biomass concentration and t is time. Y''_{sx} is the yield factor and is defined as the amount (weight) of cell material produced per amount (weight, or mole) of substrate consumed. Y''_{sx} is not always a constant.

If the medium in the fermenter is inoculated (for example, with bacteria), the culture will grow at a given rate. At the same time, a quantity of bacteria will be washed out because the culture is continuously fed and diluted with fresh medium. It thus follows that accumulation of biomass in the culture is equal to growth minus washout.

The balance equation is Eq. (4). Hence if μ is

$$\frac{dC_x}{dt} = \mu C_x - DC_x = (\mu - D)C_x \tag{4}$$

greater than D, C_x will increase, while if μ is less than D, C_x will decrease. If μ equals D, Eq. (4) will be zero and an equilibrium will exist.

It can be shown mathematically that, irrespective of the starting conditions, a steady state, with μ equal to D, must inevitably be reached, provided that D does not exceed a critical value.

In order to calculate the steady-state concentrations of biomass and the growth-limiting nutrient in the culture, mass balance equations similar to Eq. (4) for the nutrients entering, being consumed, and leaving the culture must also be made. In Eq. (5), C_s is

$$\frac{dC_s}{dt} = D(C_{si} - C_s) - \frac{\mu C_x}{Y''_{sx}} \tag{5}$$

the substrate concentration in the culture, and C_{si} the concentration of the substrate entering the vessel. The net change in C_{si} per unit of time is equal to the dilution rate multiplied by the difference in substrate concentration entering and leaving the culture, minus the substrate consumed. The substrate consumed is expressed as the growth divided by the yield, Eq. (3). At steady state, both Eqs. (4) and (5) are zero. This, when combined with Eq. (1), will lead to the equilibrium concentrations $\overline{C}_x$ for biomass [Eq. (7)] and $\overline{C}_s$ for the substrate [Eq. (6)]. Here

$$\overline{C}_s = K_s(D/\mu_{\max} - D) \tag{6}$$

$$\begin{aligned}\overline{C}_x &= Y''_{sx}(C_{si} - \overline{C}_s)\\ &= Y''_{sx}\left(C_{si} - \frac{K_s \cdot D}{\mu_{\max} - D}\right)\end{aligned} \tag{7}$$

K_s, $\mu_{\max}$, and Y''_{sx} are constants for a microorganism under the specified conditions of temperature, medium composition, and the nature of the growth-limiting substrate. For C_{si} and D, any realistic constant value can be chosen. From Eq. (6) it appears that $\overline{C}_s$ solely depends on D. Equation (7) shows that $\overline{C}_x$ depends on D and C_{si} and is proportional to C_{si} if $\overline{C}_s \ll C_{si}$, which is usually the case. If K_s, $\mu_{\max}$, and Y''_{sx} are known for a given micrognanism, the relationship between C_x or C_s, and D can be predicted at a chosen C_{si}.

J. Gijskuenen

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Chemostratigraphy

A subdiscipline of stratigraphy and geochemistry that involves correlation and dating of marine sediments and sedimentary rocks through the use of trace-element concentrations, molecular fossils, and certain isotopic ratios that can be measured on components of the rocks. The isotopes used in chemostratigraphy can be divided into three classes: radiogenic (strontium, neodymium, osmium), radioactive (radiocarbon, uranium, thorium, lead), and stable (oxygen, carbon, sulfur). Trace-element concentrations (that is, metals such as nickel, copper, molybdenum, and vanadium) and certain organic molecules (called biological markers or biomarkers) are also employed in chemostratigraphy. *See* DATING METHODS; ROCK AGE DETERMINATION.

Radiogenic isotope stratigraphy. Radiogenic isotopes are formed by the radioactive decay of a parent isotope to a stable daughter isotope. The application of these isotopes in stratigraphy is based on natural cycles of the isotopic composition of elements dissolved in ocean water, cycles which are recorded in the sedimentary rocks. The element commonly used is strontium, but osmium and neodymium isotopes are used as well. *See* ISOTOPE; RADIOISOTOPE.

Strontium (Sr) has four naturally occurring, stable isotopes, with mass numbers (sum of protons and neutrons) 88, 87, 86, and 84. Strontium-87 is radiogenic, formed by the radioactive decay of rubidium-87. Strontium replaces calcium in calcium carbonate and other calcium-bearing minerals (such as aragonite, apatite, and plagioclase). Calcite typically contains 500–2000 parts per million strontium, and aragonite (another form of calcium carbonate) contains 2000–9000 ppm. Strontium is the major cation in strontianite ($SrCO_3$) and celestite ($SrSO_4$), but its principal occurrence in minerals is as a trace element.

The ocean is a large reservoir of dissolved strontium. The isotopic composition of strontium in the oceans reflects the isotopic composition and relative proportions of strontium entering the ocean. Strontium is delivered to the oceans by dissolution in river water with an average ratio of strontium-87 to strontium-86 ($^{87}Sr/^{86}Sr$) of 0.710 and by dissolution and recrystallization of submarine carbonates. Strontium is removed from the oceans by incorporation into precipitate minerals such as calcium carbonate as well as by inorganic precipitation of evaporites, phosphorites, and ferromanganese oxides. Seawater also exchanges strontium with ocean-floor rocks at mid-ocean ridges. Ocean-floor rocks (basalt) have a relatively low average $^{87}Sr/^{86}Sr$ ratio of 0.703. The variations in the $^{87}Sr/^{86}Sr$ ratio in seawater over millions of years are largely due to the changing inputs of continent-derived strontium delivered by rivers versus strontium derived from exchange of seawater with sea-floor basalt. Comparison of the strontium isotope curve and the geologic record indicate that the $^{87}Sr/^{86}Sr$ ratio in seawater is highest during periods of mountain building and continental collision, when there is a large flux of material from the continents due to increased erosion rates. Conversely, the $^{87}Sr/^{86}Sr$ ratio is lowest in seawater during times when the continents are splitting apart and when sea-floor spreading rates are greatest. *See* SEAWATER.

Measurements of the $^{87}Sr/^{86}Sr$ ratio of calcium-bearing marine precipitates (calcium carbonate, anhydrite, gypsum, and phosphate minerals) show that the $^{87}Sr/^{86}Sr$ ratio of strontium dissolved in seawater has fluctuated over the past 600 million years between the limits of 0.7068 and 0.7092. Because the average strontium atom remains in seawater 3–4 million years before it is removed, which is much longer than the mixing time of the oceans (1000 years), the $^{87}Sr/^{86}Sr$ ratio in seawater is the same throughout the oceans at any given time. Consequently, calcite that forms in the ocean in different places at the same time has the same $^{87}Sr/^{86}Sr$ ratio. When the $^{87}Sr/^{86}Sr$ ratio is changing rapidly with time in seawater, such as between the late Eocene and the present (the past 40 million years), excellent age resolution can be obtained for stratigraphic studies. *See* EOCENE.

An assumption in using strontium isotopes (or any geochemical method) in stratigraphic studies is that the $^{87}Sr/^{86}Sr$ ratio remains unaltered during diagenesis (all the chemical and physical changes that occur in the sediment following its deposition), and hence retains the original strontium isotopic signature. Careful inspection and sample selection prior to analysis are necessary to assess the degree of diagenetic alteration. *See* DIAGENESIS; STRONTIUM.

Stable isotope stratigraphy. The elements hydrogen (H), carbon (C), nitrogen (N), oxygen (O), and sulfur (S) owe their isotopic distributions to physical and biological processes that discriminate between the isotopes because of their different atomic mass. The use of these isotopes in stratigraphy is also facilitated by cycles of the isotopic composition of seawater, but the isotopic ratios in marine minerals are also dependent on water temperature and the mineral-forming processes.

Oxygen isotope stratigraphy. Oxygen isotope stratigraphy has developed since the mid-1950s following the pioneering work of Harold Urey; it has become the most widely used method for dating and correlating marine sediments deposited during the Quaternary (Pleistocene and Holocene). Oxygen isotope stratigraphy is based on the ratio of two isotopes of oxygen (oxygen-18 and oxygen-16) in the calcium carbonate ($CaCO_3$) shells of marine fossils. *See* QUATERNARY.

Detailed measurements of the ratio of oxygen-18 relative to oxygen-16 ($^{18}O/^{16}O$) in planktonic foraminifera from sediments cored in the deep ocean show that the ocean changed periodically over the past 3 million years because of alternating glacial (or ice age) and interglacial conditions. During glacial periods, water depleted in oxygen-18 is transferred to and stored on the continents as glaciers, leaving the oceans enriched in oxygen-18 (higher $^{18}O/^{16}O$ ratio). Although both the water temperature and the $^{18}O/^{16}O$ ratio in the water determine the $^{18}O/^{16}O$ ratio in the carbonate shells, the fluctuations of the $^{18}O/^{16}O$ ratio between interglacial and glacial periods are mainly caused by fluctuating continental ice volume. Each isotopic fluctuation representing a glacial-interglacial cycle has been assigned a stage number, with odd numbers corresponding to interglacial periods and even numbers corresponding to glacial periods (numbered 1 through 23). These stages are globally synchronous and can be intercalibrated with other stratigraphic scales, such as magnetostratigraphy and biostratigraphy. There is much evidence that these climatic fluctuations (called Milankovitch cycles) are a result of changes in the incoming solar radiation reaching the surface of the Earth. The dominant periodicities of these cycles are 100,000, 40,000, and 23,000 years. *See* GLACIAL EPOCH; INSOLATION.

Carbon isotope stratigraphy. Stable carbon (C) isotope stratigraphy involves measurements of the ratio of carbon-13 to carbon-12 ($^{13}C/^{12}C$) in carbonate ($CaCO_3$) fossil shells and organic matter. Organic matter and calcium carbonate are converted to carbon dioxide (CO_2) prior to simultaneous measurement of the ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ on a gas-source mass spectrometer.

The carbon isotopic composition in marine organisms (calcite shells or organic tissue) reflects the local and global changes in the cycling of nutrients and CO_2 in the ocean, as well as ocean circulation and ocean-atmosphere interactions. The $^{13}C/^{12}C$ ratio of both organic material and carbonate material can be used as a stratigraphic tool. The $^{13}C/^{12}C$ ratio of a sample depends on the $^{13}C/^{12}C$ ratio of the source [atmospheric CO_2 for land plants, both dissolved CO_2 and bicarbonate (HCO_3^-) for aquatic environments] and the isotopic fractionation produced by equilibrium and kinetic effects (the fractionation of isotopes of the same element in physical or chemical processes occurs because of their slight mass differences). In general, organic carbon is depleted in carbon-13 relative to carbonate carbon in the marine environment. A major focus of carbon isotope studies in stratigraphy is the assessment of detailed variations and excursions of the $^{13}C/^{12}C$ ratio on a stratigraphic level. For example, during periods of increased productivity in the surface layer of the ocean, the carbon-12 is preferentially removed by phytoplankton during photosynthesis, enriching the surface water in carbon-13. Calcium carbonate and organic tissue that form during these periods have an increased $^{13}C/^{12}C$ ratio. Many organic carbon-rich, laminated black shales of Jurassic and Cretaceous age contain organic carbon that is enriched in carbon-13.

Sulfur isotope stratigraphy. The isotopic composition [the ratio of sulfur-34 to sulfur,-32 ($^{34}S/^{32}S$)] of sulfur in the sulfate molecules (SO_4^{2-}) dissolved in seawater has varied systematically through Phanerozoic time (the past 600 million years). Sulfate is a major constituent of the marine evaporite minerals gypsum and anhydrite, which are the materials commonly used as recorders of the ocean isotopic ratios. The $^{34}S/^{32}S$ ratio in seawater reflects a complex balance of the sulfate delivered to the oceans by rivers; it also reflects the relative importance of sulfur removal as reduced sulfur in pyrite, as opposed to oxidized sulfur in gypsum and anhydrite. *See* ANHYDRITE; GYPSUM; PYRITE.

Radioactive isotope stratigraphy. Radiocarbon [the radioactive isotope of carbon (^{14}C)] and the isotopes uranium-234 (^{234}U) and thorium-230 (^{230}Th) are used in radioactive isotope stratigraphy.

Radiocarbon stratigraphy. Carbon-14 is used in dating and stratigraphy of both marine and terrestrial sediments younger than 50,000 years. Radiocarbon is continually produced in the upper atmosphere by the capture of neutrons by nitrogen (^{14}N), forming carbon-14, which is radioactive with a half-life of about 5730 years. The carbon-14 enters the hydrosphere and biosphere as CO_2, and it is incorporated into plant and animal organic tissues and hard parts (such as calcium carbonate). When the plant or animal dies, exchange with the atmosphere ceases; the carbon-14 begins to decay, starting the radioactive clock.

Uranium-thorium stratigraphy. Marine minerals such as calcite incorporate minor amounts of the radioactive isotope uranium-234 (^{234}U), which has a half-life of 2.4 million years and decays to thorium-230, which is also radioactive with a half-life of 70,000 years. Because marine calcite forms almost free of thorium-230, the accumulation of radiogenic thorium-230 can be used to measure the age of marine calcites up to about 300,000 years old. This technique is valuable for measuring the age of coral reefs. *See* THORIUM; URANIUM.

Molecular stratigraphy. Certain organic molecules that can be linked with a particular source (called biomarkers) have become useful in stratigraphy. The sedimentary distributions of biomarkers reflect the biological sources and inputs of organic matter (such as that from algae, bacteria, and vascular higher plants), and the depositional environment. *See* DEPOSITIONAL SYSTEMS AND ENVIRONMENTS.

One method of molecular stratigraphy uses the composition of long-chain alkenones (lipids whose molecules comprise chains of 37–39 carbon atoms). These compounds are produced by certain photosynthetic algae (coccolithophorids) that regulate the fluidity of their membranes in waters of different temperatures by biosynthetically controlling the extent of unsaturation in their alkenones. The degree of unsaturation of alkenones in marine sediments varies as a function of water temperature, which varies from glacial to interglacial times. A molecular stratigraphic record of sea surface temperatures in Quaternary sequences has been developed and intercalibrated with the oxygen isotope record for the past half million years. Alkenones are found in marine sediments throughout the Quaternary and Tertiary.

Trace elements. Certain trace metals, such as nickel, copper, vanadium, magnesium, iron, uranium, and molybdenum, are concentrated in organic-rich sediments in proportion to the amount of organic carbon. Although the processes controlling their enrichment are complex, they generally form in an oxygen-poor environment (such as the Black Sea) or at the time of global oceanic anoxic events, during which entire ocean basins become oxygen poor, resulting in the death of many organisms; hence large amounts of organic carbon are preserved in marine sediments. The trace-metal composition of individual stratigraphic units may be used as a stratigraphic marker (or “fingerprint”), making it possible to correlate, for example, black shales from location to location within a basin. *See* GEOCHEMISTRY; MARINE SEDIMENTS; STRATIGRAPHY.

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Chemotherapy and other antineoplastic drugs

Chemotherapy is the use of chemicals to treat any disease, but the term has come to be applied most commonly to the use of drugs to treat cancer and that exhibit cytotoxic activity through inhibition of cell division. Recently, several other classes of drugs (biologicals) started to be used to treat cancer, often in conjunction with conventional chemotherapy. Cancer is an abnormal growth or proliferation of cells that tends to invade locally or spread to distant parts of the body. Several treatment modalities can be used for cancer. Surgery physically removes the abnormal growth, whereas radiation, immunotherapy, hormonal therapy, and chemotherapy are directed at killing or slowing the growth of cancerous cells. *See* CANCER (MEDICINE).

History. In 1865, in an early, well-documented use of chemotherapy, Heinrich Lissauer gave potassium arsenite (Fowler's solution) to treat leukemia. Despite this work, Paul Ehrlich, a German physician and 1908 Nobel Laureate in Medicine, is generally credited with pioneering the field of chemotherapy and coining the word. However, his efforts were directed toward discovering antibiotics for infections rather than cancer drugs. He was an early advocate of understanding biochemically why certain chemicals effectively kill actively growing bacteria. He also coined the term "magic bullet" for drugs that specifically kill bacteria. *See* ANTIBIOTIC.

The first extensively utilized cancer chemotherapeutic agent was nitrogen mustard, which was used in the mid-1940s by Alfred Gilman and Frederick S. Philips for the treatment of lymphomas and chronic leukemias. During World War I it had been noted that mustard gas, used as a toxic irritant, caused destruction of lymph nodes and bone marrow, which are both sites of active cell proliferation. This observation suggested that mustard gas is toxic to actively growing cells and that it might also kill proliferating cancer cells. Nitrogen mustard is still occasionally used for the treatment of some lymphomas, although it has largely been replaced by other chemotherapeutic regimens. *See* LEUKEMIA.

Folic acid antagonists. The second group of useful anticancer drugs developed were folic acid antagonists. All actively growing cells require the chemical metabolite folic acid to grow and divide. The antagonists were designed to inhibit a cancer cell's ability to produce folic acid, and therefore they are toxic. Aminopterin was the first in this group to be employed clinically. A major breakthrough occurred in 1948, when it was reported that over half of children with acute leukemia could obtain temporary remissions by using aminopterin. This began the era of antimetabolite therapy. Methotrexate, a related drug, replaced aminopterin and is still used in acute lymphoblastic leukemia, choriocarcinoma, carcinomas of the head and neck region, and for other tumors. The first documented chemotherapeutic cure was with methotrexate, which was used in 1961 to treat a gestational choriocarcinoma.

Nucleic acid antagonists. The third group of chemotherapeutic agents was designed to have a toxic effect on the cell's DNA. The development of these drugs was based on the hypothesis, conceived by George Hitchings and Gertrude Elion, that tumor growth might be stopped with chemicals that antagonize nucleic acids, which are necessary for cancer cell growth and division. They eventually were awarded the Nobel Prize in Physiology or Medicine for the development of such compounds. The first clinically useful compound, 6-mercaptopurine, was described in 1952 and is still used for the treatment of acute lymphoblastic leukemia. Another drug, with a different site of action, 5-fluorouracil, was synthesized in 1957 by Charles Heidelberger. It is used today in the treatment of colorectal, head and neck, and breast cancer. Cytarabine (cytosine arabinoside) was reported in 1968 to be useful in adult acute leukemia. It is still used for the primary treatment of most patients with acute myeloid leukemia. Fludarabine is a modern member of this group effective in the treatment of chronic lymphocytic leukemia.

Antitumor antibiotics. Antitumor antibiotics became recognized as potential chemotherapeutic agents in 1954, when actinomycin D (dactinomycin) was studied. They differ from antimicrobial antibiotics in that their spectrum of cytotoxicity includes human cells rather than bacteria and fungi. Doxorubicin (Adriamycin) is one of the most widely used anticancer drugs for both solid tumors and blood or bone marrow tumors.

Since the mid-1950s, many new drugs have been developed. This progress was stimulated by the pharmaceutical industry, by the important preclinical work of Howard E. Skipper and Frank M. Schabel, Jr., at the Southern Research Institute, and by the establishment of a special section of the U.S. National Cancer Institute for drug development and testing, which began work in 1955. Chemotherapeutic drugs now total more than 50, many having novel mechanisms (**Table 1**). The availability of the techniques of molecular biology and a greater understanding of the genetic abnormalities of cancer are resulting in more effective therapies, which tend to be more specific for cancer cells. Drugs which inhibit angiogenesis (blood vessel formation) or which target promoting (oncogenes) or suppressing (tumor suppressor) genes are being tested and incorporated into treatment regimens.

Monoclonal antibodies. A new class of drugs involves the use of monoclonal antibodies that target specific cell receptors. Bevacizumab is a recombinant humanized monoclonal antibody against the vascular endothelial growth factor (VEGF). VEGF is found to be overexpressed in many cancers and is in part responsible for the process of intratumoral angiogenesis. Bevacizumab is currently used in metastatic colon cancer.

Cetuximab, which binds the epidermal growth factor receptor (EGFR), and Trastuzumab, which targets Her2-neu receptor in breast cancer cells, are other examples of antibodies currently used in clinical practice (Table 1). Rituximab is an important therapeutic monoclonal antibody to the B-lymphocyte cell-surface molecule designated CD20. It has important activity in inhibiting the growth of lymphomas that express CD20. It is also possible to deliver a chemotherapy agent to a specific target cell type using a monoclonal antibody. For example, gemtuzumab ozogamicin (Mylotarg) is a drug with the monoclonal antibody anti-CD33 attached to a cytotoxic antitumor antibiotic, calicheamicin. This drug is thereby targeted by the antibody to the leukemia cell. Other than a small incidence of allergic reactions during infusion, side effects of monoclonal antibodies are variable and are closely related to the function of the receptor (VEGF, EGFR, CD20) being targeted by the antibody. Monoclonal antibodies also have been combined with

TABLE 1. Groups of drugs and mechanisms of action

Group	Source	Mechanism of action	Examples	Uses
Alkylating agents	Chemical synthesis	Blocking of DNA synthesis by chemical attachment of a reactive part of the drug (alkyl portion) to DNA and other cell components to form damaging cross links	Ifosfamide, cyclophosphamide, busulfan, chlorambucil, melphalan, dacarbazine, carmustine (BCNU), lomustine (CCNU), streptozotocin, procarbazine, hexamethylmelamine, thiotepa, nitrogen mustard (mechlorethamine), estramustine, temozolomide	Many solid tumors and hematologic (blood and bone marrow) malignancies; brain tumors; often used for high-dose chemotherapy prior to bone marrow transplantation
Antifolates	Chemical synthesis	Inhibition of DNA synthesis by inhibiting the enzyme dihydrofolate reductase	Methotrexate, pemetrexed	Head and neck cancer; lung cancer, leukemia; lymphoma; breast cancer; choriocarcinoma; mesothelioma
Antipurines	Chemical synthesis	Variable, for example, incorporation into DNA as a false building block (6-mercaptopurine, cladribine), inhibition of DNA polymerase which is required for synthesis (fludarabine), and inhibition of adenosine deaminase enzyme with the accumulation of deoxyadenosine which kills lymphocytes	Fludarabine, cladribine, azathioprine, 6-mercaptopurine, 6-thioguanine, pentostatin, clofarabine	Chronic lymphocytic leukemia; acute lymphoblastic leukemia; lymphoma; hairy cell leukemia; immunosuppression after transplantation or for aplastic anemia and autoimmune blood disorders
Antipyrimidines	Chemical synthesis	Variable, for example, incorporation into DNA (cytarabine); inhibition of thymidylate synthase (5-fluorouracil), and inhibition of DNA methylation (5-azacitidine)	Cytarabine, 5-fluorouracil, floxuridine, capecitabine, gemcitabine, 5-azacitidine, nelarabine	Acute leukemia; breast, colorectal, pancreas, and head and neck cancer; myelodysplastic syndrome
Anticancer antibiotics	Fungi or bacteria or chemical synthesis	Variable, for example, oxidation of DNA and RNA (bleomycin), inhibition of RNA synthesis (actinomycin D)	Bleomycin, dactinomycin, mitoxantrone, mitomycin C, streptozotocin	Hodgkin's disease; lymphoma; testis, breast, cervix, penis, islet cell pancreas, and head and neck cancer; acute lymphoblastic leukemia
Anticancer antibiotics of the anthracycline group	Bacteria	Several may be important, including intercalation into DNA, oxygen free-radical formation, and inhibition of topoisomerase type II	Idarubicin, doxorubicin, daunorubicin, epirubicin	Acute leukemia; Hodgkin's disease; lymphomas; multiple myeloma; breast, lung, bone, and thyroid cancer
Drugs that interfere with synthesis of cell microtubules	Semisynthesis or natural occurrence	Binding of the protein tubulin and interference with polymerization which is required to form microtubules	Vincristine, vinblastine, vindesine, vinorelbine	Multiple myeloma; lymphoma; lung and testis cancer; acute lymphoblastic leukemia; Hodgkin's disease
Drugs that stabilize microtubules against depolymerization and induce mitotic block	Tree bark, fungi, or semisynthesis	Enhanced microtubule formation, inhibition of mitosis	Paclitaxel, docetaxel	Colorectal, ovarian, breast, lung, germ cell, and head and neck cancer
Cytokines	Recombinant DNA technology	Interference with intracellular signaling	α-Interferon, aldesleukin (interleukin-2)	Chronic myelocytic leukemia; melanoma; kidney cancer; hairy cell leukemia
Topoisomerase inhibitors	Semisynthesis	Inhibition of topoisomerase enzymes I and II resulting in single- or double-strand DNA cleavage	Etoposide, teniposide, topotecan, irinotecan, anthracyclines	Leukemia; lymphoma; lung, colorectal, and ovarian cancer; myelodysplastic syndrome
Platinum drugs	Chemical synthesis	Binding to and inhibiting function of DNA	Cisplatin, carboplatin, oxaliplatin	Lung, ovary, and bladder cancer

(cont.)

TABLE 1. Groups of drugs and mechanisms of action (*cont.*)

Group	Source	Mechanism of action	Examples	Uses
Enzyme therapy	Bacteria	Depletion of asparagine, an essential amino acid	Asparaginase, pegasparaginase	Acute lymphoblastic leukemia
Inhibitors of ribonucleotide reductase	Synthesis	Inhibition of ribonucleotide reduction necessary for DNA synthesis	Hydroxyurea	Myeloproliferative diseases (such as chronic myelocytic leukemia, polycythemia vera, essential thrombocytosis); acute leukemia; melanoma; head and neck cancers; sickle cell anemia
Differentiating agents	Derivative of vitamin A	Binding to receptors on cell nucleus and stimulating differentiation of some cells	Tretinoin (all-*trans*-retinoic acid)	Acute promyelocytic leukemia
Molecular targeted therapy: small-molecule kinase inhibitors	Chemical synthesis	Inhibit dysregulated cancer-related kinases	Imatinib mesylate (targets ABL tyrosine kinases such as BCR/ABL kinase), gefitinib and erlotinib (both target epidermal growth factor receptor kinases), sorafenib (multikinase inhibitor that targets serine/threonine and tyrosine kinases)	Chronic myelocytic leukemia, acute lymphoblastic leukemia with Philadelphia chromosome, gastrointestinal stromal tumors, hypereosinophilic syndrome, non-small-cell lung cancer, kidney cancer
Proteasome inhibitors	Chemical synthesis	Inhibit a large complex that degrades proteins	Bortezomib	Multiple myeloma
Forms of naturally occurring elements	Natural	Not known. Induces apoptosis and differentiation	Arsenic trioxide	Acute promyelocytic leukemia
Monoclonal antibodies	Hybridoma techniques	Monoclonal antibodies against surface proteins	Rituximab (anti-CD20), alemtuzumab (anti-CD52), bevacizumab (antivascular endothelium growth factor), cetuximab (antiepidermal growth factor receptor), trastuzumab	Lymphomas, chronic leukemias, colorectal cancer, breast cancer
Targeted immuno-chemotherapy	Hybridoma techniques and chemical synthesis	Use cancer surface receptors to target chemotherapy	Gemtuzumab ozogamicin	Acute myelocytic leukemia
Targeted immuno-radiotherapy	Hybridoma techniques and chemical synthesis	Use cancer surface receptors to target radioactive compounds	Ibritumomab tiuxetan, tositumomab/iodine I-131	Lymphomas
Immunomodulatory drugs	Chemical synthesis	Multiple (antiangiogenic, T-cell modulation, cytokine secretion modulation)	Thalidomide and lenalidomide	Multiple myeloma, myelodysplastic syndromes
DNA methylation modulators	Chemical synthesis	Reverse abnormal DNA methylation	5-Azacitidine, decitabine	Myelodysplastic syndromes, acute leukemia
Hormonal therapy	Chemical synthesis	Multiple (blocks receptors, inhibits hormones, other)	Goserelin, bicalutamide, ketoconazole, tamoxifen, anastrozole, letrozole, tamoxifen	Prostate and breast cancer

radioisotopes for the treatment of lymphomas.

Tyrosine kinase inhibitors. Another class of anticancer agents that has been recently introduced in oncology clinical practice involves small-molecule tyrosine kinase inhibitors. Among other functions, tyrosine kinase enzymes regulate several of the intracellular processes normally responsible for cell proliferation. In cancers, these processes are often found to be dysregulated. Imatinib mesylate (Gleevec) is one of the most exciting recent drugs. It is a rationally designed ABL (Abelson leukemia oncogene) specific tyrosine kinase inhibitor. It inhibits BCR-ABL, which characterizes chronic myelocytic leukemia cells, and results in hematologic, cytogenetic, and sometimes molecular complete remissions (no abnormality detectable by the most sensitive molecular techniques). Erlotinib inhibits the EGFR-associated tyrosine kinase and has been shown to produce a survival benefit in patients with advanced non-small-cell lung cancer. Special patient populations that may derive greater benefit from erlotinib are being actively studied, including those with other cancers. These tyrosine kinase inhibitors can frequently be given by mouth. A large number of other inhibitors are currently under clinical investigation.

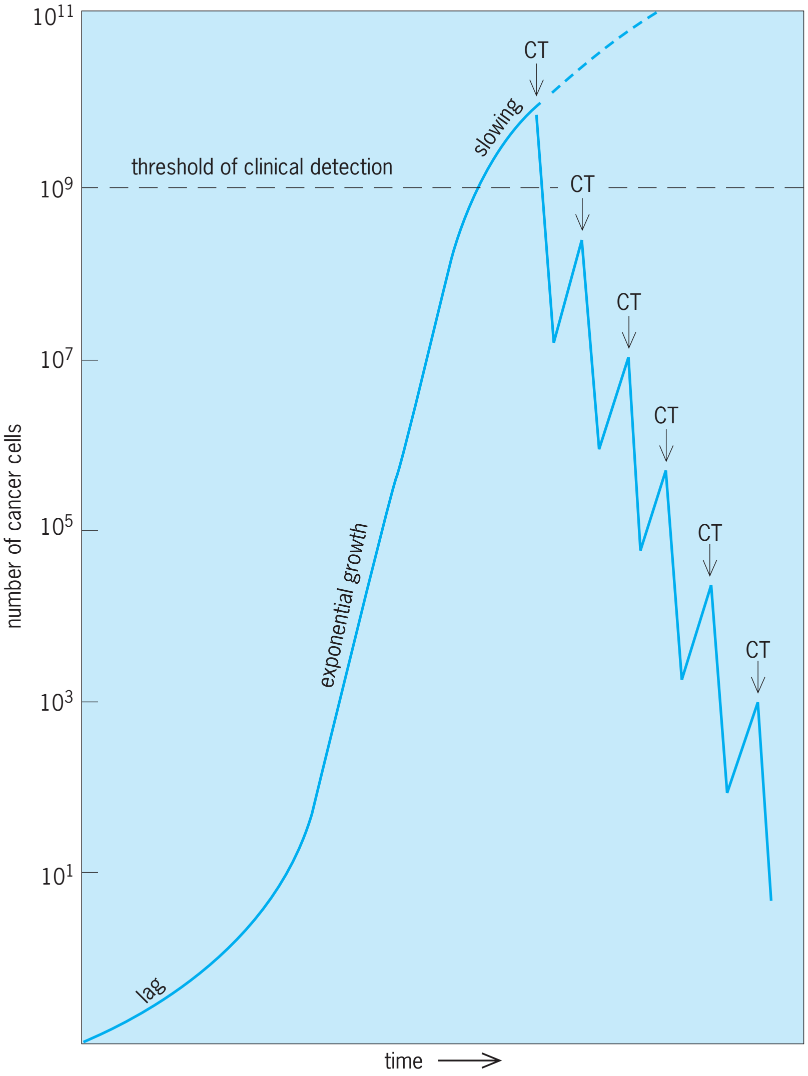
Hormonal agents. Hormonal agents have been used for several decades to inhibit cancer cells, especially in breast cancer, which frequently expresses hormone receptors on the cell surface. Representative hormonal agents include tamoxifen (a selective estrogen receptor modulator that also has partial estrogen agonist activity) and aromatase inhibitors such as anastrozole, among others. Aromatase is the enzyme responsible for conversion of androgens into estrogens and is the predominant source of estrogens in postmenopausal women. Hormonal therapy is also widely employed in metastatic prostate cancer, such as luteinizing hormone-releasing hormone (LHRH) agonists (goserelin, leuprolide), direct antiandrogen (bicalutamide), and blockers of adrenal androgen production (ketoconazole).

Sources. Chemotherapeutic drugs come from various sources. They may be extracted from natural sources—such as from bacteria, fungi, plants, or trees—or they may be chemically synthesized to target a specific protein—such as tyrosine kinase inhibitors. They may also be semisynthetic, meaning that the process starts with a complex natural compound that is then modified chemically. They may also be produced using modern recombinant DNA technology. Monoclonal antibodies may be murine (-monab); chimeric (-ximab), containing mouse variable regions and human constant regions; humanized (-zumab), containing murine binding regions (about 5% of total antibody) in a human framework; or human (-umab), derived using a variety of techniques from immunoglobulin genes with no murine immunoglobulin sequences.

Clinical trials. After basic laboratory studies suggest that a chemical might be effective in killing cancer cells, animal and then human testing begins. These tests are carried out in steps in order to systematically and safely identify those chemicals with the most usefulness. In phase I tests, the toxicity of the drug (or combination of drugs) and the maximum tolerated dose are determined by gradually increasing the dose given to patients until toxic effects are observed. In phase II studies, efficacy (tumor shrinkage) is determined in a single series of patients with a certain type of cancer. Recently, several new phase II design have been developed (for example, one called randomized discontinuation design) to identify preliminary evidence of activity of drugs that may have a greater effect on preventing cancer growth, rather than actual shrinkage. Typically, results of phase II studies are then used to proceed with larger phase III studies. In phase III tests, the drug (or combination) is randomized against the standard drug (or combination) used for that cancer to determine whether the experimental drug is more effective than the standard therapy. Phase III trials have historically been the gold standard to prove clinical efficacy.

Principles. Chemotherapy or immunotherapy is used when a cancer has spread to multiple sites (has metastasized) and cannot be removed surgically or treated with radiation therapy. It can also be used after all detectable tumor has been eradicated (complete remission) to destroy suspected but undetectable residual tumor. This type of treatment is called adjuvant, intensification, or consolidation chemotherapy. Adjuvant therapy is effective in breast and colon cancer, and consolidation in acute leukemia, for example. Neoadjuvant chemotherapy is used to shrink a tumor prior to surgery or radiation. *See* ONCOLOGY.

Fractional cell kill. For classic chemotherapy agents, the results of treatment depend upon how much chemotherapy is given, how many times it is applied, and how effective it is against the tumor. These facts are derived from a basic principle of chemotherapy that a uniform dose of a drug will destroy a constant fraction rather than a constant number of tumor cells regardless of the size of the tumor or number of cells present (fractional cell kill hypothesis). This result can be seen in the **illustration**, where the tumor



Sigmoid-shaped (Gompertzian) cancer growth (prior to first arrow) and fractional cell kill due to chemotherapy (after first arrow). Arrows indicate times of chemotherapy. Vertical axis is a log scale. The threshold for clinical detection of cancer is 10^8–10^9 total body tumor cells; since cancer probably starts from a single abnormal cell, this requires 27–30 doublings.

TABLE 2. Results of chemotherapy for disseminated disease in various cancers*

Cure in a majority of patients	Testicular cancer, childhood acute lymphoblastic leukemia, Hodgkin's disease, selected non-Hodgkin's lymphomas such as adult large B-cell lymphoma, gestational choriocarcinoma, hairy cell leukemia
Cure in a small subset of patients	Acute adult myeloid and lymphoblastic leukemia, ovarian cancer, some intermediate- and high-grade lymphomas, small-cell lung cancer
Induction of long-lasting remission	Follicular lymphoma, chronic myelocytic leukemia, gastrointestinal stromal tumor
Adjuvant† use with increased cure rates	Breast cancer, colorectal cancer, Ewing's sarcoma, Wilms' tumor, osteogenic sarcoma, rhabdomyosarcoma, glioblastoma multiforme, bladder cancer, gastric cancer
Prolongation of life but rare cures when metastatic‡	Multiple myeloma, follicular lymphoma, chronic lymphocytic leukemia, small cell lung cancer, bladder cancer, gastric cancer, colorectal cancer, pancreatic cancer, lung cancer, breast cancer, renal cell carcinoma
Palliation with unclear prolongation of life when metastatic	Head and neck cancer, hepatoma, melanoma, soft-tissue sarcoma, gallbladder cancer, cholangiocarcinoma

*These categories do not apply to cancers that have not metastasized and are treatable with surgery or radiation therapy alone, or to those that can be treated with bone marrow transplantation.

†Adjuvant refers to the use of chemotherapy in a situation where no tumor is detectable but there is a high chance that undetectable tumor cells are still present; the term for this type of therapy in blood or marrow cancers is consolidation therapy.

‡Some patients in this group can be cured by bone marrow transplantation.

number declines linearly on the log scale after the chemotherapy is applied. Drugs which are more effective in killing cancer cells give a greater slope of decline. Regrowth eventually occurs, but each subsequent dose of chemotherapy brings about a further decline in tumor cell number until eventually, in optimal circumstances, the number of tumor cells is low enough for the body to eliminate them by other mechanisms, resulting in a chemotherapy cure.

Mechanisms of cell death. Although the different groups of chemotherapeutic agents have different mechanisms of toxicity for cells, the cellular death response is often thought to be by apoptosis (programmed cell death). In this process a death signal is generated from within the damaged cells. This initiates a series of energy-requiring, choreographed cellular events leading to cellular suicide. Other mechanisms of death are necrosis and clonogenic (reproductive) death.

Goal. The goal of therapy should be determined in all patients before chemotherapy is started. The possibilities include cure, prolongation of life but not a cure, or palliation (alleviating symptoms) without likely prolongation of life (**Table 2**). The choice of chemotherapy depends not only on the type of tumor and the drug efficacy but, most importantly, on the patient. Also, it must be decided whether the chemotherapy will improve the quality of life of the patient and not just shrink the tumor. Age and the general condition of the patient influence the outcome. Those patients who are more active (better performance scores, which estimate degree of physical incapacitation by the tumor) are more likely to have a favorable outcome to chemotherapy. There are questionnaires to aid in measuring quality of life before and after drugs are given.

Dosage. For conventional chemotherapy, dosing has traditionally been based on the amount of body surface in square meters, or occasionally just on body weight. These dose calculations reflect the fact that toxicity often occurs at doses only slightly higher than those needed for therapy. In clinical trials, often the maximum tolerated dose (MTD) is the one taken forward for further testing and eventual routine use. Tyrosine kinase inhibitors, in contrast, are often prescribed at fixed doses expressed in milligrams. Knowledge of pharmacokinetic principles and drug interactions is very important when administering chemotherapy drugs.

Measurement of effect. The response of a cancer to a drug is determined by measuring the size of the cancer directly or the amount of marker substances produced by some tumors. A complete response is defined as disappearance of the tumor. A partial response means a specified decrease in tumor size that does not qualify for a complete response. In many cancers, the ultimate measure of benefit is whether the patients have a prolongation of life, which in clinical trials may require observation over a long period of time. Time to progression, or the time it takes for the cancer to recur after initial treatment, is another commonly used endpoint in cancer studies. Quality of life is another endpoint often applied in clinical studies in cancer.

Adjuvant therapy. This is a concept that is commonly used in medical oncology and accounts for significant use of chemotherapy at present. It translates into using chemotherapy after surgical removal of the cancer (for example, mastectomy for breast cancer). Chemotherapy is used to kill microscopic amounts of cancer cells that were not removed with the surgery or had spread to distant areas before the surgery. Adjuvant chemotherapy has been shown in numerous phase III trials to increase cure rates in selected common cancers. Typically, large numbers of patients need to be treated to demonstrate a benefit in the population.

Minimal residual disease. The detection of cancer cells that remain in submicroscopic numbers after therapy is referred to as minimal residual disease (MRD). Its importance is being evaluated in several malignancies, and MRD has been shown to correlate with recurrent clinical disease, especially in selected leukemias and lymphomas. The availability of improved molecular biology techniques has allowed increasing ability to detect MRD. These techniques include cytogenetics (chromosome analysis) and fluorescent in-situ hybridization (FISH), which uses DNA probes specific to regions of individual chromosomes, and these targeted areas are then identified by a fluorescent marker. Finally, reverse-transcription polymerase chain reaction (RT-PCR) is the most sensitive method currently available for detection of MRD.

Side effects. Chemotherapeutic drugs have side effects that are specific for the agent and may include transient or permanent damage to almost any organ system of the body. They cause side effects because, in addition to destroying the actively dividing cancer cells, they damage actively growing normal cells. Common sites of damage are the bone marrow, resulting in increased risk for infection, anemia, and bleeding; the gastrointestinal tract, resulting in vomiting and diarrhea; the hair follicles, causing hair loss; and the kidneys, resulting in renal failure. Today, cancer specialists have many ways of preventing or diminishing these toxicities, such as red blood cell transfusions for anemia, drugs to prevent nausea and vomiting, and growth factors which may improve anemia (erythropoietin) or shorten the time of low white blood counts (granulocyte-colony stimulating factor).

Drug resistance. Cells can become resistant to drugs of different groups, including anthracyclines, vincristine, etoposide, and paclitaxel. The general mechanism is referred to as multidrug resistance (MDR). This resistance is due to an acquired ability of the cells to pump these drugs out before they can cause irreversible damage. This pumping action is due to a transmembrane glycoprotein referred to as P-glycoprotein. These tumor cells overexpress the gene *MDR1*, which can be a useful marker of the resistance.

There are other ways by which a cancer cell can become resistant to chemotherapy. The cell may increase the amount of an intracellular drug target (for example, increased dihydrofolate reductase, which produces methotrexate resistance), reduce uptake of drugs (for example, alkylating agents), or decrease expression of a drug target (such as topoisomerase II). In some cases, resistance is due to a malfunctioning tumor suppressor gene called *p53*. The *p53* protein is an important initiator of drug-induced apoptosis; therefore, cells lacking *p53* do not commit cellular suicide in response to chemotherapies in the same way that *p53*-positive cells would.

In the case of tyrosine kinase inhibitors, resistance is often correlated with the emergence of a malignant cell clone with a new mutation in the targeted receptor, making the drug ineffective. Resistance can also be due to the presence of alternative molecular pathways that lead to cell proliferation, other than the pathway targeted by the drug.

Tumor growth. After an early lag phase, tumors grow exponentially, meaning that the time for a tumor to double in size is constant. However, as tumors grow, there is a deceleration in growth rate (see illustration), which may be due to outgrowing their blood supply, lack of sufficient nutrients, or changes in growth signals. This slowing means that there is an increase in the number of cells that are not dividing (G0 cell cycle phase), and these cells may be less susceptible to killing by drugs which act only on dividing cells. This phenomenon may compromise effective anticancer chemotherapy.

Selectivity and toxicity. Some tumors fail to respond to chemotherapy because normal tissues of the bone marrow, gut, or other organs are just as sensitive to the drug as the tumor, and unacceptable side effects preclude increasing the dose to therapeutic levels. These side effects may be early and transient such as vomiting, hair loss, or bone marrow suppression, or late and irreversible such as second malignancies, decline in fertility, lung fibrosis, and heart damage. Fortunately, effective drugs have some selectivity for the tumor, often for unknown reasons. Prednisone is an example of a drug that has the ability to destroy malignant lymphocytes with little damage to normal cells, and it is therefore selective.

Tumor heterogeneity. Cancers are not always uniform in their content of abnormal cells. There may be a mixture of cancerous cells with different features and different sensitivities to chemotherapy. Some cells may be sensitive while others are resistant to a specific drug. The use of a drug that destroys only one type of cell within a heterogeneous tumor will lead to eventual failure of therapy.

Strategies to overcome clinical resistance. Most successful modern chemotherapeutic regimens are combinations of drugs. These are usually named as acronyms, for example, CHOP therapy for lymphomas [cyclophosphamide, hydroxydaunorubicin (another name for doxorubicin), oncovin (another name for vincristine), and prednisone]. Response to combination therapy is usually superior to single-drug therapy. The use of more than one drug increases the chance of a cancer being sensitive to treatment since it is possible that a cancer cell resistant to one drug will be sensitive to another. Combinations of drugs with different mechanisms of tumor cell killing are commonly used. Also, in an effort to decrease side effects, drugs with nonoverlapping side effects are used. Drugs can also be combined with other general types of treatment such as immunotherapy. It is known from preclinical testing that chemotherapy and immunotherapy are more effective when the tumor is small. Therefore, surgery or radiation can be used in combination with chemotherapy to shrink the tumor with one modality and subsequently destroy the remaining smaller tumor with the other. Conversely, chemotherapy may be used to decrease tumor size to make surgery or radiation possible. In the case of tumors sensitive to tyrosine kinase inhibitors, resistance due to emergence of new mutations can sometimes be partially overcome by increasing the dose of the drug.

Biochemical modulation. Resistance to chemotherapy can be overcome in some instances by giving a second drug either simultaneously or in sequence. An example is the use of leucovorin (folinic acid) that potentiates 5-fluorouracil therapy administered to treat colorectal cancer by increasing reduced folates, which indirectly leads to a more stable complex of 5-fluorouracil with its target enzyme thymidylate synthetase and eventual cell death. Another example is experimental agents that increase the retention of drugs affected by multidrug-resistant cells.

High-dose chemotherapy. A strategy to kill tumors resistant to conventional doses of chemotherapy involves the use of extrahigh (supralethal) doses of chemotherapy. Because this damages the normal tissues, it is necessary to perform transplantation of hematopoietic stem cells (obtained from blood or bone marrow) afterwards to reconstitute vital bone marrow function.

Cell cycle. There has been a good deal of interest in the specific phase of the cell division cycle that is affected by chemotherapy, in the hope that this information could be used to develop more effective cures for cancer. However, the results have been disappointing overall. Some drugs kill cancer cells only in specific phases of the cell cycle (S-phase: cytarabine, methotrexate; M-phase: paclitaxel); others have no specificity (gemcitabine). Some drugs, such as the alkylating agents, cisplatin, and anthracyclines, can also kill nondividing cells. This type of information, which is usually established in tissue culture or animals, has been of limited practical use in planning human therapy. Recently, there has been renewed interest in control of the cell cycle by genes and growth factors. This may eventually lead to effective cell cycle–based drug strategies. Some of the proteins that control the cell cycle (for example, cyclins) might become targets for drug action. *See* CELL CYCLE; CELL DIVISION.

Differentiation. Tumor cells are often immature compared to normal cells and retain the ability to self-replicate. More differentiated mature cells often lose this ability and are end-stage cells. Therapy designed to induce differentiation often results in the loss of the cells' ability to reproduce. In this way tumor cells can be inactivated without administering toxic drugs, thereby avoiding toxicity to normal cells. An active drug in this group is tretinoin (all-*trans*-retinoic acid), which can lead to remissions in a large percentage of patients with acute promyelocytic leukemia. These remissions are usually of short duration unless cytotoxic drugs are added. Unfortunately, the strategy has not been useful in most cancers.

Drug delivery. Techniques are being developed to ameliorate toxicity so that higher doses of chemotherapeutic agents may be delivered directly to the tumor. One approach involves a lipid carrier to deliver more of the toxic drug to the tumor as compared to normal tissues. Thus far, the technique has some usefulness with the drugs doxorubicin in ovarian cancer and cytarabine in central nervous system lymphoma or leukemia.

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Cherry

Sweet or sour fruit of the *Prunus* genus, having cultivated and wild varieties.

Cultivated varieties. The two principal cherries of commerce are the sweet cherry (*Prunus avium*) and the sour cherry (*P. cerasus*). Both are of ancient origin and seem to have come from the region between the Black and Caspian seas. They were probably carried into Europe by birds before humans were there. The cherry was mentioned in 300 B.C. by the Greek botanist Theophrastus. It was taken to America from Europe.

Cherries of minor importance are the dwarf or western sand cherries (*P. besseyi*) of the plains region of North America; the Duke cherries, which are supposedly natural hybrids between the sweet and sour cherry; and the Padus cherries, which bear their small fruits in long clusters or racemes rather than in short fascicles.

Sweet cherries may be divided into two groups, firm-fleshed types known as Bigarreaus, represented by the Napoleon (also called the Royal Anne), and soft-fleshed types known as Hearts, represented by the Black Tartarian. Sour cherries may also be divided into two groups, clear-juice or Amarelle types, represented by the Montmorency, and colored-juice or Morello types, represented by the English Morello.

In North America the principal sweet commercial varieties are the Napoleon (white), Bing, Lambert, Van, Schmidt, and Windsor (dark). The principal commercial variety of sour cherry is the Montmorency.

Trees are propagated by budding into seedlings of the wild sweet (mazzard) cherry or of *P. mahaleb,* commonly called the perfumed cherry of southern Europe. The former is best suited to the sweet cherry, and the latter to the sour cherry. *See* PLANT PROPAGATION; REPRODUCTION (PLANT).

The sweet cherry is somewhat hardier than the peach, and the sour cherry is hardier than the sweet cherry. Cultivated varieties are usually planted 25–30 ft (7.5–9 m) apart and allowed to grow to heights of only about 15–20 ft (4.5–6 m) for ease of culture and harvest. Sour cherry trees may reach 30–40 ft (9–12 m) but are kept at 15–20 ft (4.5–6 m) and planted 18–22 ft (5.4–6.6 m) apart. Cherry trees do best in well-drained sandy loam soils. They will not tolerate wet soil. Sweet varieties require cross-pollination; common sour varieties are self-fruitful (self-pollinated). *See* FRUIT; FRUIT, TREE; ROSALES. R. Paul Larsen

Wild varieties. The wild cherry tree, *P. serotina*, grows to a height of 100 ft (30 m) and may reach an age of 200 years. It belongs to the rose family, and is an important timber species of cherry in the United States. Native in the eastern half of the United States and adjacent Canada, it reaches its largest size in the southern Appalachian Mountains. The deciduous leaves are long-pointed, thickish, and shining above (**Fig. 1**). The edible fruit is a shiny black drupe found in long clusters. The hard, strong wood is a red-brown and is used for furniture, often as an imitation mahogany.

The sweet cherry or mazzard (*P. avium*), which grows to 70 ft (21 m), is naturalized over a large part of the United States. It has fruits borne in umbel-like clusters. It also differs from the wild cherry in having more ovate leaves with rounded teeth (**Fig. 2**).

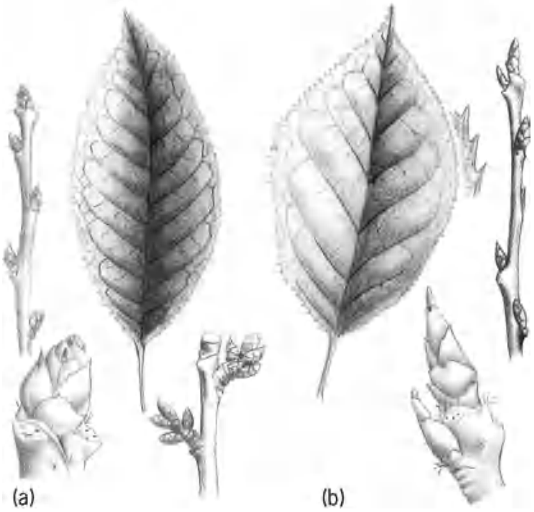

Fig. 1. Leaves, twigs, and buds of (*a*) sweet cherry (*Prunus avium*) and (*b*) choke cherry (*P. virginiana*)

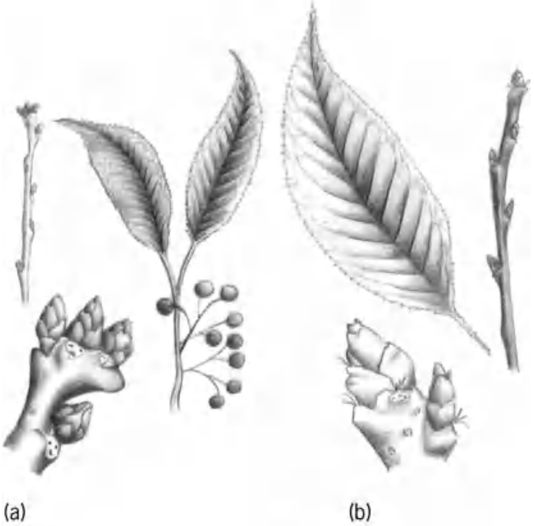

Fig. 2. Leaves, twigs, and buds of (*a*) pin or fire cherry (*Prunus pensylvanica*) and (*b*) wild cherry (*P. serotina*)

The Japanese flowering cherries are varieties of *P. serrulata*, which attract much attention at blossoming time in early May.

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Diseases. A destructive disease of cherry in the orchard and after harvest is brown rot, caused by the fungus *Monilinia fructicola*. Infections occur first in blossoms, and later in the maturing fruit, causing rot (**Fig. 3**). Cherry leaf spot, caused by the fungus *Coccomyces hiemalis*, results in leaf spotting, yellowing, and premature defoliation. Without well-functioning leaves, trees lose vigor and decline in productivity. Powdery mildew, caused by the fungus *Podosphaera oxyacanthae,* impairs the ability of leaves to supply sugars and other products needed by the tree for normal development. These three diseases can be effectively controlled with timely sprays of recommended fungicides.

Fig. 3. Brown rot disease of sweet cherry.

The major bacterial diseases of cherry are bacterial canker caused by *Pseudomonas syringae* (affecting leaves, branches, and fruit) and crown gall, due to *Agrobacterium tumefaciens*, which causes a tumorlike growth on the crown and roots.

Important virus (or viruslike) diseases are Prunus ring spot, prune dwarf, little cherry, and X disease ("buckskin"). Virus diseases affect certain tissues (wood, bark, leaves, seeds, pollen) of certain branches or even the entire tree. The symptoms vary with each disease, but usually involve small, mottled, yellow, or missing leaves, and small and poorly colored fruit. Tree growth and yield suffer. Preventive control measures include planting resistant varieties and certified virus-free stock and, where applicable, spraying for the control of insect vectors that transmit the pathogens. *See* PLANT PATHOLOGY; PLANT VIRUSES AND VIROIDS. Michael Szkolnik

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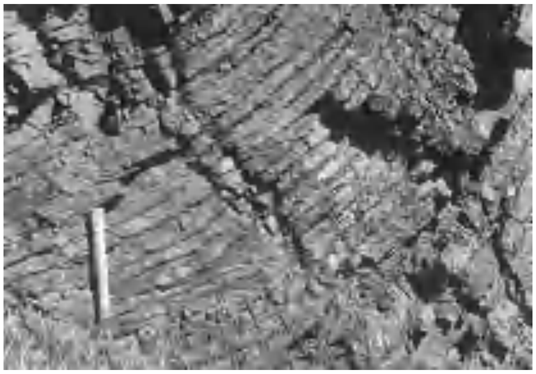
Chert

A hard, dense sedimentary rock composed of fine-grained silica (SiO_2). Chert is characterized by a semivitreous to dull luster and a splintery to conchoidal fracture, and is most commonly gray, black, reddish brown, or green. Chert is also used as a field term to describe silica-rich rocks which may be impure; common impurities include carbonates, iron and manganese oxides, and clay minerals. When impurities change the texture of the rock to the extent that it is less dense and hard than chert, and has the appearance of unglazed porcelain, the rock is then called porcellanite or siliceous shale. The term flint is synonymous with chert, but its use has become restricted to archeological artifacts and to nodular chert that occurs in chalk. The term chert, however, is preferred for the nodular deposits. Jasper refers to red or yellow quartz chert associated with iron ore or containing iron oxide. Novaculite is a white chert of great purity and uniform grain size, and is composed chiefly of quartz; the term is mostly restricted to descriptions of Paleozoic cherts in Oklahoma and Arkansas. Chert synonyms that have become obsolete include silexite, petrosilex, phthanite, and hornstone. *See* JASPER.

Composition. The silica that composes chert occurs in four forms: quartz, chalcedony, opal-CT, and opal-A. Chalcedony is a microscopically fibrous form of the mineral quartz with water trapped in void spaces parallel to the fibers. The poorly understood opal-CT phase is probably an interstratified mixture of the silica minerals cristobalite and tridymite, although it has been suggested to be solely disordered tridymite. In chert, the chalcedony, quartz, and opal-CT are secondary forms of silica derived from the dissolution and later precipitation of a primary silica phase, which for most chert is biogenic silica (opal-A). The main rock-forming types of biogenic silica are the tests and frustules of the siliceous plankton diatoms, radiolarians, silicoflagellates, and ebriidians, and the siliceous spicules of sponges. The composition of chert changes with time and temperature, beginning with opal-A, which transforms to opal-CT and finally to quartz or chalcedony. Under special conditions, opal-A can transform directly to quartz. *See* CHALCEDONY; OPAL; QUARTZ.

Diagenesis. Opal-A and opal-CT are metastable phases within the Earth's crust. The diagenetic transformation of opal-A to opal-CT and then to quartz is primarily controlled by temperature and time, but also by surface area, pore-water chemistry, sediment permeability, and host-sediment composition. The mineralogical transformations are commonly, but not invariably, accompanied by textural transformations. For example, diatom or radiolarian ooze (unconsolidated marine sediment composed mostly of diatom frustules or radiolarian tests) or diatomaceous or radiolarian earth (weakly consolidated oozes that have been incorporated into on-land deposits), which are composed of opal-A, transform into porcellanite (most commonly composed of opal-CT), which in turn transforms into chert (most commonly composed of quartz). *See* DIAGENESIS; MARINE SEDIMENTS.



Rhythmically bedded radiolarian chert from the Franciscan Complex, Diablo Range, California; of Late Jurassic age.

Occurrence. Chert occurs mainly in three forms: bedded sequences (see **illus.**), nodular, and massive. Bedded chert (called ribbon chert if beds show pinch-and-swell structure) consists of rhythmically interlayered beds of chert and shale; chert and carbonates; or in some pre-Phanerozoic formations, alternations of chert and siderite or hematite. Bedded sequences can be hundreds of feet thick stratigraphically and cover areas of hundreds of square miles. Individual beds are commonly $^1/_2$–8 in. (1–20 cm) thick. Intercalated shale layers are commonly, but not invariably, thinner than the associated chert layers. In many places individual chert beds are laminated. Chert nodules and lenses occur primarily in chalk, limestone, and dolomite, and are the only types of chert recovered by the Deep Sea Drilling Project from open-ocean sediment. Chert nodules are well known from many places in western Europe, where their dark color contrasts strikingly with the white host chalk. Nodules and lenses vary in size from $^1/_2$ in. to 30 ft (1 cm to 9 m). Fossils and sedimentary structures characteristic of the host rock are preserved within the nodules. Massive cherts occur in the interstices between basalt pillows, and as the basal member of bedded chert that overlies pillow basalts in ophiolites. *See* BASALT; CHALK; DOLOMITE ROCK; LIMESTONE.

Origin. When a supply of silica is available, chert forms in four ways: (1) by replacement of mainly carbonate rock; (2) by deposition from turbidity currents composed primarily of biogenic silica; (3) by increasing the deposition of silica relative to terrigenous input, commonly by increased productivity of biogenic silica; and (4) by precipitation of silica from water under either hydrothermal or low-temperature hypersaline conditions. The replacement of chalk and limestone by silica has been well documented in Deep Sea Drilling Project cores and in some deposits on land. The silica is derived from the dissolution of biogenic silica deposited with the biogenic carbonate. The resultant chert most commonly forms nodules, but the silica may also replace beds of limestone completely, thereby forming bedded chert. Most bedded chert, however, is probably turbidite sequences, although additional work is necessary to confirm this hypothesis. Transient, sediment-laden density currents (turbidity currents) that flowed down the sides of submarine basins carried mostly biogenic silica which settled in layers. The layers later transformed into cherts through diagenetic processes. Pelagic or hemipelagic clays were deposited in the basin between times of turbidite deposition, thus creating the rhythmically bedded chert-shale sequences found in many mountain belts. In some places, the shales may be the turbidites and the cherts the pelagic deposits. The rhythmic bedding can also be produced by productivity cycles of biogenic silica. Of relatively minor volumetric importance in post-Archean rocks is the primary precipitation of silica. Inorganic precipitation of silica takes place in hypersaline lakes and lagoons. Chert also forms by deposition of silica from hydrothermal solutions into the interstices between basalt pillows, and in other localized areas within ophiolite sequences. *See* TURBIDITE; TURBIDITY CURRENT.

Distribution. The distribution of chert is tied to the distribution of siliceous plankton, which in turn depends on oceanographic conditions. After the plankton die, their shells accumulate in great quantities on the sea floor, especially around the polar regions (diatoms) and the equatorial belt of high biological productivity (radiolarians and diatoms). Shells also accumulate in other areas where cold, nutrient-rich subsurface water upwells, such as off the west coasts of continents and in marginal seas such as the Philippine and Japan seas. Marine siliceous deposits, along with the underlying oceanic crust, are incorporated into mountain belts by uplift of oceanic crust or by obduction and thrust faulting at subduction plate margins. Such on-land cherts of every age are found at many locations around the world. *See* BACILLARIOPHYCEAE.

Radiolarians and sponge spicules occur in Phanerozoic chert. Diatoms first evolved during the Mesozoic Era and came into prominence in the Tertiary, when they became the dominant precursor of chert. The source of silica for pre-Phanerozoic cherts, which are commonly associated with banded iron formations, is equivocal. Direct evidence of a biological source is lacking, and inorganic precipitation of silica is generally postulated. Most Archean (before 2.5 billion years ago) cherts likely formed from hydrothermal or other abiotic processes. Future studies may yield information that would indicate additional sources of silica for pre-Phanerozoic cherts. *See* SEDIMENTARY ROCKS. James R. Hein

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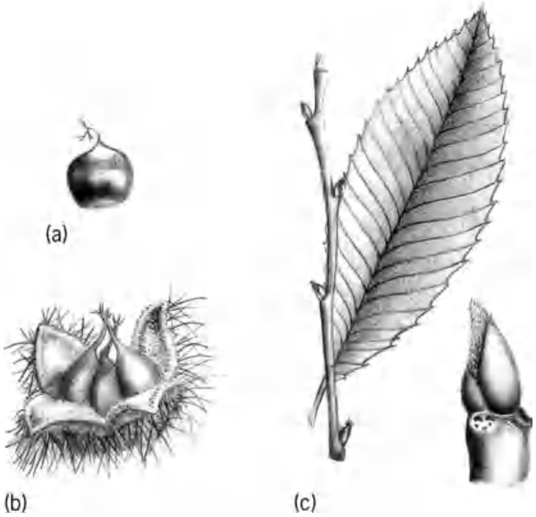
Chestnut

Any of seven species of deciduous, nut-bearing trees of the genus *Castanea* (order Fagales) native to the Northern Hemisphere and introduced throughout the world. The nuts are actually fruits, with the shells enclosing cotyledons. Trees bear both male and female flowers in late spring but must be cross-pollinated for nut production. Nuts are borne in a spiny involucre or bur that opens to release the nuts in late fall. *See* FAGALES.

Varieties. Japanese chestnuts (*C. crenata*) and Chinese chestnuts (*C. mollissima*) are grown in Asia and the United States for their nuts, and many cultivars have been selected. European chestnuts (*C. sativa*) are an important food source, both cooked whole and ground into flour. They are native to the Caucasus mountains, and distributed throughout southern Europe. American chestnuts (*C. dentata*; see **illus.**) have smaller nuts than Asian or European species and are usually sweeter. Only American trees served as an important source of lumber, because of the length of their unbranched trunks; all chestnut species have been used as a source of tannin for the leather-tanning industry. American and Chinese chinquapins (*C. pumila* and *C. henryi*) have very small nuts that are an important source of food for wildlife. All of the species can be crossed, and hybrids have been selected primarily as orchard cultivars.

Diseases. In 1838 a root disease was reported on European chestnut in Portugal, and soon after this "ink disease" was found in several other parts of southern Europe. The pathogen, *Phytophthora cinnamomi*, causes brownish-black lesions on the roots that exude an inky-blue stain. The lesions expand, coalesce, and girdle the root, resulting in tree death.



American chestnut (*Castanea dentata*). (*a*) Nut. (*b*) Bur. (*c*) Leaf, twig, and bud.

Breeding with ink disease–resistant Asian species has produced new cultivars, and careful sanitation and site selection allow European chestnuts to still be grown. In the United States, ink disease probably accounted for the recession of chestnut species from large areas in the Gulf and Atlantic states and inland to the foothills and mountains of Mississippi, Alabama, Georgia, Tennessee, Maryland, Virginia, and the Carolinas. The fungus is assumed to have entered the United States in the mid-1800s.

The second disaster for American and European chestnuts was also a fungus disease. *Cryphonectria* (formerly *Endothia*) *parasitica* was first reported in New York City in 1904 and was found to be widespread throughout the northeast region of the United States. This fungus, causing chestnut blight, had probably entered the United States on imported Japanese chestnuts in the late 1800s. The initial spread was on nursery stock (most major mail-order nurseries sold Japanese chestnuts at the turn of the century), but spores were also carried on the fur, feet, and feathers of the birds, animals, and insects that walked up and down the trees. Wounds in the bark allow access and initial fungal growth, and the resulting canker expands to kill the cambium and eventually the twigs, branches, and trunk. The fungus does not kill the root collar, and the dormant embryos there sprout and grow until wounded, infected, and killed, and the cycle is repeated. In the northern part of the natural range of American chestnut (northern Georgia to southern Maine, and west through Ohio, Kentucky, and Tennessee), sprout clumps have survived well, but farther south repeated chestnut blight cycles kill the sprout clumps. American chinquapins are also very susceptible to chestnut blight, and their sprouting system (relying on the old root system, instead of forming new roots as chestnut does) may make them more liable to be killed by blight.

Chestnut blight was first reported in Europe on chestnuts in Italy in 1938. The epidemic there proceeded as in the United States, but natural virus infection of the fungus now provides a biological control. The fungal strains with viruses are less virulent (hypovirulent), and can be inoculated into natural cankers to transmit the viruses and establish biological control in orchards. Hypovirulent strains have been used in the United States for control of blight fungus populations in orchards and forest stands of American chestnut sprouts. Improved control may result from new genetically engineered strains. In addition, trees are bred for resistance by crossing susceptible trees with resistant Chinese and Japanese chestnuts.

The next potential disaster for chestnut trees in the United States and Europe is infestation with a small wasp native to Asia called the Oriental chestnut gall wasp (*Dryocosmus kuriphilus*). Eggs laid in leaf and flower buds develop into galls and heavy infestations can kill the trees. The insect has been in the United States since 1974 (on Chinese chestnut trees in orchards in Georgia), and is now infesting American chestnut trees at the southern part of the range. Japanese chestnut breeders released cultivars with some resistance to the insect, and American chinquapins also seem to have good resistance. *See* FOREST AND FORESTRY; PLANT PATHOLOGY; TREE.

Sandra L. Anagnostakis

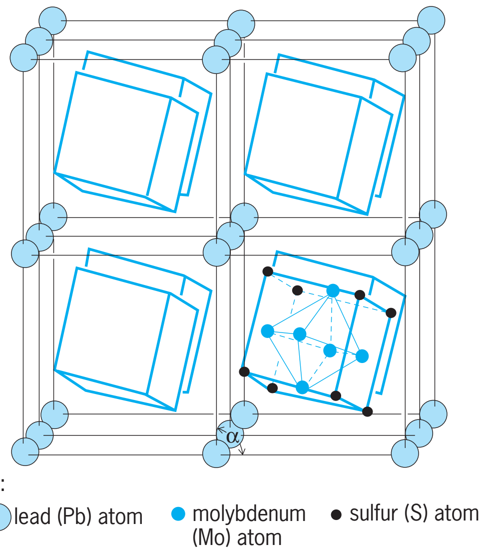
Chevrel phases

A series of ternary molybdenum chalcogenide compounds. They were reported by R. Chevrel, M. Sergent, and J. Prigent in 1971. The compounds have the general formula $M_xMo_6X_8$, where M represents any one of a large number (nearly 40) of metallic elements throughout the periodic table; x has values between 1 and 4, depending on the M element; and X is a chalcogen (sulfur, selenium or tellurium). The Chevrel phases are of great interest, largely because of their striking superconducting properties.

Crystal structure. Most of the ternary molybdenum chalcogenides crystallize in a structure in which the unit cell, that is, the repeating unit of the crystal structure, has the overall shape of a rhombohedron with a rhombohedral angle close to 90°. Some of the ternary molybdenum chalcogenides display a slight distortion of the rhombohedral crystal structure at, or below, room temperature to a triclinic structure in which the three axes of the unit cell, and the three angles between them, are unequal.

The building blocks of the Chevrel-phase crystal structure are the M elements and Mo_6X_8 molecular units or clusters. Each Mo_6X_8 unit is a slightly deformed cube with X atoms at the corners, and Mo atoms at the face centers. One of these structures, that of $PbMo_6S_8$, is shown in the **illustration**. *See* CRYSTAL STRUCTURE; CRYSTALLOGRAPHY.

Superconductivity. Many of the Chevrel-phase compounds exhibit superconductivity, a phenomenon in which a metal, when cooled below its



Crystal structure of $PbMo_6S_8$. Each lead atom is surrounded by eight Mo_6S_8 units, the structure of which is shown in the lower right part of the figure. The rhombohedral angle α is indicated also.

superconducting transition temperature T_c, loses all resistance to flow of an electric current. Several of the Chevrel-phase compounds have relatively high values of T_c, the maximum being about 15 K (−433°F) for $PbMo_6S_8$. Prior to 1986, the highest T_c of any known material was 23 K (−418°F) for the A15 compound Nb_3Ge. *See* A15 PHASES.

Since 1987, superconductivity at temperatures above the boiling point of liquid nitrogen (77 K or −321°F) has been discovered in several families of copper oxide compounds. A value of T_c of approximately 122 K (−240°F) has been observed in a compound comprising the elements thallium, barium, calcium, copper, and oxygen. As in conventional superconductors, the superconductivity is associated with electron pairs, called Cooper pairs; but the attractive mechanism responsible for the formation of the Cooper pairs may be different in the high-T_c superconducting oxides than in conventional superconductors, like the Chevrel phases and the A15 phases, where it involves the interaction between the negatively charged electrons and the positively charged ions of the crystal lattice.

The superconductivity of any superconducting compound can be destroyed with a sufficiently high magnetic field, called the upper critical magnetic field $H_{c2}(T)$, which depends on the temperature T and varies from material to material. As the temperature is lowered, $H_{c2}(T)$ generally increases from zero at T_c to a maximum value, $H_{c2}(0)$, as the temperature approaches absolute zero. The Chevrel-phase $PbMo_6S_8$ has a value of $H_{c2}(0)$ of about 60 teslas (600 kilogauss), the largest value observed for any material prior to 1986. The highest $H_{c2}(0)$ that had been previously reported for a non-Chevrel-phase material was 40 teslas (400 kilogauss) for the A15 compound Nb_3Ge. In comparison, the values of $H_{c2}(0)$ for the highest T_c copper oxide superconductors may reach several hundred teslas, values so large that they cannot readily be measured by using the magnetic fields and techniques that are presently available in the laboratory.

A number of Chevrel-phase compounds of the form RMo_6X_8, where R is a rare-earth element with a partially filled $4f$ electron shell and X is S or Se, display magnetic order at low temperatures in addition to superconductivity. The superconductivity is primarily associated with the mobile $4d$ electrons of Mo, while the magnetic order involves the localized $4f$ electrons of the R atoms which occupy regular positions throughout the lattice. Superconductivity has been found to coexist with antiferromagnetic order, but to be destroyed by the onset of ferromagnetic order. *See* ANTIFERROMAGNETISM; FERROMAGNETISM; SUPERCONDUCTIVITY.

M. Brian Maple

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Chevrotain

The name for four species of mammals which constitute the family Tragulidae in the order Artiodactyla. These animals, also known as mouse deer, are the smallest ruminants, growing to a maximum height of 12 in. (30 cm) at the shoulder. The water chevrotain (*Hyemoschus aquaticus*; see **illustration**) is found in west-central Africa along the banks of rivers in Sierra Leone through the Cameroons to the Congo. It feeds principally on aquatic vegetation. The other species are all members of the genus *Tragulus*, and range through the forested areas of Sumatra into Borneo and Java. These are the Indian chevrotain (*T. meminna*), the larger Malay chevrotain (*T. napu*), and the lesser Malay chevrotain (*T. javanicus*). They are differentiated by the pattern of markings (stripes or spots) on their coats. *Tragulus javanicus* has a coat of uniform color. The chevrotain lacks horns or antlers. There are two well-developed toes on the feet, and the upper canines of the male are elongate and protrude from the mouth as small tusks. The chevrotain is a shy animal which leads a solitary life except during the breeding season. After a gestation period of 120 days, one or two young are born. There is a total of 34 teeth with the dental formula I 0/3, C 1/1, Pm 3/3, M 3/3. The Eocene fossil traguloid, *Archaeomeryx*, which was unearthed in Mongolia, shows many general similarities to the modern chevrotains. The main line of evolutionary development of the traguloids occurred in Eurasia. *See* ARTIODACTYLA; DENTITION.

Water chevrotain (*Hyemoschus aquaticus*). (*Photo © by Brent Huffman/Ultimate Ungulate Images*)

Charles B. Curtin

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Chickenpox and shingles

Chickenpox (varicella) and shingles (herpes zoster) are two different forms of disease caused by the varicella-zoster virus, which is a deoxyribonucleic acid (DNA) virus closely related to herpes simplex and Epstein-Barr viruses. Initial infection causes varicella, a common childhood infection characterized by fever, malaise, and a rash consisting of dozens to hundreds of small fluid-filled lesions (vesicles) that are individually surrounded by reddened skin. Successive crops of lesions appear that eventually ulcerate and crust over during the two-week course of the disease. The virus is spread from person to person by the highly infectious respiratory secretions and lesion drainage. Varicella is rarely a serious disease in normal children but can be severe in immunocompromised individuals or in the rare adult who escaped childhood infection. Primary infection results in immunity to a new varicella-zoster virus, but the original virus lies dormant in nerve ganglia cells. *See* EPSTEIN-BARR VIRUS; HERPES.

At some time in their life, approximately 10% of the population suffers subsequent reactivation of latent virus, which spreads to the skin overlying the affected nerve and causes a localized eruption of vesicles called herpes zoster. The vesicles are similar in appearance and in infectiousness to varicella lesions. This syndrome is usually well tolerated, although elderly persons may develop chronic pain at the site of reactivation. Herpes zoster in immunocompromised individuals may be prolonged or may disseminate to vital organs.

Varicella or herpes zoster in a normal host is self-limited and does not typically require antiviral therapy. In individuals with underlying immune disorders, treatment with the antiviral drug acyclovir decreases the duration and severity of disease. Previously uninfected immunocompromised individuals or pregnant women recently exposed to varicella-zoster virus can be partially protected from subsequent disease through the administration of varicella-zoster immune globulin. However, antibody tests often indicate preexisting immunity from asymptomatic or forgotten childhood varicella. *See* ANIMAL VIRUS; VIRUS INFECTION, LATENT, PERSISTENT, SLOW.

Frederick P. Heinzel

Chicle

A gummy exudate used in the manufacture of chewing gum. It is contained in the bark of a tall evergreen tree, *Manilkara zapota* (see **illus.**), belonging to the sapodilla family (Sapotaceae). The species is a native of Mexico and Central America. The latex (secretion) is collected and carefully boiled to remove excess moisture. When the water content is reduced to 33%, the chicle is poured off and molded into blocks. Crude chicle contains resin, arabin, gutta, sugar, calcium, and different soluble salts. For refining, it is broken up, washed in strong alkali, neutralized with sodium acid phosphate, rewashed, dried, and powdered. The resulting product is an amorphous, pale-pink powder, insoluble in water, and forming a sticky paste when heated. In the manufacture of chewing gum, the chicle is cleaned, filtered, and sterilized, and various flavoring materials and sugar are added. *See* EBENALES; RUBBER.

Fruit of *Manilkara zapota*. (*After L. H. Bailey, The Standard Cyclopedia of Horticulture, vol. 3, Macmillan, 1937*)

Perry D. Strausbaugh; Earl L. Core

Chicory

A perennial herb, *Cichorium intybus* (Asteraceae), with a long taproot, a coarse branching stem, and a basal rosette of numerous leaves. Although the plant is a native of Europe, it has become a common weed in the United States. It is used as a salad plant or for greens. The roasted root is also used as an adulterant of coffee. *See* CAMPANULALES; SPICE AND FLAVORING.

Perry D. Strausbaugh; Earl L. Core

Child-Langmuir law

A law governing space-charge-limited flow of electron current between two plane parallel electrodes in vacuum when the emission velocities of the electrons can be neglected. It is often called the three-halves power law, and is expressed by the formula below.

$$j(\mathrm{A/cm^2}) = \frac{\epsilon}{9\pi}\left(\frac{2e}{m}\right)^{1/2}\frac{V^{3/2}}{d^2}$$

$$= 2.33 \times 10^{-6}\,\frac{V(\mathrm{volts})^{3/2}}{d(\mathrm{cm})^2}$$

Here ϵ is the dielectric constant of vacuum, $-e$ the charge of the electron, m its mass, V the potential difference between the two electrodes, d their separation, and j the current density at the collector electrode, or anode. The potential difference V is the applied voltage reduced by the difference in work function of the collector and emitter. The Langmuir-Child law applies, to a close approximation, to other electrode geometries as well. Thus for coaxial cylinders with the inner cylinder the cathode, it leads to a deviation from the true value of the current density of 13% at most. *See* SPACE CHARGE.

Edward G. Ramberg

Chilopoda

A class of the Myriapoda commonly known as the centipedes. As are all myriapods, centipedes are ground dwellers whose permeable cuticle largely restricts their distribution to moist sites and habitats. Centipedes are mostly found under stones, in moss cushions, in leaf litter, and beneath loose bark on trees; several species inhabit caves, especially those of temperate regions. All centipedes are carnivorous; their predatory habits are reflected in their great agility and fleetness and especially in the modification of the first trunk appendages into a pair of usually massive raptorial pincers, the poison claws (also called the forcipules or the prehensors). Each poison claw contains a poison gland whose duct opens near the tip of the claw. Exceptionally, the poison gland may be located in the trunk, in which case the duct connecting it to the apical opening can be as long as twenty body segments. The poison immobilizes or kills arthropod prey and even some small vertebrates. The bite of larger species, particularly of the Scolopendromorpha, may be painful to human beings, but no serious consequences have been reported. *See* ARTHROPODA.

Distribution and taxonomy. The class is divided into two subclasses, the Notostigmophora and the Pleurostigmophora. There are five orders: two are basically tropical (Scutigeromorpha, Scolopendromorpha), two are essentially temperate (Lithobiomorpha, Craterostigmomorpha), and the Geophilomorpha is abundant in both zones. Indeed, there are some Lithobiomorpha and Geophilomorpha that occur as far north as the Arctic Circle, and others at elevations as high as 4000 m (13,123 ft) on the Himalayas.

Fragmentary fossils of Scutigeromorpha are known from the Upper Silurian. Fossil Scolopendromorpha that are very similar to modern types are known from a Carboniferous site. The extinct order Devonobiomorpha, only known for the one species *Devonobius delta* from an upper Middle Devonian site near Gilboa, New York, is probably closely related to the living Craterostigmomorpha.

Morphology. Centipedes have a globular or, more often, flattened head that is distinctly articulated in respect to the long trunk. The head bears a pair of unbranched antennae, which are sometimes very long with up to more than 100 articles. The eyes are of the compound type in the Scutigeromorpha, but are simple ocelli in the other groups; however, there are no eyes in the cryptopid Scolopendromorpha, in the Geophilomorpha, and in many cave-dwelling Lithobiomorpha. The mouthparts include one pair of mandibles and two pairs of maxillae. Excluding the first segment (which bears the poison claws) and the last two or three segments (which are devoid of appendages or bear only short genital appendages), each trunk segment bears one pair of legs. In the adult centipedes, the number of leg-bearing segments is always odd: 15 in the Scutigeromorpha, Lithobiomorpha, and Craterostigmomorpha; 21 or 23 in the Scolopendromorpha; and 27 to 191 (odd numbers only) in the Geophilomorpha. Variation in segment number within the same species is the general rule among the Geophilomorpha (most species in the family Mecistocephalidae being the exception) and has also been reported in one representative of the Scolopendromorpha. Although the trunk segments are uniform ventrally, they are often unequal dorsally. This is most conspicuous in the Lithobiomorpha, in which longer and shorter segments alternate quite regularly except close to midbody.

Gas exchange occurs through lateral spiracles or through dorsal stomata (in Scutigeromorpha only). A circulatory system is present; the copper-containing respiratory pigment hemocyanin has been found in the hemolymph of Scutigeromorpha. Excretion is mainly through a pair of Malpighian tubules similar to those of the insects; in addition, Scutigeromorpha and Lithobiomorpha have a pair of maxillary reins. The genital ducts open at the posterior end of the body. *See* RESPIRATORY PIGMENTS (INVERTEBRATE).

Reproduction and development. All centipedes have separate sexes. The females of Scutigeromorpha and Lithobiomorpha have a pair of pincer-shaped appendages used in egg-laying; otherwise sexual dimorphism is usually limited to the shape of the last pair of legs, which are more elaborate in the male. Males and females of most Scolopendromorpha are virtually indistinguishable without dissection.

Fig. 1. European house centipede, *Scutigera coleoptrata* (order Scutigeromorpha); it is now commonly found in many urban sites in America. (*Photo by Marco Uliana*)

Fig. 2. Scolopender, *Scolopendra cingulata* (order Scolopendromorpha), from the Mediterranean region. (*Photo by Lucio Bonato*)

Although a few instances of parthenogenesis have been described, sexual reproduction among centipedes typically involves the transfer of sperm. Sperm transfer occurs through the production of sperm packets (spermatophores) that the male fixes to the ground (Scutigeromorpha) or, more frequently, places on a small silky web, before inviting the female to collect them. The eggs of centipedies are large. In Scutigeromorpha and Lithobiomorpha, the eggs are manipulated by the female through the posterior pincerlike appendages and finally abandoned, individually, in the soil, covered by soil particles. However, in the Craterostigmomorpha, Scolopendromorpha, and Geophilomorpha, the female not only broods her eggs but also guards the young for a time; without the attention of the female, they would succumb to the fungi and bacteria of the forest floor.

Fig. 3. Geophilomorph centipede, *Clinopodes flavidus*, from northern Italy, illustrating the very elongated, wormlike habit that is characteristic of members of order Geophilomorpha. (*Photo by Lucio Bonato*)

Many centipedes (Scutigeromorpha, Lithobiomorpha, and Craterostigmomorpha) are hemianamorphic, the young hatching with less than the adult number of pairs of legs and continue to molt until the final complement is achieved. However, even once the full complement is attained, a few more molts are required before the animal reaches sexual maturity. Postembryonic development is thus divided into a larval phase, during which the animal achieves the complete number of fully developed segments, and a postlarval phase, during which the segments do not increase further but the animal continues to grow until sexual maturity is reached.

The Scolopendromorpha and Geophilomorpha are epimorphic; that is, upon hatching, the young already possess the adult complement of leg-bearing segments, and successive molts merely permit an increase in size. Centipedes rarely reach sexual maturity in less than 1 year. There is evidence to suggest that all centipedes continue to molt even after they reach sexually maturity and perhaps throughout life; in some species this may entail many years. *See* REPRODUCTION (ANIMAL).

Notostigmophora. The subclass Notostigmophora comprises a single order, Scutigeromorpha. These centipedes are peculiar in embodying primitive as well as highly advanced characters. The group is characterized by the presence of dorsal respiratory openings (stomata); compound-type eyes; long flagellate, multisegmented antennae; and long thin legs with multisegmented tarsi. The trunk has 15 leg-bearing segments but only seven terga. The most familiar member of the order is the common house centipede, *Scutigera coleoptrata*, a species native to southern Europe but accidentally introduced to North America and elsewhere (**Fig. 1**).

Pleurostigmophora. In contrast to the Notostigmophora, the subclass Pleurostigmophora have lateral respiratory openings (or spiracles) and long, branching tracheae similar to those of the insects. Four orders are recognized: Lithobiomorpha (about 1075 species described thus far), Craterostigmomorpha (1 species), Scolopendromorpha (about 810 species), and Geophilomorpha (about 1290 species).

Lithobiomorpha and Craterostigmomorpha. The Lithobiomorpha share some primitive traits with the Scutigeromorpha, with which they were allied in some old classifications: both are anamorphic, have 15 leg-bearing trunk segments, and are rapid runners. However, members of Lithobiomorpha differ in having a flattened rather than globular head, ocelli (if present) rather than compound eyes, shorter antennae, and, mostly, two-segmented tarsi. The majority of these centipedes are rather small in size, attaining a length of up to only 4 cm (1.6 in.). Although the order is typically temperate in distribution, there are a few mainly tropical or subtropical groups; only a few species are exclusively tropical.

The order Craterostigmomorpha, represented by a single known species inhabiting Tasmania and New Zealand, resembles the Lithobiomorpha in having 15 leg-bearing segments with associated sternites; they differ, notably, in possessing 21 tergites and large, peculiar poison claws.

Scolopendromorpha. The Scolopendromorpha (**Fig. 2**) are the most abundant centipedes in the tropics, where the order exhibits its greatest diversity. They also include the largest centipedes, some of which reach a length close to 30 cm (128 in.). There are also many species, of smaller size, in the temperate zone. The order is divisible into three families: the Scolopendridae, which possess eyes, and the Cryptopidae and Scolopocryptopidae, which are blind.

Geophilomorpha. The Geophilomorpha (**Fig. 3**) represent the most specialized of all centipedes. All are dorsoventrally flattened, and their bodies are long and pliable, permitting them to squeeze through tight openings. All geophilomorphs are blind. The spiracles occur as an unbroken series from the second through the last or next-to-last leg-bearing segment. Unlike most other chilopods, which are voracious hunters that emerge at night to seek their prey in the open, the geophilomorphs are generally found in crevice-cranny habitats; they are adapted to the special requirements of life in the soil, living in the close confines of leaf litter. R. E. Crabill; A. Minelli

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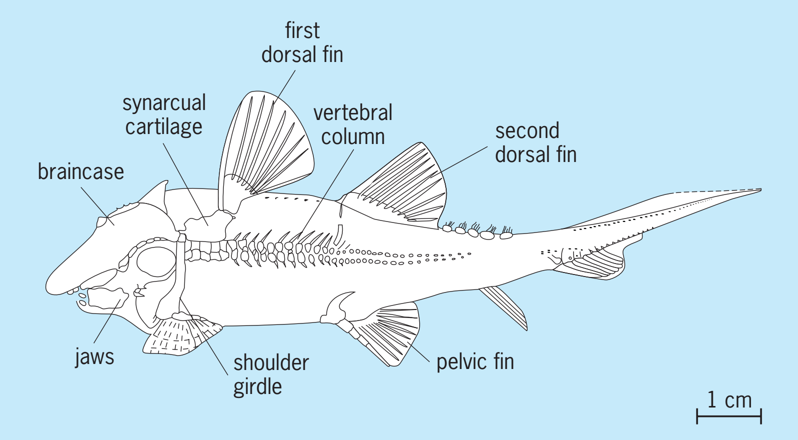

Fig. 1. Lower Carboniferous cochliodontiform *Traquairius*, lateral view. (*After R. Lund, The diversity and relationships of the Holocephali, Proc. 2d Int. Meeting Indo-Pacific Fishes, Ichthyol. Soc. Japan, 1986*)

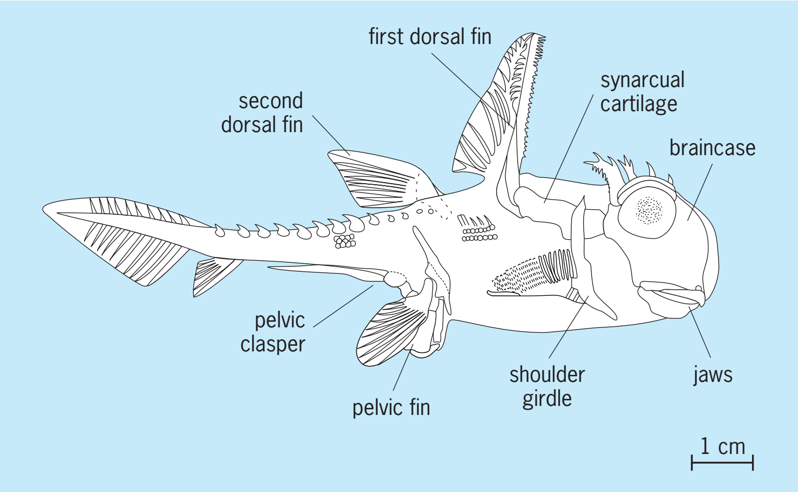

Fig. 2. Lower Carboniferous chimaeriform *Echinochimaera*, lateral view. (*After R. Lund, New Mississippian Holocephalai and the evolution of the Holocephali, Mem. Mus. Nat. Hist. Nat., Paris, 53:195–205, 1988*)

Chimaeriformes

The only extant order of the chondrichthyan subclass Holocephali, and the closest living relatives of the Elasmobranchii (sharks and rays). The chimaeriformes (ratfishes) are a distinctive group of marine fishes that mostly inhabit the deeper parts of the world's oceans, especially in the Atlantic and Pacific. Some species move to coastal waters during the winter months, and a few species may be restricted to these environments. Modern ratfishes are divided into three families, distinguished by the shape of the snout: Chimaeridae, Rhinochimaeridae, and Callorhinchidae. *See* CHONDRICHTHYES.

Morphology. Molecular sequence data and anatomical similarities (such as a cartilaginous and superficially calcified internal skeleton, urea retention mechanism, and clasper organs in the male for internal fertilization) show that chimaeriform fishes and elasmobranchs are more closely related to each other than to any other vertebrate groups. Unlike the elasmobranchs, however, chimaeriforms have the upper jaw fused to the braincase (holostylic condition); a hyoid arch that is not involved in jaw suspension; four gill slits opening into a common outer chamber covered by an opercular skinfold, with a single branchial opening on each side of the head and no spiracle in the adult; massive dental plates instead of individual teeth, with special zones of hard tissue (tritors) separated by softer dentine; a persistent and unconstricted notochord; several ringlike centra per body segment instead of a single one (polyspondylous condition); a narrow, tapering tail; and a dorsal fin with a long, barbed spine just behind the head (**Fig. 1**). A special cartilage (synarcual) connects the back of the braincase to the dorsal fin, and muscles are capable of raising the dorsal fin and its spine (Fig. 1 and **Fig. 2**). The clasper organ (Fig. 2) in males is supplemented by an anterior structure called a tenaculum, which is thought to play a role in copulation, display, or courtship. There is also a large hooklike frontal "clasper" on the head, which may play a similar role. *See* ELASMOBRANCHII. John G. Maisey

Fig. 3. Modern chimaeriform *Hydrolagus colliei* (spotted ratfish). (*Photo © by Joseph Dougherty/www.ecology.org*)

Extant forms. About 31 living species of ratfishes are categorized into six genera and three families, which can be readily distinguished as follows:

Callorhynchidae (plownose chimaeras). The four species in one genus of these chimaeras have an elongate, flexible snout with a hooklike process at the end. They occur in the Southern Hemisphere, off the southern shores of South America, Africa, New Zealand, and Australia.

Chimaeridae (shortnose chimaeras or ratfishes). This family consists of two genera and about 21 species that are known from the Atlantic and Pacific oceans. They have a short, rounded snout and long tapering ratlike tail (**Fig. 3**). The sharp dorsal spine has associated with it a poison gland that produces venom painful to humans.

Rhinochimaeridae. The three genera and six species of this family are similar to the shortnose chimaeras but differ in having a long and pointed snout lacking a hooklike process. They are known from the Atlantic and Pacific oceans, as well as the Indian Ocean off southern Africa.

Most chimaeras feed on mollusks and crustaceans and occasionally on smaller fishes. Herbert Boschung

Fossil record. The fossil record of the chimaeriforms shows that essentially modern forms were present in the Middle Jurassic (175–150 million years ago, ma). Even earlier chimaeriform-like fishes from the Devonian, Carboniferous, and Permian periods (375–250 ma) reveal a surprising variety of morphological diversity, suggesting that they occupied a wide range of exclusively marine habitats (there is no evidence of nonmarine forms). Some had rows of blunt teeth arranged across the jaws (as in sharks) instead of dental plates, while others had continuously growing, curved tooth plates (although these lack the complexity of modern chimaeriform dental plates and do not have tritors). In some, the jaws were not fused to the braincase, as in modern chimaeroids. Many were armored with bonelike plates in the skin, especially around the head. For this reason, it was once thought that chimaeriforms were related to some group of placoderms, although their "armor" is very different in form and structure and the similarities between them are probably either convergent, or represent primitive features of jawed vertebrates generally. Importantly, no placoderms are known to possess the unique features of chimaeriforms. *See* CARBONIFEROUS; DEVONIAN; JURASSIC; PERMIAN; PLACODERMI.

Evolution. The main line of chimaeriform evolution apparently began in the Late Devonian (375 ma). Many spectacular discoveries of chimaeriform-like fossils have been made in the Lower Carboniferous Bear Gulch Limestone of Montana (325 ma). These fossils suggest that several distinctive holocephalan lineages radiated during the late Paleozoic, but only one (Chimaeroidei) survived to the present day. *See* PALEOZOIC.

Two Paleozoic holocephalan orders of particular importance are the Cochliodontiformes and Menaspiformes. These are considered to be successive extinct sister groups to the Chimaeriformes, with which they share one to three pairs of tooth plates. Cochliodontiformes (Late Devonian to Late Permian; worldwide) are mostly known from isolated tooth plates, but complete fossils from Bear Gulch show they had a variety of body forms (Fig. 1). Many cochliodontiforms had a dorsoventrally flattened body; paired mandibular and occipital spines; paired, brushlike frontal spines on either side of the mouth; and "bradyodont" teeth with curved or rounded surfaces, usually with grooves or folds, and multiple small anterior tooth plates in the upper jaw plus two larger posterior tooth pairs in the upper and lower jaws. The branchial arches did not always lie beneath the head as in modern chimaeriforms, but were sometimes behind the head as in elasmobranchs. Some cochliodontiforms lacked a synarcual or dorsal fin, although most had both. Menaspiformes (Early Carboniferous to Permian; North America and Europe) had two pairs of large sickle-shaped frontal or cephalic spines anterior to the orbits, several large dermal "plates" (actually fusions of numerous small tesserae) on the top and sides of the head, holostylic jaws set a distinct angle to the body axis, with the lower jaw rami diverging at about 90°; thin tooth plates, a single pair of lower tooth plates plus anterior teeth at the midline; paired and extremely robust "prepectoral" or "mandibular" spines; a two-part synarcual but no dorsal fin or spine; a complex pattern of dermal scutes, often coalescing to form armor plates; and two rows of enlarged scales on the dorsal part of the trunk (**Fig. 4**).

The order Chimaeriformes includes four suborders: Echinochimaeroidae (Early Carboniferous; North America), Squalorajoidei (Early Jurassic; Europe), Myriacanthoidei (Late Triassic–Late Jurassic; Europe), and Chimaeroidei (Jurassic–Recent, worldwide). Until quite recently, no chimaeriforms were known before the Triassic, but the discovery of *Echinochimaera* in the Bear Gulch Limestone of Montana dramatically extended the stratigraphic

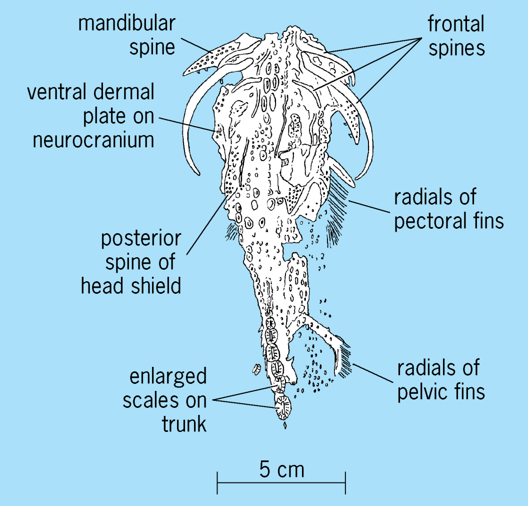

Fig. 4. Permian menaspiform *Menaspis*, dorsal view. (*After C. Patterson, The phylogeny of the chimaeroids, Phil. Trans. Roy. Soc. London, 249:101–219, 1965*)

range of the group (Fig. 2). *Echinochimaera* was remarkably modern in appearance, with a tenaculum and tooth plates (although these lack continuous tritors), but it retained a well-developed second dorsal fin instead of having a narrow, ribbonlike tail. Myriacanthoids resembled modern chimaeriforms in having tritors on at least some tooth plates, polyspondylous ring centra, reduced dermal armor, a single barbed dorsal spine attached to a movable dorsal fin, and a large frontal clasper on the head. Chimaeroids (including modern ratfishes) possess well-developed dental plates, all with specialized tritors; a laterally flattened head; and an ethmoidal canal (an enclosed space in the skull roof above the brain). Apart from the tritors, however, it is unknown whether these characters were also present in other chimaeriforms.

John G. Maisey

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Chimera

An individual animal or plant made up of cells derived from more than one zygote or otherwise genetically distinct.

Animals

Although some chimeras do arise naturally, most are produced experimentally by mixing cells of very early embryos or by tissue grafting in late embryos or adults. Experimental chimeras have been used to study a number of biological questions, including the origin and fate of cell lineages during embryonic development, immunological self-tolerance, tumor susceptibility, and the nature of malignancy. *See* CELL LINEAGE.

Mixing embryo cells. Two techniques used to form chimeras by mixing embryo cells are aggregation and injection.

Aggregation chimeras. The first experimental mammalian chimeras were produced from mouse embryos in the early 1960s, first by Andrei Tarkowski and later by Beatrice Mintz. The technique involves removing the zonae pellucidae from around 8–16 cell embryos of different strains of mice and pushing the morulae together so that the cells can aggregate. After a short period of laboratory culture, during which the aggregate develops into a single large blastocyst, the embryo is returned to a hormone-primed foster mother (**Fig. 1**). Chimeric offspring are recognized in several ways. If derived from embryos of pigmented and albino strains, they may have strips of pigmented skin and patches of pigment in the eye. Internal chimerism can be detected by use of chromosomal markers or genetically determined enzyme variants. Chimeras accept skin grafts from the two component strains but reject grafts from third-party strains. Aggregation chimeras formed from embryos of strains A and B are denoted A ↔ B, and chimeras developing from two embryos are often known as tetraparental animals. Up to 15 mouse embryos have been aggregated to form a single giant blastocyst. However, the offspring from such experiments are always normal, so that size regulation must occur after implantation. On average, 50% of aggregation

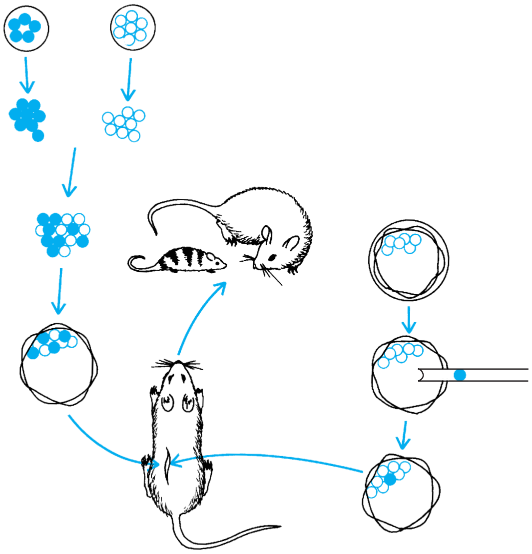

Fig. 1. Techniques for making aggregation chimeras (left) and injection chimeras (right) from early mouse embryos.

chimeras will be XX ↔ XY. Sex determination seems to depend on the relative number of XX and XY cells in the fetal gonads, and in mice most of these animals develop into phenotypic males.

Injection chimeras. This technique was first described for mouse embryos by Richard Gardner in 1968. A blastocyst of the host mouse strain is removed from its zona pellucida and held on a suction pipette. Cells of the donor strain are injected through a fine glass needle, either into the blastocoele cavity or into the center of the inner cell mass (the group of cells from which the fetus is derived). After a short period of culture, the blastocyst is returned to a foster mother. By analogy with aggregation chimeras, injection chimeras are denoted A ↔ B and are recognized by similar, genetically determined markers (pigment formation, and enzyme, serum, and urinary protein variants). A variety of cells have been injected into blastocysts in this way. Cells from adults fail to either grow or become incorporated into the fetus. Early-cleavage-stage embryos injected into the cavity of giant blastocysts (formed by aggregating several embryos in culture as described above) develop inside their zonae into "blastocysts within blastocysts." In contrast, individual cells or groups of cells isolated from embryos of about the same age as the host become incorporated into the host embryo and grow and differentiate along with it. By taking appropriately marked cells from different positions in the donor embryo, placing them in different positions in the host blastocyst, and following their contribution to the late-gestation embryo or adult, important information was obtained about cell interactions and lineages in mouse development.

Another kind of cell—the pluripotent stem cell of mouse teratocarcinomas—was found to give rise to normal tissues in adult chimeras after injection into the mouse blastocyst. Teratocarcinomas are tumors consisting of a disorganized mixture of adult and embryonic tissues. They develop spontaneously from germ cells in the gonads of certain mouse strains, or from cells in early embryos transplanted to ectopic sites. All the differentiated tissues in the tumor arise from pluripotent stem cells known as embryonal carcinoma (EC) cells. When embryonal carcinoma cells are injected into a genetically marked host blastocyst, they continue to divide and participate in normal development, and give rise to fully differentiated cells in all tissues of the adult, including skin, muscle, nerve, kidney, and blood.

Embryonal carcinoma cells from several sources, including spontaneous and embryo-derived tumors and cultured lines selected to carry specific mutations or even human chromosomes, have contributed to normal chimeras. However, embryonal carcinoma cells from some other sources fail to integrate, but produce teratocarcinomas in the newborn animal or adult. The factors controlling successful integration are not yet fully understood, but must include such things as the relative division rate of the embryonal carcinoma cells, their biochemical similarity to cells of the inner cell mass, and their chromosomal constitution. On general grounds, embryonal carcinoma cells should be expected to give rise also to fully functional germ cells, so that EC → blastocyst chimeras might be used to generate nonchimeric mice carrying specific mutations. The fact that certain embryonal carcinoma cells give rise to tumors when injected under the skin or into the body cavity but behave normally in the blastocyst has been used to support the idea that cancers can develop not only as a result of gene mutations but also as a result of disturbances in environmental factors controlling normal cell differentiation (epigenetic theory of cancer). *See* ONCOLOGY.

Interspecies chimeras. A number of interspecies chimeras have been produced by aggregating sheep and goat embryos and reimplanting them in sheep. The offspring have tissues containing a mixture of both sheep and goat cells. The goat, for example, may have patches of both wool and hair. Interspecies chimeras have also been made between rat and mouse, but these do not develop in the uterus, presumably because of immunological rejection by the foster mother. This rejection does not occur in sheep for unknown reasons.

Tissue grafting. Animals that have accepted skin or organ grafts are technically chimeras. Radiation chimeras are produced when an animal is exposed to x-rays, so that blood-forming stem cells in the bone marrow are killed and then replaced by a bone marrow transplant from a genetically different animal. Lymphoid cells in the process of differentiating from stem cells in the donor marrow recognize the recipient as "self" and do not initiate an immune response against the host cells. By removing the thymus from the irradiated host and replacing it with a thymus from another animal prior to the bone marrow transplant, it has been shown that this organ plays an important role in the generation of immunological self-tolerance. *See* TRANSPLANTATION BIOLOGY.

Natural occurrence. Naturally occurring chimeras in humans are rare and are most easily recognized when some cells are XX and others XY. Such individuals are usually hermaphrodite and probably result from fertilization of the egg by one sperm and the second polar body by another, with both diploid cells then contributing to the embryo (the small polar bodies normally degenerate). Blood chimeras are somewhat more common in animals such as cattle where the blood vessels in placentas of twins fuse, so that blood cells can pass from one developing fetus to the other. The female sibling of male and female cattle twins is sterile (a freemartin), because sex hormones from the male fetus interfere with sexual differentiation in the female. Blood chimerism always occurs in marmosets, which produce twins at most pregnancies, but no abnormalities in sexual function are found.

Brigid Hogan

Plants

In modern botanical usage a chimera is a plant consisting of two or more genetically distinct kinds of cells. Chimeras can arise either by a mutation in a cell in some part of the plant where cells divide or by bringing together two different plants so that their cells multiply side by side to produce a single individual. They are studied not only because they are interesting or ornamental but also because they help in understanding many developmental features of plants that would otherwise be difficult to investigate.

Grafting. The first type of chimera to be used in this way resulted from grafting. Occasionally a bud forms at the junction of the scion and stock, incorporating cells from both; sometimes the cells arrange themselves so that shoots derived from the bud will contain cells from both plants. A plant of this kind is *Laburnocytisus adami*, formed in 1825 by grafting *Cytisus purpureus* onto *Laburnum anagyroides*. The flowers are brown instead of the purple or yellow of the scion and stock. It has the treelike habit of *Laburnum*; its leaves resemble those of *Laburnum* except for the surfaces, which are like those of *Cytisu*; and its seeds always grow into *Laburnum* trees. Occasionally a branch grows out wholly like *Laburnum* or, more rarely, wholly like *Cytisus*. *See* PLANT PROPAGATION.

At first people thought that *Laburnocytisus* and other similar plants derived from grafting must have been nonsexual hybrids, the result of fusing two somatic cells, but there was no evidence that this could occur and result in viable hybrid cells. The occasional reversion to pure *Laburnum* or *Cytisus* branches and the fate of their seeds militated against this theory.

Further investigation showed that the plant consists of a skin of *Cytisus* cells overlying a core of *Laburnum* cells (**Fig. 2**). The skin is only one cell deep, and the flowers appear brown because a purple epidermis covers yellow cells inside the petals. The germ cells which go on to form the embryos in the seeds are always formed from the second layer of the shoot and so always produce *Laburnum* plants. Reversions are due to some buds being formed wholly from the *Cytisus* skin or by the *Laburnum* tissue bursting through the skin in bud formation.

Apical meristem. *Laburnocytisus adami* has been synthesized only once, and all the specimens in existence have been propagated vegetatively from the original. This implies great stability in the constitution of the chimera, and for a long while after the plant's origin, no one knew any mechanism whereby a shoot could maintain such a stable arrangement of genetically diverse cells. In attempts to solve this problem, it was discovered that flowering plants have growing points (apical meristems) where the outer cells are arranged in layers parallel to the surface, and that this periclinal layering is due to the fact that the outer cells divide only anticlinally, that is, by walls perpendicular to the surface of the growing point (**Fig. 3**). In many plants there are two outer (or tunica) layers and, because cell divisions are confined to the anticlinal planes, each layer remains discrete from the other and from the underlying nonlayered tissue called the corpus (Fig. 3). The epidermis of leaves, stems, and petals is derived from the outer layer of the growing point, and the discreteness of this layer accounts for the stability of the *Laburnocytisus* chimera. *See* APICAL MERISTEM.

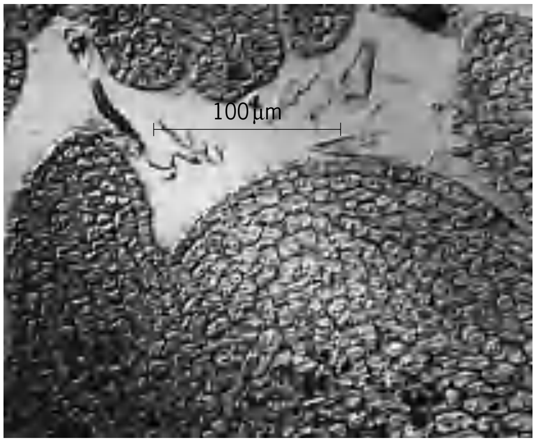

Fig. 2. Section through growing point of *Laburnocytisus adami*.

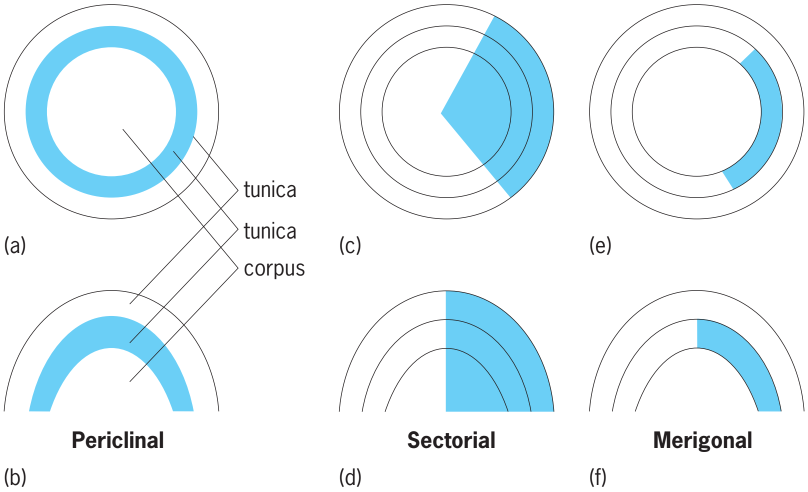

Fig. 3. The two tunica layers and one corpus layer with the three types of chimeras, (*a, b*) periclinal (*c, d*) sectorial, and (*e, f*) merigonal.

An elegant proof of the existence of these self-perpetuating layers in apical meristems came with the synthesis of polyploid chimeras in *Datura* and *Vaccinium*. This was done by treating the embryos or buds with colchicine, a drug that causes nuclei which divide in its presence to double their chromosome number. Since these tetraploid cells and their progeny are larger than ordinary diploid cells, they can be identified in sections cut through the growing point. After the treated meristems had been allowed to grow and produce lateral buds, the buds were sectioned and each tunica layer was seen to contain only cells with the same ploidy; but one layer often consisted of cells of a different ploidy from the other tunica layers and from the corpus. The exclusively anticlinal divisions of the tunica layers clearly prevent the mixing of cells of different ploidy and prevent the chimera from becoming unstable from competition between the cells of different ploidy.

Periclinal chimera. A periclinal chimera has genetically different layers (Fig. 3*a* and *b*). With this type

Fig. 4. Variegated *Pelargonium*, a periclinal chimera whose second tunica layer is genetically white and whose corpus is genetically green.

of chimera, in which the different cells can be identified under the microscope by their relative sizes, it is possible to follow into stems, leaves, and flowers which tissues are derived from each layer in the growing point. For leaves, this can also be done with variegated chimeras, a type of periclinal chimera in which the genetic difference between the cells resides in the plastids due to a mutation that prevents the synthesis of chlorophyll. Tracts of cells whose plastids lack this pigment appear white or yellow instead of green.

A common form of variegated chimera has leaves with white margins and a green center (**Fig. 4**). The white margin is derived from the second layer of the tunica, and the green center from inner cells of the growing point. (The outer tunica layer contributes no color to the leaves of most plants, because it gives rise only to the epidermis, whose cells usually do not develop chloroplasts.) The white leaf tissue overlies the green in the center of the leaf but does not mask the green color. Chimeras with green leaf margins and white centers are usually the result of a genetically green tunica proliferating abnormally at the leaf margin in an otherwise white leaf (**Fig. 5**).

Periclinal chimeras can be used to study the fate of different regions of the growing point, and how the leaves and so forth are constructed; but chimerical plants sometimes do not behave exactly like nonchimerical plants. Nevertheless, they have supplied valuable evidence, sometimes the only evidence, on which to base a view on some developmental problems. Chimeras show, for example, that there is considerable diversity in the number of layers that go to make each kind of organ, and this affects ideas about the homology of different organs.

Sectorial chimera. Since the somatic mutation that initiates most variegated and polyploid chimeras would normally occur in a single cell of a growing point or embryo, it often happens that it is propagated into a tract of mutant cells to form a sector of the plant (Fig. 3*c* and *d*). If the mutation resulted in a failure to form green pigment, the tract would be seen as a white stripe. Such chimeras are called sectorial, but they are normally unstable because there is no mechanism to isolate the mutant sector and, in the flux that occurs in a meristem of growing and dividing cells, one or other of the two sorts of cells takes over its self-perpetuating layer in the growing point. The sectorial chimera therefore becomes nonchimerical or else a periclinal chimera.

Mericlinal chimera. However, in one class of chimeras an isolating mechanism can stabilize the sectorial arrangement (Fig. 3*e* and *f*). This propagates stripes of mutant tissue into the shoot, but because the tunica and corpus are discrete from each other, the plant is not fully sectored and is called a mericlinal chimera.

Many chimeras of this type have a single tunica layer; those with green and white stripes in the leaves have the mutant cells in sectors of the corpus. It was not until C. Thielke tried to find the reason why these chimeras are stable that attention was directed to the fact that they are always plants with leaves in two

Fig. 5. Variegated *Chlorophytum*, a periclinal chimera whose outer cell layer is genetically green and proliferates at the leaf margins to give green tissue in an otherwise genetically white plant.

ranks, and consequently the lateral growth of the growing point occurs by cell expansion only in the plane connecting alternate leaves. This results in the longitudinal divisions of the corpus cells being confined to planes at right angles to the plane containing the leaves. A mutation in one cell therefore can result in a vertical sheet of mutant cells which, in the case of a plastid defect, manifests itself as a white stripe in every future leaf. Transverse sections through the bud confirm that the cells behave as predicted.

Eversports. The eversport is a special type of chimera mainly found in gymnosperms, in which a shoot becomes partially green and partially yellow at a high frequency of about 1 in every 25 nodes. It comes from a periclinal chimera with a single yellow tunica and a green corpus that becomes yellow. This change was explained by H. Derman as coming from a "replacement" periclinal cell division of the topmost cell of the tunica, with one yellow daughter cell remaining in the tunica and the lower yellow daughter cell becoming part of the corpus. This new yellow corpus cell and preexisting green corpus cells proliferate into a partially yellow and partially green corpus, thus seen as a green-yellow chimera (**Fig. 6**).

Recent studies have shown that most eversporting green-yellow chimeras in gymnosperms and dicots eventually become all yellow, leading to the conclusion that the apical meristem has a single apical cell in the top tunica layer similar to what is found in mosses and ferns. Eversports have also been used to understand which regions of a stem give rise to a node and which cells of this nodal region give rise to a leaf.

Roots. The growing points of roots may also become chimerical, but in roots there is no mechanism to isolate genetically different tissues as there is in shoots, and so chimeras are unstable. However, there can be sufficient stability to do experiments with induced root chimeras on the destiny of cells.

Cultivated plants. Since the general acceptance of the existence of organisms with genetically diverse cells, many cultivated plants have been found to be chimeras. This knowledge has explained several phenomena hitherto puzzling. In carnations, for example, white flowers have arisen from red varieties due to the red variety being a periclinal white-red chimera whose normal stability was upset. Flecks of color often indicate the chimerical nature of such plants. Color changes in potato tubers occur similarly because the plants are periclinal chimeras. *See* SOMATIC CELL GENETICS. F. A. L. Clowes; Robert W. Korn

Fig. 6. Eversporting false sawara cypress. Numerous mutant (arrows) green-yellow chimeras are present, most of which become stable mutant shoots.

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Chimney

A vertical hollow structure of masonry, steel, or reinforced concrete, built to convey gaseous products of combustion from a building or process facility. A chimney should be high enough to furnish adequate draft and to discharge the products of combustion without causing local air pollution. The height and diameter of a chimney determine the draft.

Construction specifications. For adequate draft, small industrial boilers and home heating systems depend entirely upon the enclosed column of hot gas. A draft is produced because the density of the hot gas inside is lower than that of the air outside. In contrast, stacks, which are chimneys for large power plants and process facilities, usually depend upon force-draft fans and induced-draft fans to produce the draft necessary for operation, and the chimney is used only for removal of the flue gas. Some stacks burn off the gases at the top and are known as flarestacks. *See* FAN.

For fire safety, chimneys for residential construction and for small buildings must extend at least 3 ft (0.9 m) above the level where they pass through the roof and at least 2 ft (0.6 m) higher than any ridge within 10 ft (3 m) of them. Some stacks extend as high as 500 ft (150 m) above ground level, thus providing supplementary natural draft.

A chimney or stack must be designed to withstand lateral loads from wind pressure or seismic forces (earthquakes), as well as vertical loads from its own weight. Wind pressure on a cylindrical surface is about two-thirds that on a plane surface. Thus with a wind pressure of 30 lb/ft^2 (1440 newtons/m^2), the pressure per foot of chimney height is 20 times the diameter, in feet, of the chimney (the pressure in newtons per meter of height is 960 times the diameter in meters). Depending upon geographical location, horizontal inertia loads due to an earthquake can be as high as 35% of the weight of the chimney and can result in greater overturning moments and bending stresses than wind loading. *See* LOADS, DYNAMIC.

Construction materials. Small chimneys used in residential construction are commonly made of brick or unreinforced masonry, while stacks are usually made of steel. In the early 1900s it was generally more economical to construct tall chimneys from masonry or reinforced concrete. However, modern construction costs for tall chimneys favor the use of steel since it allows for more rapid fabrication and erection compared with masonry or reinforced concrete. Where flue gases are particularly corrosive to steel, castable or masonry linings or corrosion-resistant steels (stainless) are often used; or the stack is designed with a corrosion allowance. Sometimes a steel stack has a double steel shell, consisting of concentric cylinders with an air space between the two. The inner shell serves mainly to convect the gases, while the outer shell withstands the wind or seismic loads. *See* REINFORCED CONCRETE; STAINLESS STEEL; STEEL.

Tall steel chimneys of small diameter cannot economically be made self-supporting and must be guyed. Where land costs are at a premium or where land is not available for guying, such as at congested process facilities, it is often more economical to support slender steel stacks with a derrick-type structure of steel latticed or trussed construction as opposed to constructing a self-supported stack. Modern steel stacks are usually shop welded into sections, which are then assembled in the field by flange bolting or welding. *See* JOINT (STRUCTURES); TRUSS.

Concrete chimneys may be plain or reinforced. If the bending moment due to wind or seismic forces on concrete chimneys does not produce excessive tension on the leeward side, reinforcing is unnecessary. To prevent temperature cracking, some plain concrete stacks have a fire-clay lining with an air space between the lining and the outer shell. Masonry or concrete linings are often used in construction of concrete chimneys, resulting in a chimney within a concrete chimney. The outer chimney withstands the lateral loads from wind or earthquake, and the inner one withstands the thermal loads and the acid attacks.

Except for rectangular flues and chimneys commonly used in residential construction, masonry chimneys are usually constructed of perforated radial brick molded to suit the diameter of the chimney. Because the compressive strength of the brick is much greater than that of the mortar, the design strength is determined by the tensile strength of the mortar. Unlike its steel or reinforced counterpart, a brick chimney cannot resist high tensile stresses. *See* BRICK; MASONRY; MORTAR.

Accessory structures. Tall chimneys and stacks, particularly flarestacks, are usually provided with a ladder and rest platforms to allow for inspection and maintenance. Safety regulations require either a cage around the ladder, which increases wind loading, or a safety climb device attached to the ladder to prevent a fall.

Tall stacks are usually fitted with some form of lightning protection and are always grounded at the base. Depending upon the lightning activity in a particular area, a tall stack may be fitted with a lightning dissipator at the top with a special copper line to ground to prevent static buildup and lightning strikes. *See* LIGHTNING AND SURGE PROTECTION.

Cylindrical stacks are subject to a phenomenon known as Kármán vortex oscillations due to the alternating vortices that are shed from opposite sides of the cylinder during gentle winds. Masonry (or gunite-lined stacks) and guyed stacks are generally not susceptible to this phenomenon, because the stack damping ratio is raised in the presence of an internal lining or guying, which tends to abate the buildup of oscillations from the Kármán vortex street. For unlined, self-supported, steel stacks, vortex oscillations are usually controlled by adding strakes or fins to the top third of the stack to spoil the airflow. *See* KÁRMÁN VORTEX STREET.

Foundations. Foundations for tall stacks and chimneys are made from reinforced concrete and are usually octagonal. For very soft soils, the foundation strength is augmented by piles. The design of the foundation is controlled almost entirely by the overturning moment from wind or seismic forces. *See* FOUNDATIONS; PILE FOUNDATION.

Joseph Vellozzi

Chinchilla

The name given to two species of rodents which, together with four species of viscachas, make up the family Chinchillidae. These animals are native to several areas of South America and are widely bred on farms in North America and Europe for their fur, which is long, fine, and expensive. The wild population is protected in Chile since the killing of wild stocks in the early 1900s almost led to extinction.

Species. The two species of chinchilla are *Chinchilla brevicaudata* and *C. lanigar*. These animals resemble the squirrel in size and shape and are characterized by long, muscular hindlimbs, with elongate feet bearing four toes, and short forelimbs (see **illus.**). Blunt claws occur on the flexible fingers. These animals have 20 teeth with a dental formula of I 1/1 C 0/0 Pm 1/1 M 3/3. *See* DENTITION.

Chinchillas are gregarious, nocturnally active animals and are found in arid, mountainous regions where they feed principally on vegetation. They often seek shelter in burrows or rock crevices, so

The chinchilla, with more hair per square inch than any other animal, is valued for its fur.

that their capture is difficult. The female, which is larger than the male, bears one to six offspring twice each year after a gestation period of 105–111 days.

Viscacha. There are four species of viscacha belonging to two genera, *Lagidium* (three species) and *Lagostomus*. The mountain viscacha (*Lagidium viscaccia*) lives in burrows near rocks in the foothills of the Andes. It is larger than the chinchilla and has a poor-quality fur, which is woven with wool into cloth. The plains viscacha (*Lagostomus maximus*) inhabits burrows in the pampas region of Argentina. It has coarse fur and is exclusively herbivorous. *See* RODENTIA.

Charles B. Curtin

Chinook

Amild, dry, extremely turbulent westerly wind on the eastern slopes of the Rocky Mountains and closely adjoining plains. The term is an Indian word which means “snow-eater,” appropriately applied because of the great effectiveness with which this wind reduces a snow cover by melting or by sublimation. The chinook is a particular instance of a type of wind known as a foehn wind. Foehn winds, initially studied in the Alps, refer to relatively warm, rather dry currents descending the lee slope of any substantial mountain barrier. The dryness is an indirect result of the condensation and precipitation of water from the air during its previous ascent of the windward slope of the mountain range. The warmth is attributable to adiabatic compression, turbulent mixing with potentially warmer air, and the previous release of latent heat of condensation in the air mass and to the turbulent mixing of the surface air with the air of greater heat content aloft.

In winterthe chinook wind sometimes impinges upon much colder stagnant polar air along a sharp front located in the foothills of the Rocky Mountains or on the adjacent plain. Small horizontal oscillations of this front have been known to produce several abrupt temperature rises and falls of as much as 45–54°F (25–30°C) at a given location over a period of a few hours. Damaging winds sometimes occur as gravity waves, which are triggered along the interface between the two air masses.

In the Alpine regions adverse psychological and physiological effects have been noted in humans during prolonged periods of foehn wind. These phenomena have been referred to as foehn sickness. *See* FRONT; ISENTROPIC SURFACES; PRECIPITATION (METEOROLOGY); WIND; WIND STRESS.

Frederick Sanders; Howard B. Bluestein

Chipmunk

The common name for any of 25 species of rodents in the genus *Tamias* of the mammalian family Sciuridae. Chipmunks have bright and dark stripes, large cheek pouches, and live mainly on the ground (see **illustration**). They are found primarily in forested areas in many regions of North America, south to west-central Mexico, as well as in Siberia, Mongolia, and northern and central China. The two species with the widest distribution in North America are the eastern chipmunk (*Tamias striatus*) and the least chipmunk (*T. minimus*). For the most part, the appearance and ecology of all 25 species is similar. *See* MAMMALIA; RODENTIA.

Eastern chipmunk. The eastern chipmunk is a small, fairly stout-bodied, terrestrial squirrel with five conspicuous dark dorsal stripes, a flattened and hairy tail, and large, well-developed cheek pouches. Overall dorsal coloration is tawny or reddish-brown. On each side, a broad whitish longitudinal stripe is bordered by two dark stripes. Two buff stripes are present above and below each eye. The ears are prominent and rounded. Adults are usually 200–255 mm (8.5–10 in.) in total length, including a 75–100-mm (3–4-in.) long tail, and weigh 70–140 g (2.5–5 oz).

Eastern chipmunks live in deciduous forests and brushy areas, especially near broken rocky ground, stone fences, and fallen logs. Although they spend most of their time on the ground, they occasionally climb up stumps or trees to feed or to escape an enemy. (Predators include snakes, weasels, mink, hawks, and domestic cats.) Hearing, sight, and smell are well developed in these solitary and diurnal mammals.

Habitat and hibernation. Chipmunks dig their own burrows, which provide living chambers (including a nest) and a place to store food. They become less active during the hotter summer months and hibernate during the colder winter months. Even though they hibernate, they do not store fat (as do other


Representative species of chipmunk (*Tamias*).

hibernators), so they must awaken periodically to eat. Home ranges are 0.10 to over 1.2 ha (0.04–0.5 acre), depending upon the quality of the habitat and population density. They prefer open-understory and closed-overstory habitats. Home ranges overlap broadly.

Diet. Chipmunks are chiefly vegetarians, feeding mainly on the seeds (including nuts) of woody plants. Corn, wheat, berries, and mushrooms are also eaten along with an occasional earthworm, snail, insect, frog, small snake, bird, and mouse. The large internal cheek pouches greatly assist in transporting food to underground storage chambers or to other cache sites in hollow logs or beneath rocks.

Reproduction and development. Two breeding periods may occur annually in eastern chipmunks, whereas western species have only one breeding season per year. Litters of three to five young are born after a gestation of 31 days. Young chipmunks leave the burrow for the first time at 5 to 6 weeks of age and are probably weaned before they are 40 days old. They are sexually mature at about 3 months, but most do not breed for the first time until they are one year old. Life span in the wild is usually between 2 and 4 years.

Donald W. Linzey

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Chiroptera

An order of mammals, commonly known as bats, in which the front limbs are modified as wings, thus making the chiropterans the only truly flying mammals. Bats form the second largest order of living mammals (18 families, 202 genera, 1116 species). They range from the limit of trees in the Northern Hemisphere to the southern tips of Africa, New Zealand, and South America, but most species are confined to the tropics. On many oceanic islands they are the only native land mammals. *See* MAMMALIA.

General characteristics. The wing is formed by webs of skin running from the neck to the wrist (propatagium, or antebrachial membrane), between the greatly elongated second, third, fourth, and fifth fingers (chiropatagium), and from the arm and hand to the body (usually the side) and hindlegs (plagiopatagium). There is also usually a web between the hindlegs (uropatagium, or interfemoral membrane) in which the tail, if present, is usually embedded for at least part of its length (**Figs. 1** and **2**).

Size in bats varies greatly and is well characterized by the length of the forearm (Fig. 1). As familiar reference points, the forearm of *Myotis lucifugus* is about 38 mm long (1.5 in.) and of *Eptesicus fuscus* (**Fig. 3**), about 45 mm (1.8 in.).

Most bats have one young per year, a few have two, and still fewer have three or more. This low reproductive rate is possible because of a long lifespan (up to 34 years in one species) and low predation. Bats have very few natural predators. Most predation is by chance encounters, although some predators may learn to wait at the entrance to a roost and capture bats as they emerge.

Bats are useful as pollinators, as distributors of seeds of tropical plants, and as predators of nocturnal insects. Their prey includes, many agricultural pest insects. Also, they help to maintain the balance of nature, as there are very few other nocturnal insect predators. Although the majority of bats are relatively small and feed on insects, there is great variation in their food habits. Bats can be fruit-eating (there are numerous fruit-eating bats—ranging in size up to the flying fox, with a wingspan reaching nearly 1.5 m or 5 ft); blood-feeding (the vampires); carnivorous (feeding on other small vertebrates—birds, mammals, lizards and frogs); and fish-eating.

Most bats (except pteropids) use echolocation to navigate and to capture insects or other food. Echolocation is similar to radar in that a series of clicks is produced. These clicks bounce off objects, including food items, and return as an echo to the bat, indicating the size, speed, and distance of the object. Most insects are captured by bats in flight using echolocation. Bats catch insects in the air with their mouth, wings, or tail membrane. *See* ECHOLOCATION.

Roost types vary greatly, bats may roost in buildings, in cracks or hollows of trees, under sloughing bark, under bridges, in caves or mines, solitary among foliage, in clusters of leaves, in rolled-up leaves, and in other protected places.

Most temperate bats hibernate during winter; they waken about every 2 weeks for a few hours and then reenter hibernation. About 75% of the fat energy stored for hibernation is used during arousals, leaving only about 25% to support bats throughout hibernation.

The 18 living families of bats may be briefly characterized as follows.

Pteropodidae (Old World fruit bats). These are in general the most primitive of living bats, characterized by more primitive ears and shoulder joints, and are the only family placed in the suborder Megachiroptera. The family, with 42 genera and 186 species, is widely distributed in the tropics and subtropics of the Old World, east to Australia and the Caroline and Cook islands. While some species are quite small, the family includes the largest of all bats, with wingspreads up to 5.5 ft (1.5 m) [Fig. 2]. The external ear of Old World fruit bats is elongate and oval, and there is no tragus. Most still retain a claw on the second digit (absent in all other bats, which constitute the suborder Microchiroptera), as well as the claw on the thumb. The teeth, however, are highly modified for eating fruit or nectar. The tail is short and rudimentary, or absent.

Few have developed the echolocation (radar) mechanism found in all Microchiroptera. One genus emits ultrasonic sounds, but most do not. These bats navigate visually. Many make long flights between feeding and roosting areas. They are slow but strong flyers. Many of the larger fruit bats congregate in large groups, whereas the smaller ones are usually solitary. Most Old World fruit bats find their food by smell. Most feed on ripe fruit, crushing the pulp in their teeth and spitting out the seeds. These bats may get food by hovering, or they may hold onto a branch with their feet and press the fruit to their chest with a foot to extract it. They sometimes eat flowers. Although some appear to breed at variable times, most breed at well-defined times. Most produce only one young. Some individuals in captivity have lived up to 20 years.

Rhinopomatidae (mouse or long-tailed bats). This insect-eating family, with one genus and four species, is found chiefly in arid regions of northern Africa and southern Asia and is characterized by long wirelike tails and rudimentary nose leaves (dermal outgrowths of unknown function above the nostrils). The tails of rhinopomatids are nearly as long as the head and body combined, and the tail membrane is very short and narrow. Rhinopomatids have large ears connected by skin across the forehead. The tragus (cartilaginous flap at the notch of the ear, Fig. 1) is well developed but rather small. These bats roost in caves, houses, and rock clefts, and are also found in pyramids of Africa. Some roost in very large colonies.

Emballonuridae (sac-winged bats). This insectivorous family includes 13 genera with 51 species and is found in the tropics of both the Old and New worlds. Like the Pteropodidae, but unlike other families of bats, members of Emballonuridae have well-developed bony processes behind the eye sockets. The tail extends only partly across the uropatagium. There is a great deal of variation in this family, with adults varying in weight from 5 to 105 g (0.18 to 3.7 oz). Members lack a nose leaf, but a tragus is present. The tail goes through the tail membrane and appears on the upper surface.

Members of Emballonuridae are commonly known as sac-winged bats because of their glandular wing sacs that open on the upper surface of the wing near the shoulder. These glands secrete a pungent red substance. The sacs are best developed in males and thus may function as a sexual attractant. If present, the sacs are located in the antebranchial membrane (the skin ahead of the upper arm and forearm) and can be seen by partially extending the wing against a light.

Roosting may occur in caves, buildings, ruins, trees, curled leaves, hollow logs, and rock crevices. Although many species form large colonies, some form smaller colonies, and some species are solitary.

Noctilionidae (bulldog or fish-eating bats). This tropical American family, represented by two species in one genus (*Noctilio*), includes a highly specialized fish-eating species. Fish are detected by echolocation and gaffed by the bats' long-clawed feet. The nostrils open forward and down, and the tubular nose extends slightly beyond the lips. There is no nose leaf. The ears are large and pointed, are separate, and a tragus is present. The tail, as in the Emballonuridae, is present but extends only to about the middle of the tail membrane and then perforates the membrane, with the tip being free. The fish-eating bat *Noctilio leporinus* has long hindlegs and large hindfeet with well-developed claws that are useful for catching fish. The other species in the family, *N. albiventris*, is not as well modified for fishing. *Noctilio* is one

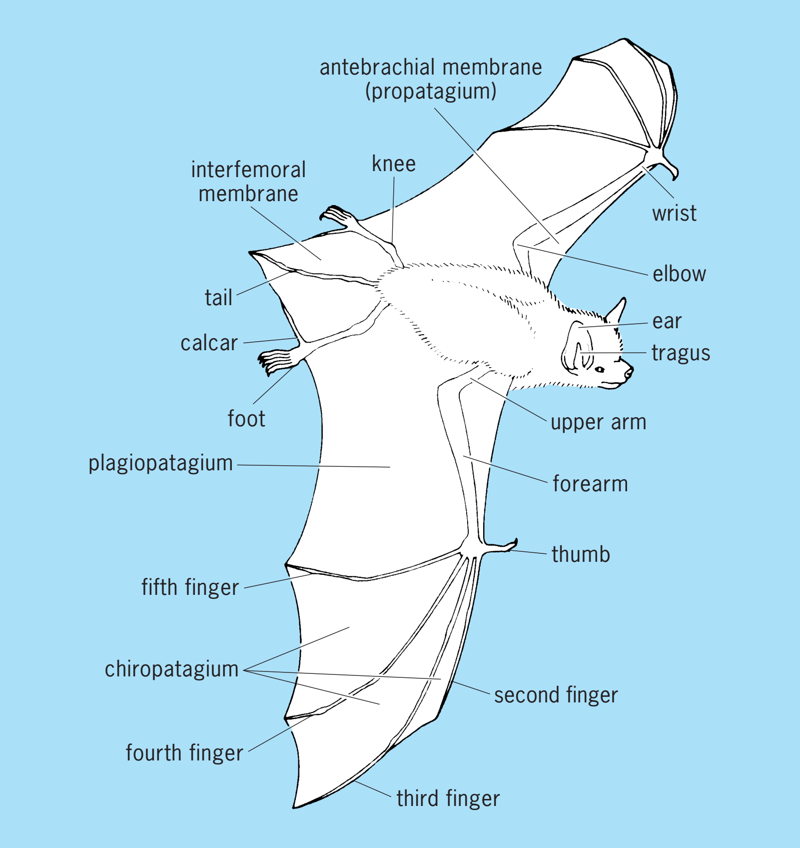

Fig. 1. Anatomical features of bat. (*After R. Peterson, Silently by Night, McGraw-Hill, 1964*)

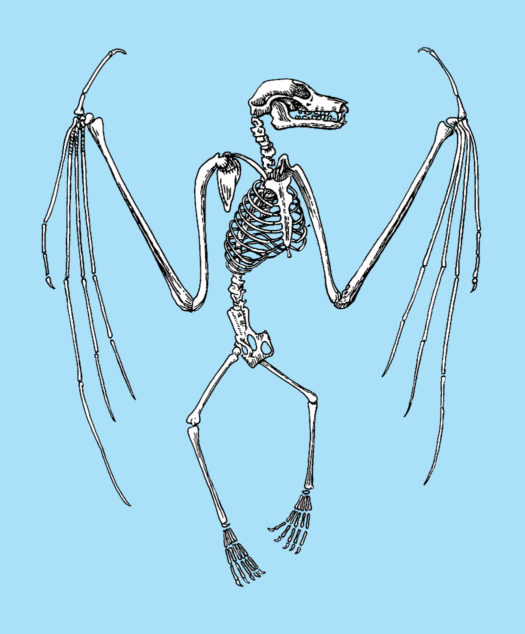

Fig. 2. Skeleton of *Pteropus*, giant fruit bat (lacking tail). (*After R. Peterson, Silently by Night, McGraw-Hill, 1964*)

Fig. 3. *Eptesicus fuscus* (family Vespertilionidae), big brown bat, from Huntington Lake, California. (*Photo by Dr. Lloyd Glenn Ingles; © 1999 California Academy of Sciences*)

of only three genera of bats that feed on fish. The others are *Myotis* (*M. vivesi* and *M. adversus*) and *Megaderma*. *Noctilio leporinus* apparently uses its echolocation to find fishes and then uses its claws to capture them. Besides fish, it will eat aquatic crustaceans, ants, crickets, scarab beetles, and stinkbugs. *Noctilio albiventris* will also eat fish, although this species has been observed using echolocation to capture insects from the surface of the water.

Nycteridae (slit-faced bats). This family of insect eaters, with one genus and 16 species, is found in Africa and southern Asia. These bats have an extensive basin behind the nose, which is partly bridged over by flaps of skin, leaving a mere slit between them. Slit-faced bats have large ears united at the base. They have a small tragus. They feed mainly on insects, spiders, and sun spiders, but some have been known to eat vertebrates, including fish, frogs, birds, and other bats.

Megadermatidae (false vampire and yellow-winged bats). The four genera (with five species) of this family occur in tropical Africa, southeastern Asia and adjoining islands, and northern Australia. The nose leaf is well developed and simple; the ears are very large and are joined across the forehead. An external tail is lacking. There are no upper incisors. Some species are insect-eating; others feed on small vertebrates, including other bats. The name "false vampire" is from earlier times when these bats were thought to feed on blood.

Rhinolophidae (horseshoe bats). The 77 species (in one genus) of these insect-eating bats are widely distributed in the temperate and tropical areas of the Old World. Horseshoe bats are remarkable for their extremely complex nose leaf expansion of the skin surrounding the nostrils. The lower part is horseshoe-shaped and covers the upper lips, surrounds the nostrils, and has a notch on the lower edge. Above the nostrils is an erect structure (the lancet), connected only at the base and pointed upward. The ears are large but lack a tragus. A tail is present. There are two thoracic teats, but females also have two "dummy teats" on the abdomen that the young grasp as they are being transported. Horseshoe bats roost in many different types of locations, including caves, buildings, trees, and foliage. They feed on insects and spiders. Those in temperate areas hibernate. Some species have delayed fertilization.

Phyllostomidae (New World leaf-nose bats). While most of the 160 species (in 55 genera) of this tropical and subtropical American family possess simple nose leaves (less complex than in Old World leaf-nosed bats), there is tremendous variety in structure, reflecting an equal diversity in food habits. Primitively insect-eating, many have become fruit- or nectar-feeders, and a few are predators on small vertebrates, including other bats. The nose leaf structure is usually present and can be very large, but it may be reduced or absent. The tail may be present or absent. A tragus is present. Phyllostomid bats vary greatly in size, from small species to a false vampire bat, *Vampyrum spectrum*, which is the largest New World bat; its head and body length is about 5 in. (130 cm) and the wingspread can be up to about 3 ft (0.9 m). *Vampyrum spectrum* does not feed on blood. It is carnivorous, feeding on birds, bats, and rodents, and (possibly) on fruit and insects.

The true vampire bats (three species) were previously placed in their own family but are now included among the Phyllostomidae, subfamily Desmodontinae. The vampires are essentially confined to the mainland of tropical America. *Desmodus rotundus* is the best-known species. The vampire bats feed only on fresh blood; *D. rotundus* often feeds on cattle. Vampire bats feed by using the very sharp front incisor teeth (not the canines, as commonly believed) to scratch the surface of the skin so that blood oozes out. There is no sucking of blood; the blood is lapped up with the tongue, but the saliva of the bat contains an anticoagulant which helps keep the blood flowing.

Natalidae (funnel-eared bats). These bats (three genera and eight species) are tropical American insect-eating species with large funnellike ears with glandular papillae on the inside. These are relatively small bats, with the forearm ranging up to about 41 mm (1.7 in.) and the adults weighing 7–10 g (0.25–0.35 oz). The eyes and tragus are small. The tail reaches to the end of the membrane. There is no nose leaf, and the thumb claw is prominent. There is a large "natalid organ" on the face of males which bears a resemblance to sensory cells; it is not always noticeable, and appears to be unique to natalids. These bats often roost in caves, but some have been found in trees. Natalids are often found in large groups.

Furipteridae (smoky or thumbless bats). This insect-eating family, confined to tropical Central and South America, is represented by two species in two genera. Bats of this family are small (with forearm lengths of only 30–40 mm or 1.2–1.6 in.). The thumb is present but is enclosed in the wing membrane and is so small it appears to be absent. The ears are funnel-shaped and not connected at the base, and the tragus is small. The eyes are close together and point downward. There is no nose leaf, and the tail is long. The third and fourth toes are joined.

Thyropteridae (disk-winged or New World sucker-footed bats). The three species (in one genus) of this insectivorous family are confined to the tropical American mainland. These are small bats, with a forearm length ranging up to 38 mm (1.5 in.). The average weight of *Thyroptera tricolor* is only about 4.2 g (0.15 oz). The large suction disks on short stalks on the thumbs and hindfeet enable them to roost on the smooth inner surfaces of large rolled-up leaves. Unlike the Old World sucker-footed bats, they have a well-developed thumb claw. The tail extends slightly beyond the tail membrane. The third and fourth toes are joined. These bats differ from most others in that they usually hang with the head upward. These bats cling to surfaces, even smooth surfaces, by the suckers.

Myzopodidae (Old World sucker-footed bat). The single species of this family is unique among bats in that it is confined to Madagascar. It eats insects and has suckers on the thumbs and feet rather like those of the Thyropteridae. However, the suckers on this bat are sessile, whereas those of thyropterids are on a short stalk.

Mystacinidae (New Zealand short-tailed bats). The two insect-eating species of this family (both in the genus *Mystacina*) are confined to New Zealand; one (*M. robusta*) is probably extinct, and the other (*M. tuberculata*) is considered vulnerable to extinction. Their body and hindlegs are stout, and they have short tails that do not reach the edge of the uropatagium. The male has a large claw with a projection from it, and the toes also have extra projections. The tail goes through the tail membrane and appears on the upper surface. These bats are very agile, running on the ground and up sloping branches.

Molossidae (free-tailed and mastiff bats). This family includes 100 species in 16 genera and is widely distributed in the tropics and subtropics. They have long tails that extend beyond their uropatagia, and the body and hindlegs are stoutly built. These bats show great size variation, with forearm measuring 27–85 mm (1.1–3.3 in.) in length. The body hair is short and velvetlike in texture.

One genus, *Cheiromeles*, is referred to as the naked or hairless bat. The naked bats are large (with forearm lengths of 70–86 mm or 2.8–3.4 in.), and the hair is so short that the bats appear to be naked. The eyes are small. The ears are leathery and united across the forehead and possess a tragus. There is no nose leaf. The wings are long and thin, and these bats are rapid fliers.

Free-tailed bats feed on insects, and they roost in caves, buildings, tunnels, trees, foliage, and crevices, that is, almost anywhere that bats can roost. They have a strong musky odor and often occur in huge numbers. For example, *Tadarida brasiliensis* number about 20 million in Bracken Cave, Texas, constituting one of the largest vertebrate congregations in the world. They do not hibernate and apparently are generally active throughout the year. They usually have one young per year.

Craseonycteridae (bumblebee bat). Bumblebee bats were described in 1974 as a new species, genus, and family. This family includes only one species. It is from Thailand and is of special interest because it is the smallest bat, and may be the smallest mammal, in the world. Bumblebee bats weigh about 2 g (0.07 oz), or about the same weight as the other two contenders for "world's smallest mammal," the Eurasian pygmy shrew (*Suncus etruscus*) and southern Indiana populations of the American pygmy shrew (*Sorex hoyi*). It apparently feeds on insects and spiders.

Mormoopidae (ghost-face bats). This family includes two genera and 10 species of insectivorous bats, all in the New World. It was formerly placed in the family Phyllostomidae. They occur in tropical lowland habitats from southern Arizona and Texas, south through Mexico, Central America, and northern South America. The largest of these bats, *Pteronotus parnellii*, has a forearm measuring 54–65 mm (2.1–2.6 in.). Mormoopids differ from phyllostomids in lacking the nose leaf. They do, however, have flaps that form a funnel when the mouth is open. The nostrils are in the upper lip, and there are bristles on the outside of the lip flaps that further push air toward the mouth. The eyes of mormoopids are smaller than those of phyllostomids. Members of this family form large colonies in caves.

Hipposideridae (Old World leaf-nosed bats). The hipposiderids include nine genera and 81 species found in the tropics of Asia and Africa, the Philippines, Solomons, and Australia; they were previously considered a subfamily of the Rhinolophidae, but they are currently are recognized as a full family. Old World leaf-nosed bats, like horseshoe bats, have a nose leaf, although the structure differs between the two families. (Members of the genera *Trianops* and *Cloetis* have three leaf points on the nose.) The tail may be absent, but varies greatly in length and may be up to 60 mm (2.4 in.) long. These bats may live in caves, buildings, or hollow trees.

Vespertilionidae (mouse-eared or vespertilionid bats). This nearly cosmopolitan family, with 404 species in 48 genera, occurs almost everywhere that bats occur. All members have a long tail that extends to the edge of the uropatagium. In spite of its many species, the family shows little structural diversity. Most vespertilionids have no special facial modifications. A few have very large ears or small simple nose leaves. Echolocation, present in all families of bats except the Pteropodidae, is perhaps most highly developed in vespertilionids and is used for catching insects as well as avoiding obstacles. Most species are relatively small, with forearm lengths ranging 22–75 mm (0.9–2.9 in.), and with adults weighing up to 50 g (1.8 oz). Most species have two mammary glands, except for the genus *Lasiurus*, which has four. The many species of this family roost in a very wide variety of locations. Most species appear to have delayed fertilization; however, in a few tropical species, fertilization immediately follows mating. Gestation is usually 40–70 days, but sometimes can last more than 100 days. Almost all are insect-eating, but at least three species of *Myotis* will catch fish. The pallid bat, *Antrozous pallidus*, often comes to the ground to feed on spiders, beetles, and scorpions, and perhaps occasionally even on small vertebrates. This family includes many of the common North American bats, such as *Myotis, Eptesicus* (Fig. 3), *Pipistrellus, Nycticeius*, and *Corynorhinus*.

Fossil record. Bats have a poor fossil record but have been distinct at least since the Eocene, some 50 million years ago. One unusually well-preserved early form, *Icaronycteris*, combined a primitive insect-eating dentition and a retained claw on the second digit with the advanced type of shoulder joint seen in the Vespertilionidae.

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Chlamydia

A genus of bacteria with a growth cycle differing from that of all other microorganisms. Chlamydiae grow only in living cells and cannot be cultured on artificial media. Although capable of synthesizing macromolecules, they have no system for generating energy; the host cell's energy system fuels the chlamydial metabolic processes. The genome is relatively small; the genomes of *C. pneumoniae* and *C. trachomatis* have been completely sequenced.

Infectious particle. The chlamydial infectious particle, called the elementary body, is round and about 350–450 nanometers in diameter. It enters a susceptible host cell and changes to a metabolically active and larger (approximately 800–1000 nm in diameter) reticulate body that divides by binary fission. The entire growth cycle occurs within a vacuole that segregates the chlamydia from the cytoplasm of the host cell. The reticulate bodies change back to elementary bodies, and then the cell lyses and the infectious particles are released. The growth cycle takes about 48 h.

Chlamydial diseases. Human diseases are caused by three species of *Chlamydia*. *Chlamydia trachomatis*, occurring in humans, is susceptible to sulfonamides and produces inclusions that stain with iodine because they contain glycogen. *Chlamydia psittaci*, occurring in birds, lower animals, and humans, is sulfa-resistant and the inclusions do not stain with iodine. The so-called TWAR strains have been given their own species category, *C. pneumoniae*. The TWAR elementary body is pear-shaped rather than round, and there is little deoxyribonucleic acid (DNA) relatedness. The species *Chlamydia pecorum* is not an important cause of human disease, but infects domestic mammals.

Chlamydia trachomatis. *Chlamydia trachomatis* is almost exclusively a human pathogen, and one of the most common. Those strains infecting humans have no known animal reservoir. Infections occur in two distinct epidemiologic patterns. In many developing countries, *C. trachomatis* causes trachoma, a chronic follicular keratoconjunctivitis. It is the world's leading cause of preventable blindness, affecting approximately 500 million people, with millions losing their sight. In areas where this condition is highly endemic, virtually the entire population is infected within the first few years of life. Most active infections are found in childhood. Scarring can develop as a result of severe inflammation of the conjunctiva. Over a period of years, the scars shrink and distort the upper eyelid, causing an in-turning of the eyelashes which damages the cornea and causes blindness. By age 60, more than 20% of a population can be blinded as a result of trachoma. *See* EYE DISORDERS.

Chlamydia trachomatis is the most common sexually transmitted bacterial pathogen; an estimated 3–4 million cases occur each year in the United States, and there are close to 90 million worldwide. The most common manifestation is nongonococcal urethritis in males. The cervix is the most commonly infected site in women. Ascending infections can occur in either sex, resulting in epididymitis in males or endometritis and salpingitis in females. Chlamydial infection of the fallopian tube can cause late consequences such as infertility and ectopic pregnancy, even though the earlier infection is asymptomatic. For some women, their first knowledge of having had a chlamydial infection occurs when they are being evaluated for infertility or are hospitalized with an ectopic pregnancy. Thus, chlamydial infection in the female can be particularly insidious and dangerous. *See* SEXUALLY TRANSMITTED DISEASES.

The infant passing through the infected birth canal can acquire the infection and may develop either conjunctivitis (called inclusion conjunctivitis of the newborn, or inclusion blennorrhea) or pneumonia. In the United States, *C. trachomatis* is the leading cause of conjunctivitis in the first month of life, and of pneumonia in the first 6 months.

All of the diseases mentioned above involve mucous membranes. There is a more invasive form of *C. trachomatis* that causes a systemic sexually transmitted disease called lymphogranuloma venereum. Lymphogranuloma venereum has a worldwide distribution, although it is more common in some tropical countries. This disease has a predilection for lymphoid tissue involvement. It occurs in stages: the primary stage involves small, superficial, usually painless genital lesions; in the secondary stage, inguinal buboes (infected lymph nodes) are the common finding. If untreated, the disease may progress to stages involving widespread tissue destruction of genital and intestinal tracts.

Chlamydia psittaci. *Chlamydia psittaci* is virtually ubiquitous among avian species and is a common pathogen among lower mammals. It is economically important in many countries as a cause of abortion in sheep, cattle, and goats. It causes considerable morbidity and mortality in poultry, particularly turkeys and ducks. *Chlamydia psittaci* can infect humans, causing the disease psittacosis. Psittacosis can occur as pneumonia or a febrile toxic disease without respiratory symptoms. Apparently, the chlamydiae that infect turkeys, ducks, and psittacine birds are most infectious for humans. Psittacosis is a potential threat to the health of pet-bird owners and is an occupational hazard in the poultry industry. *Chlamydia psittaci* derived from mammals can also infect humans.

Chlamydia pneumoniae (TWAR). *Chlamydia pneumoniae* appears to be a human pathogen with no animal reservoir. It is of worldwide distribution and may be the most common human chlamydial infection. It appears to be an important cause of respiratory disease, being found in association with sporadic cases of community-acquired pneumonia and epidemics of mild pneumonia. Some evidence has been generated to associate *C. pneumoniae* infections with acute and chronic asthma. In addition, *C. pneumoniae* infection has been linked to coronary artery disease. *Chlamydia pneumoniae* infections start early in life, usually about school age. Infections are likely acquired by the respiratory route. Seroprevalence increases rapidly up to the ages of 30 or 40, where a plateau is approached. Age-specific seroprevalence ultimately reaches 60–70% in many populations. It is believed that asymptomatic, chronic infections are common.

Treatment. Azithromycin is the drug of choice for uncomplicated chlamydial infection of the genital tract. With an antimicrobial spectrum similar to that of erythromycin, it concentrates in cells where the organism grows, and it is effective as a single dose. Two therapeutic agents require longer treatment regimens: doxycycline, a tetracycline antibiotic, is the first alternate treatment; erythromycin may be used for those who are tetracycline-intolerant, as well as for pregnant women or young children. *See* MEDICAL BACTERIOLOGY.

Julius Schachter

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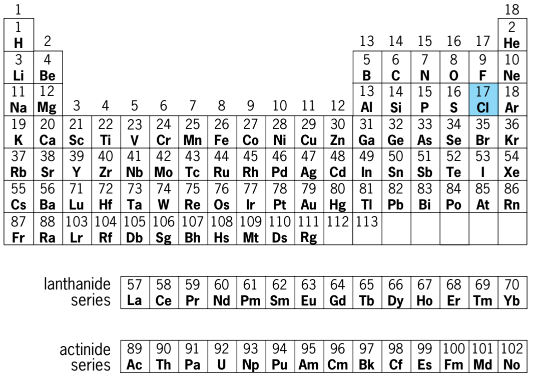
Chlorine

A chemical element, Cl, atomic number 17 and atomic weight 35.453. Chlorine exists as a greenish-yellow gas at ordinary temperatures and pressures. It is second in reactivity only to fluorine among the halogen elements, and hence is never found free in nature, except at the elevated temperatures of volcanic gases. It is estimated that 0.045% of the Earth's crust is chlorine. It combines with metals, nonmetals, and organic materials to form hundreds of chlorine compounds, the most important of which are discussed here. *See* PERIODIC TABLE.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H**																	2 **He**
3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
55 **Cs**	56 **Ba**	71 **Lu**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	103 **Lr**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112	113					

lanthanide series	57 **La**	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**
actinide series	89 **Ac**	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**

Chlorine and its common acid derivative, hydrochloric (or muriatic) acid, were probably noted by experimental investigators as early as the thirteenth century. C. W. Scheele identified chlorine as "dephlogisticated muriatic acid" in 1774, and H. Davy proved that a new element had been found in 1810. Extensive production started 100 years later. During the twentieth century, the amount of chlorine used has been considered a measure of industrial growth.

Physical properties. The atomic weight of naturally occurring chlorine is 35.453 (based on carbon at

12). It is formed of stable isotopes of mass 35 and 37; radioactive isotopes have been made artificially. The diatomic gas has a molecular weight of 70.906. The boiling point of liquid chlorine (golden-yellow in color) is −33.97°C (−29.15°F) at 760 mm Hg (10^2 kilopascals) and the melting point of solid chlorine (tetragonal crystals) is −100.98°C (−149.76°F). The critical temperature is 144°C (292°F); the critical pressure is 78.7 atm; the critical volume is 1.745 ml/g; and density at the critical point is 0.573 g/ml. Thermodynamic properties include heat of sublimation at 7370 ± 10 cal/mole at 0 K, heat of evaporation at 4882 cal/mole at −33.97°C, heat of fusion at 1531 cal/mole, vapor heat capacity at a constant pressure of 1 atm of 8.32 cal/(mole °C) at 0°C (32°F) and 8.46 cal/(mole °C) at 100°C (212°F). Chlorine forms solid hydrates, $Cl_2 \cdot 6H_2O$ (pale-green crystals) and $Cl_2 \cdot 8H_2O$. It hydrolyzes in water as shown in reaction (1).

$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad (1)$$

Chemical properties. Chlorine is one of four closely related chemical elements which have been called the halogen elements. Fluorine is more active chemically, and bromine and iodine are less active. Chlorine replaces iodine and bromine from their salts. It enters into substitution and addition reactions with both organic and inorganic materials. Dry chlorine is somewhat inert, but moist chlorine unites directly with most of the elements. *See* HALOGEN ELEMENTS.

Compounds. Sodium chloride, NaCl, is used directly as mined (rock salt), or as found on the surface, or as brine. It may also be dissolved, purified, and reprecipitated for use in foods or when chemical purity is required. Its main uses are in the production of soda ash and chlorine products. Farm use, refrigeration, dust and ice control, water treatment, food processing, and food preservation are other uses. Calcium chloride, $CaCl_2$, is usually obtained from brines or as a by-product of chemical processing. Its main uses are in road treatment, coal treatment, concrete conditioning, and refrigeration. *See* HALITE.

Wet chlorine reacts with metals to form chlorides, most of which are soluble in water. It also reacts with sulfur and phosphorus and with other halogens as in reactions (2).

$$\begin{aligned} H_2 + Cl_2 &\rightarrow 2HCl \\ 2Fe + 3Cl_2 &\rightarrow 2FeCl_3 \\ 2S + Cl_2 &\rightarrow S_2Cl_2 \\ S + Cl_2 &\rightarrow SCl_2 \\ S + 2Cl_2 &\rightarrow SCl_4 \qquad (2) \\ P_4 + 6Cl_2 &\rightarrow 4PCl_3 \\ P_4 + 10Cl_2 &\rightarrow 4PCl_5 \\ Br_2 + Cl_2 &\rightarrow 2BrCl \\ 2F_2 + Cl_2 &\rightarrow ClF + ClF_3 \end{aligned}$$

The oxides of chlorine, dichlorine monoxide, Cl_2O, chlorine monoxide, ClO, chlorine dioxide, ClO_2, chlorine hexoxide, Cl_2O_6, and chlorine heptoxide, Cl_2O_7, are all made indirectly. Cl_2O is commonly called chlorine monoxide also. Chlorine dioxide, a green gas, has become increasingly important in commercial bleaching of cellulose, water treatment, and waste treatment.

Hydrogen chloride, HCl, is a colorless, pungent, poisonous gas which liquefies at 82 atm at 51°C (124°F). It boils at −85°C (−121°F) at 1 atm (10^2 kPa). Its major production is as the by-product of many organic chlorinations. It can be made by direct reaction of chlorine and hydrogen in an open combustion chamber submerged in cooled, aqueous hydrochloric acid solution. It is used as a strong acid and as a reducing agent.

Aluminum chloride, $AlCl_3$, is an anhydrous, white, deliquescent, hexagonal crystalline substance. Either scrap aluminum or the oxide (bauxite) may be chlorinated. Aluminum chloride is a catalyst for production of cumene, styrene, and isomerized butane. Of the aluminum chloride uses in anhydrous form, ethylbenzene production uses 25%, dyes 30%, detergents 15%, ethyl chloride 10%, drugs 8%, and miscellaneous production 12%. Hydrated and liquid forms are also available, 50% of which are used in drug and cosmetic production.

Ferric chloride, $FeCl_3$, is a solid composed of dark, hexagonal crystals. Much chlorine from chemical processes is converted to ferric chloride, which is then used for the manufacture of salts, pigments, pharmaceuticals, and dyes and for photoengraving, preparation of catalysts, and waste and sewage treatment.

Natural occurrence. Because many inorganic chlorides are quite soluble in water, they are leached out of land areas by rain and ground water to accumulate in the sea or in lakes that have no outlets. Seawater contains 18.97 g of chloride ion per kilogram (3% sodium chloride). Solar evaporation produces large deposits of salts in landlocked areas. Similar evaporation in the past is responsible for vast underground deposits of rock salt and brines in Michigan, central New York, the Gulf Coast of Texas, Stassfurt in Germany, and elsewhere. These deposits are mainly of sodium chloride, the supply of which is unlimited for practical purposes. Other rocks and minerals in the Earth's surface average slightly over 0.03% chloride. *See* HALOGEN MINERALS; SALINE EVAPORITE.

Manufacture. The first electrolytic process was patented in 1851 by Charles Watt in Great Britain. In 1868 Henry Deacon produced chlorine from hydrochloric acid and oxygen at 400°C (750°F) with copper chloride absorbed in pumice stone as a catalyst. The electrolytic cells now used may be classified for the most part as diaphragm and mercury types. Both make caustic (NaOH or KOH), chlorine, and hydrogen. The economics of the chlor-alkali industry mainly involve the balanced marketing or internal use of caustic and chlorine in the same proportions as obtained from the electrolytic cell process.

Uses. Chlorine is an excellent oxidizing agent. Historically, the use of chlorine as a bleaching agent in the paper, pulp, and textile industries and as a germicide for drinking water preparation, swimming pool purification, and hospital sanitation has made community living possible. Chlorine is used to produce bromine from bromides found in brines and seawater. The automotive age increased the production of bromine tremendously for the manufacture of ethylene dibromide for use in gasoline. Compounds of chlorine are used as bleaching agents, oxidizing agents, solvents, and intermediates in the manufacture of other substances. *See* HERBICIDE.

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Chlorite

One of a group of layer silicate minerals, usually green in color, characterized by a perfect cleavage parallel to (001). The cleavage flakes are flexible but inelastic, with a luster varying from pearly or vitreous to dull and earthy. The hardness on the cleavage is about 2.5. The specific gravity varies between 2.6 and 3.3 as a function of composition.

Chlorite is a common accessary mineral in low- to medium-grade regional metamorphic rocks and is the dominant mineral in chlorite schist. It can form by alteration of ferromagnesian minerals in igneous rocks and is found occasionally in pegmatites and vein deposits. It is a common constituent of altered basic rocks and of alteration zones around metallic ore bodies. Chlorite also can form by diagenetic processes in sedimentary rocks. *See* DIAGENESIS.

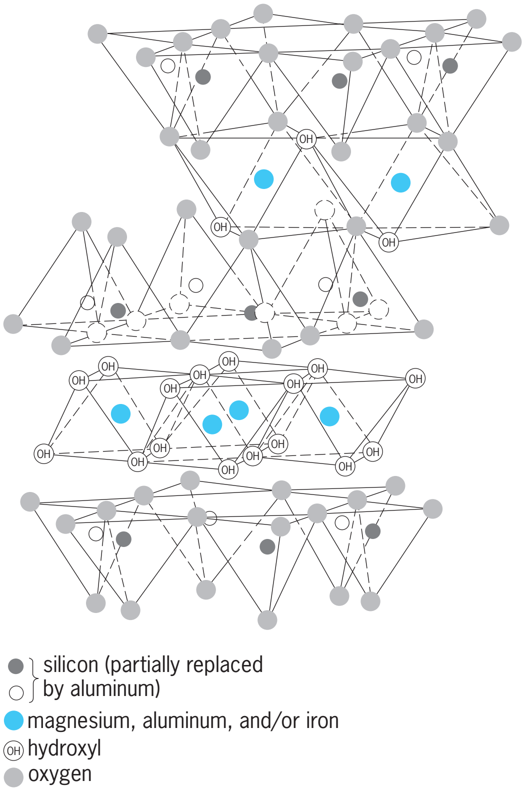


Diagram of the structure of chlorite. (*After R. E. Grim, Clay Mineralogy, McGraw-Hill, 1953*)

The crystal structure of chlorite consists of a 2:1 layer, similar to that in mica, with octahedrally coordinated cations sandwiched between two tetrahedral sheets that are inverted relative to one another. Substitution of Al or Fe^{3+} for Si in the tetrahedral sheets gives a net negative charge to the 2:1 layers, which must be balanced by a positively charged octahedral sheet in the interlayer space. The composition of the 2:1 layer can be expressed as

$$\left(\mathrm{R}^{2+}_{3-a-b-c}\mathrm{R}^{1+}_{a}\mathrm{R}^{3+}_{b}\square_{c}\right)\left(\mathrm{Si}_{4-x}\mathrm{R}^{3+}_{x}\right)\mathrm{R}_{10}(\mathrm{OH})_{2}$$

and that of the interlayer as

$$\left(\mathrm{R}^{2+}_{3-d-e-f}\mathrm{R}^{1+}_{d}\mathrm{R}^{3+}_{e}\square_{f}\right)(\mathrm{OH})_{6}$$

with $\square$ = vacancy. Enough R^{3+} cations must be present in the interlayer to create a net positive charge on that sheet. Long hydrogen bonds link basal oxygens of each tetrahedral sheet with surface hydroxyl groups of the interlayer sheet (see **illus.**). Different stacking arrangements of the layers and interlayers are possible. *See* MICA.

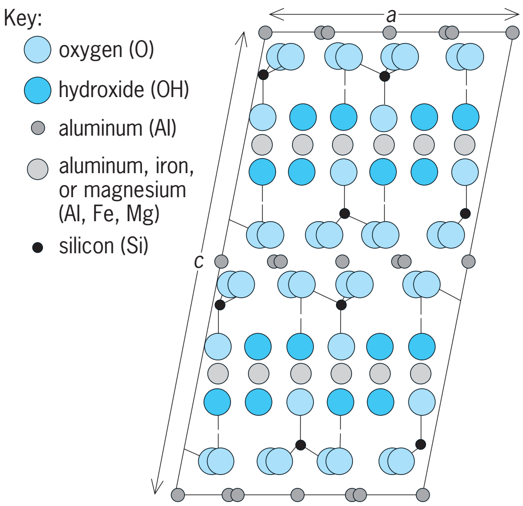
Most chlorites are trioctahedral with close to 3.0 octahedral cations present in both the 2:1 layer and the interlayer. The main octahedral cations present in these sheets are Mg, Fe^{2+}, Fe^{3+}, and Al, but with important substitutions of Cr, Mn, Ni, V, Cu, or Li in certain species. Species names are given according to the dominant divalent octahedral cation present: clinochlore for Mg dominant, chamosite for Fe^{2+} dominant, nimite for Ni dominant, and pennatite for Mn^{2+} dominant. A few dioctahedral chlorites are known also. *See* AUTHIGENIC MINERALS; CLAY MINERALS.

S. W. Bailey

Chloritoid

A hydrous iron aluminum silicate mineral with an ideal formula of $Fe_2^{2+}Al_4O_2(SiO_4)_2(OH)_4$. Chloritoid occurs as platy, black or dark green crystals, rarely more than a few millimeters in size. Its density ranges from 3.46 to 3.80 g/cm^3, and its hardness on the Mohs scale is 6.5.

Crystal form. Chloritoid most commonly forms monoclinic crystals, having a single twofold rotation axis perpendicular to a mirror plane. This is the symmetry of the prismatic crystal class, symbolized as $2/m$. The atomic structure of chloritoid is characterized by silicon atoms surrounded by four oxygen atoms in a tetrahedral arrangement. These tetrahedral clusters form layers that alternate with layers of ferrous iron (Fe^{+2}) and aluminum (Al; see **illus.**) The iron and aluminum are surrounded by six oxygen (O) and hydroxide (OH) ions in an octahedral arrangement in the ratio $[Fe_2^{2+}AlO_2(OH)_4]^-$ and are sandwiched between layers of $(SiO_4)^{4-}$ tetrahedra. The sandwiches of silica tetrahedra–iron and aluminum octahedra–silica tetrahedra are stacked alternately with layers of aluminum. Other structural forms of chloritoid, called polytypes, are created by variations in the stacking of the



Crystal structure of chloritoid, projected on (010). The unit cell for one structural type of chloritoid, $2M_2$, is shown. The unit cell parameters are $a = 0.9482$ nanometers, $b = 0.5485$ nm, $c = 1.8180$ nm, $\beta = 101.8°$. (*After P. H. Ribbe, ed., Orthosilicates, Reviews in Mineralogy, vol. 5, Mineralogical Society of America, 1980*)

tetrahedral-octahedral-tetrahedral sandwiches. *See* CRYSTAL STRUCTURE; CRYSTALLOGRAPHY.

In thin section under the polarizing microscope, chloritoid can appear to be rectangular, with a length two or three times the width. It is observed to be pleochroic, having a color of bluish or greenish gray if the long dimension of the crystal is parallel to the polarizing direction, and pale gray to colorless if the long dimension of the crystal is perpendicular to the polarizing direction. Crystals are commonly twinned across planes parallel to the long dimension. The indices of refraction range from 1.713 to 1.740, with a birefringence (δ) of about 0.010. The mineral has a higher-than-average index of refraction and tends, therefore, to stand out from the other minerals in thin section. Chloritoid exhibits anomalous interference colors in cross-polarized light. *See* BIREFRINGENCE; PLEOCHROISM.

Composition. The composition of chloritoid typically deviates from the ideal formula. Magnesium (Mg) substitutes for as much as 40% of the iron, although the ratio Mg/(Mg + Fe) is generally 0.15 to 0.20. Manganese has been found to substitute for 17% of the iron, but manganese contents are generally less than 1% of the iron. A variety of chloritoid, called ottrelite, contains manganese in substitution for iron in amounts of about 60%. Ferric iron (Fe^{3+}) substitutes for less than 14% of the aluminum, and titanium occurs in trace amounts.

Occurrence. Chloritoid is typically found in low-grade, metamorphosed shales, which are commonly called pelitic schists. It occurs as a comparatively large mineral set in a matrix composed of quartz and fine-grained muscovite. It first appears in most metamorphic terrains near the biotite isograd, that is, near the first appearance of biotite; however, the first appearance of chloritoid depends on many factors, including pressure, oxidation state, and availability of proper rock compositions in the metamorphic terrain. In low-grade rocks, chloritoid is found in association with chlorite, muscovite, and, in some rocks, paragonite. At medium grades of metamorphism, chloritoid can be found with garnet or staurolite in a muscovite and quartz matrix.

The reaction responsible for the synthesis of chloritoid in pelitic schists is not well documented but may occur as in reaction (1), where H_2O may be water or a supercritical fluid phase.

$$\text{12 pyrophyllite} + \text{4 chlorite} \rightarrow \text{9 chloritoid} + \text{49 quartz} + 10\,H_2O \quad (1)$$

Chloritoid breaks down during metamorphism by either reaction (2) or (3).

$$\text{Chloritoid} + \text{quartz} \rightarrow \text{garnet} + \text{staurolite} + \text{chlorite} + H_2O \quad (2)$$

$$\text{Chloritoid} + \text{muscovite} + \text{quartz} \rightarrow \text{garnet} + \text{staurolite} + \text{biotite} + H_2O \quad (3)$$

The stoichiometric coefficients in these two reactions depend on the Fe/Mg ratios in the minerals, which in turn depend on the pressure and temperature of the reaction. Reaction (2) is found to occur in medium- to high-pressure terrains, whereas reaction (3) occurs in low-pressure terrains.

Experimental studies of the stability of chloritoid have been conducted over a limited range in temperature and pressure and in the possible compositions of chloritoid. The low-temperature stability limit of chloritoid has not been well determined. Calculations indicate that reaction (1) proceeds at a temperature near 400°C (750°F) at 500 megapascals (5 kilobars). The high-temperature stability limit of chloritoid has been studied experimentally under conditions appropriate for reaction (2). The results indicate that chloritoid is stable up to temperatures near 550°C (1020°F) at 500 MPa (5 kbar) and 575°C (1070°F) at 1000 MPa (10 kbar), although the precise temperature and pressure conditions of reaction (2) have not been determined. Reactions at low pressures, including reaction (3), have not been investigated.

Chloritoid is increasingly being recognized as a constituent in rocks that formed under high-pressure conditions. It is found in association with glaucophane in blueschist-facies metamorphic rocks, and with amphibole and pyroxene in eclogite-facies metamorphic rocks. These are rocks that formed under conditions thought to prevail at the base of the Earth's crust or in the mantle. Experimental studies of metamorphism of basalt under these conditions indicate the formation of chloritoid at pressures exceeding 2300 MPa (23 kbar) and at a temperature of 650°C (1200°F). In these high-pressure occurrences of chloritoid, the chloritoid is rich in magnesium, having a value of Mg/(Mg + Fe) ranging from 0.38 to 0.40. *See* METAMORPHIC ROCKS. Theodore C. Labotka

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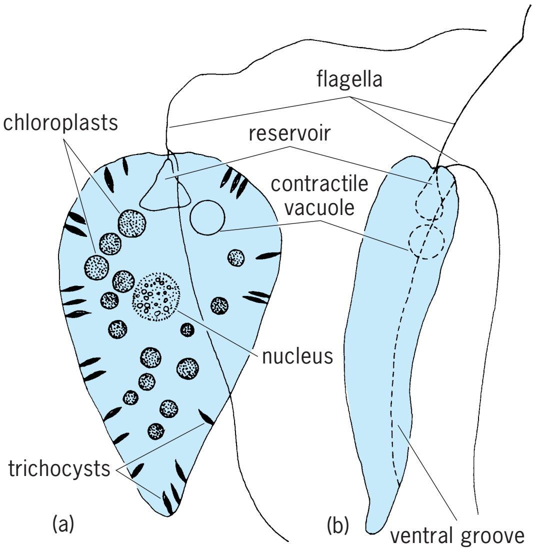
Chloromonadida

An order of the class Phytamastigophorea, also known as the Chloromonadina. These poorly known flagellates are grass-green or colorless, somewhat flattened, and have two equal flagella, one anterior, the other trailing. All known genera are free-swimming, although *Reckertia* and *Thaumatomastix* form pseudopodia. They vary in size from 30 to 100 micrometers. Chromatophores are small disks, stigmas are lacking, and fat is the storage product. Trichocysts are found in three genera. The nucleus is large, with nucleoli and chromosomes visible during interphase. One or two anterior vacuoles are present and a reservoir seems to be present in *Trentonia* and *Gonyostomum* (see **illus.**). Life cycles are unknown, but longitudinal division occurs. *Gonyostomum* sometimes occurs as bloom in cedar swamps, and *Vacuolaria* is sometimes common there. The taxonomic position of the class is poorly defined. *See* CILIA AND FLAGELLA; PHYTAMASTIGOPHOREA; PROTOZOA. James B. Lackey



***Gonyostomum semen*. (*a*) Dorsal view. (*b*) Side view.**

Chlorophyceae

A large and diverse class of plants, commonly called green algae, in the chlorophyll *a-b* phyletic line (Chlorophycota). Estimated number of taxa varies widely; 560 genera and 8600 species are conservative estimates. *See* CHLOROPHYCOTA.

Characteristics. The green algae exhibit great morphological diversity while sharing fundamental biochemical and ultrastructural features. Their photosynthetic pigments are similar to those in higher plants and include chlorophyll *a* and *b*, α-, β-, and γ-carotene, and various xanthophylls, especially lutein, violaxanthin, zeaxanthin, antheraxanthin, and neoxanthin. Chloroplasts vary in number and shape, but always have two membranes, two to five thylakoids per lamella, and usually one or more pyrenoids. A cell wall, which may be calcified, is usually present, and often contains cellulose, hydroxyproline glycosides, xylan, and mannan. The chief food reserve is starch, stored in the chloroplast as granules which often sheathe a pyrenoid. Motile cells usually have two or four apically inserted smooth flagella of approximately equal length. In a few genera, motile cells have more than four apical flagella, one or two pairs of subapical flagella, or a subapical crown of numerous flagella. Flagellar scales and hairs are rare. There is sometimes an eyespot, which lies within the chloroplast. *See* CELL PLASTIDS; CHLOROPHYLL.

Phylogeny. Almost all somatic cell types known for algae occur among the Chlorophyceae, the exceptions being rhizopodial unicells and complex multicellular thalli differentiated into macroscopic organs. In the traditional view of phylogeny within the green algae, the progenitor is a motile unicell (monad) with a wall and a pair of equal, smooth, apical flagella, similar to present-day *Chlamydomonas*. In one line of evolution (volvocine), monads joined to form motile colonies. In a different evolutionary line, monads lost their flagella, forming nonmotile solitary cells and colonies (tetrasporine line), which then underwent specialization and elaboration (chlorococcine line). Multicellular thalli (ulotrichine line) were made possibly by the evolution of desmoschisis, a type of cell division in which the wall of the progeny and that of the parent become an integral structure. Traditionally, the ulotrichine line has been considered to lead from unbranched filaments (Ulotrichales) through forms with both prostrate and erect branched systems (Chaetophorales) to the higher plants, with two very distinctive groups (Zygnematales and Oedogoniales) as early offshoots and a third equally distinctive group (charophytes) diverging from a more advanced position. Siphonous and vesicular green algae (siphonine line) were believed to have evolved prior to the origin of desmoschisis.

Ultrastructural studies, however, have revealed differences in details of nuclear and cell division, cell coverings, plasmodesmata, pyrenoids, and flagellar structure that are correlated among themselves and with certain traditional characters to a degree that strongly suggests that the ulotrichine line is polyphyletic, with desmoschisis having evolved at least four times. Moreover, these studies suggest that the ultimate ancestral green flagellate was prasinophycean (asymmetrical and covered with scales) rather than *Chlamydomonas*-like. Integration of these studies and inferences suggests four phyletic lines: chlorophycean, ulvophycean, charophycean, and pleurastrophycean.

Chlorophycean phyletic line. This phyletic group has motile cells that are usually walled and with two or more apically arising flagella, their basal bodies associated with four or more relatively narrow bands of microtubules in a cruciate arrangement. The group includes the volvocine, tetrasporine, and chlorococcine lines, as well as the Chlorosarcinales, Microsporales, Sphaeropleales, Oedogoniales, and Chaetophorales. It is believed to be the most derived of the four phyletic lines and the only one with a chlamydomonad ancestor.

Volvocales and Chlorococcales. The order Volvocales includes all Chlorophyceae that normally are flagellate and motile. The cells are solitary or united into colonies of definite structure, called coenobia. Some taxonomists place the unicellular forms in a separate order, Chlamydomonadales, and interpret the coenobial forms as being multicellular. *Chlamydomonas*, presumably similar to the volvocalean archetype, has two smooth flagella, a chloroplast that commonly is cup-shaped or H-shaped, a pyrenoid, a nucleus, an eyespot, and contractile vacuoles. The protoplast is enclosed in a wall (theca). Within the Volvocales there are notable evolutionary trends: isogamy through anisogamy to oogamy; increase in number of cells; and increase in polarity, resulting in morphological and functional differentiation of component cells. *Volvox*, terminating these trends, has a spherical coenobium composed of as many as 50,000 cells. The Tetrasporales, regarded by some taxonomists as a suborder of the Volvocales, are essentially unicellular Volvocales that have lost their flagella and become nonmotile in their vegetative phase. The cells generally have an internal organization similar to that of *Chlamydomonas*. They are usually massed in gelatinous colonies of indefinite shape, but in some genera the thallus is saccate, dendroid, or reticulate. *See* VOLVOCALES.

The order Chlorococcales comprises a large and diverse assemblage of nonmotile algae that appear to follow the Tetrasporales phylogenetically, sharing their inability to form multicellular thalli, but differing cytologically in that vegetative cells lack eyespots and contractile vacuoles and tend to be nonpolar. Most Chlorococcales are solitary cells of various shapes (spherical, ellipsoid, reniform, lunate, acicular, polygonal) and sizes (to 200 micrometers maximum dimension). Cells are free or attached by a gelatinous stalk. The wall is plain or ornamented (spines, bristles, knobs, horns) and uniformly or asymmetrically thickened. In many genera, however, the cells are joined into colonies of indefinite or definite structure. Colonies of indefinite structure result from coalescence of gelatinous envelopes (Coccomyxaceae) or joining of successive progenies by persistent remnants of parental walls (Dictyosphaeriaceae, **Fig. 1***f*). Colonies of definite structure (coenobia) result from coherence of the cells of a progeny, whether the cells are nonmotile (Scenedesmaceae, Fig. 1*i*) or initially motile (Hydrodictyaceae, Fig. 1*d*, *e*, *g*). Asexual reproduction is by cleavage of a protoplast to form autospores or autocolonies (cells or colonies having the same shape as the parent) or zoospores. After being released from the parental wall, autospores and autocolonies enlarge to adult size. Zoospores either metamorphose individually into nonmotile cells or settle collectively to form an autocolony. Sexual reproduction is usually isogamous.

The Chlorococcales constitute an important component of fresh-water plankton and soil microflora, but occupy other aquatic and subaerial habitats, including snow and ice. Some are the algal component (phycobiont) of lichens, while others occur in the tissues of aquatic and terrestrial plants and aquatic animals. *Oophila*, for example, lives in the mucilage of salamander eggs. *Prototheca* is an intestinal pathogen of various domestic animals and humans. *Chlorella*, commonly found in a wide variety of aquatic habitats, is used extensively in physiological research and is grown in mass cultures as a protein source for poultry, livestock, and humans.

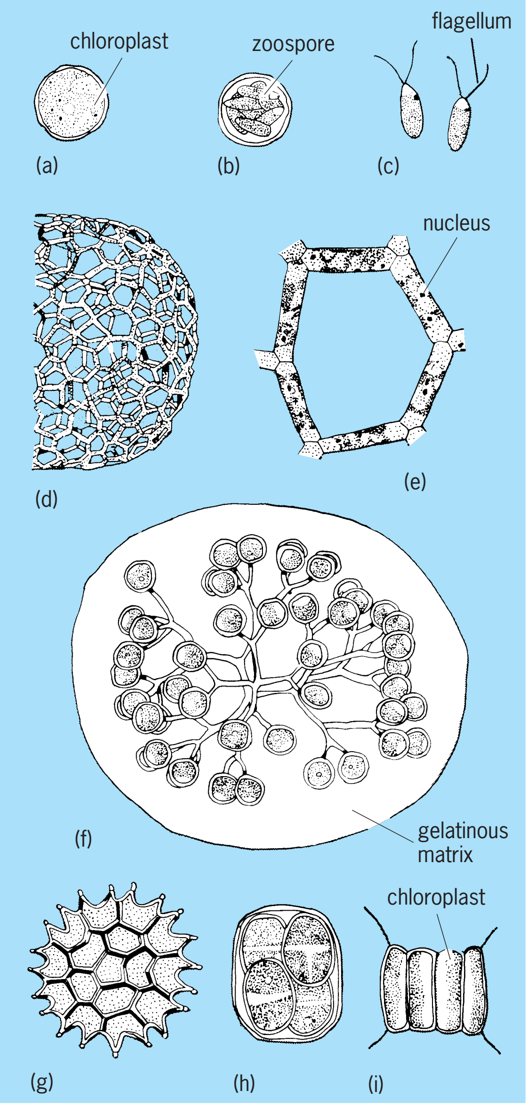


Fig. 1. Chlorococcales. (*a*) *Chlorococcum* (Chlorococcaceae), vegetative cell; (*b*) cell with zoospores; (*c*) zoospores; (*d*) *Hydrodictyon* (Hydrodictyaceae), portion of coenobium; (*e*) portion enlarged; (*f*) *Dictyosphaerium* (Dictyosphaeriaceae), colony in gelatinous matrix; (*g*) *Pediastrum* (Scenedesmaceae), coenobium; (*h*) *Oocystis* (Oocystaceae), colony (*from G. M. Smith*, *Fresh-water Algae of the United States*, *2d ed.*, *McGraw-Hill*, *1950*); (*i*) *Scenedesmus* (Scenedesmaceae), coenobium (*from G. M. Smith*, *Cryptogamic Botany*, *vol. 1*, *2d ed.*, *McGraw-Hill*, *1955*).

Nearly 200 genera of Chlorococcales are recognized, distributed among 15 or 16 families. They are almost exclusively freshwater.

In the orders Volvocales, Tetrasporales, and Chlorococcales, cell division is of the type termed eleutheroschisis, in which the daughter protoplasts either remain naked or secrete new walls separate from the parental wall, which ruptures or gelatinizes to release the progeny (zoospores, autospores, or gametes). In theory, multicellularity was made possible by the evolution of desmoschisis, a process by which daughter cells make permanent contributions to the parental wall. In multicellular algae with uninucleate cells, there is a regular sequence of karyokinesis, cytokinesis, and cell-wall deposition. The relationship between daughter and parental walls is not always clear, however; numerous intermediate situations have been demonstrated. A relatively small group of green algae (mainly in soil) exhibit desmoschisis but lack intercellular connections (plasmodesmata) and thus form only cuboidal (sarcinoid) or irregular packets. Both chlorophycean and charophycean phyletic lines are represented, with members of the former assigned to the order Chlorosarcinales and those of the latter to the order Chlorokybales. In a few genera, rudimentary filaments result from end-to-end coherence of daughter cells that do not contribute to the parental wall and thus are equivalent to autospores. Such genera can be assigned to the Chlorococcales. Long but unbranched filaments can also be produced in the absence of desmoschisis of which there are two well-known freshwater examples. In *Microspora* (**Fig. 2*a***), each daughter cell forms a partial wall, so that the filament wall is composed of segments that are H-shaped in optical section, each segment covering the lower half of one cell and the upper half of the subtending cell. The cells are quadrate, each with a reticulate chloroplast lacking pyrenoids. The nucleus lies in a bridge of cytoplasm that crosses the middle of the central vacuole. In *Sphaeroplea* (Fig. 2*b*), daughter cells secrete an entire wall, but the parental wall soon breaks apart. Mature cells are 15–16 times longer than wide and have a curious coenocytic organization, in which a linear series of vacuoles is separated by transverse cytoplasmic bands, each containing several nuclei and a parietal girdle-shaped chloroplast with several pyrenoids or numerous discoid chloroplasts, certain of which contain pyrenoids. Sexual reproduction involves oogamy or an advanced form of anisogamy. *Microspora* and *Sphaeroplea* are traditionally assigned to their own families and, in the present classification, to their own orders.

Oedogoniales. The order Oedogoniales and the coextensive family Oedogoniaceae comprise three genera of filamentous fresh-water algae with several unique features, including (1) an elaborate method of cell division that results in the accumulation of apical caps; (2) zoospores and antherozoids with a subapical crown of numerous flagella; and (3) a highly specialized type of oogamy. *Oedogonium*, with simple filaments, comprises several hundred species that grow attached to various substrates, including stones, wood, and aquatic angiosperms. In *Bulbochaete* and *Oedocladium*, which have fewer species, the filaments are branched. *See* OEDOGONIALES.

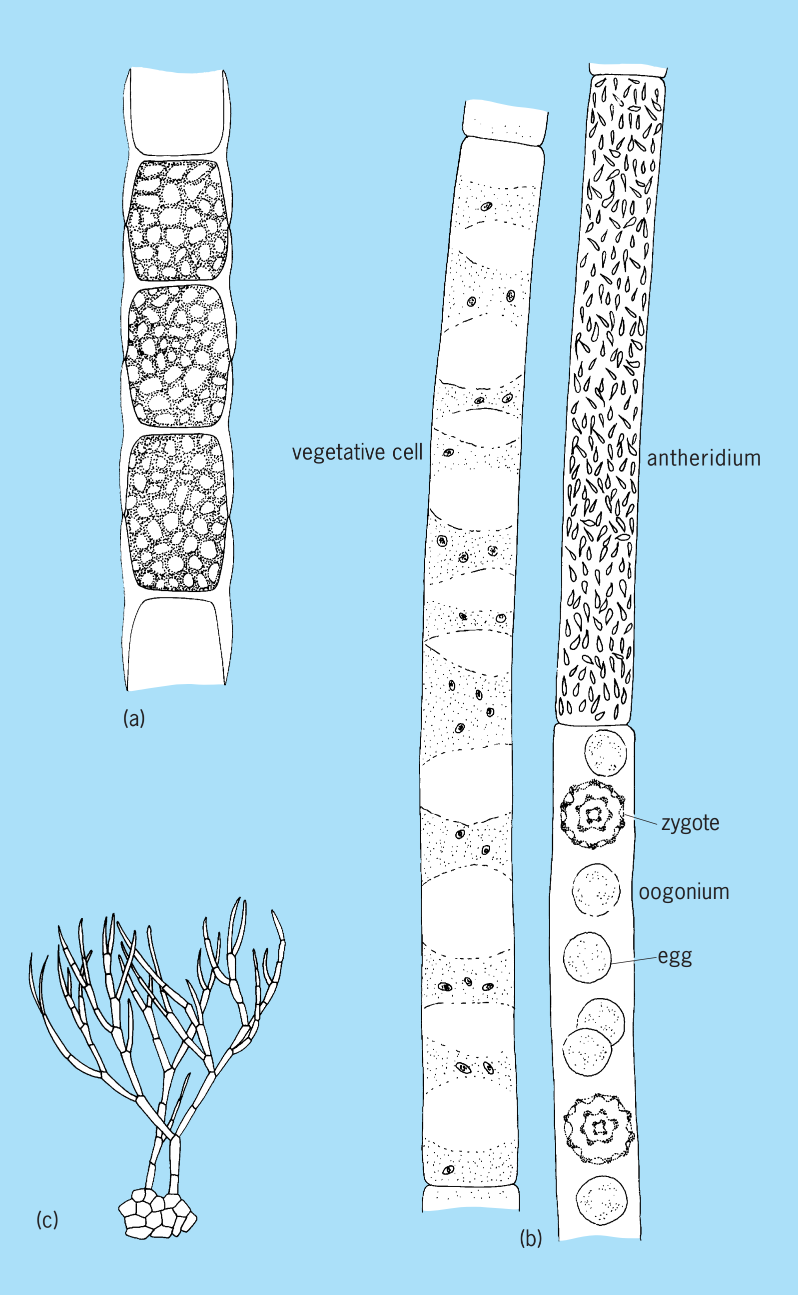


Fig. 2. Filamentous green algae with chlorophycean ultrastructure. (*a*) *Microspora* (Microsporales), showing H-shaped wall segments; (*b*) *Sphaeroplea* (Sphaeropleales); (*c*) *Chaetophora* (Chaetophorales), heterotrichous thallus (erect and prostrate systems).

Chaetophorales. Traditionally, the ulotrichine line was considered to begin with the unbranched filaments of *Ulothrix* and continue through various genera with branched filaments composed of uninucleate cells, each containing a parietal laminate chloroplast. If more than one order (Ulotrichales) was recognized, the branched forms were separated as the Chaetophorales. Modern studies have shown, however, that this morphological spectrum encompasses four phyletic lines as defined by ultrastructural features. *Ulothrix* is ulvophycean, as are *Trentepohlia* and probably all marine genera previously assigned to the Chaetophorales. *Microthamnion* is pleurastrophycean, while *Coleochaete* is charophycean. Residual chlorophycean forms, which include *Uronema* (unbranched) and *Chaetophora* (branched), constitute the order Chaetophorales *sensu stricto* with about 28 genera distributed among three families. Except for *Uronema*, members of the family Chaetophoraceae typically have a thallus differentiated into a prostrate portion composed of loose or pseudoparenchymatous filaments and an erect, freely branched portion (heterotrichous thallus, Fig. 2*c*). Ultimate branches are usually attenuate, often terminating in a long multicellular hyaline hair. In the Aphanochaetaceae, many cells bear unsheathed unicellular hairs, often with a bulbous base. In *Schizomeris*, the only member of the family Schizomeridaceae, the juvenile is similar to *Ulothrix*, but during maturation all cells in the upper portion of a filament undergo repeated division in various planes, resulting in a parenchymatous cylinder indistinctly marked into bands by the persistent transverse walls of the uniseriate cells.

Ulvophycean phyletic line. Ulvophyceae have motile cells that are scaly or naked, are radially symmetrical, and have two or more flagella arising apically from a cruciate root system, but the distal ends of the basal bodies lie in counterclockwise rotation rather than the clockwise rotation seen in Chlorophyceae. Cytokinesis is effected by a precocious cleavage furrow that impinges on microtubules of the persistent spindle. This phyletic line, which is predominantly marine, includes the Ulotrichales, Ctenocladales, Ulvales, Trentepohliales, Acrosiphoniales, Cladophorales, Siphonocladales, Bryopsidales, Dasycladales, and possibly Cylindrocapsales and Prasiolales.

Ulotrichales. The simplest thallus in the ulvophycean phyletic line is the unbranched filament of *Ulothrix* (**Fig. 3**), the only certain member of the family Ulotrichaceae and the order Ulotrichales. Other genera previously aligned with *Ulothrix* have been shown to be chlorophycean (such as *Uronema*, now in the Chaetophorales) or charophycean (such as *Klebsormidium, Stichococcus*, and *Raphidonema*, now in the Klebsormidiales) or to be reinterpreted as filamentous Chlorococcales (such as *Binuclearia*). Each cell of the *Ulothrix* filament has a nucleus and a parietal laminate or cylindrical chloroplast with one or more pyrenoids. Filaments attach (at least initially) by a modified basal cell to stones or wood, forming extensive stands in various aquatic habitats, such as the shores of lakes and harbors. The life history of fresh-water species involves only one somatic phase, a haploid gametophyte, with meiosis occurring in the production of zoospores during germination of the zygospore. Alternation of a filamentous gametophyte with a filamentous sporophyte has been reported for a marine species.

Ctenocladales. Small green algae with branched filaments are widespread in marine habitats, and have traditionally been assigned to the Chaetophorales, but all prove to have ulvophycean rather than chlorophycean ultrastructure. The order Ctenocladales has been proposed to receive them, but some workers refer them to the Ulvales, an order usually restricted to algae with parenchymatous thalli. In these marine forms, which constitute the family Ulvellaceae, the thallus usually consists solely of prostrate filaments that are free or coherent and pseudoparenchymatous. It is affixed to, or immersed in, a solid substrate, usually an aquatic organism. Free erect filaments, if produced, are short, the cells moniliform or irregularly swollen. Colorless anucleate setalike projections of the cell wall are produced in many genera. Sporangia and gametangia are often

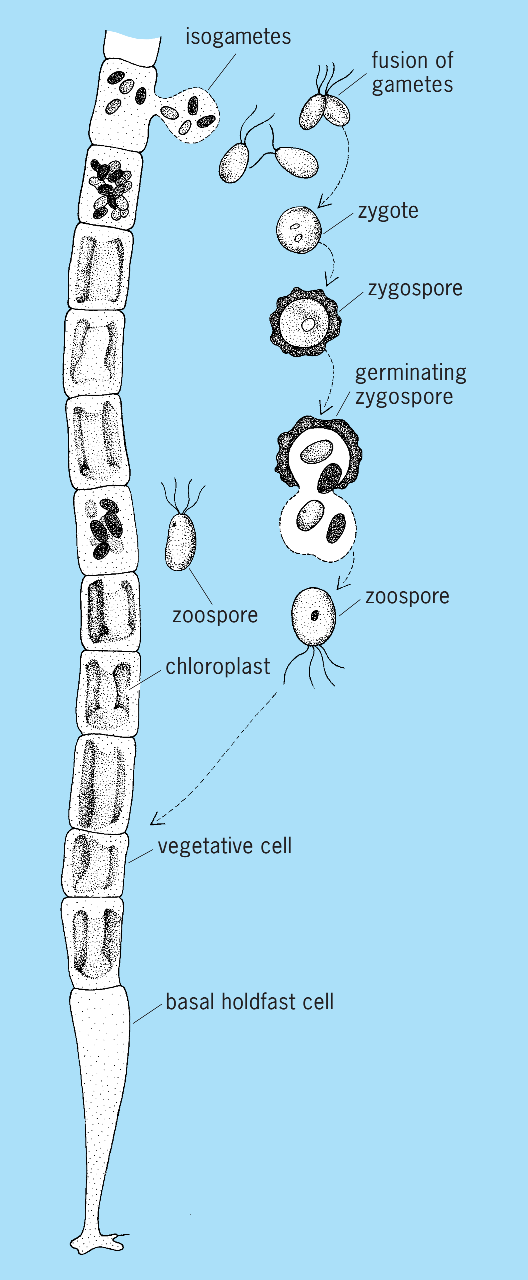


Fig. 3. *Ulothrix* (Ulotrichales).

conspicuously larger than vegetative cells and undergo sequential cleavage. Swarmers are released by the abrupt rupture of an elongate exit papilla. Various ulvophycean genera that previously were assigned to the Chaetophorales but that lack the special features of the Ulvelaceae are tentatively placed in the Ctenocladaceae.

Ulvales. The order Ulvales comprises green algae with thalli in the form of biseriate filaments, monostromatic blades, tubes, or sacs, and distromatic blades. Cytologically, they are similar to *Ulothrix*, and some workers do not segregate them from the Ulotrichales. Various life histories have been demonstrated. *Ulva* (sea lettuce) and its close relative *Enteromorpha* occur abundantly in the intertidal zone, especially in harbors and estuaries. As treated here, the order comprises five families (Capsosiphonaceae, Percursariaceae, Ulvaceae, Monostromataceae, and Gomontiaceae) with about 12 genera.

Trentepohliales. The order Trentepohliales, with the single family Trentepohliaceae, comprises a small, specialized group of subaerial algae. The thallus is composed of branched uniseriate filaments loosely arranged in an erect tuft or cohering laterally to form a prostrate disk. Sporangia and gametangia are clearly differentiated from vegetative cells. Starch is lacking. Carotenoid pigments are abundant, coloring the thallus yellow-green, yellow, orange, or red, and often imparting the odor of violets. *Trentepohlia*, which has both prostrate and erect systems, grows on rocks, tree trunks, leaves, and wooden structures. *Cephaleuros* grows within the leaves and twigs of various plants in tropical and subtropical regions, including those of commercial plantings of tea and coffee. It is parasitic, inducing a massive wound response in many hosts.

Acrosiphoniales. Thalli in the order Acrosiphoniales are composed of unbranched or branched filaments, each cell usually containing many nuclei and a perforate cylindrical chloroplast with numerous pyrenoids. The life history often includes a vesicular sporophyte derived from the zygote. The vesicle produces haploid quadriflagellate zoospores that give rise to filamentous gametophytes. Gametes and zoospores are liberated through a distinct pore, which is operculate in one family. The order includes two families, Codiolaceae with unbranched filaments and Acrosiphoniaceae with profusely branched filaments, comprising three or four genera restricted to cold marine and brackish waters.

Cladophorales. In the order Cladophorales, the simple or branched filaments have multinucleate cells, as in most Acrosiphoniales, but the characteristic life history is an alternation of isomorphic somatic phases. The cell wall is thick and lamellate. The chloroplast is a parietal network with numerous pyrenoids. *Cladophora* is one of the most common algae in all parts of the world and in all aquatic habitats. Certain species form spherical masses (*Cladophora* balls) that roll to and fro on the bottom of shallow lakes.

Siphonocladales. In the Siphonocladales, an order of tropical marine algae closely related to the Cladophorales, the multinucleate cells are often vesicular rather than cylindrical, and when cylindrical may anastomose in one or more planes. The chief feature of the order supposedly is the occurrence of a unique process of cell division, called segregative division. The protoplast cleaves into multinucleate portions of varying size, which round up, secrete a wall, and expand until they are in complete mutual contact. In some genera the daughter vesicles expand outward and upward, forming branches. The enormous size of the primary vesicle of certain species of *Valonia* has made this genus a favorite subject of biophysical studies, especially in the fields of permeability and solute absorption. In the few species of Siphonocladales in which sexual reproduction has been observed, the thalli are diploid gametophytes, with meiosis occurring during the production of biflagellate isogametes. The failure to observe segregative division in more than a few members of the Siphonocladales and the paucity of information on life histories obscure the border between this order and the Cladophorales. Some authors combine the two orders.

Bryopsidales. Many green algae (almost entirely marine) have thalli composed of nonseptate multinucleate filaments or tubes. These forms, which constitute the order Bryopsidales, are abundant and diverse in most tropical waters. *Halimeda*, which has a calcified thallus, is a major contributor to the buildup of coral reefs and infilling of atoll lagoons. *See* BRYOPSIDALES; HALIMEDA.

Dasycladales. In another group of tropical, essentially marine green algae, the thalli are noncellular, but unlike those in the Bryopsidales, they exhibit radial symmetry, with whorls of loosely arranged or densely aggregated branches arising from the primary axis. These forms constitute the order Dasycladales. Most members have calcified thalli, and there is a rich fossil record extending at least to the Cambrian and including more than a hundred extinct genera. Some genera have a unique life history, involving the fragmentation of an enormous primary nucleus to form numerous small secondary nuclei, which migrate into gametangia. The gametangia cleave into uninucleate units, which develop into operculate cysts containing biflagellate isogametes. Meiosis is believed to occur prior to or during fragmentation of the primary nucleus. *Acetabularia* (mermaid's wine glass) is frequently used in morphogenetic experimentation, since its large and readily accessible nucleus is quite amenable to manipulation. *See* DASYCLADALES.

Charophycean phyletic line. This phyletic group has motile cells that are scaly or naked, asymmetrical, devoid of eyespots, and with two laterally or subapically arising flagella, their basal bodies associated with a broad band of microtubules (multilayered structure) and usually an additional, smaller microtubular root. The distal ends of the basal bodies show counterclockwise rotation. Cytokinesis is effected either by centripetal growth of a furrow that impinges on microtubules of the persistent spindle or by means of a cell plate in the presence of a phragmoplast, the microtubules of which proliferate from the persistent spindle. This group includes the Chlorokybales, Klebsormidiales, Zygnematales, and Coleochaetales, as well as the charophytes (treated here as the class Charophyceae).

Chlorokybales. Packet-forming algae with charophycean ultrastructure have been segregated from the Chlorosarcinales as the order Chlorokybales. So far only one genus, *Chlorokybus*, is known.

Klebsormidiales. Rudimentary filaments that dissociate easily and lack holdfast cells are formed by members of the order Klebsormidiales. Plasmodesmata are absent. Each cell contains a nucleus and a parietal laminate chloroplast. Zoospores, which lack eyespots, are formed singly in unspecialized cells. Two families (Klebsormidiaceae and Elakatotrichaceae) with at least seven genera are tentatively recognized.

Zygnematales. The order Zygnematales is a large and well-known group of freshwater and subaerial green algae exhibiting two somatic types, unicells (desmids) and unbranched uniseriate filaments. The cell wall is composed of inner fibrillar cellulose layers and an outer slippery pectic layer. Plasmodesmata are absent. Each cell has a nucleus and one or more distinctly shaped chloroplasts. The most distinctive feature of the order is sexual reproduction by conjugation of ameboid or passive gametes (hence the alternate name, Conjugales). Flagellate cells are unknown. The zygote secretes a thick wall and undergoes a period of dormancy. Meiosis occurs at some point (variable, depending upon the species) between conjugation and germination.

Members of the Zygnemataceae (especially *Spirogyra* and *Zygnema*) form the slippery skeins common in stagnant water. Mesotaeniaceae, often called saccoderm desmids, are essentially unicellular Zygnemataceae. The Desmidiaceae and Peniaceae together constitute the placoderm desmids. The cells vary in shape, but are always composed of mirror-image semicells often demarcated by a median constriction. The cell wall has pores and is frequently ornamented. Placoderm desmids are abundant in slightly acidic fresh water. *See* ZYGNEMATALES.

Coleochaetales. Members of the order Coleochaetales are aquatic epiphytes or endophytes. The thallus consists of cells that are clustered or united into filaments. In *Coleochaete*, the only genus in the family Coleochaetaceae, the thallus may be filamentous, pseudoparenchymatous, or rudimentarily parenchymatous. Most or all cells bear one or more cytoplasmic setae, each with a basal gelatinous sheath. Each cell contains a nucleus and usually a parietal laminate chloroplast with a pyrenoid traversed by one or more thylakoids. Asexual reproduction is by scaly biflagellate zoospores, lacking eyespots and formed within ordinary cells. Sexual reproduction is oogamous, with minute colorless antherozoids being formed singly in conical antheridia, and eggs singly in spherical or flask-shaped oogonia. Fertilization occurs in place. The zygote enlarges greatly and secretes a thick wall. Neighboring branches produce a pseudoparenchymatous or parenchymatous sheath around the zygote, suggesting the possibility of the transfer of substances. After a period of dormancy (winter), the zygote germinates meiotically to form 8–32 biflagellate zoospores. Although exhibiting features conducive to the development of a terrestrial life, *Coleochaete* probably is not in the direct line of evolution of any extant embryophyte.

Pleurastrophycean phyletic line. Pleurastrophyceae have motile cells that are thecate or naked and more or less flattened. The flagella have a cruciate microtubular root system showing counterclockwise rotation of the basal bodies. The ancestral flagellate is believed to resemble *Tetraselmis*, a marine genus usually aligned with Prasinophyceae. The Pleurastrophyceae, while apparently a distinct group, is small. The few genera that have been assigned to it have been taken from several orders, including Chlorococcales, Chlorosarcinales, and Chaetophorales.

Micromonadophyceae. In addition to the four phyletic lines described here, each of which includes monads as well as multicellular algae, there is a residual group of primitive green flagellates for which the name Micromonadophyceae has been proposed. These monads are scaly or secondarily naked and have one to four flagella arising from an apical pit or lateral depression. The interzonal mitotic spindle persists during cytokinesis. This group corresponds to the class Prasinophyceae in the present classification.

The ultrastructural classification described in this article could be incorporated in the traditional scheme with minimal difficulty by according the rank of subclass to each major group, a treatment in keeping with the presumed monophyletic origin of green algae. For the sake of consistency, however, Prasinophyceae and Charophyceae are treated elsewhere in this work as separate classes. *See* ALGAE; CHAROPHYCEAE; PRASINOPHYCEAE.

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Chlorophycota

A division of the plant kingdom (also known as Chlorophyta or Chlorophycophyta) comprising all algae that have chlorophyll *a* and *b* except the Euglenophyceae, and that in all other respects are so different as to suggest a separate origin of their photosynthetic pigments. Three classes, Charophyceae (charophytes), Chlorophyceae (green algae), and Prasinophyceae, are recognized. *See* ALGAE; CHAROPHYCEAE; CHLOROPHYCEAE; PRASINOPHYCEAE.

Paul C. Silva; Richard L. Moe

Chlorophyll

The generic name for the intensely green, blue, or purple tetrapyrrolic pigments found in higher plants, algae, and photosynthetic bacteria that serve as photoreceptors and transducers of light energy to chemical energy in photosynthesis. *See* PHOTOSYNTHESIS.

Occurrence and Distribution of Major Cholorophylls

Although only about 20 chlorophylls are discussed here, new chlorophylls are found every year, especially in marine microalgae and photosynthetic bacteria of lakes and tidal flats. Chlorophylls *a*, *b*, and *d* are found in oxygenic photosynthetic organisms. All members of the chlorophyll *c* group are found in oxygenic, marine microalgae. Bacteriochlorophylls *c*, *d*, *e*, and *g* are found in anoxygenic (non-oxygen-producing) photosynthetic bacteria. All members of the chlorophyll *c* group are found in oxygenic, marine microalgae.

Chlorophylls a and b. The principal chlorophylls of higher plants and green algae are chlorophylls *a* and *b*. Chlorophyll *a* is found in the light-harvesting pigment-protein complexes (also called antennae) and reaction-center complexes (where the chemistry takes place) of all oxygen-evolving organisms, while chlorophyll *b* is found only in the antennae.

In higher plants, chlorophylls *a* and *b* are contained in the chloroplast (a type of cell plastid). At the highest magnification of the light microscope, one may just see tiny grana in the plastids of higher plants. A granum is made up of 10–100 discs (known as thylakoids), which are the basic photosynthetic apparatus. Chlorophylls *a* and *b* are attached to specific proteins located in the thylakoid membrane. In addition to the outer light-harvesting antennae complexes, two functionally and structurally distinguishable groups of chlorophyll-protein complexes exist: photosystem I and photosystem II. Each photosystem, with the associated antenna, contains about 300 chlorophyll molecules (and a few carotenoid molecules). The majority of these chlorophylls serve as light-harvesting antennae and funnel the energy they absorb to the special reaction-center chlorophylls of photosystem I and II. These reaction-center chlorophylls are special as they are two chlorophyll *a* molecules held in close juxtaposition by a unique protein environment. *See* CAROTENOID; CELL PLASTIDS; PLANT CELL.

Chlorophyll c. The chlorophyll *c* group is a rapidly expanding group of at least eight antenna chlorophylls. All members of the chlorophyll *c* group are found in oxygenic marine microalgae and brown algae. *See* ALGAE.

Chlorophyll d. Chlorophyll *d* has been shown to be the major chlorophyll in the cyanobacterium *Acaryochloris marina* which is a free-living epiphytic bacterium growing in association with red algae. *See* CYANOBACTERIA.

Bacteriochlorophylls. Photoheterotrophic bacteria, which do not evolve O_2, contain bacteriochlorophyll *a* as their reaction-center pigment but may contain bacteriochlorophylls *a, b, c, d, e*, and *g* as antenna pigments. Purple photosynthetic bacteria contain bacteriochlorophylls *a, b*, and *g*, and the green bacteria contain bacteriochlorophylls *a, c, d*, and *e*. *See* BACTERIA; BACTERIAL PHYSIOLOGY AND METABOLISM.

Function

Chlorophyll molecules have three functions: (1) They serve as antennae to absorb light quanta. (2) They transfer this energy from one chlorophyll to another over distances usually of 1.5–2 nm by a process of resonance transfer, so that the energy finally comes to reside in the special chlorophyll molecules P700 or P680 (the number after P represents their long-wavelength absorption maxima) in the reaction centers of photosystem I or II. (3) The special reaction-center chlorophyll molecules P680 and P700, having in their excited states (symbolized as $P680^*$ and $P700^*$) the energy of the photon, undergo chemical oxidation by transferring one of their electrons to a neighboring acceptor molecule. Specifically, $P680^*$ transfers one electron to a pheophytin molecule (in case of photosystem II) and $P700^*$ to another chlorophyll molecule (in the case of photosystem I). In this way the energy of the fleeting light quanta is converted into stable chemical energy.

Light-induced oxidation of reaction-center chlorophyll molecules leads to photobleaching, which is detected spectroscopically by an absorbance decrease. Loss of an electron oxidizes the reaction-center chlorophyll molecules. P680 is transformed to $P680^+$ and P700 to $P700^+$. Analogous bacteriochlorophyll species, P840+ or P890+, is produced in nonoxygenic photosynthetic bacteria. These cationic species are detected both optically as well as by the electron spin resonance technique, because each has an unpaired electron. *See* SPECTROSCOPY.

Chemical Structure

Chlorophylls contain up to four pyrrole rings that are joined by four methine (—CH═) bridges at C5, C10, C15, and C20. However, all chlorophylls also contain a fifth cyclopentanone ring, designated E. Chlorophylls with four pyrrole rings are called phytoporphyrins, and the chlorophylls of the *c* group belong to this family, the members of which are emerald green in color. Chlorophyll *a* contains three pyrrole rings (rings A, B, and C) and one dihydropyrrole ring (ring D) with a hydrogen atom at C17 and C18 (**Fig. 1**). Such chlorophylls are called chlorins, and chlorophylls *a*, *b*, and *d*, and bacteriochlorophylls *c*, *d*, and *e* belong to this family: chlorophyll *a* is blue and the other five are green. Some chlorophylls contain two dihydropyrrole rings (rings B and D) with hydrogen atoms at C7, C8, C17 and C18. These chlorophylls are called bacteriochlorins. Bacteriochlorophylls *a*, *b*, and *g* belong to the bacteriochlorin family and they are purple. These different-colored chlorophylls allow the organisms that possess them to efficiently use (as photosynthetically active radiation) those parts of the visible and near-infrared spectrum of solar radiation that permeate their environment.

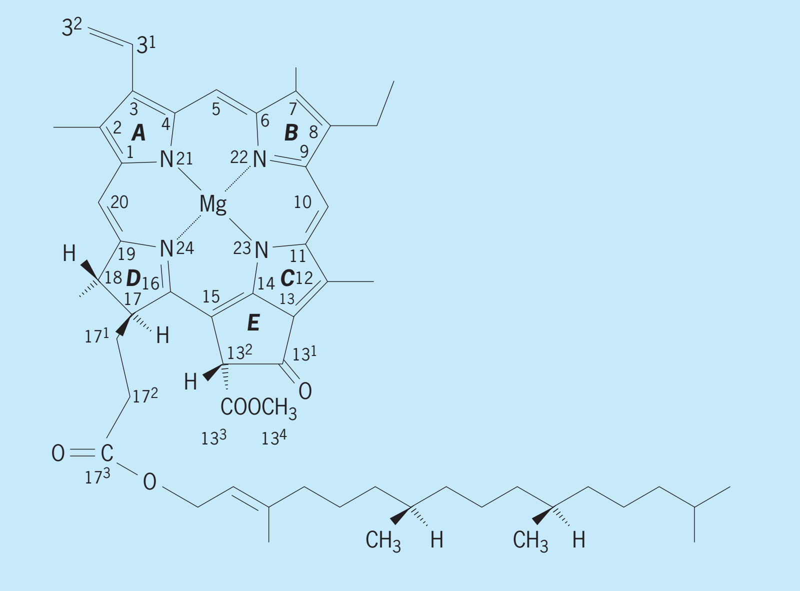

Fig. 1. Structure of chlorophyll *a* ($C_{55}H_{72}O_5N_4Mg$).

Central metal atom. Chlorophyll molcecules contain a central magnesium (Mg) atom that binds extra ligands (besides the four pyrrolic nitrogens) so strongly that it seldom exists only as a four-coordinate metal: one or both of the axial positions are occupied by an electron donor (nucleophile) group so that the Mg is generally a six-coordinate metal, but also sometimes exists as a five-coordinate metal. Axial coordination to the central Mg atom is important for understanding the ligation of chlorophyll to histidine, glutamine, or asparagine residues of chlorophyll apoproteins. Due to the greater than 4 coordination number of Mg, chlorophyll can exist as a monomer, dimer, trimer, tetramer, and as an aggregate of *n* number of chlorophyll molecules. The monomers absorb red light maximally in the 660–670-nm region, whereas the aggregates absorb (darker) red light in the 680–700-nm region. On the other hand, the chlorophyll-H_2O-chlorophyll adduct is suggested to absorb as far as 740 nm; the (chlorophyll·H_2O)$_2$ adduct may absorb around 700 nm.

Chlorins. The structure of chlorophyll *a*, which is a 3-monovinyl compound, is shown in Fig. 1. This molecule has now been synthesized in the laboratory. The characteristic feature of chlorophyll *a* is that it is a Mg-chlorin. Because rings A, B, C, and D are linked through methine bridges at C5, C10, C15, and C20 (Fig. 1), a large resonating 16-membered inner ring of carbon and nitrogen atoms attached to each other through alternating single and double bonds is formed. Closely related derivatives of chlorophyll *a* (the monovinyl pigment shown in Fig. 1) include [3,8-divinyl]-chlorophyll *a* which sometimes has long-chain alcohols other than phytol esterified at C17^3. Some widely dispersed marine phytoplanktonic *Prochlorococcus* strains contain 3,8-divinyl derivatives of chlorophylls *a* and *b*: it has been calculated that these divinyl pigments are responsible for approximately 25% of global photosynthesis.

Other chlorophylls closely related to chlorophyll *a* possess formyl (—CH═O) groups. Chlorophyll *b* is [7-formyl]-chlorophyll *a* and chlorophyll *d* is [3-formyl]-chlorophyll *a*.

Bacteriochlorophylls *c* and *d*, like chlorophyll *a*, belong to the chlorin family. The common features include a hydroxyethyl (—CHOHCH$_3$) group at C3, while the carboxymethyl (—COOCH$_3$) group at C13^2 of chlorophyll *a* is replaced by a H atom and the long-chain alcohol esterified at C17^3 is frequently farnesol ($C_{15}H_{25}OH$) of chlorophyll *a*, which replaces the phytol ($C_{20}H_{39}OH$). Bacteriochlorophylls *c* and *e* in addition have a C20 methyl (—CH$_3$) substituent.

Phytoporphyrins. The chlorophyll *c* group is a diverse group of Mg-phytoporphyrins including [3,8-divinyl]-protochlorophyllide *a*, which is also shown as a biosynthetic intermediate in the biosynthesis of chlorophyll *a* (**Fig. 2**). Most chlorophylls *c* have a free C17^3 carboxyl group, but two recently discovered nonpolar chlorophylls *c* are esterified at C17^3 to the sugar residue of a monogalactosyldiacylglycerol (MGDG) moiety. Frequently, the propionate group at C17 is replaced by an acrylic acid (—CH═CH—COOH) side chain.

Bacteriochlorins. Bacteriochlorophylls *a, b*, and *g* belong to the bacteriochlorin family of chlorophylls. There are several forms of bacteriochlorophyll *a*: one is esterified at C17^3 with phytol and the other is esterified with geranyl-geranol. Both forms have an acetyl (—CO—CH$_3$) group at C3 and an ethyl (—C_2H_5) group at C8. Bacteriochlorophylls *b* and *g* have an ethylidene (═CH—CH$_3$) group at C8 but bacteriochlorophyll *b* has an acetyl group at C3 where bacteriochlorophyll *g* has a vinyl (—CH═CH$_2$) group. In *Acidiphilium rubrum* the central Mg of bacteriochlorophyll *a* is replaced by a zinc (Zn) atom.

Chlorophyll derivatives. Pheophytins are chlorophyll derivatives lacking the central Mg atom; they occur naturally as electron acceptors in photosystem II. Bacteriopheophytin *a* is a derivative of bacteriochlorophyll *a* and serves as an electron acceptor in bacterial reaction centers. Pheophorbides are chlorophyll derivatives that have lost the central Mg atom and the long-chain alcohol ester moiety.

Biosynthesis

The two major plant tetrapyrrole pigments, chlorophylls and hemes, are both synthesized from ALA (5-aminolevulinic acid). ALA is converted to protoporphyrin in a series of enzymatic steps, which are identical in plants and animals. Thereafter, the pathway branches to form hemes text are porphyrins chelated with iron (Fe^{2+}), which are present in many respiratory hemoproteins including cytochromes. In the other branch, porphyrins are chelated with Mg^{2+} to form precursors of chlorophyll (Fig. 2). *See* HEMOGLOBIN; PORPHYRIN.

ALA is formed by the condensation of succinyl coenzyme A and glycine by ALA-synthase in non-plastid-containing eukaryotes (animals, yeasts and fungi) and in the α subgroup of proteobacteria (which includes the well-known genera of photosynthetic bacteria *Rhodopseudomonas,* *Rhodobacter*, and *Rhodospirillum*). However, in plants, algae, Archaea, and most bacteria (excluding the α-proteobacteria), ALA is formed from glutamate, a 5-carbon amino acid, by the C_5 pathway. This is the more ubiquitous pathway of ALA formation in nature. All of the enzymes necessary for converting glutamate to ALA (and further to chlorophyll) are contained in the chloroplasts of higher plants and green algae. The $C13^1$, $C13^2$, and $C13^3$ of ring E (Fig. 1) arise from the propionic acid ($—CH_2—CH_2—COOH$) group of Mg-protoporphyrin. An oxygen is introduced to form a 13^1-oxo-propionic acid ($—CO—CH_2—COOH$) moiety and spontaneous bonding then occurs between $C13^2$ and C15, thus forming ring E with a $C13^3$ carboxymethyl ($CHOOCH_3$) substituent. In higher plants and green algae, the oxygen for the 13^1-oxo-group comes from molecular oxygen (O_2), by activity of an oxygenase-type enzyme; in anaerobic photosynthetic bacteria, it comes from water (H_2O), by a hydratase enzyme activity.

In higher plants, a light-dependent and reduced nicotinamide adenine dinucleotide phosphate (NADPH)-dependent protochlorophyllide reductase (LPOR) introduces a hydrogen atom at both C17 and C18, thus converting protochlorophyllide to chlorophyllide. Cyanobacteria, green algae, mosses, ferns, and gymnosperms contain both LPOR and a dark (that is, light-independent) DPOR enzyme so that these organisms can synthesize chlorophyllide in light or dark. The esterification of a geranylgeranyl pyrophosphate forms chlorophyll *a* with a geranylgeranyl ester, which is followed by reduction to a phytyl ester: the esterification and reduction are both catalyzed by chlorophyll synthase, thus completing chlorophyll *a* formation. Among additional cofactors required for chlorophyll formation are Fe^{2+}, Mg^{2+}, adenosine triphosphate (ATP), nicotinamide adenine dinucleotide (NAD), and O_2. Concomitant with chlorophyll synthesis, the disk, or thylakoid, membranes are also synthesized. The possible origins of the phycobilin pigments, chlorophylls *b*, *c*, and *d*, and the bacteriochlorophylls are shown in Fig. 2.

Fluorescence

Chlorophylls reemit a fraction of the light energy they absorb as fluorescence. Regardless of the wavelength of the absorbed light, the emitted fluorescence is always on the long-wavelength side of the lowest energy absorption band, in the red or infrared region of the spectrum. The fluorescent properties of a particular chlorophyll are functions of the structure of the molecule and its immediate environment. Thus, the fluorescence spectrum of chlorophyll in the living plant is always shifted to longer wavelengths (peak at 685 nm) relative to the fluorescence spectrum of a solution of the same pigment (peak at approximately 660 nm). This red shift is characteristic of chlorophyll-protein complexes.

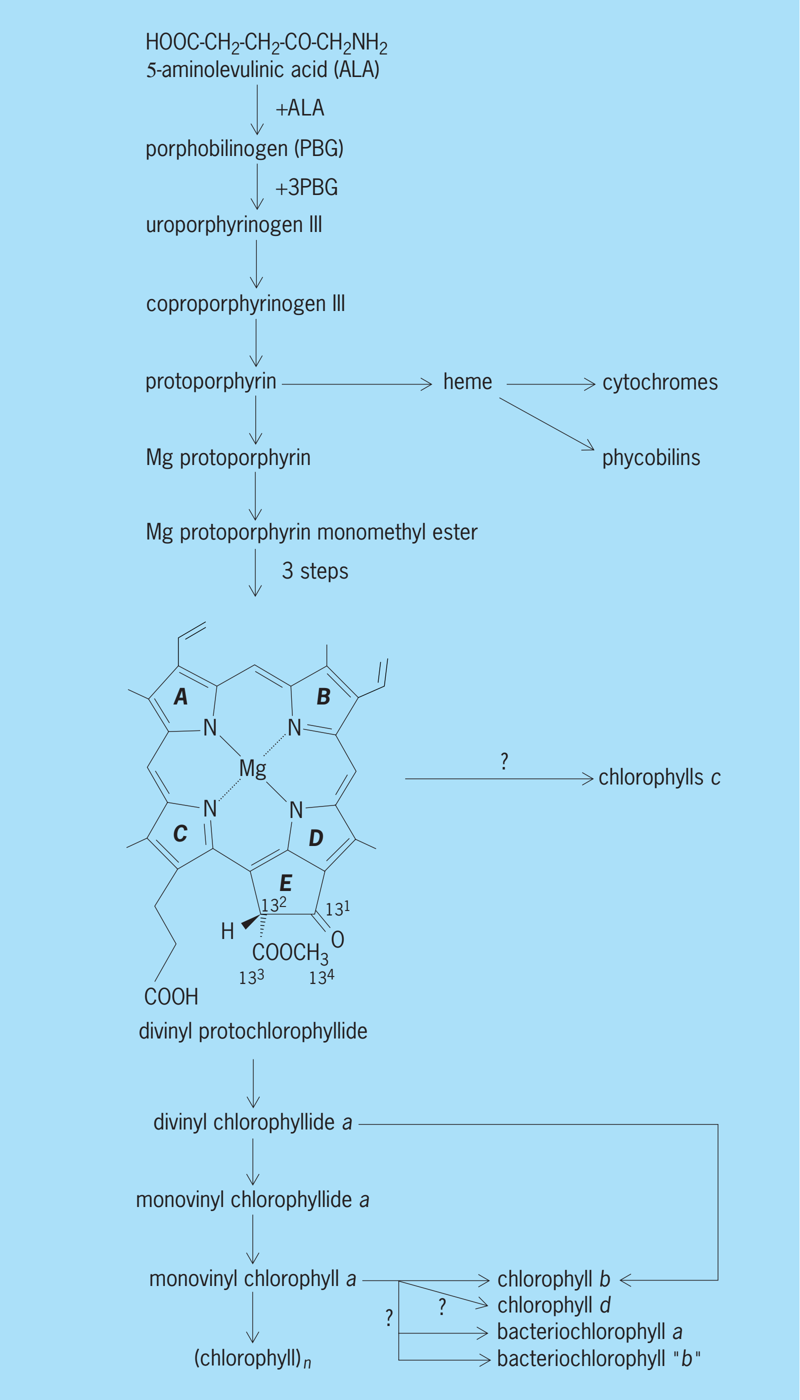

Fig. 2. Simple biosynthetic route for chlorophyll *a* and some related compounds. (In reality most of the pathways are much more complex and are often branched.) The tetrapyrrole structure shown above is Mg 3,8-divinyl protochlorophyllide.

Even in dilute solutions, the capacity of chlorophyll to fluoresce depends on the nature of the solvent. In solvents that can combine with the central Mg atom of chlorophyll by donating a pair of electrons to it, chlorophyll is fluorescent. In solvents that lack this property, chlorophyll is dimeric or polymeric and nonfluorescent at room temperature. The aggregates are formed by combining the carbonyl group of one molecule with the Mg atom of the neighboring molecule.

An excited chlorophyll *a* in diethyl ether has a mean lifetime of 5×10^{-9} s (5 nanoseconds), whereas in the living plant this is reduced to $0.5–2 \times 10^{-9}$ s (0.5–2 ns). A long-lived excited state of chlorophyll *a* (the triplet state) has been observed under special conditions, such as illumination of concentrated solutions in dry hydrocarbon solvents at low temperatures. Under these conditions, chlorophyll *a* emits phosphorescence at a spectral maximum of 750 nm. Weak phosphorescence of chlorophyll *a* has been recently observed in living cells.

The most widespread chlorophylls in nature, chlorophylls *a* and *b*, fluoresce with a quantum efficiency of 0.33 and 0.16, respectively, in dilute solution in diethyl ether. In the living cell the quantum efficiency drops to 0.03 for chlorophyll *a* and to zero for chlorophyll *b*. This is due to the property of chlorophyll *b* to transfer all its excitation energy to chlorophyll *a*, which, in turn, channels most of its excitation to photosynthesis, allowing only a small fraction to escape as fluorescence.

Measurements of chlorophyll *a* fluorescence are of great practical use as these have been shown to be a probe of the efficiency of photosynthesis. Applications of fluorescence are numerous and include measurements of the photosynthetic efficiency of plants under field conditions; advance estimations of the impact of abiotic and biotic environmental stresses on anticipated crop and biomass and yields; and, the assessment of the photosynthetic efficiency and productivity of plant communities in terrestrial, inland water, and marine ecosystems by remote sensing of chlorophyll *a* fluorescence. *See* FLUORESCENCE.

Govindjee; Robert J. Porra; George C. Papageorgiou

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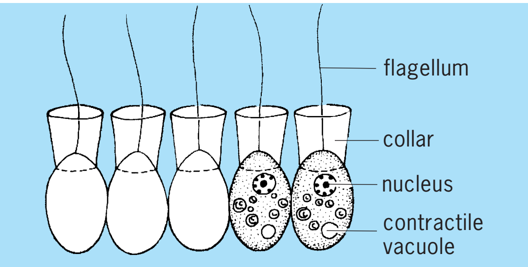
Choanoflagellida

An order of the class Zoomastigophorea, superclass Mastigophora, subphylum Sarcomastigophora, in the phylum Protozoa. They are principally small, single-celled or colonial, structurally simple, colorless flagellates distinguished by having the anterior end surrounded by a thin protoplasmic collar, within which is an ingestive area for particulate matter, for example, bacteria. A single flagellum arises from the center of this collar. The genus *Monosiga* is single, sometimes with a stalk, sometimes free in the plankton. *Desmarella* is a linear colony (see **illus.**), and *Astrosiga* and *Sphaerosiga* are colonies radiating from a center. *Proterospongia* cells arise in a common jelly, the zooids being organically connected. *Diploeca* lives in an attached lorica. *Stelexomonas* and *Aulomonas* inhabit tubular loricae. *Diplosiga* has a double colony. *Sportelloeca* and *Pleurasiga* live in complex loricae. *See* PROTOZOA; SARCOMASTIGOPHORA; ZOOMASTIGOPHOREA.



A linear colony of the choanoflagellate, *Desmarella moniliformis*.

The botanist P. Bourrelly puts these organisms in the order Monosigales. It is generally agreed, however, that the group shows relationships to the sponges. They are widespread in fresh and salt water and are common in inshore waters. James B. Lackey

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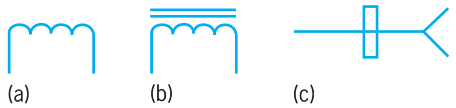
Choke (electricity)

An inductor that is used to prevent electric signals and energy from being transmitted along undesired paths or into inappropriate parts of an electric circuit or system. Power-supply chokes prevent alternating-current components, inherent to a power supply, from entering the electronic equipment. Radio-frequency chokes (RFCs) prevent radio-frequency signals from entering audio-frequency circuits. The printed circuit boards used in virtually all electronic equipment such as computers, television sets, and high-fidelity audio systems typically have one or more chokes. The purposes of these chokes are the (1) attenuation of spurious signals generated in the equipment itself so that these signals will not be transmitted to other parts of the circuit or beyond the overall system to other electronic devices; (2) prevention of undesired signals or electrical noise generated in other parts of the system from adversely affecting circuit performance; and (3) prevention of ripple from the power supply from degrading system behavior. Waveguide chokes keep microwave energy from being transmitted to the wrong part of a waveguide system. *See* ELECTRICAL



Graphic symbols for chokes or inductors in electric circuits. (*a*) Choke or inductor with air core. (*b*) Choke or inductor with magnetic core. (*c*) Waveguide choke.

NOISE; ELECTRONIC POWER SUPPLY; PRINTED CIRCUIT; RIPPLE VOLTAGE; WAVEGUIDE.

In its simplest form, a choke or an inductor is a coil of wire (usually copper) wound around and insulated from a core, which may or may not be ferromagnetic. Ferromagnetic cores tend to increase inductance, reduce physical size, and reduce electromagnetic coupling between circuit elements, and they may increase power loss and resultant heating. Such cores often lead to nonlinear or swinging chokes, commonly found in power supplies, where the nonlinearity may be an advantage. The basic principle of operation derives from the fact that it is impossible to change instantaneously the energy stored in a magnetic field. The various configurations are designed to control the magnetic field in an appropriate manner. The graphic symbols used to represent the various types of chokes or inductors in electric circuits are shown in the **illustration**.

Chokes come in a wide variety of inductance ranges, power-handling capabilities, fabrication technologies, and intended applications. In many cases they are specially designed for a particular situation. Chokes are available in inductance sizes ranging from a fraction of a microhenry to tens of henrys or higher. The frequency range of intended use is a major consideration. *See* INDUCTANCE; INDUCTOR.

Edwin C. Jones, Jr.

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Choked flow

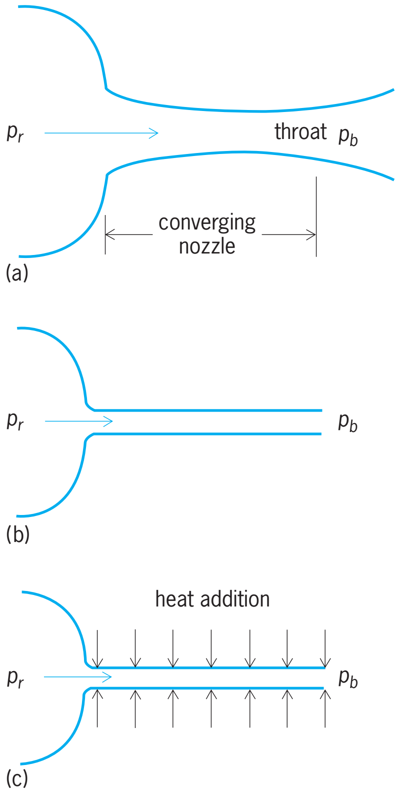
Fluid flow through a restricted area whose volume flow rate reaches a maximum when the fluid velocity at the minimum area reaches sonic speed. The phenomenon of choking exists only in compressible flow and can occur in several flow situations. *See* COMPRESSIBLE FLOW.

Flow through varying-area duct. Choked flow can occur through a convergent flow area or nozzle attached to a huge reservoir (**illus.** *a*). Flow exits the reservoir through the nozzle if the back pressure is less than the reservoir pressure. In all cases considered here, the reservoir pressure is assumed to be a constant. When the back pressure is decreased slightly below the reservoir pressure, a signal from beyond the nozzle exit is transmitted at sonic speed to the reservoir. The reservoir responds by sending fluid through the nozzle. Further, the maximum velocity of the fluid exists at the nozzle throat where the area is smallest.

When the back pressure is further decreased, fluid exits the reservoir more rapidly. Eventually, however, the velocity at the throat reaches the sonic velocity. Then the fluid velocity at the throat is sonic, and the velocity of the signal is also sonic. Therefore, further decreases in back pressure are not sensed by the reservoir, and correspondingly will not induce any greater flow to exit the reservoir. The nozzle is thus said to be choked, and the mass flow of fluid is a maximum for a given reservoir pressure. Thus, choking in a converging nozzle occurs when the Mach number (defined as the ratio of fluid velocity to the sonic velocity) at the throat equals 1. *See* MACH NUMBER; NOZZLE; SOUND; SUPERSONIC DIFFUSER.

Flow with friction. Choked flow can also occur through a long constant-area duct attached to a reservoir (illus. *b*). As before, flow from the reservoir through this duct is induced when the back pressure is decreased below the reservoir pressure, and a signal is transmitted through the duct to the reservoir.

As fluid flows through the duct, friction between the fluid and the duct wall reduces the pressure acting on the fluid. As pressure is reduced, other fluid properties are affected, such as sonic velocity, density, and temperature. The maximum Mach number occurs at the duct exit. As the back pressure is decreased, flow exits more rapidly through the duct,



Examples of choked flow. (*a*) Flow through a varying-area duct or nozzle. (*b*) Flow through a constant-area duct. (*c*) Frictionless flow through a constant-area duct with heat addition. P_b = back pressure; P_r = reservoir pressure.

but eventually the Mach number at the exit reaches 1. Any further decrease in back pressure is not sensed by the reservoir and so causes no increase in flow rate. Thus, when the Mach number is 1 at the duct exit, the flow is said to be choked, and the mass flow rate through the duct is a maximum.

Frictionless flow with heat addition. A reservoir with a constant-area duct attached may also be considered in the case that the flow through the duct is assumed to be frictionless, but heat is added to the system along the duct wall (illus. *c*). As fluid receives energy in the form of heat, fluid properties again change. The maximum Mach number occurs at the duct exit. As the total amount of heat increases, the Mach number at the duct exit increases, and eventually reaches 1. At this point, the mass flow through the duct is a maximum and the flow is said to be choked. Any further heat addition results in a decrease in mass flow through the duct. *See* FLUID FLOW; GAS DYNAMICS.

William S. Janna

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Cholera

A severe diarrheal disease caused by infection of the small bowel of humans with *Vibrio cholerae*. This facultatively anaerobic, curved, gram-negative, rod-shaped bacterium is rapidly motile by means of a single sheathed polar flagellum. Cholera is transmitted by the fecal-oral route. From its ancestral home in the Indo-Pakistani subcontinent, through movement of people by ships and other means of transportation, cholera has swept the world in seven pandemic waves. These involved the Western Hemisphere several times in the 1800s, and again in Peru in 1991. Whereas previous cholera outbreaks were associated with high mortality rates, through understanding of its pathophysiology it can now be said that no one should die of cholera who receives appropriate treatment soon enough.

Cholera produces a secretory diarrhea caused by the protein cholera enterotoxin (CTX), which is composed of two kinds of subunits: five B subunits responsible for binding to a glycolipid, the GM1 ganglioside, on host membranes; and a single A subunit, which is an enzyme. The latter, an adenosine ribosyl transferase, transfers adenosine diphosphate P–ribose from nicotinamide adenine dinucleotide to a host cell regulatory protein, G_s. This causes permanent activation of adenylate cyclase and a consequent increase in cyclic adenosine monophosphate. The result is hypersecretion of chloride and bicarbonate and inhibition of sodium absorption, leading to the secretion of the large volumes of isotonic fluid which constitute the diarrhea of severe cholera. The B subunit also activates arachidonic acid metabolism, leading to the production of eicosanoids, which may contribute to the diarrhea as well as to the immune response. The treatment consists of replacing the fluids and electrolytes lost in the voluminous cholera stool. This can be done intravenously, which may be essential initially in comatose patients, or perorally using oral rehydration salt solutions containing a utilizable carbon (energy) source (glucose, rice powder). The oral rehydration solutions are a relatively recent development, can also be used in the treatment of other diarrheal diseases, and have been responsible for saving millions of lives. Appropriate antibiotics can also be used adjunctively to decrease the excretion of the vibrios and the duration of the disease. The incubation period may be less than one day or up to several days; properly treated, the patient should recover in 4 or 5 days. The disease produces immunization, and convalescents rarely get cholera again. *See* DIARRHEA.

Despite the fact that the cholera vibrios were first discovered by Robert Koch in 1883 and a cholera vaccine was introduced 3 years later, there is still no effective, economical, and nonreactogenic vaccine. Use of a killed whole-cell vaccine administered parenterally was eliminated because of expense, reactogenicity, and lack of efficacy. Experimental vaccines currently being evaluated include genetically engineered living attentuated preparations administered perorally (or intranasally), killed whole-cell vaccines administered perorally, and conjugated vaccines (polysaccharide and toxin antigens) administered parenterally. Efforts are also being made to include cholera antigens transgenically in edible plants. A recently developed candidate attenuated vaccine has a deletion in the CTXφ (which carries the genes for CTX) and is also defective in its hemagglutinin/protease. The latter is a zinc metalloprotease which apparently causes detachment of the vibrios (to find another host) and may contribute significantly to the diarrhea which is still produced by CTX$^-$ strains.

A complicating feature is the fact that of approximately 150 recognized serogroups of *V. cholerae*, until 1992 only the two biotypes, classical (first described by Koch) and El Tor (recognized later), of serogroup O1 have been responsible for all epidemic cholera (El Tor first emerged in pandemic form in 1961). In 1992 a recently recognized serogroup, O139, caused epidemic cholera in India and Bangladesh and, for a time, replaced the resident El Tor vibrios. O139 resembles El Tor except for the distinctive O139 (instead of O1) polysaccharide somatic antigen and the possession of a capsule. They are antigenically distinct, so a new vaccine will be required for O139. The emergence of O139 raises the specter that other serogroups of *V. cholerae* may acquire virulence and epidemicity by some means of horizontal genetic transmission. It has recently been recognized that CTX is genetically encoded by a bacteriophage, CTXφ, which has become integrated in the *V. cholerae* chromosome. Virulent cholera vibrios also produce toxin-coregulated pili, surface fibrils, which are essential for colonization and also serve as receptors for CTXφ. Other non-O1/O139 vibrios carry CTXφ but apparently do not have other essential attributes of virulence, including the ability to adhere and colonize the small bowel and to spread epidemically. Another pilus, the mannose-sensitive hemagglutinin, serves as the receptor for another temperate filamentous choleraphage, 493, which may play a role in horizontal genetic transmission and cholera vibrio territoriality.

The best ways to avoid cholera are by chlorination of water, sanitary disposal of sewage, and avoidance of raw or improperly cooked seafood, which may have become infected by ingesting infected plankton in epidemic areas.

Richard A. Finkelstein

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Cholesterol

A cyclic hydrocarbon alcohol commonly classified as a lipid because it is insoluble in water but soluble in a number of organic solvents. It is the major sterol in vertebrate cells and the most common sterol of eukaryotes, but it is absent from most prokaryotes. In vertebrates, the highest concentration of cholesterol is in the myelin sheath that surrounds nerves and in the plasma membrane that surrounds all cells. Insects and most invertebrates cannot synthesize cholesterol; therefore, they rely on dietary cholesterol for use in their membranes and as a precursor of ecdysone, a molting hormone required during growth and development. *See* ECDYSONE; LIPID.

Function. All vertebrate cells require cholesterol in their membranes to function normally. Cholesterol helps maintain normal cell membrane function by associating with the phospholipid acyl chains within the membrane, thereby adjusting up or down the degree of molecular motion or fluidity within the membrane that allows proteins to carry out their tasks. Cholesterol is also the required precursor molecule for the formation of steroid hormones, bile acids, and vitamin D, which are required in the execution of various essential bodily processes.

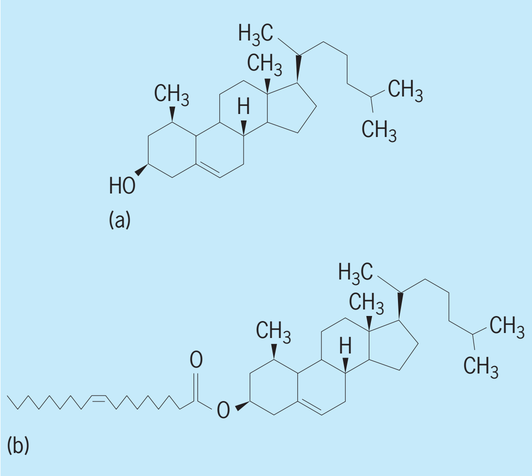

Fig. 1. Cholesterol. (*a*) Structure of unesterified, or free, cholesterol with the hydroxyl group in the 3β, position. (*b*) Structure of a cholesteryl ester molecule with a fatty acid (oleate in this case) attached to the 3β-hydroxy position via an ester bond.

Free and esterified forms. Cholesterol can exist either in the free (unesterified) form, in which the hydroxyl group (OH) at carbon-3 exists in the beta (β) configuration (**Fig. 1***a*), or as a cholesteryl ester to which a fatty acid is attached through an ester bond to the 3β-hydroxyl group (Fig. 1*b*). The free form is found in cell membranes and on the surface of plasma lipoproteins (lipid-protein emulsion-like complexes that transport cholesterol among tissues via the blood), with the hydroxyl group at the membrane aqueous environment interphase and the hydrocarbon tail buried among the fatty acyl chains of the phospholipids forming the membrane or surface layer. The cholesteryl ester molecule is usually found within lipid droplets in the cytoplasm of cells or within the neutral lipid core of plasma lipoproteins.

Cholesterol can be esterified by tissue enzymes termed acyl-coenzyme A (CoA):cholesterol *O*-acyltransferases 1 and 2 (ACAT1 and ACAT2) and by the plasma enzyme lecithin-cholesterol acyltransferase or LCAT. ACAT1 catalyzes the esterification of cholesterol for storage within cells in steroidogenic (steroid-producing) tissues. In the liver, the organ that serves as the central clearinghouse for cholesterol in the body, cholesterol esterification via ACAT2, leads to its storage or its secretion in the form of lipoproteins. Esterification via ACAT1 also occurs in macrophages (phagocytic immune cells) in the arterial wall, forming the lipid-filled foam cells of atherosclerosis in a process apparently designed to protect the cell membrane from becoming overly enriched in free cholesterol. In steroidogenic tissues, cholesteryl ester can be hydrolyzed via catalysis by cholesterol ester hydrolase (CEH), and the resulting cholesterol is then converted into steroid hormones. In macrophage foam cells, hydrolysis via CEH allows for cholesterol mobilization and removal from the cell; and in the liver, hydrolysis via CEH permits the cholesterol molecule to be used for any of the multiple pathways within the liver, including those resulting in the formation of bile and plasma lipoproteins and those involved in membrane function. *See* CELL MEMBRANE; LIPOPROTEIN; PHOSPHOLIPID.

Sources. Cellular cholesterol is obtained both from the diet, following its absorption in the intestine, and from synthesis within all cells of the body.

Intestinal cholesterol absorption. Much of the cholesterol in the body can be obtained in the diet. Foods that contain cholesterol come from animal sources, and those highest in cholesterol include eggs, dairy products, and organ meats such as liver and brain. The cholesterol from the human diet, typically about 250 mg per day, becomes mixed with endogenous (originating from within the body) cholesterol (about 750 mg per day), secreted into the intestine in bile. Through the processes of digestion, dietary cholesterol is solubilized by bile acids (detergents that facilitate fat and cholesterol absorption) into micelles (water-soluble particles) and transferred through a protein called Niemann-Pick C1-like 1 into enterocytes (cells lining the intestine), whereupon it is esterified by ACAT2, incorporated into absorptive lipoproteins called chylomicrons, and brought into the circulation and deposited in the liver. This process is only about 50% efficient, and about half of the cholesterol in the intestine is excreted each day.

While all cell types have the enzymatic machinery to synthesize cholesterol, only the liver has enzymes to degrade the cholesterol molecule in significant amounts by converting it into bile acids. Assembly of bile acids and cholesterol into bile micelles in the liver with subsequent secretion into the intestine, followed by absorption and return of the absorbed cholesterol to the liver constitutes the process termed enterohepatic recirculation. In a normal day, the bulk of the removal of cholesterol from the body occurs through fecal excretion of approximately equal amounts ($\sim$1 g combined) of cholesterol and bile acid. *See* ABSORPTION (BIOLOGY); LIVER.

Biosynthesis and feedback regulation. Cholesterol synthesis occurs in all vertebrate cells, with perhaps the highest rates occurring in the liver, skin, intestine, and in the brain at the time of myelination. The process involves the conversion of two-carbon acetate molecules into isoprenoid units continuing on to produce a 30-carbon precursor known as lanosterol. This molecule is then rapidly converted into the 27-carbon cholesterol molecule. The whole process requires over 40 enzymes and is highly regulated by the cholesterol status of the cell through the process of feedback regulation. The key rate-limiting enzyme in the biosynthetic process is 3-hydroxy-3-methylglutaryl coenzyme A reductase (HMG-CoA reductase). This is the target enzyme for the statin drugs that are used clinically to reduce blood cholesterol concentrations. These drugs work in part by binding to and inactivating HMG-CoA reductase, resulting in a decrease in the rate of cholesterol synthesis. *See* COENZYME; ENZYME.

Although the presence of feedback regulation of cholesterol synthesis was identified some 70 years ago, only recently have we come to understand the complexity of the process. The systematic identification of the many individual steps in this process has provided new fundamental information about the structure and function of cell membranes. A whole series of protein molecules has been evaluated, and the identification of the processes that govern the behavior of these proteins has provided unique insights into how membranes function as molecular sensors responding to changes in the cholesterol availability within the cell.

In the 1950s, the liver was shown to be the site of much of the feedback regulation; nevertheless, many of the details about the feedback mechanism have been identified in skin fibroblasts and in other cells in culture that can be manipulated to induce mutations in individual steps in the regulatory process (**Fig. 2**). Initially, cholesteryl ester-rich low-density lipoproteins (LDL) bind to receptors on the cell surface termed LDL receptors. These receptors localize in regions within the membrane, termed clathrin-coated pits in cell types other than liver cells. These structures bud off the membrane and move into the cell. The bound LDL is delivered to lysosomes (cellular organelles containing digestive enzymes), whereupon the cholesteryl esters are hydrolyzed, making the cholesterol available to the cell. In liver hepatocytes, where most of the LDL clearance from plasma occurs, the LDL receptors do not cluster in coated pits. Rather, the receptor appears to interact with an as yet unidentified protein molecule for internalization of bound LDL particles.

Within cells, the amount of the LDL receptor produced is regulated through transcriptional mechanisms. The cholesterol molecules brought into the cell as a result of receptor activity will eventually transmit the signal for downregulation (a decrease) of receptor-mediated uptake of LDL. This occurs by shutting down the transcriptional activation of the LDL receptor gene in an analogous fashion to the regulation of the genes that participate in cholesterol biosynthesis.

The transcription factor responsible for stimulating transcription of the enzymes of the biosynthetic pathway as well as the LDL receptor is termed the sterol regulatory element-binding protein (SREBP). This protein controls gene transcription by binding to a nucleotide sequence (typically 5′-TCACNCCAC-3′, where N can be any base) within the promoter region of genes. There appear to be a family of three SREBPs (SREBP1a, SREBP1c, and SREBP2), each of which may be involved in regulation of different aspects of lipid metabolism. These proteins are initially integral membrane proteins within the endoplasmic reticulum. As such, they have no access to the nucleus without protein processing. To gain access to the nucleus, the SREBPs must move within vesicles

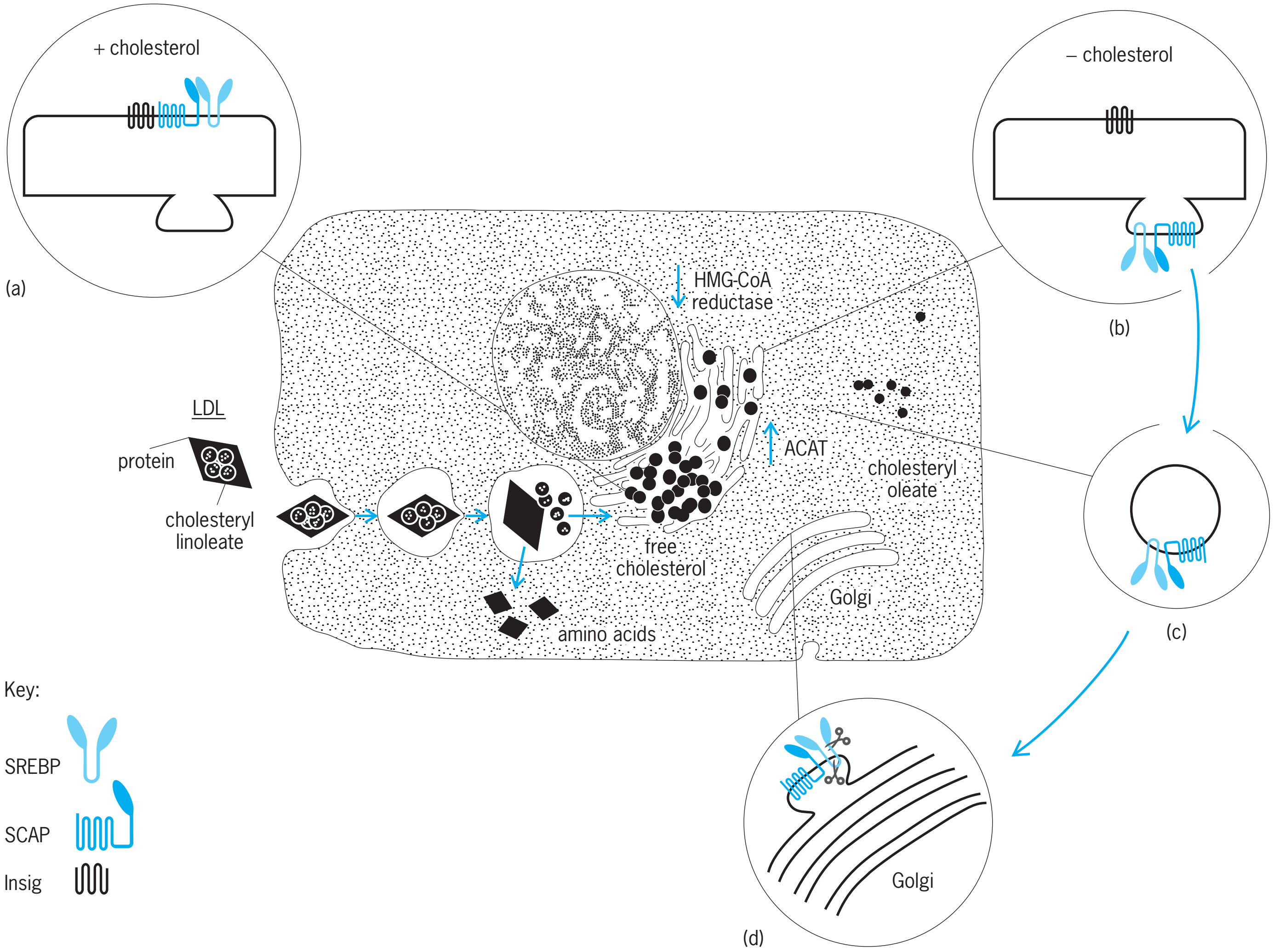

Fig. 2. Insights into the low-density lipoprotein (LDL) receptor internalization pathway, including the uptake of LDL, disassembly in the lysosome, and conversion of the LDL cholesteryl esters into cholesterol, which becomes a part of the regulatory pool of cholesterol inside the cell. (*a*) When cellular cholesterol levels are normal, sterol-regulatory element-binding protein (SREBP), SREBP cleavage-activating protein (SCAP), and Insig-1 form a macromolecular complex in the endoplasmic reticulum (ER). (*b*) Lowering the cholesterol level in the ER stimulates the release of Insig-1 from the complex, which allows SCAP to escort SREBP to vesicles. (*c*) These vesicles bud off and are targeted to carry the SCAP-SREBP complex to the Golgi apparatus. (*d*) In the Golgi, SREBP is cleaved at two sites by proteases, and the sterol-regulatory element-binding fragment is released into the cytoplasm from where it migrates into the nucleus. (*Reprinted from R. G. W. Anderson, J. Goldstein, and M. Brown, From cholesterol homeostasis to new paradigms in membrane biology, Trends Cell Biol., 13:534–539, © 2003, with permission from Elsevier*)

to the Golgi complex inside cells, where the SREBP protein undergoes proteolytic cleavage at two sites by two different proteases, the so-called site 1 and site 2 proteases (Fig. 2*d*). The result is the release of a 480-amino-acid N-terminal portion of the protein that is a transcription factor that travels to the nucleus, where it can bind to the sterol-regulatory element within genes and participate in signaling for their transcription. The SREBP1 transcription factors bind to numerous genes that are involved in fatty acid metabolism, whereas SREBP2 is more involved in promoting the transcription of genes in cholesterol metabolism.

Initially, it appeared that regulation of the release of the processed transcription factor via proteolytic cleavage would be the key regulatory step responsive to cholesterol, but in reality it turned out to be a protein termed SREBP cleavage activating protein, or SCAP (Fig. 2*b*). This protein contains an amino acid sequence termed the sterol-sensing domain (SSD), which is made up of eight membrane-spanning regions that define a signature sequence that is shared with other proteins known to be sensitive to regulation by cholesterol. Several amino acid mutations that abolish cholesterol-mediated regulation occur in the SSD of SCAP. Identification of this fact signaled that it was SCAP that actually detected the level of cholesterol in the membrane. When SCAP binds cholesterol, a conformational change occurs in SCAP that allows the protein to bind to proteins called insigs, which serve as endoplasmic reticulum membrane anchors. When SCAP is bound to insigs, the SCAP–SREBP complex is retained in the endoplasmic reticulum and cannot participate in vesicular traffic to the Golgi compartment (Fig. 2*a*). The result is that SREBP cannot be processed and the transcriptional component of SREBP cannot be generated and travel to the nucleus and activate cholesterol biosynthetic enzymes. The decrease in nuclear content of processed SREBPs results in a decrease in cholesterol biosynthesis. *See* ENDOPLASMIC RETICULUM; GENE; GENE ACTION; GOLGI APPARATUS.

Metabolism. Steroid hormones are derived from cholesterol and are required for the control of many different cell functions. The conversion of cholesterol to the steroid hormones including cortisol, aldosterone, and androgens occurs in the adrenal glands. Conversion of cholesterol to estrogen, progesterone, or testosterone occurs in the ovary, placenta, or testes. *See* HORMONE; STEROID.

Cholesterol is also a precursor of the bile acids that are synthesized in the liver. Bile acids together with cholesterol and phospholipids are secreted into the bile canaliculi (minute ducts or channels) in the liver. The detergent property of bile acids permits these lipids to become micelles. When the fat in food enters the intestine after a meal, the gallbladder contracts and the liver is stimulated to produce more bile that is secreted into the small intestine, where the bile acids participate in the emulsification (solubilization) of the fat in the diet. The emulsification process allows digestion of the fat to take place efficiently, and the products of digestion, including cholesterol, are absorbed into the intestinal cells. Sometimes, cholesterol in the gall bladder crystallizes and becomes gallstones. The size of the gallstones can vary widely from about the size of a grain of gravel to a lima bean. *See* GALLBLADDER; GALLBLADDER DISORDERS.

A cholesterol biosynthetic precursor, 7-dehydro cholesterol is also the precursor of vitamin D, a hormone that is required for control of normal calcium metabolism. The initial step in the conversion of 7-dehydro cholesterol to vitamin D occurs in the skin in response to ultraviolet light; however, further modifications are required in the liver and kidney in order to form the biologically active form of the vitamin. *See* CALCIUM METABOLISM; LIPID METABOLISM; VITAMIN D.

Plasma lipoproteins and atherosclerosis. Cholesterol and cholesteryl esters are essentially insoluble in water so that, in order to transport these molecules among tissues in the blood, the liver and intestine produce lipid–protein complexes termed lipoproteins. These particles solubilize cholesterol and other lipids, including triglycerides (fats) and phospholipids, so that they can move between tissues to satisfy their metabolic needs. Triglyceride-rich lipoproteins are the largest particles and include the chylomicrons and very low density lipoproteins (VLDL). The LDLs are the major lipoprotein class in human blood, and these particles are enriched in cholesteryl esters, while the smallest particles are the high-density lipoproteins (HDLs).

All of the cholesterol in the blood plasma (after blood cells are removed) is present in the lipoproteins. The relative amounts of the lipoprotein classes are often measured in terms of their cholesterol concentrations as risk factors for the development of atherosclerosis, or hardening of the arteries. The best profile is to have low concentrations of LDL cholesterol (preferably below 100 mg/dl) and to have higher concentrations of HDL cholesterol (above 50 mg/dl). When the concentrations of LDL cholesterol get too high, deposition of cholesterol within the arteries occurs that, over years, can result in accumulations that lead to lesions or plaques in the arterial wall. Higher levels of HDL appear to protect against this deposition. The instability or tendency of plaques to rupture can lead to complications of coronary heart disease, such as myocardial infarction (heart attack). Diets high in cholesterol and saturated fat often result in higher LDL cholesterol concentrations and increased risk for the development of atherosclerosis. *See* ARTERIOSCLEROSIS; HEART DISORDERS.

Lawrence L. Rudel; Peter Edwards

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Choline

A compound used by the animal organism as a precursor of acetylcholine and as a source of methyl groups. It is a strongly basic hygroscopic substance with the formula below. It is questionable whether

$$(CH_3)_3{\equiv}N^+{-}CH_2{-}CH_2OH$$

this very necessary metabolite should be considered a vitamin. Choline is determined microbiologically by using a mutant of the mold *Neurospora crassa*.

A choline deficiency has been produced in a number of animal species. The degree of deficiency achieved depends on the amount of choline precursors, particularly methyl donors such as methionine, present in the diet. Choline deficiency is associated with fatty livers, poor growth, and renal lesions. It is a lipotropic agent. There is no direct evidence of disease in humans due to choline deficiency, although there have been suggestions that some of the liver, kidney, or pancreas pathology seen in various nutritional deficiency states may be related to choline insufficiency. Choline is found in acetylcholine, which is necessary for nerve impulse propagation, and in phospholipids.

There is no evidence that choline acts as a coenzyme. Choline functions as a donor of methyl groups to quaternary nitrogen and sulfonium compounds.

Human beings eat 50–600 mg of choline per day, but only excrete 2–4 mg. Consequently, conventional load tests are of no value in studying choline requirements, and no knowledge of human requirements exists. *See* ACETYLCHOLINE; VITAMIN.

Stanley N. Gershoff

Choline, trimethyl-β-hydroxyethylammonium hydroxide, is a quaternary compound which is made by the reaction of trimethylamine and ethylene oxide in either an aqueous or an alcoholic solvent. If choline salts are desired, the reaction can be carried out with the corresponding trimethylamine salt, or the base can be neutralized with the corresponding acid. The salts in common use are choline chloride, choline bitartrate, choline dihydrogen citrate, and tricholine citrate.

Choline salts are sold as liquids and solids. The liquids, such as a 65% solution of tricholine citrate, are prepared by the aqueous quaternization procedure, decolorized with charcoal, and then evaporated to the desired strength. The solid types are prepared in either aqueous or alcoholic media and are crystallized by cooling concentrated solutions.

Richard J. Turner

Chondrichthyes

A class of fishes characterized by well-developed jaws and bony teeth; pectoral and pelvic girdles, each supporting paired fins; a cartilaginous skeleton that lacks true bone; toothlike scales of ectodermal and mesodermal origin; paired nostrils with blind olfactory sacs (not opening into the mouth); a vertebral column having either a straight or heterocercal posterior end; absence of a swim bladder; cranium without sutures; and internal fertilization.

Chondrichthyes has traditionally included the subclasses Holocephali (chimaeras) and Elasmobranchii (sharks, rays, and skates). A group of Devonian armored fishes, the Placodermi, has been regarded as ancestral to the Chondrichthyes, but this derivation is not certain. Another group of primitive jawed fishes called acanthodians, considered by many as ancestral to the higher bony fishes, exhibit certain primitive elasmobranch-like features. In any case, it is probable that the elasmobranchs and chimaeras arose independently of each other some time during the Silurian or Early Devonian. Because even calcified cartilage is rarely preserved, the fossil record of the Chondrichthyes is represented mainly by teeth and spines, with only occasional associated skeletons. *See* ACANTHODII; PLACODERMI.

Holocephali. The Holocephali differ from the Elasmobranchii in having only four pairs of gill arches and gills that open to the exterior from a single pair of apertures; in the erectile dorsal fin and spine; in the naked skin in adults; and in the absence of a cloaca and ribs. Males of some species are equipped with a frontal clasper on the head. The teeth are consolidated into six pairs of plates, and the upper jaw is immovably fused with the brain case; these adaptations function in grinding mollusks, their chief food. Chimaeras date from the Early Mesozoic. *See* CHIMAERIFORMES.

Elasmobranchii. The elasmobranchs have five to seven pairs of gill clefts, all opening separately; one or two dorsal fins; rigid spines preceding the fins of some taxa; spiracles either present or absent; placoid scales; numerous teeth that are not set in sockets and arranged in several rows; the inner margin of the pelvic fins of males modified to form a copulating organ called claspers; and oviparous, ovoviviparous, or viviparous development. *See* BATOIDEA; ELASMOBRANCHII; SELACHII.

Herbert Boschung

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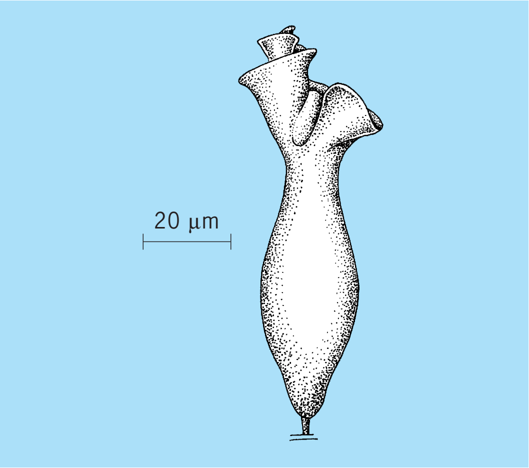
Chonotrichida

An order of the Holotrichia. This is a small group of curious, vase-shaped ciliates, commonly found as ecotocommensals on marine crustaceans. They attach to their hosts by a short, secreted stalk, and their bodies are practically devoid of ciliature.



***Spirochona*, an example of a chonotrichid.**

Spirochona (see **illus.**) is a common example of this order. *See* CILIOPHORA; HOLOTRICHIA; PROTOZOA.

John O. Corliss

Chopping

The act of interrupting an electric current, beam of light, or beam of infrared radiation at regular intervals. This can be accomplished mechanically by rotating a vibrating mirror in the path of the beam to deflect it away from its intended source at regular intervals. A current can be chopped with an electromagnetic vibrator having contacts on its moving armature. A current can also be chopped electronically by passing it through a multivibrator or other switching circuit. Chopping is generally used to change a direct-current signal into an alternating-current signal that can more readily be amplified. Control systems for guided missiles make extensive use of chopping. *See* MULTIVIBRATOR.

Chopping has been increasingly used inside analog integrated circuits. Solid-state switches and capacitors are used to chop operational amplifiers, greatly improving their offset voltages. Chopping is also used in analog large-scale-integrated switched-capacitor filters as a means for reducing their undesirable $1/f$ (inverse-frequency) noise. *See* AMPLIFIER; INTEGRATED CIRCUITS; OPERATIONAL AMPLIFIER; SWITCHED CAPACITOR.

Eric J. Swanson

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Chordata

The phylum of animals characterized by possession of a notochord, which includes the Cephalochordata (lancelets), Urochordata (tunicates), and Craniata (vertebrates and hagfishes). The phylum also may include the extinct Yunnanozoons and Vetulicolians. Members of the first two groups are small and strictly marine. The vertebrates include the fishes, amphibians, reptiles, birds, and mammals; they are usually free-living and are found in many environments from marine to freshwater and in almost all terrestrial biomes. Some workers include the acorn worms, pterobranchs, and graptolites (Hemichordata) as a subphylum within Chordata, but here it is considered as a separate phylum, because recent morphological and molecular data indicate these organisms are closely related to echinoderms and do not possess a notochord. However, the phylogenetic position of these animals is still controversial. *See* CEPHALOCHORDATA; HEMICHORDATA; TUNICATA; VERTEBRATA.

Characteristics. The typical chordate characteristics include a notochord, a dorsal hollow nerve cord, pharyngeal slits, and a postanal tail. All chordates are deuterostomes, and most chordates also have bilateral symmetry and a somatic arrangement that includes a head, trunk, and tail region, which they share with their common ancestor. *See* DEUTEROSTOMIA.

Notochord. The notochord arises in the chordate embryo as a slender, flexible rod filled with gelatinous cells and surrounded by a tough fibrous sheath. It contains, at least in some chordates, transverse striated muscle fibers and lies above the developing gut. The notochord persists as the axial support for the body throughout the animal's life in cephalochordates and some urochordates, but it is surrounded and gradually replaced by segmental vertebrae in the Vertebrata, starting with the early fishes.

Nerve cord. The dorsal hollow nerve cord grows from a specialized band of neurectoderm along the middorsal surface of the embryo by folding together two parallel ridges. The anterior end enlarges slightly in larval tunicates and somewhat more in lancelets, but enlarges greatly in the vertebrates to form the brain. Vertebral evolution is characterized by continual enlargement of the brain. Moreover, the amount of neurectoderm in the vertebrates is larger than that in the other two groups, and the lateral rims form the neural crests, the cells of which migrate to all parts of the embryo and develop into a number of diverse structures in the body. In the vertebrates or craniates, the brain is enclosed in the braincase or cranium, and the spinal cord is enclosed by the neural arches. *See* NERVOUS SYSTEM (VERTEBRATE).

Pharyngeal slits. Pharyngeal slits are paired slits that develop as outpocketings from the sides of the embryonic pharynx and connect the lumen of the digestive system to the external environment; they are retained as gills in all aquatic chordates. Pharyngeal slits originated as adaptatations for filter feeding but soon became the primary respiratory organ, as blood vessels line the fine filaments on the margins of each slit. Internal gills were lost with the origin of tetrapods. Larval and some adult amphibians possess external gills that are different in structure from the earliest internal gill slits. In embryonic tetrapods, the pharyngeal slits close early in ontogeny, with the pharyngeal pouches becoming the site for development of glands, such as the parathyroids, thymus, and tonsils in mammals. *See* RESPIRATORY SYSTEM.

Postanal tail. The chordate tail is part of the skeletal, muscular, and nervous system of the animal and continues posterior to the anus. It is a feature not found in any other animal group and serves to increase the force available to the organism for locomotion.

Affinities. Much controversy still exists about the origin and affinities of the chordates, although there is no question that the Hemichordata (acorn worms and pterobranchs) are closely related and part of the pharyngeal-slit filter-feeding radiation. Almost all workers agree that the Echinodermata are allied to the Chordata because of evidence ranging from embryonic development (they are both deuterostomes) to biochemical similarities, but early chordate affinities are just now coming to light. *See* ECHINODERMATA.

Evolutionary origins. With the discovery of *Yunnanozoon lividum* in China, the earliest fossil record of putative chordates now dates back to the Early Cambrian (525 million years ago). *Myllokunmingia*, from the early Cambrian Chengjiang fossil site in southwestern China, and *Pikaia*, from the Middle Cambrian Burgess Shale in Canada, are also considered to be the earliest chordates. These organisms appear to have chordate characteristics (though they are still being debated), including an impression of a notochord, segmented muscles, and what appear to be pharyngeal slits. *Pikaia* resembles the present-day lancelet or amphioxus (Cephalochordata), which burrows in shifting sands. Presumably all other chordates developed from this ancestral type, with their differing characteristics evolving because of differing habitat conditions.

There are a number of hypotheses for how chordates evolved. One theory postulates that chordates arose from an echinoderm ancestor, because they share similar embryonic developmental patterns (for example, they are both deuterostomes and exhibit similar cleavage and coelomic formation). Another hypothesis suggests that chordates have evolved from tunicate larval form; however, it is far more likely that the vertebrates descended directly from an amphioxus-like form.

What is known is that the first chordate evolved the notochord, which provided a stronger skeleton and permitted the reduction of the transverse and circular muscles. A notochord resulted in a fixed body length and the loss of peristaltic locomotion. Having a notochord for support permitted the appearance of pharyngeal slits through the lateral walls of the anterior parts of the body, which served for increased filter feeding and subsequently for respiration. The presence of the notochord also permitted the appearance of a postanal tail and increased force for locomotion. The dorsal longitudinal muscles enlarged, and with this modification came the evolution of the dorsal hollow nerve cord (dorsal because of closer proximity with the major muscle masses).

Tunicates (Urochordata) are either sessile organisms that live on hard substrates (Class Ascidiacea) or are planktonic (Class Thaliacea and Class Larvacea). Ascidians and thaliaceans have lost the notochord feature in the metamorphosed adult but retain the pharyngeal gill slits and an endostyle (a glandular ciliated groove along the ventral side of the pharynx). Larvae of all tunicate groups (and adult larvacians) have retained the ancestral chordate features (gill slits and notochord).

The most recently evolved group was the Vertebrata, which are presumed to have left the oceans to invade freshwaters and then the land. They retained the full set of chordate features but had to evolve several additional ones. Size and swimming ability increased to swim upstream against the currents. Because of an increased inward flow of water across the body surface, the problem of water balance was solved when the kidneys, with the nephron as the basic unit, evolved to rid the body of excess water. Finally, dermal bone evolved as armored protection against predators. Embryological development of the nerve cord also changed with the appearance of the neural crest, a unique vertebrate feature that is involved in the development of bony scales, teeth, gill bars, pigment cells, and several parts of the nervous system. *See* AMPHIBIANS; ANIMAL KINGDOM; AVES; MAMMALIA; REPTILIA. Walter J. Bock

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Chorion

The outermost of the several extraembryonic membranes in amniotes (reptiles, birds, and mammals) enclosing the embryo and all of its other membranes. The chorion, or serosa, is composed of an outer layer of ectodermal cells and an inner layer of mesodermal cells, collectively the somatopleure. Both layers are continuous with the corresponding tissue of the embryo. The chorion arises in conjunction with the amnion, another membrane that forms the outer limb of the somatopleure which folds up over the embryo in reptiles, birds, and some mammals. The chorion is separated from the amnion and yolk sac by a fluid-filled space, the extraembryonic coelom, or body cavity. In those mammals in which the amnion forms by a process of cavitation in a mass of cells, instead of by folding, the chorion forms directly from the trophoblastic capsule, the extraembryonic ectoderm, which becomes gradually underlain by extraembryonic mesoderm.

In reptiles and birds the chorion fuses with another extraembryonic membrane, the allantois, to form the chorioallantois, which lies directly below the shell membranes. An extensive system of blood vessels develops in the mesoderm of this compound membrane which serves as the primary respiratory and excretory organ for gaseous interchanges. In all mammals above the marsupials, the chorion develops special fingerlike processes (chorionic villi) extending outward from its surface. To a varying degree in different species of mammals, the villous regions of the chorion come into more or less intimate contact with the uterine mucosa, or uterine lining, of the mother, thereby forming the various placental types. *See* ALLANTOIS; AMNIOTA; FETAL MEMBRANE; GERM LAYERS. Nelson T. Spratt, Jr.

Chromadorida

An order of nematodes in which the amphid manifestation is variable but within superfamilies some constancy is apparent. The various amphids are reniform, transverse elongate loops, simple spirals, or multiple spirals not seen in any other orders or subclasses. The cephalic sensilla are in one or two whorls at the extreme anterior. In all taxa the cuticle shows some form of ornamentation, usually punctations that are apparent whether the cuticle is smooth or annulated. When developed, the stoma is primarily esophastome and is usually armed with a dorsal tooth, jaws, or protrusible rugae. The corpus of the esophagus is cylindrical; the isthmus is not seen; and the postcorpus, in which the heavily cuticularized lumen forms the cresentic valve, is distinctly expanded. The esophagointestinal valve is triradiate or flattened. The females usually have paired reflexed ovaries.

There are four chromadorid superfamilies: Choanolaimoidea, Chromadoroidea, Comesomatoidea, and Cyatholaimoidea. Choanolaimoidea is distinguished by a complex stoma in two parts. The group occupies marine habitats; some species are predaceous, but for many the feeding habits are unknown. Chromadoroidea comprises small to moderate-sized free-living forms that are mainly marine but are also found in fresh water and soil. Known species either are associated with algal substrates or are nonselective deposit feeders in soft-bottom sediments. Comesomatoidea, containing only one family, the Comesomatidae, is found in marine habitats, but the feeding habits are unknown. Cyatholaimoidea is found in marine, terrestrial, and fresh-water environments. *See* NEMATA.

Armand R. Maggenti

Chromatic aberration

The type of error in an optical system in which the formation of a series of colored images occurs, even though only white light enters the system. Chromatic aberrations are caused by the fact that the refraction law determining the path of light through an optical system contains the refractive index n, which is a function of wavelength λ. Thus the image position and the magnification of an optical system are not necessarily the same for all wavelengths, nor are the aberrations the same for all wavelengths.

In this article the chromatic aberrations of a lens system are discussed. For information on other types of aberration *see* ABERRATION (OPTICS); REFRACTION OF WAVES.

Dispersion formula. When the refractive index of glass or other transparent material is plotted as a function of the square of the wavelength, the result is a set of dispersion curves which appear to have an asymptote in the near-ultraviolet region and a straight portion in the near-infrared (up to 1 micrometer). In the glass catalogs the indices are given for selected wavelengths between 0.365 and 1.01 μm, which are the absorption (emission) bands of certain chemical elements. For an extended discussion of dispersion *see* ABSORPTION OF ELECTROMAGNETIC RADIATION; DISPERSION (RADIATION); OPTICAL MATERIALS.

For the visible region, the Hartmann formula, Eq. (1), where a and b are constants for a given glass,

$$n = a/(\lambda - b) \tag{1}$$

has been much used. However, if an attempt is made to apply it to the near-ultraviolet or the near-infrared, it proves to be insufficient. Over this more extended range, n can be given as a function of the wavelength by Eq. (2).

$$n = a + b\lambda^2 + \frac{c}{\lambda^2 - 0.028} + \frac{d}{(\lambda^2 - 0.028)^2} \tag{2}$$

Values of the four universal functions $a(\lambda)$ for various wavelengths

λ	a_1	a_2	a_3	a_4
1.0140	0.000000	0.000000	0.000000	+1.000000
0.7682	+0.031555	−0.276197	+1.051955	+0.192687
0.6563	0.000000	0.000000	+1.000000	0.000000
0.6438	−0.004774	+0.051075	+0.966511	−0.012813
0.5893	−0.024952	+0.326272	+0.744598	−0.045919
0.5876	−0.025492	+0.336338	+0.735480	−0.046326
0.5461	−0.033080	+0.597795	+0.479049	−0.043764
0.4861	0.000000	+1.000000	0.000000	0.000000
0.4800	+0.009340	+1.036699	−0.052699	+0.006659
0.4358	+0.143980	+1.193553	−0.394569	+0.057036
0.4047	+0.366779	+1.045064	−0.487634	+0.075791
0.3650	+1.000000	0.000000	0.000000	0.000000

This formula, in which c and d are additional constants, enables one to compute n for any wavelength if it is given for four. An equivalent formula is shown by Eq. (3), where $a_1(\lambda)$, $a_2(\lambda)$, ... are functions of

$$n = n_1 a_1(\lambda) + n_2 a_2(\lambda) + n_3 a_3(\lambda) + n_4 a_4(\lambda) \tag{3}$$

the form of Eq. (2), which assume for $\lambda_1, \lambda_2, \ldots$ the values 1, 0, 0, 0; 0, 1, 0, 0; 0, 0, 1, 0; and 0, 0, 0, 1, respectively. Choosing $\lambda_1 = 0.365 = \lambda^{**}$, $\lambda_2 = 0.4861 = \lambda_F$, $\lambda_3 = 0.6563 = \lambda_C$, $\lambda_4 = 1.014 = \lambda^*$, one finds in the **table** the four universal functions $a(\lambda)$ tabulated for different values of λ. Note that for any wavelength Eq. (4) holds.

$$a_1 + a_2 + a_3 + a_4 = 1 \tag{4}$$

Instead of giving the indices of a glass for the wavelengths specified, one can specify the glass by the refractive index n_F at one wavelength F, the dispersion $\delta = n_F - n_C$, and the partial dispersions in the ultraviolet and infrared, defined respectively by Eqs. (5).

$$P^{**} = \frac{n^{**} - n_F}{n_F - n_C} \qquad P^{*} = \frac{n_F - n^{*}}{n_F - n_C} \tag{5}$$

The partial dispersion for an arbitrary wavelength λ is then given by Eq. (6).

$$P = P^{**} a_1(\lambda) + a_2(\lambda) + P^{*} a_4(\lambda) \tag{6}$$

In the literature the Abbe number, defined by Eq. (7), where n_D is the mean index for the D lines of

$$\nu = (n_D - 1)/(n_F - n_C) \tag{7}$$

sodium, is frequently used to designate optical glass.

In **Fig. 1**, $(n_F - 1)$ is shown plotted against $(n_F - n_C)$ for various optical materials. One sees that in this kind of plot glasses of the same type lie on a straight line, while on the ordinary plot of n_D versus ν they lie on hyperbolas.

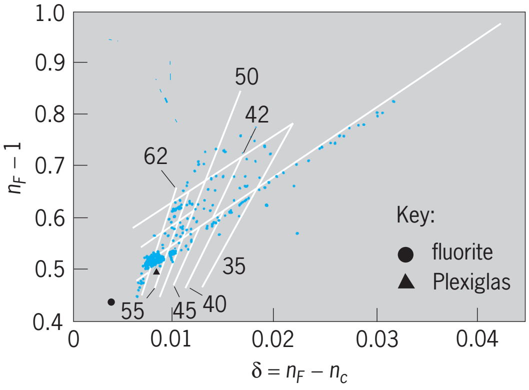

Fig. 1. Plot of (n_F − 1) versus δ for selected glasses and for fluorite and Plexiglas. The numbers on the lines dividing the glasses into groups represent ν values.

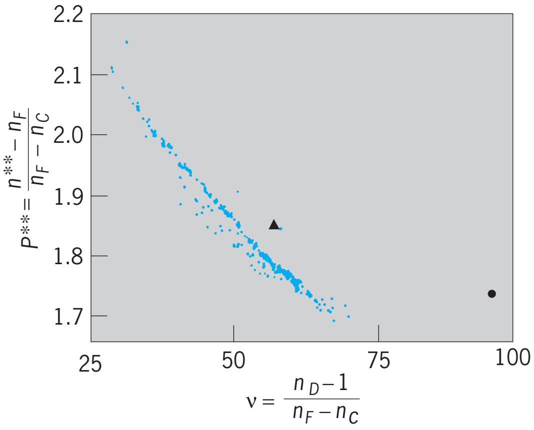

Fig. 2. Plot of P^{**} versus ν for materials of Fig. 1.

Color correction. A system of thin lenses in contact is corrected for two wavelengths λ_A and λ_B if the power of the combination is the same for both wavelengths as in Eq. (8), where the K_κ's are the dif-ference s between the first and last curvatures of the lenses, and the summation is over all the lenses, each with its particular value of n_A, n_B, and K_κ. Two cemented lenses are corrected for wavelengths C and F, for instance, if Eqs. (9) hold.

$$\phi_A = \phi_B = \Sigma(n_A - 1)K_k = \Sigma(n_B - 1)K_k \tag{8}$$

$$\begin{aligned} \phi_1 + \phi_2 &= \phi \\ \phi_1/\nu_1 + \phi_2/\nu_2 &= \phi_C - \phi_F = 0 \end{aligned} \tag{9}$$

See LENS (OPTICS).

The two lenses are also corrected for a third wavelength if and only if, in addition, one has $P_1 = P_2$, where P_1 and P_2 are given by Eq. (6).

A system corrected for three colors is called an apochromat (in microscopy this term traditionally demands freedom from asymmetry in addition). An apochromat for the ultraviolet portion of the spectrum is possible only if the two glasses in **Fig. 2** have the same P^{**} value. For the infrared, the glasses must have the same P^* value (**Fig. 3**). The $\nu - 1$ values for the two glasses should lie as far apart as possible to give low values for the powers.

Three lenses can be corrected for four wavelengths and therefore practically for the whole spectrum if the glasses lie on the straight line on the plot of P^{**} against P^* (**Fig. 4**). Such a system may be called a superachromat.

In lenses with finite thicknesses and distances, there are in gaussian optics two errors to be corrected. One is a longitudinal aberration, which means that the gaussian images do not lie in the same plane, and the other is a lateral aberration, which means that the images in different colors have different magnifications.

In the presence of longitudinal aberration, it is best to balance the lateral aberration so that the apparent sizes of the images as seen from the exit pupil coincide.

A system of two uncorrected lenses, such as a simple ocular, with one finite distance, cannot be corrected for both color errors. Two finite distances are needed to balance both color errors at the same time.

In a general system, all image errors are functions of the wavelength of light. However, in a lens system corrected for color, it is easily possible, with a small adjustment, to balance the correction of the aperture rays (spherical aberration) with respect to

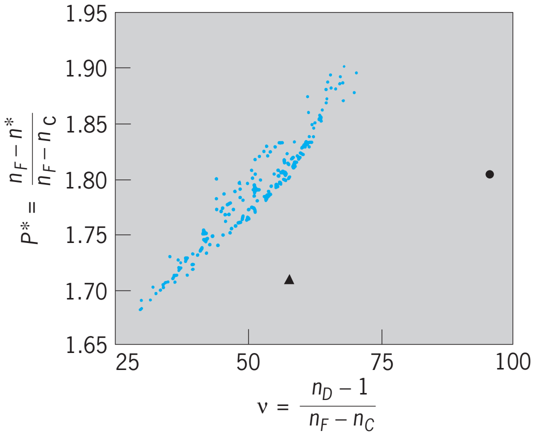

Fig. 3. Plot of P^* versus ν for materials of Fig. 1.

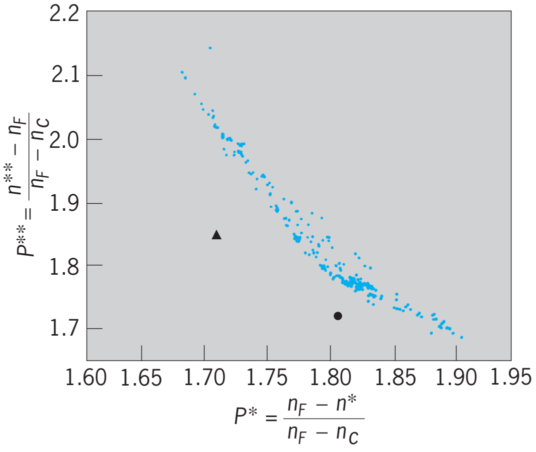

Fig. 4. Plot of P^{**} versus P^* for materials of Fig. 1.

color by introducing a small amount of lateral color aberration.

If only two colors can be corrected, the choice of the colors depends on the wavelength sensitivity of the receiving instrument. For visual correction, the values for *C* and *F* are frequently brought together. Some optical systems contain filters to permit only a narrow spectral band to pass the instrument. This makes correction for color errors easier.

If light of a large band of wavelengths traverses the instrument, it is frequently desirable to use catadioptric systems, such as the Schmidt camera. The mirror or mirrors of these systems are used to obtain the necessary power without introducing color errors, and an afocal lens system can be added to correct monochromatic aberrations. *See* SCHMIDT CAMERA.

Max Herzberger

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Chromatography

A physical method of separation in which the components of a mixture of substances are separated from each other by differences in their distribution between two phases, one (stationary phase) is stationary and the other (mobile phase) moves through the stationary phase in a definite direction. The substances must interact with the stationary phase to be retained and separated by it.

Retention and separation. Retention results from a combination of reversible physical interactions that can be characterized as adsorption at a surface, absorption in an immobilized solvent layer, and electrostatic interactions between ions. When the stationary phase is a porous medium, accessibility to its regions may be restricted and a separation can result from size differences between the sample components. More than one interaction may contribute simultaneously to a separation mechanism. The general requirements are that all interactions must be reversible, and that the two phases can be separated (two immiscible liquids, a gas and a solid, and so forth) in such a way that a distribution of sample components between phases and mass transport by one phase can be established. *See* ABSORPTION; ADSORPTION.

Reversibility of the interactions can be achieved by purely physical means, such as by a change in temperature or by competition; the latter condition is achieved by introducing substances into the mobile phase that have suitable properties to ensure reversibility for the interactions responsible for retention of the sample components. Since this competition with the sample components is itself selective, it provides a general approach to adjusting the outcome of a chromatographic experiment to obtain a desired separation. It is an absolute requirement that a difference in the distribution constants for the sample components in the chromatographic system exist for a separation to be possible.

Methods. A distinction between the principal chromatographic methods can be made in terms of the properties of the mobile phase and configuration of the stationary phase. In gas chromatography the mobile phase is an inert gas, in supercritical fluid chromatography the mobile phase is a fluid (dense gas above its critical pressure and temperature), and in liquid chromatography the mobile phase is a low-viscosity liquid. The stationary phase can be a porous, granular powder with a narrow particle-size distribution packed into a tube (called a column) as a dense homogeneous bed. This configuration is referred to as a packed column and is nearly always used in liquid and supercritical fluid chromatography, and is sometimes used in gas chromatography. Alternatively, the stationary phase can be distributed as a thin film or layer on the wall of an open tube of capillary dimensions, leaving an open space through the center of the column. This configuration is referred to as an open tubular column (or incorrectly as a capillary column); it is commonly used in gas chromatography, but rarely used in supercritical fluid or liquid chromatography.

Thin-layer chromatography is a form of liquid chromatography in which the stationary phase is spread as a thin layer over the surface of a glass or plastic supporting structure. The stationary phase must be immobilized on the support by using a binder to impart the desired mechanical strength and stability to the layer. The samples are applied to the layer as spots or bands near the bottom edge of the plate. The separation is achieved by contacting the bottom edge of the plate below the line of samples with the mobile phase, which proceeds to ascend the layer by capillary action. This process is called development and is performed in a chamber, with the lower edge of the layer in contact with the mobile phase and the remaining portion of the layer in contact with solvent vapors from the mobile phase. The chamber may be a simple device such as a covered jar or beaker or a more elaborate device providing control of the mobile-phase velocity and elimination or control of the vapor phase. Thin-layer chromatography is the most popular form of planar chromatography having virtually replaced paper chromatography in laboratory practice. *See* GAS CHROMATOGRAPHY; GEL PERMEATION CHROMATOGRAPHY; LIQUID CHROMATOGRAPHY; SUPERCRITICAL-FLUID CHROMATOGRAPHY.

Uses. Chromatographic methods provide a means of analyzing samples (to determine component identity and relative amount), isolating significant quantities of purified material for further experimentation or commerce, and determining fundamental physical properties of either the samples or the mobile or stationary phases (for example, diffusion coefficients, partition coefficients, or thermodynamic properties). There are virtually no boundaries to the sample types that can be separated. Examples include organic and inorganic compounds in the form of fixed gases, ions, polymers, as well as other species. Applications are found in all areas of science and technology, making chromatography one of the most widely used laboratory procedures in chemistry. Depending on intent, chromatography can be applied to trace quantities at about the limit of detector response (for example, 10^{-15} g) or to kilogram amounts in preparative separations.

Instrumentation. Modern chromatographic methods are instrumental techniques in which the optimal conditions for the separation are set and varied by electromechanical devices external to the column or layer. Separations are largely automated, with important features of the instrumentation being control of the flow and composition of the mobile phase, introduction of the sample onto the stationary phase, and online detection of the separated components. In column chromatography, the sample components are detected in the presence of the mobile phase after they have exited the stationary phase. In thin-layer chromatography, the sample components are detected in the presence of the stationary phase, resulting in different detection strategies.

Instrument requirements differ by the needs of the method used. Gas chromatography uses a mobile phase of constant composition at a few atmospheres of column inlet pressure and variation in the temperature of the column to effect a separation. Liquid chromatography uses a pump to select or vary the composition of the mobile phase with a high column inlet pressure (typically a few hundred atmospheres) and a constant temperature for the separation. These differences in optimized separation conditions result in different equipment configurations for each chromatographic method.

Interpretation. The results of a chromatographic experiment are summarized in a chromatogram (**Fig. 1**), a two-dimensional record of the detected response to the sample components (*y* axis) plotted against the residence time of the components in column chromatography or migration distance in planar chromatography (*x* axis). Individual compounds or mixtures of unseparated compounds appear as peaks in the chromatogram. These peaks are ideally symmetrical and occur at positions in the chromatogram that are characteristic of their identity, with a distribution around the mean position (apex of the peak) that is characteristic of the kinetic properties of the chromatographic system. The area inscribed by the peak is proportional to the amount of substance separated in the chromatographic system.

Information readily extracted from the chromatogram includes an indication of sample complexity (the number of observed peaks), qualitative substance identification (determined by peak position), relative composition of the sample (peak dimensions; area or height), and a summary of the kinetic characteristics of the chromatographic system (peak shapes).

There is a synergistic relationship between the peak profiles and the properties of the detector. The detector may have an approximately equal response to all substances, in which case the peak sizes are roughly equal to their relative concentration in the sample; or the detector may have a selective response to some property of the sample components, such as a particular chromophore or the presence of a particular element, in which case the peak sizes have to be interpreted with respect to prior knowledge of the way a particular compound responds to the detector. This is also a useful feature, because the information in the chromatogram can be edited to suit an individual application. For example, the determination of organophosphorus pesticides in environmental samples by gas chromatography can be made with a detector that responds selectively to phosphorus, so that the information contained in the chromatogram is limited to the number of phosphorus-containing compounds in the sample and is easier to interpret than a chromatogram in which all compounds present in the sample are revealed by the detector.

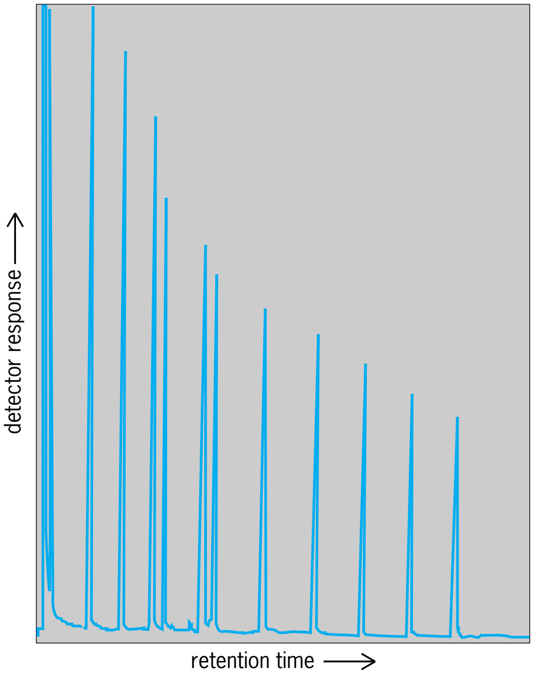

Fig. 1. Typical chromatogram obtained by gas chromatography.

Quality of separation. The object of a chromatographic separation is to obtain a minimum acceptable separation (resolution) between all components of interest in a sample within the shortest possible time. The resolution between two peaks in a chromatogram depends on how well the peak maxima are separated and how wide the two peaks are. This can be expressed numerically, at least for peaks of approximately equal height, by the ratio of the separation of the two peak maxima divided by the average peak widths at their base. When two peaks are separated such that they are just touching at their base, the value calculated for their resolution is 1.5; for difficult-to-separate samples a lower resolution value of 1.0, representing 94% peak separation (6% of the peak areas overlap), is an adequate goal for identification and quantification based on the characteristic shape of the individual peaks. Resolution is also simply related to the properties of the chromatographic system by the equation below,

$$R_s = \frac{N^{1/2}}{4}\,\frac{\alpha - 1}{\alpha}\,\frac{k_2}{1 + k_2}$$

where R_s is the observed resolution, N is the column efficiency measured as the plate number, α is the separation factor (a measure of the relative peak maxima positions; $\alpha = k_2/k_1$), k is the retention factor (the ratio of the time a substance spends in the stationary and mobile phases), and the subscripts 1 and 2 refer to the peak order (peak 2 emerges from the column after peak 1). The equation is derived with the assumption that the average of the two peak widths is identical to the peak width of the second peak, generally a reasonable assumption for peaks that are close to each other in the chromatogram. To a first approximation, the three terms in the equation can be treated as independent variables and optimized separately to obtain a desired separation in the chromatogram.

Efficiency. The efficiency of a chromatographic system is expressed as the plate number. This terminology was adopted from the application of the theory of fractional distillation columns to gas chromatography when this technique was introduced. The term has remained in use, although any analogies between chromatography and fractional distillation are inappropriate and the concept of a theoretical plate has no physical meaning as presently used in chromatography. From a mathematical perspective, efficiency is a characteristic property of the extent of peak dispersion that occurs during the time a compound is resident in the chromatographic system.

Systems with large numerical values for their efficiency are preferred to optimize resolution. Since the resolution is proportional to $N^{1/2}$, unless N can be increased by large increments only small changes in resolution will be obtained. The numerical value for N is governed by kinetic factors that control peak broadening (N affects only peak widths and not peak positions). The chromatographic system should be optimized to minimize peak broadening, leading to better separations. All things being equal, N could never be too large, and chromatographic systems with intrinsically large values of N are desirable. The corollary is also true that systems with intrinsically small values of N are undesirable and diminish the prospects of achieving a desired separation unless other factors in the chromatographic system can be adjusted to compensate for the poor kinetic performance of the column (**Fig. 2***a*).

The rate theory of peak broadening recognizes three processes that contribute to peak widths beyond purely instrumental contributions: (1) resistance to mass transfer between phases prevents instantaneous equilibrium within the chromatographic system; (2) flow anisotropy in packed beds results from variations in the flow characteristics of the bed in regions of unequal packing density; (3) longitudinal diffusion is the natural consequence of molecular diffusion along the axis of migration of the mobile phase. The purpose of column design is to minimize these contributions to peak broadening to achieve the most favorable value of N. The optimum column design is different for each chromatographic method, although it can be easily predicted from the characteristic properties of the chromatographic system and the desired operating conditions (see **table**).

Resistance to mass transfer is often the major cause of peak dispersion in chromatography, and it is related to the absolute magnitude and the relative magnitude of the solute diffusion coefficients in the mobile and stationary phases, and the fact that the relative velocity of the mobile phase is significant on the time scale for these other processes. Resistance to mass transfer, therefore, prevents true equilibrium from being established in the chromatographic system, resulting in additional peak dispersion from that predicted from an equilibrium model.

In gas chromatography, the rate of radial diffusion defines the useful range of column radii for open

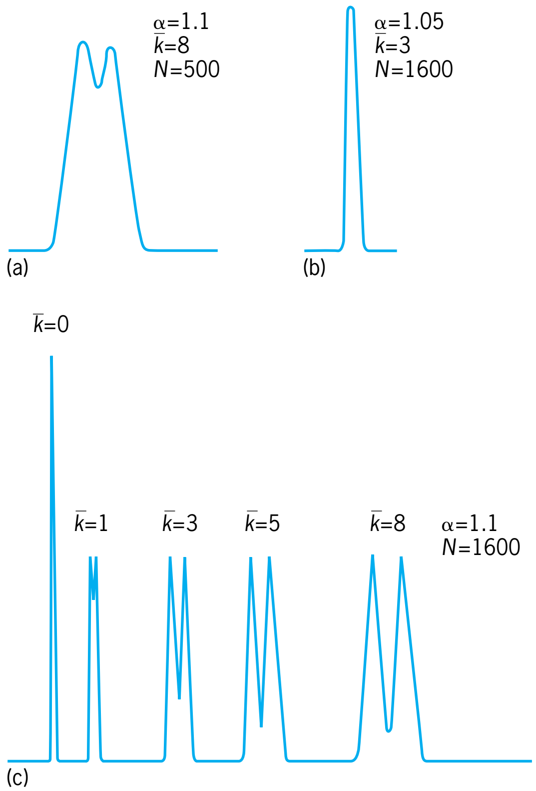

Fig. 2. Observed changes in resolution in a two-component separation for different values of the separation factor, average retention factor, or plate number. (*a*) Viewed vertically, this chromatogram indicates the change in resolution at the same average retention factor and separation factor values when the plate number is varied. (*b*) Viewed vertically, this chromatogram indicates the relationship between resolution and changes in the separation factor with the same plate number and average retention factor value. (*c*) Viewed horizontally, this chromatogram illustrates the change in resolution as the average retention factor is varied with the same value for the separation factor and plate number. (*After P. J. Schoenmakers, Optimization of Chromatographic Selectivity, Elsevier, 1986*)

Approximate values of characteristic parameters in predicting peak broadening

Parameter	Gas	Supercritical fluid	Liquid
Diffusion coefficient (m^2/s)	10^{-1}	10^{-4} to 10^{-3}	10^{-5}
Density (g/cm^3)	10^{-3}	0.3–0.8	1
Viscosity (poise)	10^{-4}	10^{-4} to 10^{-3}	10^{-2}
Column length (m): packed	1–5	0.1–1.0	0.05–1.0
open tubular	10–100	5–25	
Column diameter (mm), open tubular	0.1–0.7	0.02–0.1	
Average particle diameter (μm)	100–200	3–10	3–10
Column inlet pressure (atm)	<10	<600	<400
Efficiency (N): packed	10^3 to 10^4	10^4 to 8×10^4	5×10^3 to 5×10^4
open tubular	10^4–10^6	10^4–10^5	

tubular columns, and the difference in diffusion processes between the mobile and stationary phases dictates that the liquid stationary-phase film should be thin compared to the dimensions of the column radius. High efficiency in gas chromatography can be obtained with open tubular columns of 0.1–0.5 mm diameter, liquid films of 0.1–2.0 micrometer thickness, and column lengths of 5–100 m or more. Open tubular columns of these dimensions offer little flow resistance, and since gases have low viscosities, long columns are practically feasible and compatible with the low operating pressures favored in modern instrument design. Packed columns provide lower efficiencies, since long columns have undesirably high column inlet pressure requirements and the column packing structure results in peak broadening from flow anisotropy, which is unimportant for open tubular columns.

The mobile-phase diffusion coefficients are less favorable in supercritical fluids and liquids than they are for gases. To minimize the contribution of radial mass transfer to peak broadening, the dimensions of an open tube must be reduced proportionately, requiring columns with internal diameters less than 0.10 mm. Small column diameters present significant problems in column preparation and instrument design. These are difficult but possible to achieve for supercritical fluids, but cause exceptional problems in liquid chromatography. Packed columns are invariably used in the practice of supercritical fluid and liquid chromatography. To minimize flow anisotropy and stationary-phase mass-transfer contributions to peak broadening, the columns must have homogeneously packed beds of small particles with a narrow average particle diameter (3–10 μm); the total column length, and therefore the maximum plate number, is limited by the viscosity of the mobile phase and the available column operating pressure (see table). These same restrictions apply to supercritical fluids; however, since their characteristic physical properties are more favorable than those for liquids, supercritical fluids are capable of more efficient separations (larger value for N) than can be obtained in liquid chromatography. Thus, it is generally feasible to optimize resolution through varying N only in gas chromatography and in a more limited way in supercritical fluid chromatography. For liquid chromatography, the largest practical value for N is used for the separation, and the other parameters in the equation are varied to improve resolution. *See* SUPERCRITICAL FLUID.

Selectivity. The separation factor α in the equation is determined by the difference in the distribution coefficients for the two peaks, which is responsible for their relative positions in the chromatogram. Thus, it is the thermodynamic properties of the system that are responsible for the mechanism by which the two components are selectively recognized and therefore retained to different extents. Numerical analysis of the term selectivity reveals its critical importance to obtaining a desired separation. First of all, a separation can result only when α has a value greater than 1.0 ($\alpha = 1$ corresponds to the observed resolution $R_s = 0$), but only a relatively small increase in the value of α close to its minimum value considerably increases the possibility of obtaining a separation (Fig. 2*b*).

In gas chromatography, the mobile phase behaves essentially as an ideal gas and does not contribute to the selectivity of the system. To vary α, a new stationary phase (column) must be selected or the temperature of the system varied. In liquid chromatography, there is a high level of flexibility gained by being able to easily modify the properties of the mobile phase, as well as the possibility of exploiting retention mechanisms that are not available in gas chromatography. These factors account for its widespread use. The properties of the mobile phase are easily varied by changing either the identity or composition of the mobile phase from the wide range of solvents available, or by using additives in the mobile phase to change the properties of individual sample components (for example, buffers, complexing agents, and micelles), as well as by changing the type of stationary phase (column) used for the separation.

In practice, gas chromatography and liquid chromatography should be considered as complementary techniques. Separations by gas chromatography are restricted to thermally stable compounds with significant vapor pressure at the temperatures required for their separation. The upper temperature limit for common stationary phases is in the range 200–400°C (390–750°F). Few compounds with a molecular weight above 1000 have sufficient vapor pressure to be separated in this temperature range, and many low-molecular-weight compounds are known to be labile at temperatures required for their vaporization.

The only requirement for separation by liquid chromatography is that the sample has sufficient solubility in an available solvent whose properties are suitable for the separation. This criterion is much easier to meet in general and results in many of the applications for liquid chromatography as being those for which gas chromatography is unsuitable. Included are applications to high-molecular-weight synthetic polymers, biopolymers, ionic compounds, and many thermally labile polar compounds of chemical interest.

Supercritical fluids have solvating properties that are intermediate between those of gases and liquids. Liquids are virtually incompressible under the conditions used in liquid chromatography, so their capacity for intermolecular interactions is fixed. By contrast, fluids are highly compressible, and their density, which is proportional to their solvating capacity, can be varied over a wide range by simply changing the operating pressure or temperature of the column. This feature is unique to supercritical fluid chromatography, and it is the principal method of varying the separation factor α. The most common mobile phase is carbon dioxide, a relatively nonpolar fluid. More polar fluids, such as water, ammonia, or methanol, tend to have unfavorable critical constants or are highly corrosive to columns and instrument components, limiting their use. Mixed mobile phases, such as carbon dioxide–methanol mixtures, can be used to vary the selectivity but miscibility problems and high critical constants for the mixed mobile phases may restrict the range of properties available for experimentation. Supercritical fluid chromatography can provide faster and more efficient separations than liquid chromatography, but it is more restricted than liquid chromatography in the choice of mobile phases and retention mechanisms to vary the selectivity. However, it finds applications in many areas where the results from gas and liquid chromatography are unsatisfactory. Examples are the separations of low-molecular-weight organic polymers, fats and oils, and enantiomers. *See* CHEMICAL SEPARATION TECHNIQUES.

Separation time. The retention factor k in the equation represents the compromise between the need for retention to achieve resolution and the overall separation time. Numerical evaluation of this term indicates that a minimum value of k is required to obtain close-to-maximum resolution in the chromatographic system, but larger values of k do not increase this resolution significantly and lead to unfavorable separation times (Fig. 2*c*). The most difficult components to separate in a mixture will ideally have k values between 1 and 3, while k values greater than 10–20 have little further influence on resolution. Increasing the residence time of substances in a chromatographic system beyond a certain point does not contribute to their further separation. In practice, larger values than the optimum values may be required to provide sufficient space to fit all the components of a complex mixture into the chromatogram.

Planar chromatography. The separation mechanisms for thin-layer and column liquid chromatography are essentially the same. However, the two processes differ in that in column liquid chromatography all substances migrate the same distance and become separated in time, while in thin-layer chromatography all substances have the same separation time and are separated in space. In column liquid chromatography, the mobile phase moves through the column at a constant velocity, while in thin-layer chromatography its velocity is usually controlled by capillary forces and declines with distance from the solvent entry position. These forces are generally too weak to achieve the optimum velocity required to minimize zone broadening. Compared to a constant mobile-phase velocity, longer separation times and a reduced separation potential result. The useful development distance for a separation is restricted, since eventually the mobile-phase velocity becomes so low that zones begin to broaden faster than their centers are moving apart. The optimum development length depends on properties of the mobile and stationary phases, particularly the average particle size of the layer; and it is typically between 5 and 15 cm for commercially available materials.

A general discussion of zone broadening in thin-layer chromatography is inherently more complex than in column liquid chromatography for reasons which relate to both the practice of the technique and the limitations of subsequent theoretical treatments. Because substances are separated in space, individual zones experience only those theoretical plates through which they travel; and therefore the efficiency N is a function of the migration distance of the substance in the chromatogram. The migration of individual zones occurs across several regions of different local velocity and can be represented only by some average value that is difficult to determine. In practice, when the mobile-phase velocity is controlled by capillary forces, the major contribution to zone broadening is longitudinal diffusion supplemented by a smaller contribution from flow anisotropy. Separations in thin-layer chromatography occur with a plate number of 0–5000, depending on migration distance, and with a capacity for baseline resolved peaks of about 10–14 in the chromatogram.

The general variation of resolution with migration distance is more complex than for column liquid chromatography and is approximately represented by a special curve (**Fig. 3**). The fundamental parameter used to characterize the position of a sample zone in a thin-layer chromatogram is the retardation factor, or R_f value. It represents the ratio of the distance migrated by the sample to the distance traveled by the solvent front in the same time. The boundary conditions for R_f values are $1 \geq R_f \geq 0$ (Fig. 3). There is no separation possible for substances that do not migrate from their origin ($R_f = 0$) or do not interact with the stationary phase and move with the solvent front ($R_f = 1$). A maximum in the resolution of two closely spaced peaks is observed at an R_f of about 0.3, but the resolution does not vary much in the range $R_f = 0.2$–0.5, which is the optimum region in which to obtain a separation. When the difference in R_f values for two substances exceeds 0.1,

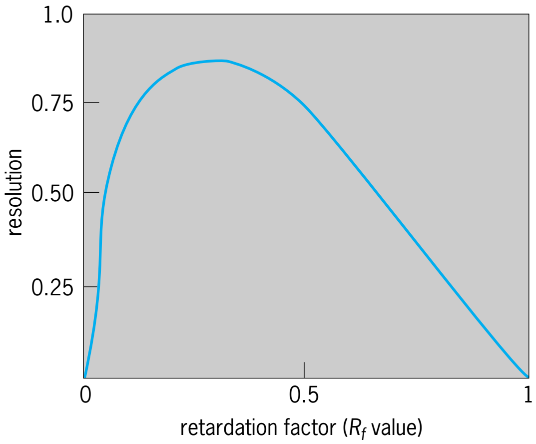

Fig. 3. Variation of resolution of two closely migrating zones as a function of the R_f value of the faster moving zone. (*After C. F. Poole and S. K. Poole, Chromatography Today, Elsevier, 1991*)

separations are easy to achieve; for R_f values less than 0.05, a separation is very difficult or impossible to achieve because of an inadequate range of efficiency values. Therefore, selective separation systems are required.

A common method of improving the separation potential of thin-layer chromatography is to increase the number of development steps used for the separation. This process is known as multiple development. A reduction in zone dimensions is achieved by a refocusing mechanism that is well understood from a phenomenological perspective but is difficult to characterize quantitatively. At the start of each development, the solvent front contacts the bottom portion of the zone first, and this region of the zone starts moving forward before the more distant regions of the zone still ahead of the solvent front. The result is a compression of the sample zone such that its width is reduced in size compared to zones migrated the same distance in a single development. This process can be automated so that a large number of developments can be used in an individual separation, resulting in a peak capacity for baseline resolved peaks of about 25–40, a considerable increase over the separation capacity obtained by using a single development.

The ultimate separation capacity of column liquid chromatography is greater than that of thin-layer chromatography. However, for simple separations where a high sample throughput is required, where crude samples are to be analyzed with minimum sample preparation, and where chemical reactions are to be used for detection, thin-layer chromatography is often preferred to column liquid chromatography. The reasons are that the stationary phase is not reused and multiple samples can be separated in parallel lanes in contrast to the single-sample sequential separations characteristic of column chromatography. After the separation, the components are immobilized on the stationary phase and can be treated with chemical reagents to change their detection properties without time constraints. The types of samples that are suitable for analysis by thin-layer chromatography are the same as those normally separated by column liquid chromatography, and a choice between the two approaches is made on the basis of practical considerations such as those outlined above. *See* ANALYTICAL CHEMISTRY. Colin F. Poole

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Chromatophore

A pigmented structure found in many animals, generally in the integument. The term is usually restricted to those structures that bring about changes in color or brightness. A majority of chromatophores are single cells that are highly branched and contain pigment granules that can disperse or aggregate within the cell. However, in coleoid cephalopod mollusks (all mollusks except *Nautilus*), the chromatophores function as miniature organs, and changes in the dispersion of pigment are brought about by muscles. Although the mode of action of the two types of chromatophore is completely different, the effect is the same: pigment either is spread out over a large area of the body or is retracted into a small area.

The movement of pigment takes place in many chromatophores simultaneously, so that the effect is a change in the quality of light reflected from the surface of the animal. The color change functions as a camouflage from predator or prey, but it may also serve for regulating temperature, protecting against harmful radiation, and in some animals, signaling. Light stimulates the responses of chromatophores, and although in some species light may affect the chromatophores directly, light generally acts indirectly via the eyes and central nervous system.

Occurrence. Single-cell chromatophores are found in some annelids, in insects (migratory locusts, some grasshoppers, and stick insects), and in echinoderms (some sea urchins). They are much more conspicuous in crustaceans (shrimps and prawns), in fishes (especially in bony fish and teleosts), in anuran amphibians (frogs and toads), and in a few reptiles.

The chromatophores may be uniformly distributed in the skin (chameleons), or they may occur in patches (flounders) or lines (around the abdomen in shrimps). Chromatophores of various colors may be distributed unevenly across the body, and occur at different depths in the skin. This characteristic can be important for enhancing or suppressing colors produced in the skin by reflecting structures.

Colors produced. Chromatophores produce their colors by reflection after absorption of light. Generally, the light comes from above, but it may come from below after reflection from an underlying structure. The most common type of chromatophore contains melanin (and is, therefore, often called a melanophore), which absorbs all wavelengths so that the chromatophore appears black; other types have red (erythrophores) or yellow (xanthophores) pigments. These pigments generally derive from carotenoids in vertebrates and from ommochromes in invertebrates. It should be noted that although a chromatophore may appear red in the laboratory or in a shallow tidal pool, it will appear black at depths of 165 ft (50 m) or more, and many of the red chromatophores of marine animals may act (like the black ones) as neutral-density filters for matching background brightness rather than for providing color.

Chromatophores do not usually contain green or blue pigments. These colors are often produced structurally, by reflecting or refracting structures (iridophores, also called iridocytes). The skin of many animals contains structures known as leucophores which, being broadband reflectors, can also produce greens and blues. Chromatophores in cephalopods and amphibians often function in conjunction with iridophores and leucophores to produce beautiful and complex color patterns over the whole body.

Crustaceans and vertebrates. Chromatophores contain pigment granules that move within them, giving them an appearance that ranges from spotted to fibrous on the five-stage scale that is widely used to measure the degree of chromatophore expansion. If the pigment within the particular cell is black or brown, the integument takes on a dark appearance when most of the chromatophores are in the last stage of dispersion (stage 5). If the pigment color is yellow or cream, the animal tends to look paler if all the chromatophores are at that stage.

Shrimp or frog chromatophores respond actively to the background illumination (**Fig. 1**). After only an hour or two, changes in the state of the chromatophores become evident with the aid of a microscope. These changes are usually brought about by hormones that are released from a particular site and circulated throughout the body. In shrimp, the hormones acting on the chromatophores originate in organs located in the eyestalk and also in the central nervous system. In the frog, the hormone responsible for color change comes from the pars intermedia of the pituitary organ; it is a peptide, called melanocyte-stimulating hormone, that disperses the pigment granules, thus making the skin darker. In teleosts, the control system is more complicated because there is a second hormone, melanin-concentrating hormone from the hypothalamus, that suppresses melanocyte-stimulating hormone, causing pigment aggregation in all color classes of chromatophores, and hence paling.

In crustaceans, elasmobranch fishes, anurans, and lizards, control of the chromatophores is thought to be exclusively hormonal. Such hormonal control is true also of some teleosts; in others the control is part hormonal and part neural; while in still others control is purely neural, as in the chameleon. Where nerves are involved, the speed of the response is faster, the chromatophores responding in minutes rather than hours. *See* NEUROSECRETION.

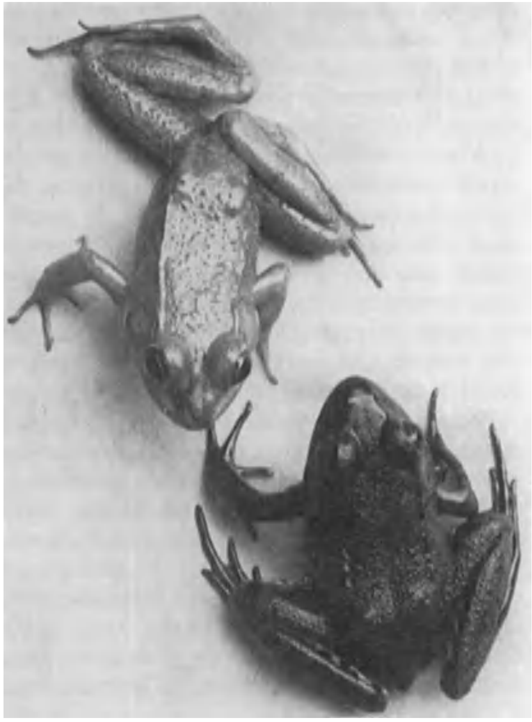

Fig. 1. Light- and dark-adapted frogs. (*After J. Pierce, J. Exp. Zool., 89:293–295, 1942*)

The chromatophores of crustaceans often have pigments of different colors, and they enable the integument to take on the background hue for concealment. When they form patterns, such as lines and bands, they may also serve to conceal the animal disruptively by breaking up the outline of the body. In fish, anurans, and reptiles, camouflage is again a major function, but in terrestrial vertebrates with chromatophores, changes in color may also serve for temperature regulation, at least when the temperature is excessively high or low. In some teleosts, neurally controlled chromatophores permit the rapid color changes that are used for social signaling, for example during sexual or territorial encounters.

Cephalopods. Each cephalopod chromatophore organ comprises an elastic sac containing pigment granules. Attached to the sac is a set of 15–25 radial muscles that are striated and contract rapidly. Associated with the radial muscles are axons from nerve cell bodies that lie within the brain. Active nerve cells cause the radial muscles to contract and the chromatophore sac expands; when the nerves are inactive, energy stored in the elastic sac causes the chromatophore to retract as the muscles relax. The chromatophores receive only nerve impulses, and there is no evidence that they are influenced by hormones.

The chromatophores are ultimately controlled by the optic lobe of the brain under the influence of the eyes. Two consequences follow from the fact that cephalopod chromatophores are under the direct control of the brain. First, color change is

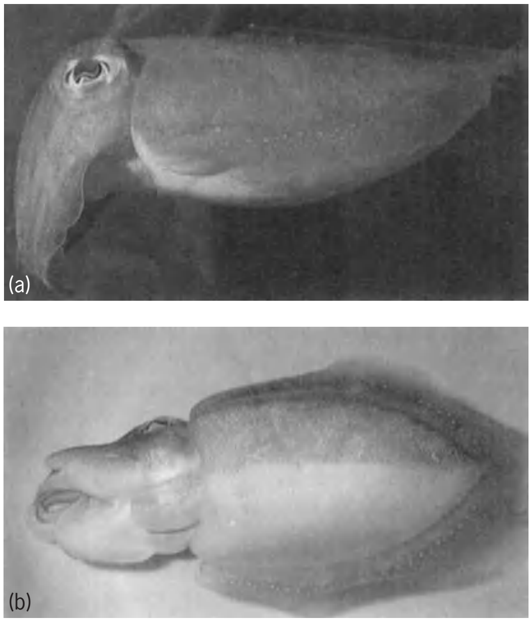

Fig. 2. Orientation of a cuttlefish. (*a*) The animal has a pale underside because all the chromatophores on the ventral mantle are retracted. (*b*) When the cuttlefish is rolled over onto its right side, the chromatophores of the upper (left) half of the ventral mantle expand to maintain the countershading.

instantaneous (an octopus can change from almost white to jet black in less than a second). Such a rapid change may cause a predator to hesitate, permitting escape; also, when the animal reaches the sea floor, it can vanish almost at once. Second, patterns can be generated in the skin in a way impossible in other animals. Thus, cephalopods can use the chromatophores not just to match the background in general color but to break up the body visually (disruptive coloration) so that the predator does not see the whole animal.

Concealment is obviously a major function. It is possible that cephalopod chromatophores evolved for purposes of camouflage after the ancestral cephalopods had abandoned the molluscan shell in the interest of speed and agility. However, because the chromatophores are neurally controlled and patterns can be produced in the skin, they can also be used for signaling. A characteristic of cephalopods is that some species make displays as conspicuous as those of fish or birds. Included are sexual signals destined for members of the same species, and warning signals, such as the large black eyespots used against predators. Signaling is especially well developed in some shallow-water forms, such as the Caribbean reef squid.

Finally, cephalopod chromatophores can be used for countershading and for maintaining countershading after disorientation. Animals that are generally illuminated from above tend to have a dark upper surface and a light lower surface, concealing them from a viewer from the side. This characteristic is true of fish and cephalopods. However, when a fish becomes momentarily disorientated and rolls over on its side, it becomes conspicuous because its countershading is fixed. When a squid rolls over, the chromatophores on the ventral surface of the body expand to maintain the countershading (**Fig. 2**). Such versatility is possible only because the chromatophores are neurally controlled. *See* PIGMENTATION; PROTECTIVE COLORATION.

J. B. Messenger

Chromium

A chemical element, Cr, atomic number 24, and atomic weight 51.996, which is the weighted average for several isotopes weighing 50 (4.31%), 52 (83.76%), 53 (9.55%), and 54 (2.38%). The orbital arrangement of the electrons is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^5$, $4s^1$. The stability of the half-filled *d* shell doubtless accounts for this rather unusual arrangement. In the crust of the Earth, chromium is the twenty-first element in abundance, which ranks it along with vanadium, zinc, nickel, and copper. Traces of chromium are present in the human body; in fact, it is essential to life. *See* PERIODIC TABLE.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H**																	2 **He**
3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
55 **Cs**	56 **Ba**	71 **Lu**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	103 **Lr**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112	113					

lanthanide series	57 **La**	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**
actinide series	89 **Ac**	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**

The element was discovered in 1797 and isolated the following year by the French chemist L. N. Vauquelin. It was named chromium because of the many colors of its compounds. It occurs in nature largely as the mineral chromite ($FeO \cdot Cr_2O_3$), which is a spinel, but the ore is usually contaminated with Al^{3+}, Fe^{3+}, Mn^{2+}, and Mg^{2+}. Smaller quantities are found as the yellow mineral crocoite ($PbCrO_4$).

As a transition metal, chromium exists in all oxidation states from 2− to 6+. The chemistry of its aqueous solutions, at least in the 3+ (chromic) state, is complicated by the fact that the compounds exist in many isomeric forms, which have quite different chemical properties.

Pure chromium metal has a bluish-white color, reflects light well, and takes a high polish. When pure, it is ductile, but even small amounts of impurities render it brittle. The metal melts at about 1900°C (3452°F) and boils at 2642°C (4788°F). Chromium shows a wide range of oxidation states; the compounds in which the metal is in a low oxidation state are powerful reducing agents, whereas those in which it shows a high oxidation state are strong oxidizing agents.

The bright color and resistance to corrosion make chromium highly desirable for plating plumbing fixtures, automobile radiators and bumpers, and other decorative pieces. Unfortunately, chrome plating is difficult and expensive. It must be done by electrolytic reduction of dichromate in sulfuric acid solution. This requires the addition of six electrons per chromium ion. This reduction does not take place in one step, but through a series of steps, most of which are not clearly understood. The current efficiency is low (maybe 12%), and the chromium plate contains microscopic cracks and other flaws, and so it does not adequately protect the metal under it from corrosion. It is customary, therefore, to first plate the object with copper, then with nickel, and finally, with chromium.

In alloys with iron, nickel, and other metals, chromium has many desirable properties. Chrome steel is hard and strong and resists corrosion to a marked degree. Stainless steel contains roughly 18% chromium and 8% nickel. Some chrome steels can be hardened by heat treatment and find use in cutlery; still others are used in jet engines. Nichrome and chromel consist largely of nickel and chromium; they have low electrical conductivity and resist corrosion, even at red heat, so they are used for heating coils in space heaters, toasters, and similar devices. Other important alloys are Hastelloy C (Cr, Mo, W, Fe, Ni), used in chemical equipment which is in contact with HCl, oxidizing acids, and hypochlorite. Stellite [Co, Cr, Ni, C, W (or Mo)], noted for its hardness and abrasion resistance at high temperatures, is used for lathes and engine valves, and Inconel (Cr, Fe, Ni) is used in heat treating and in corrosion-resistant equipment in the chemical industry. *See* ALLOY; HEAT TREATMENT (METALLURGY); STAINLESS STEEL.

Several chromium compounds are used as paint pigments—chrome oxide green (Cr_2O_3), chrome yellow ($PbCrO_4$), chrome orange ($PbCrO_4 \cdot PbO$), molybdate orange (a solution of $PbSO_4$, $PbCrO_4$, and $PbMoO_4$), chrome green (a mixture of $PbCrO_4$ and Prussian blue), and zinc yellow (potassium zinc chromate). Several of these, particularly zinc yellow, are used to inhibit corrosion. The gems ruby, emerald, and alexandrite owe their colors to traces of chromium compounds. *See* CORROSION; EMERALD; PAINT; RUBY.

Dichromates are widely used as oxidizing agents, as rust inhibitors on steel, and as wood preservatives. In the last application, they kill fungi, termites, and boring insects. The wood can still be painted and glued, and retains its strength. Other chromium compounds find use as catalysts, as drilling muds, and in photochemical reactions. The last are important in the printing industry. A metal plate is coated with a colloidal material (for example, glue, shellac, or casein) containing a dichromate. On exposure to strong light under a negative image, the dichromate is reduced to Cr^{3+}, which reacts with the colloid, hardening it and making it resistant to removal by washing. The unexposed material is washed off, and the metal plate is etched with acid to give a printing plate. *See* PRINTING.

Chromium is essential to life. A deficiency (in rats and monkeys) has been shown to impair glucose tolerance, decrease glycogen reserve, and inhibit the utilization of amino acids. It has also been found that inclusion of chromium in the diet of humans sometimes, but not always, improves glucose tolerance. Certain chromium(III) compounds enhance the action of insulin.

On the other hand, chromates and dichromates are severe irritants to the skin and mucous membranes, so workers who handle large amounts of these materials must be protected against dusts and mists. Continued breathing of the dusts finally leads to ulceration and perforation of the nasal septum. Contact of cuts or abrasions with chromate may lead to serious ulceration. Even on normal skin, dermatitis frequently results. Cases of lung cancer have been observed in plants where chromates are manufactured.

John C. Bailar, Jr.

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Chromophycota

A division of the plant kingdom (also known as Chromophyta) comprising nine classes of algae: Bacillariophyceae (diatoms), Chrysophyceae (golden or golden-brown algae), Cryptophyceae, Dinophyceae (dinoflagellates), Eustigmatophyceae, Phaeophyceae (brown algae), Prymnesiophyceae, Raphidophyceae, and Xanthophyceae (yellow-green algae). Some of these classes are closely related, while others stand so far apart that they are sometimes assigned to their own divisions. The chief unifying character is the presence of chlorophyll *c* rather than chlorophyll *b* as a complement to chlorophyll *a* (although only chlorophyll *a* is present in Eustigmatophyceae). The chloroplasts are usually brown or yellowish because of large amounts of β-carotene and various xanthophylls, many of which are restricted to one or more classes. Storage products include lipids, starch, and glucans (glucose polymers with β-1,3 linkages). In all classes except Dinophyceae, the chloroplast is surrounded by chloroplast endoplasmic reticulum that is continuous with the nuclear envelope, and the deoxyribonucleic acid of the chloroplast forms an annular genophore. Except in Cryptophyceae, thylakoids are in groups of three. In most classes, motile cells bear two unequal flagella, one of which may be almost completely reduced and at least one of which bears two rows of hairlike appendages. Algae in this division range in size and complexity from unicellular flagellates to gigantic kelps. *See* ALGAE; BACILLARIOPHYCEAE; CHRYSOPHYCEAE; CRYPTOPHYCEAE; DINOPHYCEAE; EUSTIGMATOPHYCEAE; PHAEOPHYCEAE; PRYMNESIOPHYCEAE; RAPHIDOPHYCEAE; XANTHOPHYCEAE.

Paul C. Silva; Richard L. Moe

Chromosome

A DNA–protein complex in the nucleus of eukaryotic cells. Chromosomes were so named because after staining, nineteenth-century light microscopists saw chromosomes as colored bodies in cells. The combination of DNA and proteins in chromosomes is called chromatin. Collectively the DNA from all the chromosomes in a nucleus is the hereditary blueprint for the species. Eukaryotes (plants, animals, fungi, and protists) usually have one nucleus in each cell. A nucleus is a double membrane-bound compartment in which chromosomes are located in interphase between cell divisions. In contrast, prokaryotes, such as bacteria and their allies (including mitochondria and chloroplasts), do not have true chromosomes or nuclei because prokaryotes do not confine their small, single circle of DNA in a membrane-bound compartment. *See* DEOXYRIBONUCLEIC ACID (DNA).

Interphase chromosomes. Chromosomes are usually described when they are easily observed in a condensed state during mitosis (M phase of the cell cycle). However, chromosomes are not visible during interphase, which comprises the largest part of the cell cycle. Interphase consists of G_1 (the first gap in interphase without DNA synthesis from the end of telophase to the beginning of DNA synthesis), followed by S (the synthesis phase, during which the DNA is replicated so each chromosome has two identical chromatids), and finally G_2 (the second gap phase, beginning after S and lasting until M phase begins). Nuclei in cells that stop dividing usually arrest in G_0, which is a G_1 interphase-like state that may persist indefinitely.

During interphase, chromosomes are decondensed to form an apparently homogenous mass of chromatin that consists of long DNA double helices associated with proteins. Chromosomes are still present as individual units in interphase nuclei, but their boundaries are difficult to distinguish, something like looking at a clear bottle full of cotton balls and trying to tell where one cotton ball ends and another begins. *See* CELL CYCLE; MITOSIS.

Structure and composition of mitotic chromosomes. Each chromatid of a chromosome consists of one long, linear DNA double helix that is associated with proteins to form chromatin. A DNA double helix is composed of two parallel polymeric chains of nucleotides that are twisted around each other. Each strand consists of alternating phosphate and sugar molecules with bases extending from each sugar. There are four bases: adenine (A), which forms hydrogen bonds with thymine (T) in the opposite DNA strand, and guanine (G), which forms hydrogen bonds with cytosine (C) in the opposite DNA strand. As a result, the two single DNA strands of polynucleotides in a double helix are complementary. This relationship is used when DNA is replicated during interphase of the cell cycle and when RNA is transcribed using DNA as a template. The DNA double helix of one chromatid is usually millions of base pairs (bp) long.

When chromosomes condense during mitosis, DNA becomes so highly folded that each double helix is approximately 10,000 times as long as the chromatid in which it is packed. (The necessity of this level of folding is apparent when one considers that diploid human cells contain about 2 m of DNA divided between 46 chromosomes in a nucleus that is about 5 μm in diameter.) In a current model for the structure of an average chromosome, the hierarchy of folding begins with formation of nucleosomes. A nucleosome consists of a core of eight basic proteins called histones (two molecules each of histones H2a, H2b, H3, and H4) and DNA. Histones are positively charged so they are attracted to negatively charged DNA. To form a nucleosome, 146 base pairs (bp) of DNA wraps 1.65 times around the core histone particle. There are about 50 bp of coiled DNA between adjacent nucleosomes. A chain of nucleosomes linked by a continuous DNA double helix forms a fiber with a diameter of about 10 nm and a 6:1 packing ratio of DNA length to 10-nm fiber length. Next, the 10-nm fiber associates with other proteins to coil or fold into a fiber with a diameter of 30 nm and a 42:1 ratio of DNA length to 30-nm fiber length. The 30-nm fiber forms ~1-μm-long loops that are attached to a proteinaceous chromosome core (scaffold). The loops condense against the core under the influence of a protein complex called condensin that is found in the core. The condensed loops and core constitute a strand called the chromonema with a diameter of ~0.2 μm. The chromonema coils, possibly due to contraction of the proteinaceous core, to form a chromatid about 1 μm in diameter with a ratio of DNA length to chromatid length of ~10,000:1. Coiling does not occur at the primary constriction (=centromere), resulting in a narrow part of the chromatid (**Fig. 1**). *See* NUCLEOSOME.

Without resorting to special treatments, chromosomes are visible only when they become condensed into sausage-shaped bodies during division of the nucleus (mitosis and meiosis). Although they are always microscopic, mitotic chromosomes in different species and even within a species can vary enormously in size, for example, from 1 to 40 μm in length and 1 to 2 μm in width. A chromosome can consist of either two identical sister chromatids (during G, prophase, prometaphase, and metaphase of mitosis) or of one chromatid (during G_1, anaphase and telophase of mitosis). Having one or two chromatids per chromosome does not change ploidy (the number of complete chromosome sets in a nucleus).

At a gross morphological level, chromosomes often can be distinguished from one another on the basis of their relative lengths and the positions of their primary constriction. The segments of chromosomes to either side of the primary constriction (centromere) are called arms. If the arms are roughly of equal length, the chromosome is metacentric. If the centromere is near one end, the chromosome is acrocentric, and there is a short (p) arm and a long (q) arm. If the centromere is truly at the end (rare), the chromosome is telocentric.

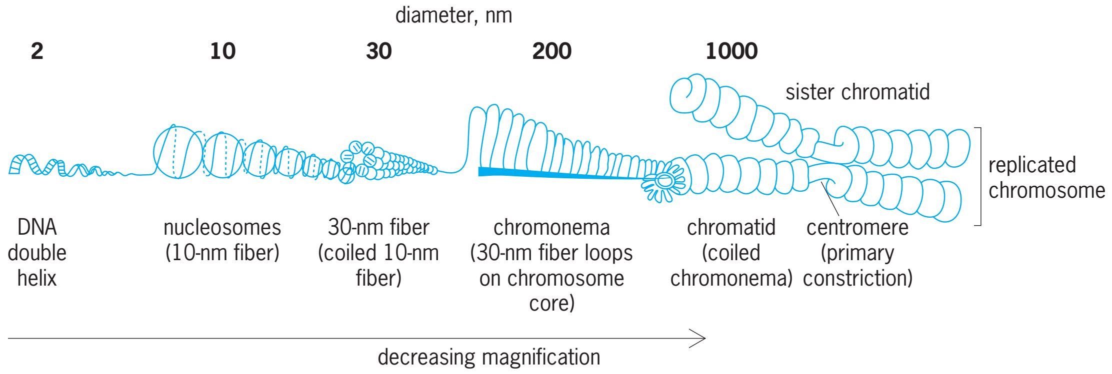

Fig. 1. Model of hierarchy of chromosome structure. Objects on the left are magnified more than those to the right. On the left and progressing to the right, a DNA double helix is associated with nucleosomes to form a 10-nm fiber that is coiled or folded to form a 30-nm fiber that forms loops on the chromosome core to form the chromonema that is coiled to form one chromatid. Note the lack of coiling in the primary constriction (centromere).

Chromosomes with primary constrictions in intermediate positions are described as submetacentric and subacrocentric (**Fig. 2**).

Kinetochores. A kinetochore is a nucleoprotein structure that forms in the centromere on each chromatid. Depending on the species, a kinetochore may appear as an amorphous sphere or a layered disk. The DNA involved in kinetochores often consists of a 150-bp tandem repeat sequence; the exact sequence varies from species to species. [In addition, there are often additional repeated sequences in the centromere and in heterochromatin (chromatin that is tightly coiled even in the nondividing nucleus and stains darkly in interphase). Proteins found in kinetochores are more evolutionarily conserved than the DNA sequences. During mitosis, microtubules grow from the spindle poles and attach to kinetochores. Force is applied through these kinetochore microtubules to move chromosomes to the metaphase plate during prometaphase and then to move sister chromatids (now sister chromosomes) to opposite poles during anaphase.

Telomeres. The ends of chromosomes are called telomeres. Although telomeres usually have no

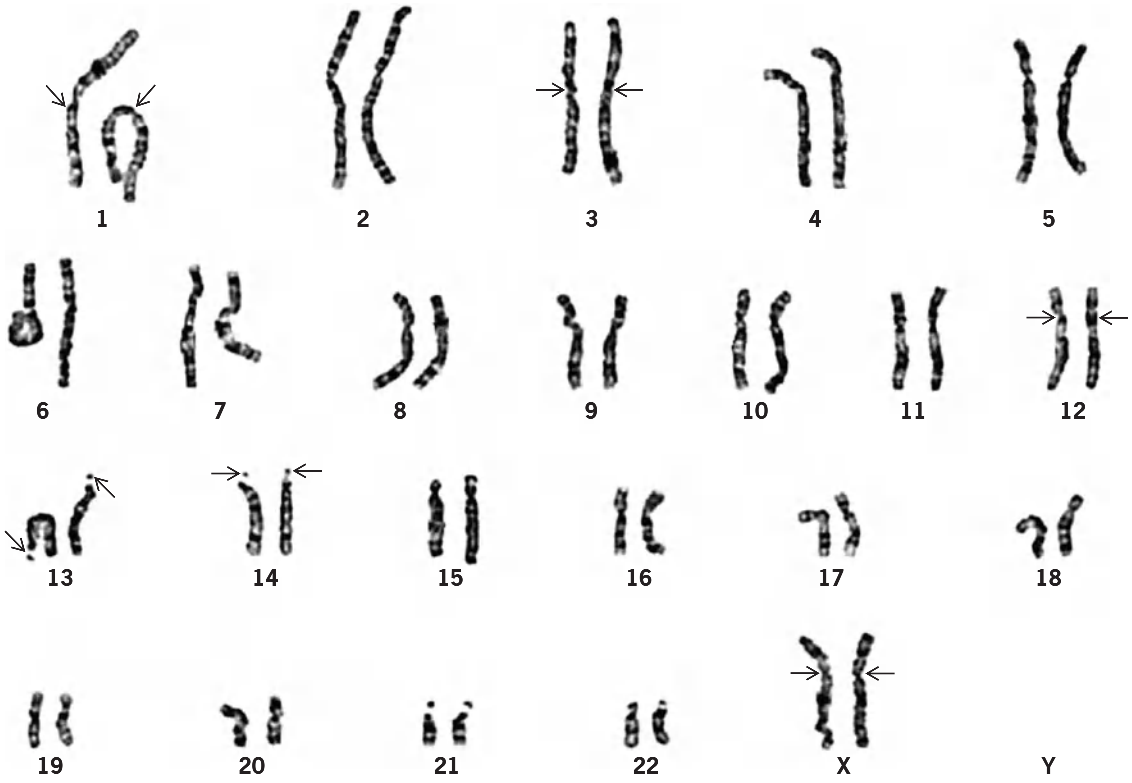

Fig. 2. Diploid set of normal human female chromosomes that have been G-banded for identification. G bands stain more darkly than the lighter R bands, and G bands have more AT-rich DNA than R bands. To construct an idiogram, chromosomes were cut out of a photograph and pasted in a row from longest to shortest with homologs together. Arrows indicate some centromeres. Note metacentric (such as chromosomes 1 and 3), acrocentric (such as chromosomes 13 and 14), submetacentric (such as the X chromosome), and subacrocentric (such as chromosome 12). Since these are chromosomes from a female, there are two X chromosomes and no Y chromosome. (*Courtesy of Genzyme Corporation*)

visibly distinct structure, they are necessary for the survival of chromosomes; without telomeres, chromosomes would be nibbled away slowly from their ends during every round of DNA replication, during which a little of the DNA double helix is lost from both ends of a chromatid. The telomere is the site where an enzyme called telomerase adds expendable DNA, usually in the form of a short repeat sequence such as TTAGGG. Most differentiated animal cells have no telomerase activity, but they inherit telomeres that are thousands of bp long from telomerase activity during meiosis that occurred just before gametes were formed. Telomere lengths are adequate for the normal number of divisions the cells undergo during development. This protects the body from cells that are dividing out of control, because cells that divide too frequently are eventually destroyed when their telomeres are lost. One cost of this protection is aging, and, as one might expect, cancer cells often have telomerase activity that permits them to divide indefinitely.

Euchromatin and heterochromatin. Chromatin is divided into euchromatin and heterochromatin based on its level of condensation during interphase and G_0. Euchromatin is decondensed and available for transcription. However, euchromatin still requires the proper proteins to mark genes (DNA segments) for transcription, that is, genes are not transcribed just because they are in decondensed chromatin, but genes must be in decondensed chromatin to be transcribed. In contrast, heterochromatin generally remains condensed, and its DNA is not used for transcription, if for no other reason than transcription factors and RNA polymerase are sterically hindered from access to the DNA. However, even heterochromatin becomes euchromatic when its DNA is replicated during S phase. There are two types of heterochromatin: constitutive heterochromatin that is always condensed (except during S phase) and facultative heterochromatin that is condensed only in certain cells or in only one sex. Facultative heterochromatin seems to be a way to control gene activity.

During mitosis, euchromatin and heterochromatin are similarly condensed and stained with most dyes. However, heterochromatin in condensed chromosomes can be stained differently from euchromatin after special procedures that typically utilize Giemsa stain. One technique, called C-banding, stains constitutive heterochromatin intensely so that a simple pattern of dark bands is visible on chromosomes. C-bands often occur around centromeres, nucleolus organizers, or at the ends of chromosomes, but they can be anywhere on a chromosome. C-banding has been used successfully on both plant and animal chromosomes. The other technique, called G-banding, stains facultative heterochromatin intensely and results in a relatively complex banding pattern. G-banding works well on mammalian and avian chromosomes and has been important for identifying individual chromosomes in these groups (Fig. 2).

Methyl groups can be added to cytosines in DNA, and this generally causes DNA to become facultatively heterochromatic and unusable for transcription. The pattern of methylation is duplicated during S phase, so methylation is inherited from one cell generation to the next. While spermatozoa and eggs carry genes for the same traits, some genes are differently methylated in spermatozoa compared with eggs. Thus, only the maternal or paternal versions of these genes are active in developing embryos. This is an epigenetic phenomenon (gene activity not determined by DNA sequence, but rather through chemical modification of DNA like methylation) called imprinting.

Chromosome sets, genomes, ploidy, and homologs. Generally, eukaryotes are capable of sexual reproduction that involves fusion of two gametes. Gametes usually carry a haploid set of chromosomes, defined as one copy of each chromosome that is characteristic of the species. An unreplicated haploid set of chromosomes, in which each chromosome consists of one chromatid, contains one genome of DNA called the 1C amount (C standing for "constant" for each species). For example, the human genome (1C amount of DNA) consists of about 3.5 picograms of DNA or 3.4 billion base pairs of DNA or 1 m of DNA. Other species have different genome sizes (1C). Normally each human gamete (spermatozoon or egg) carries a haploid chromosome set (often denoted $1n$) of 23 chromosomes. After fertilization the zygote is usually diploid ($2n$) with 46 chromosomes (Fig. 2 and **Colorplate 1**). If an organism has one or more complete sets of chromosomes with no extra or missing chromosomes, it is euploid. If an organism has more than two sets, it is polyploid. If chromosomes are added or missing from a set, the organism is aneuploid. *See* POLYPLOIDY.

A special class of chromosomes called B chromosomes (or supernumerary chromosomes) occurs sporadically in many organisms. B chromosomes generally have few, if any, active genes, and they are not necessary for the life of the organism. B chromosomes may be thought of as molecular parasites, and their presence or absence does not constitute aneuploidy. Aside from B chromosomes, the numbers of chromosomes in a set vary enormously from one species to another. Generally, haploid numbers above 15 are rare in plants, and haploid numbers above 50 are rare in animals. There are two ways in which chromosomes numbers can change: by breaking one chromosome into two smaller chromosomes or by fusing two chromosomes into one larger chromosome. DNA breaks are usually caused by radiation or chemicals. While breaks usually are repaired without a trace, sometimes repair leads to permanent breaks, fusion of chromosomes, trading segments between chromosomes (translocation), and inversion within a chromosome.

Most eukaryotic organisms are diploid with two sets of chromosomes, so each chromosome is represented twice (one derived from the egg and one from the spermatozoon). These pairs of chromosomes are called homologs or homologous chromosomes. Homologs are the same size and shape, have the same banding pattern, and carry genes for the same traits (but not necessarily the same alleles of those genes) (Fig. 2 and Colorplate 1).

Karyotypes and idiograms. Although the terms karyotype and idiogram have sometimes been used interchangeably, it less confusing to restrict karyotype to a word description of a set of chromosomes (for example, the haploid set of chromosomes is represented by three large metacentric, two large acrocentric, five small acrocentric, and two small metacentric chromosomes), whereas the term idiogram is used for a diagrammatic representation of a chromosome set, in which the chromosomes are arranged in a row from largest to smallest. In general, the longest chromosome is numbered 1, the next longest numbered 2, and so on. The chromosomes can be drawn, but usually they are cut out of a photograph of a chromosome spread and pasted in position. If the cell was diploid, homologs are positioned together in pairs (Fig. 2 and Colorplate 1).

Techniques for spreading and staining chromosomes. To make chromosome preparations suitable for observation by light microscopy, cells are usually fixed (killed and preserved) in a freshly prepared solution of one part acetic acid and three parts ethanol or methanol. The chromosomes are then spread and flattened onto a glass microscope slide, either by squashing cells under a cover glass or by bursting cells that have been hypotonically swollen cells and permitting the chromosomes to dry on the slide. Chromosomes can then be stained for examination by light microscopy.

Many stains have been used for chromosomes. Without special treatments, dyes such as crystal violet, Giemsa stain, orcein, and carmine stain chromosomes homogeneously throughout their length. Historically the Feulgen technique has been important because the intensity of staining is a direct indicator of the amount of DNA present. Some techniques result in the formation of “bands” on chromosomes due to differential staining based on the location of euchromatin and heterochromatin or differences in base composition of DNA along the length of chromosomes. The latter type of banding is observed with fluorescent dyes such as Hoechst 33258, daunomycin, chromomycin A, mithramycin, DAPI, and quinacrine dihydrochloride that either bind better or fluoresce more strongly in AT-rich or GC-rich DNA (Fig. 2).

Fluorescence in-situ hybridization (FISH). Important new tools for cytogenetics have been introduced during the past 30 years. One of these is fluorescence in-situ hybridization (FISH). In this technique, a specific DNA probe is prepared by attaching a small molecule, such as biotin, to a DNA sequence of interest (for example, a gene). A solution containing the DNA probe is placed on a glass microscope slide with chromosome spreads and heated to denature both the probe and the chromosomal DNA, that is, the hydrogen bonds between AT and GC base pairs are broken so that DNA double helices separate into single, complementary DNA strands. When the slide and solution are cooled to a temperature appropriate for renaturation (reformation of double helices by hydrogen bond formation between complementary strands), the probe will renature with any complementary DNA sequence in the chromosomes. Next, an antibody specific for biotin that is itself attached to a small fluorescent dye molecule (such as fluorescein isothiocyanate, FITC) is placed on the slide. This antibody selectively binds to the biotin in the probe and then the slide is examined under a microscope that has an ultraviolet (UV) light source and the appropriate filters for the dye. The dye will fluoresce to show the location of the probe on the chromosome(s) [**Colorplate 2**]. FISH has proven to be a powerful technique for be a powerful technique for locating DNA sequences on chromosomes.

Other forms of FISH include genomic painting, chromosome painting, and multicolor FISH. In genomic painting, the DNA of one species is isolated and labeled with biotin. The labeled DNA is used as a probe to identify chromosomes from that species among the chromosomes from one or more different species in a hybrid. In chromosome painting, one chromosome is isolated and its DNA is amplified by the polymerase chain reaction (a technique for amplifying specific sequences of DNA) involves copying and amplifying the complementary strands of a target DNA) and labeled with biotin; this labeled DNA is then used as a probe to locate a specific chromosome in a group of chromosomes. In multicolor FISH, probes can be prepared for each chromosome in a set, and every chromosome can be identified simultaneously using different dye combinations. *See* GENE AMPLIFICATION.

Immunofluorescence. Immunofluorescence can be used to locate specific proteins on chromosomes. The first step is the preparation of a primary antibody that will specifically bind to the protein of interest in chromosomes on a slide. Next, the primary antibody is bound by a secondary antibody that is labeled with a fluorescent dye that is visualized using fluorescence microscopy. Immunofluorescence is useful for relating proteins to the structure and function of chromosomes (Colorplate 1). *See* IMMUNOFLUORESCENCE.

Function. The nucleus is a molecular library of instructions for building an organism, responding to the environment, and reproducing. Chromosomes are like molecular books, and DNA is the molecular text. In a library, most of the books and the vast majority of the text are stored compactly when not in use, but they must be available when needed. Decondensation of euchromatin in interphase makes the DNA physically available for interaction with proteins called transcription factors that recognize specific base sequences and prepare the DNA for transcription by the enzyme RNA polymerase. During transcription, complementary single-stranded ribonucleic acid is made using one of the DNA strands as a template. Transcribed segments of DNA are called genes. Many RNAs are messages (mRNAs) that are transferred to the cytoplasm, where they associate with ribosomes. There, the base sequence of mRNA is used to determine the amino acid sequence of proteins in a process known as translation of the genetic code. During translation, the linear sequence of bases in mRNA is used to determine the linear sequence of amino acids in a protein. *See* GENE; GENETIC CODE.

Other RNAs are transcribed that are not messages, but instead function as structural components, enzymes, suppressors of gene activity, or signals in the pathway to forming heterochromatin. Four of these other RNAs are components of ribosomes. Most ribosomal RNA is transcribed from nucleolus organizer regions (NORs), where hundreds or thousands of copies of the ribosomal RNA gene are located. Active NORs appear as secondary constrictions on certain chromosomes, that is, chromosome constrictions in addition to centromeres. *See* RIBONUCLEIC ACID (RNA); RIBOSOME.

During mitosis, when the duplicated DNA is being divided equally between the daughter cells, the DNA is so compactly packaged in condensed chromosomes that it is temporarily unavailable for transcription, like books that are crated for shipping to another library. At the end of mitosis (telophase), chromosomes decondense and return to their interphase condition, that is, the books are uncrated, and the library is open for business.

Special chromosomes. Special chromosomes include sex chromosomes, polytene chromosomes, and the chromosomes of meiosis.

Sex chromosomes. Some animals determine whether embryos develop as males or females by the combination of sex chromosomes they carry. Mammals and birds are prominent examples.

In mammals, males normally have only one large X chromosome and one Y chromosome that is usually small and heterochromatic. The Y carries the *SRY* gene, which determines that testes will be formed rather than ovaries. Females have two X chromosomes and no Y chromosome, so they form ovaries by default (Fig. 2 and Colorplate 1). However, because the number of X chromosomes differs in males and females, there is a problem with the dosage of genes on the X chromosome. Either the male with only one X has half enough genes or the female with two X's has twice too many genes. The problem is solved in mammals by converting one of the two X chromosomes in each cell of females into facultative heterochromatin in a process known as lyonization. This involves transcription of a gene on the mostly inactive X to produce RNA molecules that coat and play a role in inactivating the X chromosome. As a result, females, like males, have only one active (euchromatic) X chromosome in each cell. X inactivation occurs early in embryonic development, appears to be random with respect to which X is inactivated, and is inherited in subsequent cell divisions. Thus, the body of female mammals is a patchwork (mosaic) of tissues in which genes from one or the other X is active. During interphase, the inactive X chromosome in the nuclei of female cells stains darkly and is called a Barr body. Male cells seldom show Barr bodies.

In birds, the system is reversed so females have one Z chromosome and one small W chromosome, while males have two Z chromosomes. Presumably the presence of the W chromosome somehow determines that ovaries rather than testes will form in females. Barr bodies are not visible in male birds, indicating that birds deal with dosage compensation differently than mammals. *See* SEX DETERMINATION.

Fig. 3. *Drosophila melanogaster* polytene chromosomes.

Polytene chromosomes. A few insects, plants, and protozoa have cells that undergo endoreduplication, a process involving round after round of DNA synthesis without nuclear division to produce polytene chromosomes. The best-known example of polytene chromosomes occurs in Dipteran (fly) salivary glands. A polytene chromosome often consists of a thousand or more identical DNA double helices lying parallel in a bundle. Polytene chromosomes show intricate patterns of banding, where in some cases a band corresponds to a specific gene. Often euchromatin is selectively replicated, so heterochromatin

Fig. 4. Electron micrograph of a tomato synaptonemal complex. The kinetochore looks like a fuzzy ball, and a single recombination module is indicated by an arrow.

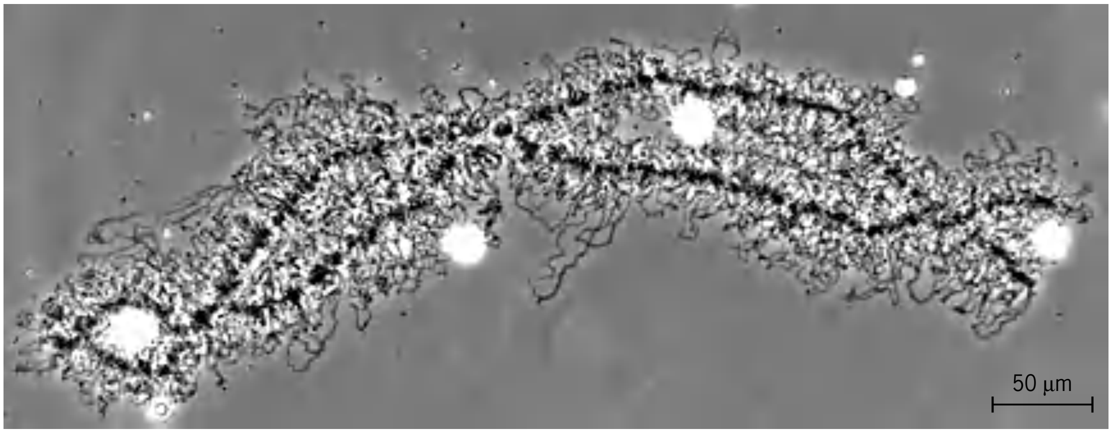

Fig. 5. Lampbrush chromosomes from a salamander (axolotyl) primary oocyte. Chromatin loops extend from the axes of two homologous chromosomes that come together at the chiasmata, where crossing over has occurred. Bright spots are nucleolar material. (*Courtesy of Garry Morgan, University of Nottingham*)

has little representation. Polytene chromosomes are not comparable to mitotic chromosomes; rather they are a special class of interphase chromosomes. Aside from protozoa that produce polytene chromosomes on the way to forming macronuclei, cells with polytene chromosomes are differentiated cells that will never divide again (**Fig. 3**).

Chromosomes of meiosis. Meiosis consists of two special cell divisions referred to as Meiosis I (MI) and Meiosis II (MII). MI is unique among nuclear divisions because crossing over occurs between homologous chromosomes and the chromosome number is reduced from diploid to haploid. For this, elongate homologous chromosomes synapse (come together side-by-side) in a gene-for-gene alignment during prophase I. Synapsed homologs are held together by a proteinaceous structure called the synaptonemal complex (SC) [**Fig. 4**]. The synaptonemal complex looks like a railroad track, with the rails represented by two lateral elements. One lateral element is associated with the two sister chromatids of one chromosome, and the other lateral element is associated with the two sister chromatids of the homologous chromosome. Chromatids in homologs are called nonsister chromatids. Thin transverse filaments span the central region between the lateral elements. It is at this time that new gene combinations are created by crossing over. Pairs of homologous chromosomes held together by synaptonemal complexes or chiasmata are called bivalents. *See* MEIOSIS.

Crossing over involves breakage and repair of DNA in such a way that nonsister chromatids exchange equivalent segments. These events probably occur in recombination nodules, proteinaceous ellipsoids about 100 nm in diameter that reside between the lateral elements of the synaptonemal complex (Fig. 6). The pattern of crossing over (recombination) can be mapped on synaptonemal complexes by examining synaptonemal complexes and recombination nodules using electron microscopy or by locating recombination nodules using immunofluorescent antibodies targeted to a protein in recombination nodules called MLH1 (**Colorplate 3**). Recombination nodule maps show the pattern and frequency of crossing over on chromosomes and thereby link genetic linkage maps to chromosome structure. *See* CROSSING-OVER (GENETICS); RECOMBINATION (GENETICS).

Primary oocytes (immature eggs) of most animals enter a synthetic period right after crossing over is completed and the synaptonemal complex breaks down. During this time, many components that will be needed by the developing embryo are synthesized and stored in the oocyte. Apparently to enhance transcription at this time, the pairs of homologous chromosomes (held together at sites of crossing over called chiasmata) become extremely long to permit rapid RNA synthesis on loops of chromatin extending from the chromosome axes. These bivalents (pairs of homologous chromosomes) are called lampbrush chromosomes because nineteenth-century cytologists thought they looked like the brushes used to clean glass chimneys of oil lamps (**Fig. 5**). Stephen M. Stack; Lorinda K. Anderson

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Chromosome aberration

Any numerical or structural change in the usual chromosome complement of a cell or organism.

Heteroploidy. Numerical changes (heteroploidy) are of two types, polyploidy and aneuploidy.

Polyploidy is a change in the number of chromosome sets. The polyploid condition has both advantages and disadvantages. For example, tetraploid ($4n$) plants can be fertile because each chromosome can pair in meiosis with a homologous chromosome and segregate properly to form euploid $2n$ gametes or germ cells. These plants are larger than diploid varieties and produce larger fruit making them valuable commercially. Triploid ($3n$) plants, however, are usually sterile because of the inability of every chromosome to find a homologous chromosome to pair with in meiosis. The result is improper segregation (nondisjunction) of chromosomes and aneuploidy in the progeny. Triploidy rarely occurs in animals. Triploid reptiles and frogs are seen only in populations that reproduce parthenogenetically from unfertilized eggs that have not undergone the meiotic divisions that could produce aneuploid ova. Triploidy occurs in about 1% of human pregnancies, but it is almost always an embryonic lethal condition. *See* MEIOSIS; MITOSIS; POLYPLOIDY.

Aneuploidy is a change in the number of chromosomes from the diploid ($2n$) number (usually found in the somatic cells of sexually reproducing organisms, including animals and plants) or the haploid (n) number (usually found in germ cells and the haplophase of some unicellular organisms.) Aneuploidy involves either an increase or a decrease in the number of chromosomes. It usually involves a single chromosome, and any chromosome in the complement can be involved. Aneuploidy is the result of aberrant segregation of one or more chromosomes during meiosis or mitosis. If malsegregation or nondisjunction occurs during meiosis, one daughter cell receives two copies of the chromosome and the other daughter cell receives none. Fertilization of such an aneuploid germ cell by a euploid gamete will produce a zygote that has either three copies (trisomy) or one copy (monosomy) of the chromosome. Malsegregation of a chromosome can also take place during a mitotic division in a somatic cell, producing trisomic or monosomic cells in an otherwise euploid individual. This outcome is important primarily in the origin and progression of some forms of cancer. In humans, nearly 20% of ova and 7% of sperm may be aneuploid, and at least 3% of recognized pregnancies are trisomic and 1% are XO, that is, having a single sex chromosome per cell. Also, nearly half of all miscarriages and 3% of stillbirths are the result of aneuploidy.

Autosomal trisomy. The most common trisomy in human liveborns is trisomy 21, or Down syndrome, which is a major cause of mental retardation and congenital heart disease. Individuals with trisomy 18 and trisomy 13 also occur but are much less common. Most autosomal trisomies are lethal to embryos, leading to spontaneous abortion. The incidence of trisomy for any autosome increases exponentially with maternal age. For trisomy 21, the risk is about 1 in 100 for women over 35 years of age, and much greater for women over age 40. In about 80% of cases, the extra chromosome 21 is inherited from the mother and in 20% from the father, the latter case showing no paternal age effect on incidence. *See* DOWN SYNDROME.

Sex chromosome aneuploidy. In humans, there are more types of aneuploidy involving the sex chromosomes than the autosomes. The most common is XO, occurring in about 1% of pregnancies, with the risk being slightly higher in very young mothers. Although 99% of XO fetuses die early in pregnancy, the other 1% (about 1 in 10,000 liveborn females) survive. The high frequency of deaths of most XO fetuses is somewhat puzzling because the somatic cells in XX females have only a single active X chromosome. It is believed that the cause of death may be the presence of one or more genes on the tiny shared (homologous) segment of X and Y that remain active on both the Y and the otherwise inactive X chromosome. Adults who are XO tend to be short, with some webbing of the neck. They rarely develop secondary sexual characteristics or have children because the germ cells essential for ovarian development are usually absent. These features are characteristic of Turner syndrome. *See* HUMAN GENETICS.

Trisomy for the human X chromosome, commonly called XXX, is not associated with embryonic death or congenital malformations. The reason is that in all mammals, including humans, only a single X chromosome is active in each somatic cell; additional X chromosomes are inactivated, so almost all of their genes fail to be expressed. These are adult individuals with as many as five X chromosomes, and while they are physically normal they do show some degree of mental retardation.

In contrast to autosomal trisomy, sex chromosome aneuploidy increases only slightly with maternal age, and the extra X chromosome comes from the mother in only about 60% of the cases. About 1 of every 1000 liveborn females is XXX, while 1 of every 1000 liveborn males is XXY and 1 is XYY. An additional X chromosome can be present in either egg or sperm; additional Y chromosomes can be present only in sperm. The XXX and XXY individuals display minimal phenotypic manifestations of their increased number of chromosomes, although XXY males are usually sterile and have an increased risk of mild mental retardation. Individuals who are XYY generally are indistinguishable from XY individuals, although they are questionably at a slightly increased risk of antisocial behavior. The presence of a Y chromosome leads to male sex differentiation no matter how many X chromosomes are present, because of the presence of a single, critical gene, called *SRY*, on the Y chromosome. A mutation of this gene has been found in some XY individuals who developed as females.

Structural abnormalities. Structural abnormalities (chromosome mutations) involve the gain, loss, or rearrangement of chromosome segments after the continuity of the deoxyribonucleic acid (DNA) strand in one or more chromosomes is disrupted (**Fig. 1**).

Deletion. A deletion involves the loss of a chromosome segment and the genes it carries. A terminal deletion involves the loss of a segment extending from the point of disruption (breakpoint) to the end

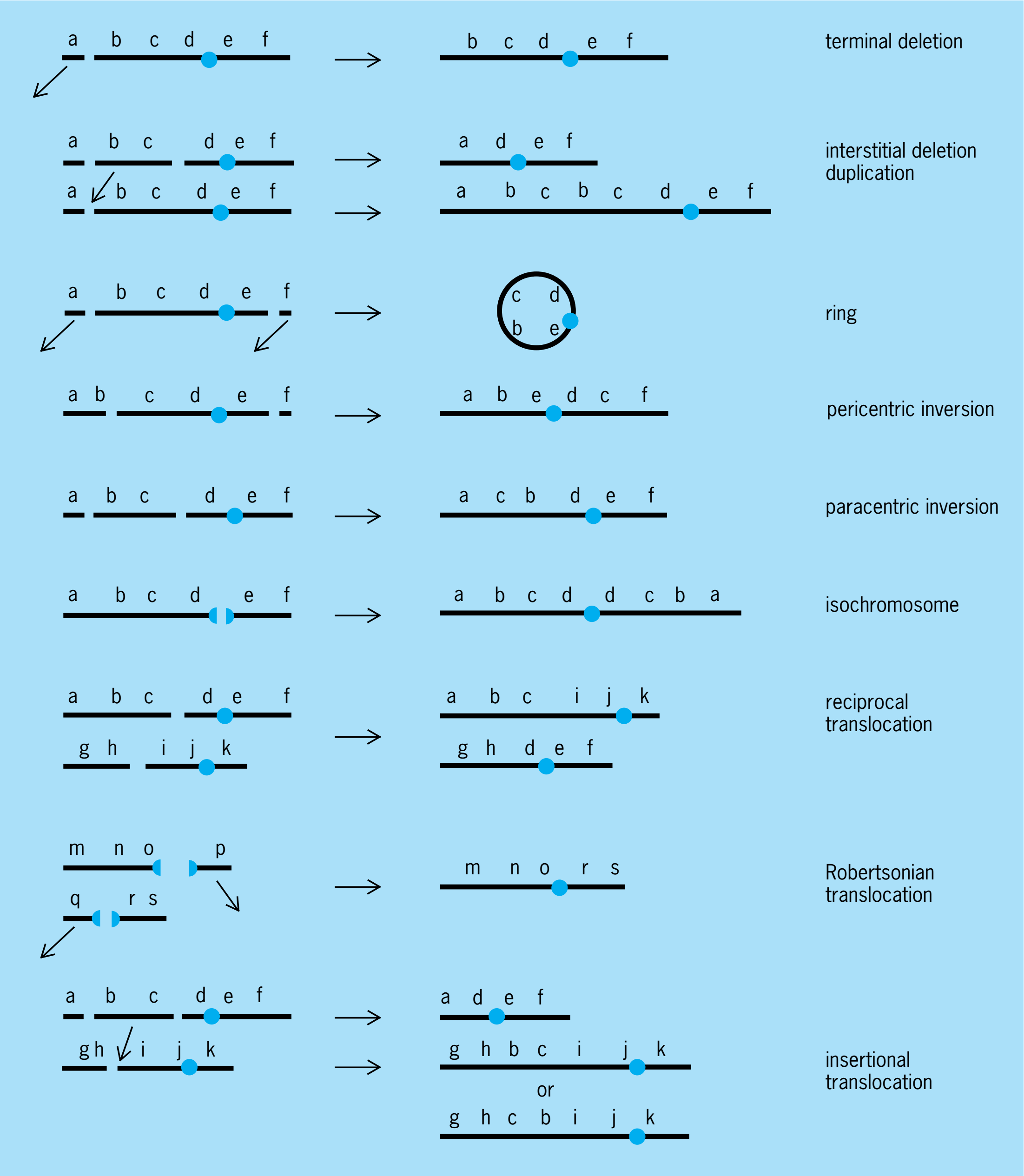


Fig. 1. Diagram of various types of structural abnormalities.

of the same arm of a chromosome. It is relatively uncommon because the broken end of the chromosome is usually repaired during DNA replication, resulting in a dicentric chromosome that is unstable because its two centromeres tend to be pulled toward opposite spindle poles at anaphase of cell division. The result is the breakage and eventual loss of the chromosome. An interstitial deletion involves the loss of the segment between two breakpoints in one arm of a chromosome (**Fig. 2**). The effect of such a loss depends on the genes that are included in the missing segment. If a deletion is associated with a genetic disease, the chromosome breakpoint provides a clue to the location of the gene responsible for the disease. For example, deletions were useful in mapping and isolating the human gene for retinoblastoma.

Fragments and duplication. When one break occurs in each arm of a chromosome, the broken ends of the internal centromeric fragment may join, resulting in the formation of a stable ring chromosome (Fig. 2). Each of the two end segments lacks a centromere, and such acentric fragments are lost during cell division, resulting in deletion of both end segments. Ring chromosomes are subject to reduction in size, as well as doubling. An individual who has a ring chromosome may thus show phenotypic effects not only of deletion but of duplication of part of the chromosome. A duplication more commonly occurs in other ways. For example, a chromosome segment can undergo tandem or inverted duplication at the usual chromosome site, or the second copy of the segment may be carried on another chromosome.

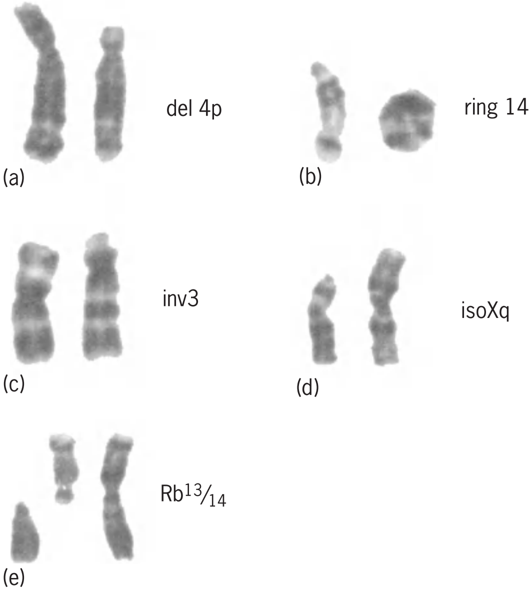


Fig. 2. G-banded human chromosomes illustrating structural chromosome abnormalities present in different individuals. The normal chromosome(s) is on the left in each case. (*a*) Terminal deletion of the short arm of chromosome 4 (4p). (*b*) Ring chromosome 14. (*c*) Pericentric inversion of chromosome 3. (*d*) Isochromosome of the long arm of the X. (*e*) Robertsonian translocation of chromosomes 13 and 14.

Inversion. An inversion is generated by disrupting the DNA strand in a chromosome at two breakpoints and rejoining the broken ends with the interstitial segment in the opposite orientation. This process will invert the order of the genes on the segment (Fig. 2). The centromere is included in the inverted segment in pericentric inversions but not in paracentric inversions. Thus, pericentric inversions can often be identified by an altered position of the centromere, while paracentric inversions can be identified only by an altered banding pattern or altered gene order.

Translocation. A translocation involves the interchange of one or more chromosome segments between two or more chromosomes. A reciprocal translocation involves the reciprocal exchange of the segment produced by a single break in one chromosome for the segment produced by a single break in another chromosome. A Robertsonian translocation (Fig. 2) is produced by the rejoining of the long arms and centromere of two acrocentric or telocentric chromosomes after disruptions in the short arm or at the centromere. It results in the reduction of chromosome number by one, except in the rare case in which the two short arms rejoin and the tiny fragment retains a functional centromere. An insertional translocation is produced when the interstitial segment between two breakpoints in one chromosome is inserted into a breakpoint in another chromosome. A complex translocation involves rearrangement of segments from three or more chromosomes. *See* GENE AMPLIFICATION; MUTATION.

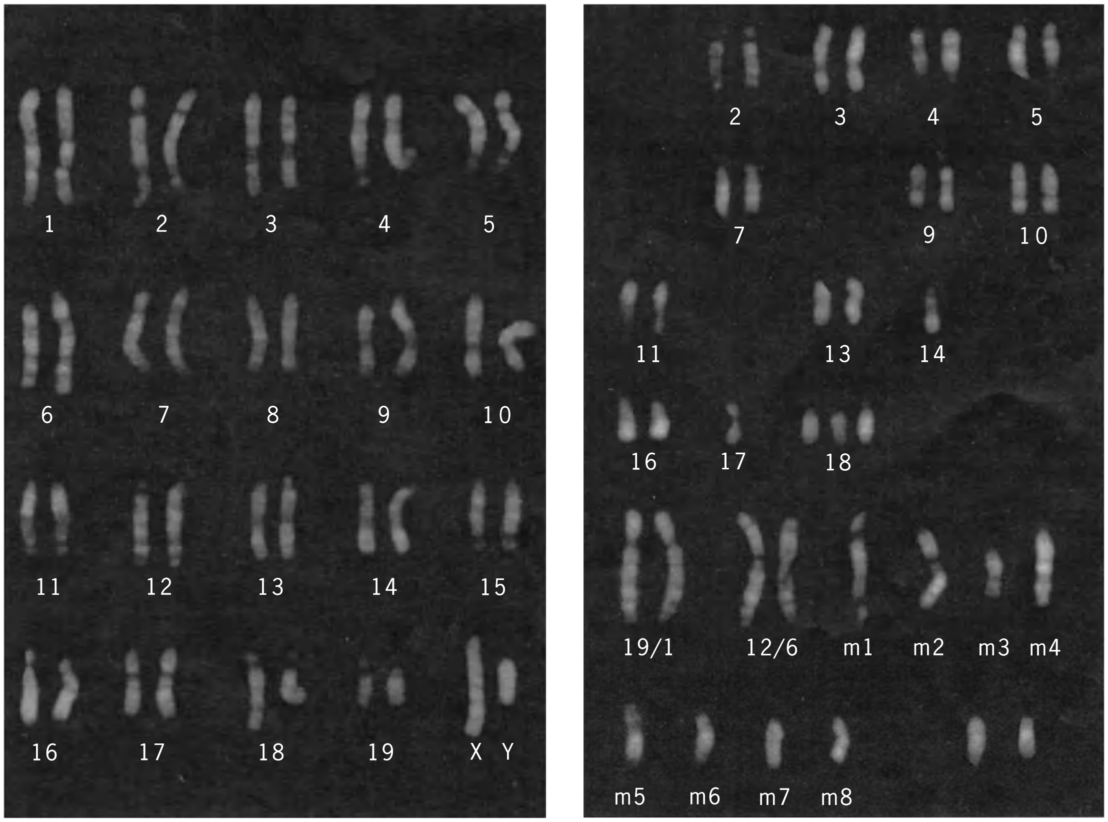
Consequences of translocations and inversions. If a translocation breakpoint disrupts a gene, the gene's function will be blocked or abnormal, and such can have deleterious effects on development or function. Sometimes a normally silent gene is activated by a chromosome rearrangement that places it next to a strong promoter of gene expression, and this change is important as a cause of cancer. If a translocation does not block the function of an essential gene or activate a normally silent gene, the individual carrying the rearrangement will be normal.

In an individual carrying an inversion on one of a pair of homologous chromosomes, pairing leads to the formation of a loop containing the inverted segment. Crossing over within the loop leads either to the formation of gametes with a duplication of one segment of the inversion and a deficiency of the other segment, or to two abnormal chromosomes, one with two centromeres and the other lacking a centromere. *See* CROSSING-OVER (GENETICS).

Causes. Structural aberrations can occur spontaneously or be induced by agents that break chromosomes, such as x-rays, radioactive substances, ultraviolet rays, and certain chemicals. The most frequent cause may be the presence of enormous numbers of a few types of short interspersed elements (SINES), that is, DNA sequences that occur once every few thousand base pairs throughout the genome of most metazoans, including humans. These elements predispose to the occurrence of errors during DNA replication or genetic recombination at meiosis that can lead to the deletion or duplication of the region between two nearby interspersed repeats on one chromosome. They may also play a role in the formation of inversions and, possibly, translocations. *See* MUTAGENS AND CARCINOGENS.

Another cause of structural aberrations is also inherent in the genome: the great abundance of short repeats of a 2-, 3-, or 4-base-pair unit. Some trinucleotide repeats, such as $(CGG)_n$ or $(CAG)_n$, can undergo expansion during meiotic and mitotic cell divisions. This expansion sometimes affects gene function and leads to disease. The most common type of X-linked mental retardation in humans is the result of heritable expansions, in the *FMR-1* gene, of a specific trinucleotide repeat, $(CGG)_n$, where the number of expansions (n) is increased from the normal 8–20 or so to 50–200 or more. For unknown reasons, this expanded region tends to undergo breakage under some conditions, and this particular form of mental retardation is called the fragile X syndrome. There are dozens, if not hundreds, of similar fragile sites in the human and other genomes.

Imprinting. The function of a gene that is inherited from the father may differ from that of the same gene inherited from the mother, a phenomenon known as imprinting. The mechanism for imprinting is not fully understood, but differences in DNA methylation of genes in sperm compared to ova appear to be involved. Imprinting is important in some human diseases, such as Prader-Willi and Angelman syndromes. Although deletions of the same region on chromosome 15 have been observed in some individuals with either of these syndromes, individuals who received the deleted chromosome 15 from the father developed the Prader-Willi syndrome, whereas those



(a) (b)

Fig. 3. Q-banded chromosomes of (*a*) normal mouse metaphase cell, arranged according to the standard karyotype, (*b*) and metaphase karyotype of a mouse cancer cell showing numerical and structural changes. Chromosomes 2–18 are structurally normal, but noteworthy are the monosomy 17 and 14 and trisomy 18.

who received the deleted chromosome 15 from the mother developed Angelman syndrome. Thus, although each syndrome is associated with the presence of a single undeleted chromosome 15, the outcome depended on the parental origin.

Abnormal chromosomes in tumor cells. Specific chromosome aberrations play an important role in the development of many, if not all, cancers. For example, most patients with chronic myelogenous leukemia have a translocation between chromosome 9 and 22 which fuses the normally silent *c-abl* oncogene with the expressed *bcr* gene. The result is the production of an abundant *bcr-abl* fusion gene product and tumor development (**Fig. 3***a* and *b*). Tumor cells tend to be chromosomally unstable, and further chromosome aberrations may enhance tumor malignancy. Translocations and trisomies may lead to additional oncogene products, whereas deletions may remove genes that suppress tumor growth.

Some tumor cells have an elongated region on a chromosome arm that contains an increased number of copies (amplification) of an oncogene. Such regions stain uniformly, rather than being banded, and are called homogeneously staining regions (HSRs). The amplified oncogenes are sometimes extrachromosomal, that is, are present on very tiny collections of chromatin resembling small chromosomes that lack centromeres; these are called double minutes (DMs). *See* ONCOGENES; ONCOLOGY.

Evolution. Chromosome complements are remarkably diverse throughout both plant and animal kingdoms, and chromosome aberrations may have played an important role in the reproductive isolation that fosters speciation. For example, polyploidization creates a reproductive barrier that favors the formation of a new, polyploid species. Some species contain very large chromosome numbers, such as a fern with about 1000 chromosomes, a crayfish with over 350 chromosomes, and a butterfly with over 400 chromosomes.

Structural chromosome changes have also been a common occurrence in evolution. As described above, when a translocation or inversion involves one of a pair of homologous chromosomes, abnormal gametes are produced and fertility is reduced. However, in a small, inbreeding population, both male and female parents could receive a copy of the rearranged chromosome or chromosomes, and each parent could pass them on to an offspring, who would thus have a matched set of rearranged chromosomes. The latter would pair normally at meiosis, leading to the production of normal gametes. In this way, the altered chromosome could spread through a small, inbreeding population and might replace the initial chromosome arrangement, becoming fixed in the population. *See* POPULATION GENETICS.

Chromosome rearrangements do not change the banding patterns of the chromosome segments.

Therefore, it is possible to compare the karyotypes of species to determine what changes have been fixed in their evolution. For example, there is a preponderance of Robertsonian translocations in lemurs compared to other primates, and a preponderance of pericentric inversions in the chromosomes of the great apes and humans. The telocentric chromosomes of the European mouse, *Mus musculus domesticus*, undergo frequent Robertsonian translocations and, indeed, one mouse was found in which 18 of the 19 autosomes had undergone such translocations. At this time there is no evidence that chromosome changes alone have led to the creation of a new species, but it is clear that they can lead to sterility in certain outcrosses and to the reproductive isolation that is critical for speciation. *See* CHROMOSOME; RECOMBINATION (GENETICS); SPECIATION.

Orlando J. Miller; Dorothy A. Miller

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Chromosphere

A complex structure of warm gas above the visible surface, or photosphere, of the Sun and most stars. The term “chromosphere” was first applied to the red ring and large prominences seen at the edge of the eclipsed Sun with the unaided eye. Emission in the Balmer-alpha line of hydrogen at 653-nanometer wavelength accounts for the red color. The chromosphere is transparent in visible light, but is opaque and bright in the ultraviolet continuum and in strong lines of abundant elements, including hydrogen, helium (first observed during the 1868 solar eclipse), oxygen, calcium, and magnesium. Gas temperatures range from 3500 to 30,000 K (5800 to 54,000°F) and densities are between 10^9 and 10^{12} particles per cubic centimeter.

Structure of solar chromosphere. The solar chromosphere extends from roughly 500 km (300 mi) above the photosphere to where hydrogen becomes fully ionized and the gas temperature rises rapidly to more than 10^6 K (1.8×10^6 °F) in the corona. High-resolution images of the Sun taken in strong emission lines reveal a filamentary structure consisting of many magnetic loops. In the chromospheric network at the edges of 30,000-km-wide (19,000-mi) supergranule cells, the magnetic field is strong, the gas is dense and hot, and the chomosphere may be only 500 km (300 mi) thick. Here the magnetic heating rate is 10 or more times higher than average. Thin gas jets called spicules are clustered in the network. In the center of supergranule cells, where the magnetic field is weak, the chromospheric gas cools to 3500 K (5800°F) and extends upward several thousand kilometers. Here molecular carbon monoxide (CO) is abundant enough to keep this gas cool. *See* SUPERGRANULATION.

Chromospheres of other stars. Stars with effective temperatures less than about 8000 K (14,000°F; the Sun is 5770 K or 9930°F) show the same emission lines as the solar chromosphere and are thus thought to have analogous regions. Slowly rotating old stars show chromospheric emission at minimal levels comparable to those seen in the centers of solar supergranule cells. This weak emission indicates a basal level of chromospheric heating that is probably produced by the damping of nonmagnetic acoustic waves generated by convection in the lower atmosphere. Young, rapidly rotating stars show chromospheric emission at levels 10 or more times higher than is observed in regions of strong magnetic fields on the Sun. The highest levels of this emission correspond to saturated heating by magnetic-field reconnection events (often called microflaring) or the damping of magnetoacoustic waves.

Wilson-Bappu effect. In 1957 Olin C. Wilson and M. K. V. Bappu discovered that the widths of the near-ultraviolet emission lines of singly ionized calcium (Ca^+) increase with stellar luminosity. The Wilson-Bappu effect is now explained by the increased amount of gas in the chromospheres of lower-gravity stars, which have higher luminosities. Wilson began a long-term program to monitor the strength of the stellar Ca^+ emission, which led to the discovery of magnetic cycles on stars analogous to the 11-year solar cycle. Continued monitoring of this emission feature in many stars revealed that some are going through phases of no magnetic cycle, like the Maunder minimum of sunspots observed between 1645 and 1715. The energy budget and dynamics of stellar chromospheres have been studied with the *Hubble Space Telescope* and the *International Ultraviolet Explorer* satellite. *See* SATELLITE (ASTRONOMY); SUN.

Jeffrey L. Linsky

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Chronic fatigue immune dysfunction syndrome

A condition resulting in massive, debilitating fatigue accompanied by diverse symptoms including memory loss, diminished powers of concentration, sleep disorder, headache, low-grade fever, muscle and joint pains, sore throat, tender lymph nodes, and a postexertional malaise lasting more than 24 hours. This condition is also known as postviral fatigue, chronic fatigue syndrome, and myalgic encephalomyelitis. It is often associated with stress.

The severity of chronic fatigue immune dysfunction syndrome (CFIDS) varies considerably. Some patients are bedridden while others suffer only mildly debilitating symptoms. The cause of the disease is unknown, although there are hypotheses relating it to an abnormal immune response due to concurrent stress and a previous infection, perhaps viral. The Epstein-Barr virus, human herpes virus 6, cytomegaloinclusion virus, Coxsackie virus, various stealth viruses, and a retrovirus have been implicated. All of these viruses are common, and the general population is frequently exposed to them. Nevertheless, the general population does not suffer from the syndrome. One possibility is that exposure to the virus occurs during a period of either physical or emotional stress. Genetic and environmental factors may also be implicated. An abnormal immune response to viral or bacterial activity could explain many symptoms of CFIDS. Among possible sources of immune "dysregulation" in CFIDS are decreased natural killer cell (NK) cytotoxity, increased T and B lymphocyte activation, and elevated cytokine production. *See* EPSTEIN-BARR VIRUS; HERPES; INFECTION.

CFIDS is not life-threatening and is not considered communicable. However, it often occurs within families or within a defined geographical area, which, at least in some cases, suggests the possible involvement of an infectious agent. If a viral cause is proven, there would be an infective phase during or immediately after the incubation of the virus.

There is no definitive diagnostic test for CFIDS; thus it is necessary to first eliminate all other potential symptom etiologies. A diagnosis of the syndrome should be made only after alternative medical and psychiatric causes of chronic fatigue have been excluded. Fatigue can occur in the simplest to the most complex diseases. Conditions that must be excluded include simple iron deficiency anemia, familial or genetically related anemias, hematomachrosis, chronic infections (such as tuberculosis and Lyme disease), inflammatory conditions (such as sarcoidosis and thyroid dysfunction), autoimmune diseases (such as lupus erythematosus, Hashimoto's thyroiditis, and hemolytic anemia), and cancer.

While the majority of individuals with confirmed CFIDS have positive antibodies to one or more of the implicated viruses, the viruses are so common that antibody titers may be suggestive but are not diagnostic. *See* ANTIBODY.

There have been suggestions that CFIDS is a psychiatric state manifesting itself as a primary chronic depressive neurosis. This means that the individual is not physically ill but imagines somatic illness and may be labeled as neurotic or lazy. Despite many similarities in the somatic presentation of CFIDS and depression, various psychological, immunologic, and neurological tests indicate clear differences between the two disorders.

There is no standard method of treatment. However, some believe that treatment based on reversal of the abnormal immune response is helpful. Cognitive behavioral therapy and certain approaches to exercise have also demonstrated efficacy as treatments. Some individuals affected by CFIDS improve with time; when untreated, most remain functionally impaired for several years.

Derek Enlander; Christopher Snell

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Chronograph

Any device that measures a time interval. The term is usually restricted to measurements that have a small percentage error. Early time measurements used the human pulse rate or counted the number of swings of a pendulum for small time intervals. Astronomers used a regulated rotating drum to measure the time intervals of short changes in objects in the sky. Physicists did the same in the laboratory. The term chronograph seems to have stuck even when the device is digital rather than a graph. The term chronometer is often used interchangeably with chronograph, although again the result may be an electronically produced number rather than a meter reading. *See* CHRONOMETER.

Modern chronographs range from accurate wristwatch chronometers, used to time sporting events, to Doppler or other electronic or atomic means used in the laboratory or everyday living. *See* ATOMIC CLOCK; DOPPLER EFFECT; QUARTZ CLOCK; TIME-INTERVAL MEASUREMENT; WATCH. John L. Safko

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Chronometer

A large, strongly built watch especially designed for precise timekeeping on ships at sea. The name is sometimes loosely applied to any fine watch. *See* WATCH.

The features that distinguish a chronometer from a watch are (1) a heavy balance wheel, the axis of which is kept always vertical by mounting the entire instrument within two concentric rings, so pivoted as to permit the chronometer to remain undisturbed despite considerable tilting of the box containing it, as the ship rolls and pitches; (2) a balance spring wound in cylindrical shape, instead of a nearly flat helix; (3) a special escapement; and (4) a fusee, by means of which the power of the mainspring is made to work through a lever arm of continuously changing length, being shortest when the spring is tightly wound and longest when it has run down, thus regulating the transmitted power so that it is approximately constant at all times. *See* ESCAPEMENT; SPRING (MACHINES).

These mechanical chronometers are being replaced by quartz digital chronometers, which operate on the same principle as a quartz watch. *See* QUARTZ CLOCK.

Oceangoing ships formerly relied completely on chronometers keeping Greenwich mean time to determine longitude. The broadcast of radio time signals that became widespread in the 1920s, and subsequently the loran, Omega, and satellite navigation systems, have made Greenwich mean time available to mariners at almost any instant, and chronometers are no longer indispensable for determining longitude at sea. However, they are still a necessary backup, and naval vessels will not leave port without one or more chronometers aboard. *See* CLOCK (MECHANICAL); HOROLOGY; LORAN; SATELLITE NAVIGATION SYSTEMS; TIME. Steven J. Dick

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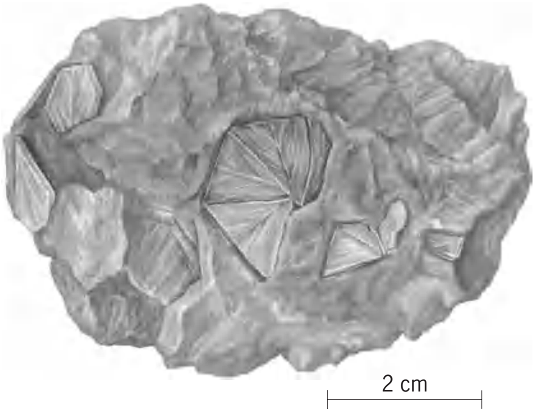
Chrysoberyl

A mineral having composition $BeAl_2O_4$ and crystallizing in the orthorhombic system. Chrysoberyl crystals are usually tabular parallel to the front pinacoid and frequently in pseudohexagonal twins (see **illus.**). There is good prismatic cleavage. The hardness is 8.5 (Mohs scale) and the specific gravity is 3.7–3.8. The luster is vitreous and the color various shades of green, yellow, and brown. There are two gem varieties of chrysoberyl. Alexandrite, one of the most prized of gemstones, is an emerald green but in transmitted or in artificial light is red. Cat's eye, or cymophane, is a green chatoyant variety with an opalescent luster. When cut en cabochon, it is crossed by a narrow beam of light. This property results from minute tabular cavities that are arranged in parallel position.



Chrysoberyl crystals in pegmatite, Greenwood, Maine. (*Specimen from Department of Geology, Bryn Mawr College*)

Chrysoberyl is a rare mineral found most commonly in pegmatite dikes and occasionally in granitic rocks and mica schists. Gem material is found in stream gravels in Ceylon and Brazil. The alexandrite variety is found in the Ural Mountains. In the United States chrysoberyl is found in pegmatites in Maine, Connecticut, and Colorado. *See* BERYLLIUM; GEM. Cornelius S. Hurlbut, Jr.

Chrysocolla

A silicate mineral with composition essentially $(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$; iron, and more rarely manganese, may substitute for copper. Although acicular monoclinic crystals have been reported, the wide variation in the composition of analyzed specimens suggests that chrysocolla is a hydrogel or gelatinous precipitate rather than a well-crystallized mineral. This suggestion is reinforced by the fact that x-ray diffractions are weak and ill defined. The mineral characteristically occurs in impure amorphous-to-cryptocrystalline crusts and masses with conchoidal fracture.

There is a wide variation in physical properties commensurate with the variation in chemical composition. The hardness varies from 2 to 4 on Mohs scale, the specific gravity varies from 2.0 to 4.0, and the refractive index is given variously from 1.40± to 1.60. The luster is vitreous to greasy; and the color is normally green to greenish blue but may be brown or, with manganese present, black.

Chrysocolla is a secondary mineral occurring in the oxidized zones of copper deposits, where it is associated with malachite, azurite, native copper, and cuprite. It is also found in alluvial gravels, indicating that copper is carried in solution far from its primary source. Chrysocolla is a minor ore of copper and a minor gem. Most gem material is essentially chalcedony colored by incorporated chrysocolla. *See* GEM; SILICATE MINERALS. Cornelius S. Hurlbut

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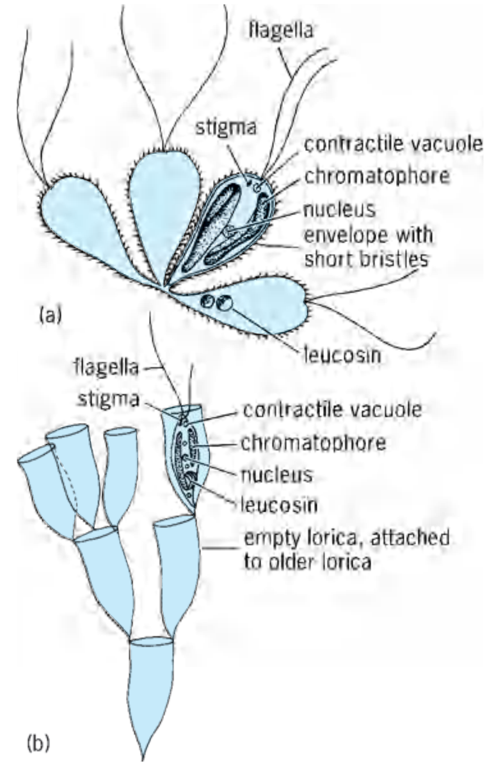
Chrysomonadida

An order of the class Phytamastigophorea. Many botanists consider this group a part of the class Chrysophyceae, the golden-brown algae. Chrysomonads, also known as Chrysomonadina, are usually small flagellates, *Mallomonas* being about the largest. They are yellow to brown because of



Chrysomonads. (*a*) Portion of colony of *Synura uvella*. Cell size is 20–40 μm, and colonies 100–400 μm. (*b*) *Dinobryon sertularia* colony. Cells measure 30–44 μm.

phycocrysin in the usual one or two chromatophores, but some lack chromatophores. *Uroglena* colonies may be quite large. Many species form diagnostic siliceous cysts. Palmelloid colonies (*Hydrurus*) consist of a tough, gelatinous matrix holding many nonflagellate cells. Starch is not formed, but fats are, and the refractive carbohydrate leucosin is common. The flagella are usually two, rarely three, and are subequal. Nuclei are small. *See* CILIA AND FLAGELLA.

Synura and *Dinobryon* are colonial types which produce enough oil to be a source of tastes and odors in drinking water (see **illus.**). *Dinobryon* often shows large numbers of cysts in the open ends of empty tests of old colonies. Chrysomonads may ingest food through the area near the flagellar base. Chrysomonadida are common in cooler fresh water, and certain types (Coccolithophora and Silicoflagellata) abound in the ocean. *See* CHRYSOPHYCEAE; COCCOLITHOPHORIDA; PHYTAMASTIGOPHOREA; PROTOZOA; SILICOFLAGELLATA. James B. Lackey

Chrysophyceae

A relatively large and diverse class of algae in the chlorophyll *a–c* phyletic line (Chromophycota). In protozoological classification, these organisms constitute an order, Chrysomonadida, of the class Phytomastigophora. Some workers align Chrysophyceae (golden or golden-brown algae) with Bacillariophyceae (diatoms) and Xanthophyceae (yellow-green algae) in the division Chrysophyta.

Chrysophytes typically are flagellate unicells, either free-living or attached, and solitary or colonial. There are, however, ameboid and plasmodial forms, solitary or colonial nonflagellate cells, filaments, and blades. Fresh-water forms, which are usually found in cold clear water, are more common than marine forms.

Although many unicellular chrysophytes have naked protoplasts, others are covered with organic or siliceous scales, or surrounded by a siliceous, cellulosic-pectic, or (rarely) calcareous lorica. Cells that compose blades and filaments have a polysaccharide wall. The statospore, an internally formed resting stage or cyst, occurs in the life history of most chrysophytes. It is urn-shaped, with a siliceous spiny body and a pectic plug. Similar cysts, assigned to the families Archaeomonadaceae and Chrysostomaceae, are found in the fossil record as far back as the Late Cretaceous.

Motile cells bear two subapically inserted, unequal flagella—a hairy (mastigoneme-bearing) flagellum directed forward, and a shorter, smooth flagellum directed backward. In some genera, the smooth flagellum is greatly reduced and may be represented only by its basal region, which may be transformed into a photoreceptive system, often in combination with an eyespot. Contractile vacuoles may be present in fresh-water forms.

Most chrysophytes are photosynthetic, but some are osmotrophic or phagotrophic. Each cell contains one or two chloroplasts (rarely more), which conform to the biochemical and ultrastructural patterns typical of Chromophycota. The chlorophylls are masked by carotenoids (especially β-carotene and fucoxanthin), producing the characteristic golden-brown color. Chloroplast endoplasmic reticulum is present, thylakoids are in groups of three, and chloroplast deoxyribonucleic acid is distributed in a ring. The chief storage product is chrysolaminaran, which is a glucose polymer with β-1,3 linkages, but lipids are also stored.

Asexual reproduction in unicellular forms is by longitudinal binary fission, autospores (nonflagellate cells that are miniatures of the parent), or zoospores, and in multicellular forms by fragmentation or zoospores. Sexual reproduction, observed rarely and in only a few species, is isogamous.

A satisfactory classification of the approximately 1000 species of chrysophytes has not yet been elaborated. One scheme emphasizes somatic organization, by analogy with green algae (Chlorophyceae), while another scheme emphasizes details of flagellation. Studies using electron microscopy and laboratory culture have led to the removal of certain groups to other classes. The choanoflagellates—collared, colorless flagellate unicells—were formerly aligned with chrysophytes or placed in their own class (Craspedophyceae), but similarity to sponge choanocytes supports their placement among animals, as the order Choanoflagellida of the class Zoomastigophora. Members of the order

Isochrysidales, characterized by having two equal flagella, have been transferred to the class Prymnesiophyceae. The bicosoecids, a small group of colorless unicells with a lorica formed of spiral or annular elements and with one of the two flagella serving as a contractile stalk, are sometimes appended to the Chrysophyceae or, alternatively, assigned to the Zoomastigophora. Finally, silicoflagellates, which are characterized by an elaborate siliceous endoskeleton and a unique protoplast, are placed in the subclass Dictyochophycidae or referred to their own class. They are a relictual group common in the fossil record as far back as the Early Cretaceous but represented in modern seas by only a few taxa. *See* ALGAE; BACILLARIOPHYCEAE; BICOSOECIDA; CHOANOFLAGELLIDA; CHRYSOMONADIDA; XANTHOPHYCEAE. Paul C. Silva; Richard L. Moe

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Chrysotile

Chrysotile is a fibrous mineral with a tubular morphology for each fibril (**Fig. 1**). It is a member of the serpentine mineral group, as are antigorite and lizardite. Chrysotile aggregates make up serpentine asbestos, which is the most important type of commercially mined asbestos. Russia and Canada are the main producing countries. Chrysotile displays interesting properties such as being thermally and electrically insulating, sound insulating, chemically inert, fire-resistant, mechanical energy–absorbing, and flexible with enough high tensile strength to be woven. There are hundreds of applications for chrysotile including fire retarder in buildings, roofing tiles, brake pads, weavable material for refractory clothes, filters, and fibers in fibrocement and road surfaces. *See* ASBESTOS; SERPENTINE; SERPENTINITE.

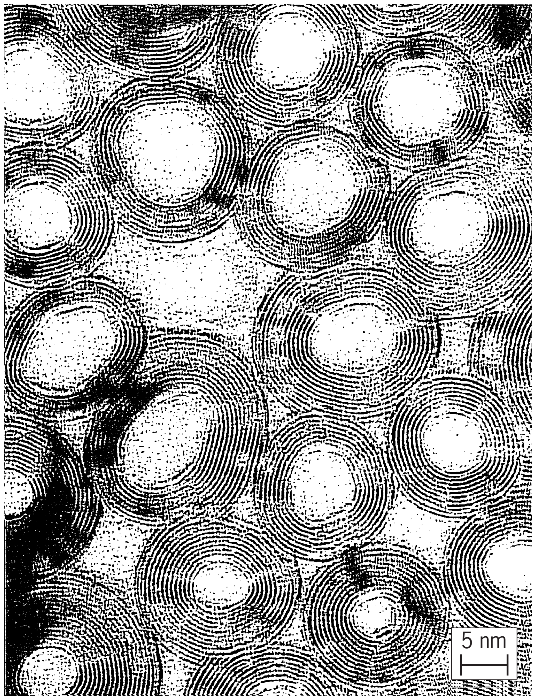

Fig. 1. Cross section of parallel chrysotile fibrils seen with a high-resolution transmission electron microscope (TEM). Black circular fringes image a chrysotile layer containing an octahedral and tetrahedral sheet.

Intensive inhalation of long and thin asbestos fibers over a considerable time period can induce pulmonary diseases such as asbestosis and lung cancers, as well as pleural diseases such as plaques, fibrosis, and mesothelioma. Such health hazards have drastically reduced the use of chrysotile, which is strictly regulated by law in western countries. *See* RESPIRATORY SYSTEM DISORDERS.

Geological occurrence. Chrysotile asbestos shows up mainly as cross-cutting veins in serpentinized green rocks, such as peridotites. It often forms from hydrothermal alteration ($T \leq 350°C$ or 662°F) of magnesium-rich olivines. In general, most serpentines are reacted on and below the sea floor, at slow-spreading mid-ocean ridges, as heated seawater interacts with exposed rocks from the upper mantle of the Earth. Obduction of such rocks accounts for serpentinites in some orogenic belts (for example, the Western Alps). *See* OLIVINE; PERIDOTITE.

Parallel assemblages of chrysotile fibrils in veins are either at a moderate angle (slip fibers) or more commonly normal (cross-fibers) to the vein walls. Progressive shear or opening of the vein by tectonic events seems to be required for massive development of long fibers.

Crystal-chemical properties. The chemical composition of chrysotile expressed as its formula unit is close to $Mg_3Si_2O_5(OH)_4$ [Mg = magnesium, Si = silicon, O = oxygen, OH = hydroxyl], with minor amounts of aluminum (Al) and iron (Fe) and traces of nickel (Ni) and chromium (Cr). This silicate layer is characterized by a tubular shape of each fibril as the basic unit of this material. Each tubule is made of 0.73-nanometer-thick cylindrical layers fitted into each other as telescopic tubes or coils. Most common tubule dimensions are 20 nm outer diameter, 5–7 nm inner diameter, and from 1 micrometer to several centimeters length. Fibrils may aggregate as fibers with a more or less close-packed arrangement of the tubules.

Each curved chrysotile layer is made of two assembled sheet components when viewed at the atomic scale: an outer octahedral sheet (Oc) and an inner tetrahedral sheet (Te). Silicate tetrahedra combine as a honeycomb network to form the tetrahedral sheet. Each silicate tetrahedron consists of a silicon atom surrounded by four close-packed oxygen atoms, and any tetrahedron shares three oxygen atoms with its neighbors whereas the fourth oxygen points toward the octahedral sheet. The octahedral sheet is built up by edge-sharing octahedra all lying on one of the faces, and each is centered by magnesium atoms (**Fig. 2**). All octahedron corners opposed to the tetrahedral sheet are hydroxyl groups. One-third of the inner corners are occupied by hydroxyl groups, whereas the two-thirds left are completed by the above-mentioned nonbridging oxygens of the tetrahedral sheet.

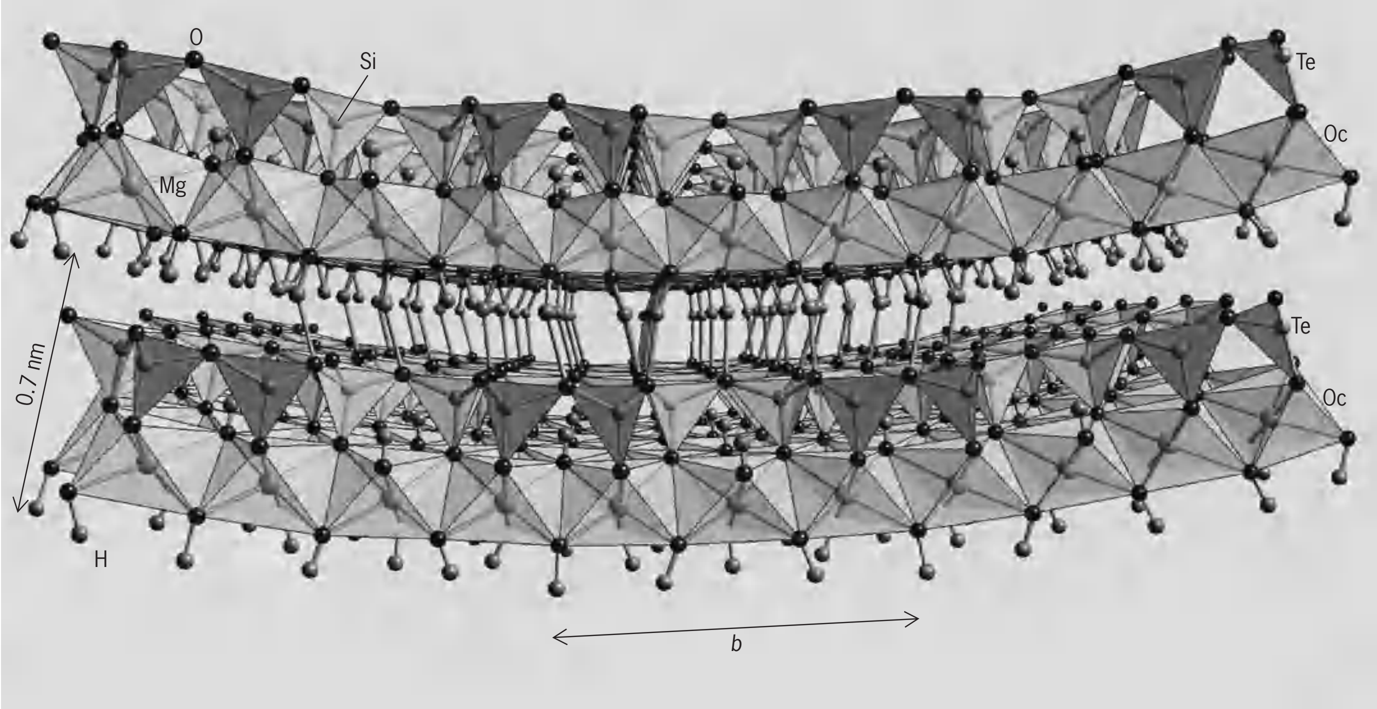

Fig. 2. Atomic structure of a portion of two contiguous chrysotile layers (Oc = octahedral sheet, Te = tetrahedral sheet). Atoms and bonds are seen on and inside translucent coordination polyhedra. Note the progressive deformation and breaking of hydrogen (H) bonds between the layers. This three-dimensional representation was done with CRYSTALMAKER^{TM} software.

The curvature of the serpentine layer of chrysotile is thought to arise from the larger lattice dimensions of the octahedral sheet compared to those of the tetrahedral sheet. Accordingly, curvature is concave toward the tetrahedral sheet, and this partially compensates for any misalignment along with other tetrahedral sheet distortions. Such curvature disturbs the hydrogen (H) bonding between successive layers, that is, the linkage between hydroxyl groups of the octahedral sheet and bridging oxygen of the tetrahedral sheet of the next layer. Due to a progressive structural glide between consecutive layers, a periodic modulation of the hydrogen-bonding strength is observed along the fibril circumference (Fig. 2). This may weaken the average interlayer bonding compared to the case of lizardite, the flat serpentine. *See* HYDROGEN BOND.

Topologies of fibrils. Chrysotile tubules have layers arranged either as pure tube-in-tube cylinders or as spirally wound scrolls. The fibrils elongate either along the x axis (0.53 nm repeat) for normal chrysotile, or along the y axis (0.90 nm repeat) for para-chrysotile. Less frequently, helically wound (chiral) chrysotile tubules are found with curvature axes inside the lattice layer (similar to carbon nanotubes). *See* FULLERENE.

Flat serpentine layers of lizardite are translationally periodic in structure. Once such layers are curved and fitted into each other (as in chrysotile), the tubule loses both radial and circumferential periodicity. Periodicity is maintained along the tubule axis only, thus making chrysotile a kind of a one-dimensional crystal.

Fivefold symmetry. Each time a new cylindrical layer is added on the external surface of a normal chrysotile tubule, five more unit cells of b length are necessary to close up the circumference, because the increment of the perimeter is equal to five times the b length. The uniform distribution of such extra length along a turn implies that any interlayer configuration is recovered regularly five times per turn. Consequently, whatever the stacking sequence of curved unit cells along a tubule radius, the same sequence is recovered at integral multiples of $2\pi/5 = 72^\circ$. Accordingly, fivefold symmetry may be foreseen for the cylindrical lattice of chrysotile tubules as shown by the diffraction pattern of model lattice masks. More direct evidence of fivefold symmetry came from the numerical Fourier transforms of lattice images of tubule cross sections observed by high-resolution transmission electron microscopy (**Fig. 3**). From the above, chrysotile would be the first mineral having a normally forbidden fivefold symmetry axis. This axis would be macroscopic and unique, and in coincidence with the fibril axis. Accordingly, such fivefold symmetry might differ from that of quasicrystals of binary and ternary intermetallic alloys where six distinct fivefold axes are present at both macroscopic and microscopic scales. *See* CRYSTAL STRUCTURE; CRYSTALLOGRAPHY.

Polygonal serpentines. In serpentinite veins of ultrabasic rocks, long and thin chrysotile fibers coexist frequently with shorter but thicker polygonal fibers of serpentine. When observed with the transmission electron microscope, cross sections of polygonal serpentines exhibit either 15 or 30 radially distributed sectors of flat serpentine, each akin to lizardite (**Fig. 4**). *See* ELECTRON MICROSCOPE.

There are geological occurrences where either 15-sectored or 30-sectored fibers are present, others where both types coexist. In the latter case, 30-sectored fibers are statistically larger in diameter (up to several micrometers) than 15-sectored ones. Electron diffraction patterns of single polygonal fibers have fivefold symmetry (Fig. 4). Reasons for such symmetry are the same as those invoked for chrysotile. In polygonal serpentines, flat sectors develop where the interlayer hydrogen bonding is satisfied along the radius of the fiber. Such bonding occurs easily 15 times per turn, or less easily 30 times per turn. *See* ELECTRON DIFFRACTION.

Experimental evidences support a transformation of chrysotile into polygonal serpentines, that is, a polygonization process of cylindrical tubules. Such a transition would take place for growing chrysotile when its diameter overshoots 50–100 nm. Further development of polygonal serpentine to micrometer size would occur by nucleation and further growth of serpentine layers inside and outside the polygonal tube.

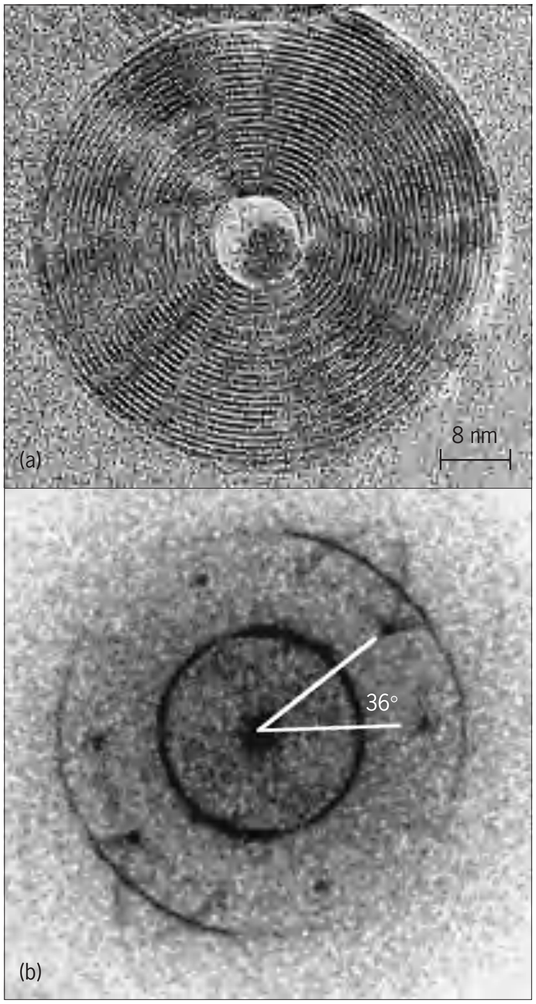

Fig. 3. Chrysotile tube. (*a*) High-resolution TEM image. (*b*) Numerical Fourier transform. The fivefold symmetry of the pattern shows up from the 36° angle between visible spots. (*Courtesy of B. Devouard*)

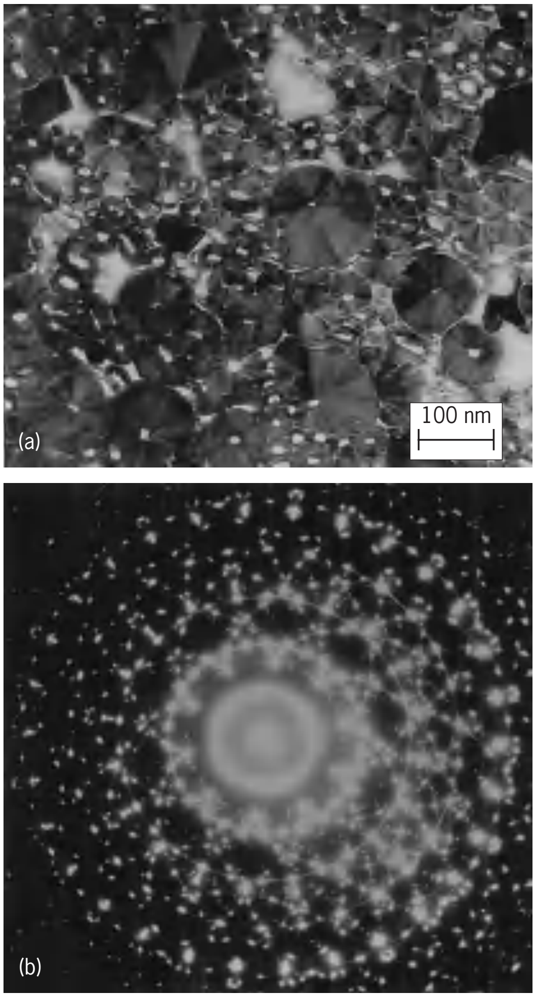

Fig. 4. Polygonal serpentine. (*a*) TEM image of cross-sectioned serpentines, with 15 sectors each. (*b*) Electron diffraction pattern of a serpentine as a rose with fivefold symmetry. (*Courtesy of A. Baronnet and B. Devouard*)

Fiber type and associated hazards. Pure material made of close-packed, poorly coherent chrysotile tubules is finely fibrous and silky. Scratching it with a nail or pouring water droplets on it produces a cottonlike or liquid soap aspect, respectively. Easy separability and thus dispersion of such fibrils in air or in a liquid are likely, so that such material is potentially harmful when inhaled or ingested by humans. Aggregates of polygonal serpentine fibrils that are tightly intergrown and short may be considered less hazardous since they are not able to produce dusts containing long fibers.

Alain J. Baronnet

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Chytridiomycota

A phylum of primitive fungi characterized by production of predominantly aquatic fungi characterized by production of uniflagellate zoospores (asexually produced motile spores). Chytrids are basal in the fungal lineage and are thought to have diverged about 1 billion years ago from an ancestor shared with protistian groups such as the Choanoflagellates and Mesomycetozoa. *See* CHOANOFLAGELLIDA; FUNGI.

Phylogeny. Chytridiomycota includes five orders: Blastocladiales, Chytridiales, Monoblepharidales, Spizellomycetales, and Neocallimastigales. Ultrastructural studies reveal distinct zoospore architecture in each order. Molecular analyses indicate that phylum Chytridiomycota is not monophyletic; rather order Blastocladiales is most basal, evolving among members of the Zygomycota and diverging from the core chytrids. Based on thallus structure, 90 genera and over 1500 species of chytrids have been named. Recent molecular and ultrastructural phylogenetic studies, however, have demonstrated unexpected genetic diversity among chytrid fungi, indicating that the actual species richness of this group is untapped. *See* ZYGOMYCOTA.

Morphology and reproduction. Chytrids exist in a variety of morphological forms, enabling them to adapt to life in diverse habitats. All thallus forms ultimately produce zoospore-generating structures called sporangia (**Fig. 1**). Members of the Blastocladiales and Monoblepharidales commonly form filaments, similar to hyphae of higher fungi. Simpler thallus forms consist of sporangia and rootlike rhizoids, and can vary in structure from a holocarpic thallus, in which the entire thallus has developed into a sporangium, to repeating sporangial units in polycentric rhizomycelia. Sexual recombination is achieved with fusion of motile gametes, fusion of contributing thalli, or fusion of motile gametes with nonmotile gametes. Zoospores function in asexual reproduction, in which stored lipids are used as an energy source through the coordinated interactions of organelles in the microbody–lipid complex. Positioned near the flagellum, the microbody–lipid complex can be viewed as the "battery" of the zoospore (**Fig. 2**). The microbody of the complex contains enzymes that help convert stored lipids to energy with the aid of mitochondria, and the membrane cisterna sequesters calcium, suggesting a role in signal transduction and the regulation of flagellar beating.


Fig. 1. Light micrographs of zoospore discharge. The spherical sporangium (diameter 30 μm) of a chytrid thallus growing on sweet gum pollen (the pollen grain is the sphere at the left) progressively releases a globular mass of zoospores into a vesicle. Zoospores swarm within the vesicle for about 5 min before swimming away as uniflagellate zoospores. (*Micrographs by Peter Letcher*)


Fig. 2. Electron micrograph of a longituditudal section through a chytrid zoospore (length 6 μm) with two visible lipid globules (homogenous gray circles at bottom left and upper right of the zoospore). The single flagellum is at the posterior end of the zoospore. The nucleus is surrounded by a dense, granular mass of ribosomes. Mitochondria cluster near microbodies that encircle the anteriorly located lipid globule. A fenestrated cisterna surrounds the posteriorly located lipid globule.

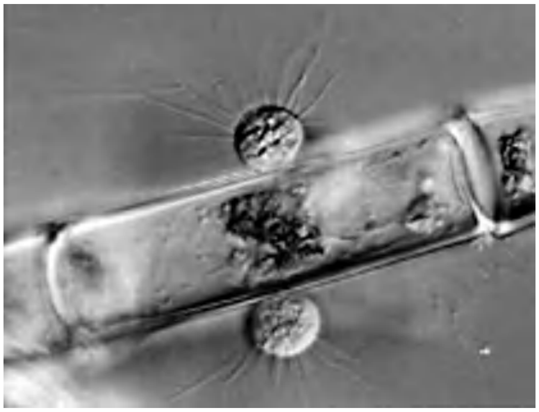
Fig. 3. Light micrograph of two chytrid thalli infecting the filament of a green alga. Hairlike appendages extend from the sporangia (diameter 30 μm) of the chytrid thalli. The contents of the host cell are collapsed.

Ecology. Chytrids are important saprotrophs, feeding on dead and decaying organisms in both aquatic and terrestrial habitats, and have been collected from the Arctic to the tropics. They are biodegraders and nutrient recyclers of resilient materials such as chitin, keratin, cellulose, and pollen. *Rhizophlyctis rosea* is a chytrid resistant to desiccation and a ubiquitous cellulose degrader found in soils. The Neocallimastigales, a group of obligately anaerobic chytrids that live in the digestive tracts of ruminant animals such as cows and sheep, are especially important in improving feed value of cellulosic and hemicellulosic foods. *See* FUNGAL ECOLOGY.

Parasitic activity. Chytrids are also common parasites of algae (**Fig. 3**), other fungi, insects, plants, and animals. Algal parasites are implicated in the natural control of algal blooms. *Coelomomyces* decreases mosquito populations by parasitizing mosquito larvae and inducing adult female mosquitoes to oviposit its sporangia rather than mosquito eggs. *Synchytrium endobioticum* causes black wart of potatoes and makes potato production difficult in infested soils due to the longevity of chytrid resting spores which remain dormant for long periods before germination, withstanding adverse conditions. *Caulochytrium protostelioides* parasitizes hyphal fungi on plant leaves. *Batrachochytrium dendrobatidis*, discovered in the mid-1990s and considered a primary culprit in the global deaths and mass extinctions of frogs and other amphibians, is the first documented chytrid parasite of vertebrate animals. *See* PARASITOLOGY. Martha J. Powell

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Ciconiiformes

An order of predominantly long-legged, long-necked wading birds including herons, ibises, spoonbills, storks, and their allies, and also the hawklike New World vultures which were previously placed in the Falconiformes. The flamingos have traditionally been placed in this order; however, they show a number of unique features and differences and so are placed in a separate order, Phoenicopteriformes. Some workers have suggested that the ibises are members of the Charadriiformes and that the herons should be placed in a separate order; however, these suggestions are controversial. *See* CHARADRIIFORMES; FALCONIFORMES; PHOENICOPTERIFORMES.

Classification. The order Ciconiiformes is divided into four suborders and seven families: Ardeae, with the family Ardeidae (herons; 62 species; worldwide); Balaenicipites, with the family Balaenicipitidae (shoe-billed stork; one species; Africa); Ciconiae, with the families Scopidae (hammerhead; one species; Africa); Threskiornithidae (ibises and spoonbills; 33 species; worldwide); Ciconiidae (storks; 17 species; worldwide); and Cathartae, containing the families Teratornithidae (Miocene to Pleistocene of South and North America) and Cathartidae (New World vultures; seven species; New World).

Several of these families are divided into subgroups, the most distinct of which are the ibises (Threskiornithinae) and spoonbills (Plataleinae). The affinities of the New World vultures to the ciconiiforms, and especially to the storks (Ciconiidae), have been demonstrated rather convincingly. For many decades, numerous ornithologists have queried the inclusion of these birds in the Falconiformes, but their true affinities had been obscure.

Great blue heron (*Ardea herodias*), Galápagos Islands, Ecuador. (*Photo by H. Vannoy Davis; © 2001 California Academy of Sciences*)

Fossil record. Except for the Cathartae, the fossil record of the Ciconiiformes is scattered, considering that these are large wading birds, and does not illustrate anything special about the relationships and distribution of these birds. The New World vultures have an extensive fossil record, including in the Old World; the Teratornithidae are found in both North and South America and include the longest winged birds.

Characteristics. The herons (Ardeidae, see **illustration**), shoe-billed stork (Balaenicipitidae), hammerhead (Scopidae), ibises and spoonbills (Threskiornithidae), and storks (Ciconiidae) are mainly wading birds with strong legs, living in marshes and other wet areas. They feed on crustaceans, fish, amphibians, and other animals, which are caught in various ways depending on the structure of the bill. Most are diurnal, but a few are nocturnal. Some of the storks are scavengers. Most species are colonial and nest in mixed, often huge, colonies in trees or on the ground, as well as a few on cliff ledges; the hammerhead builds a huge, domed nest. All are strong fliers, usually having to cover a long distance between the nesting site and feeding areas; some are excellent soarers.

Most species have elaborate courtship displays and form tight pair bonds; many species of herons possess specialized courtship plumes. The young remain in the nest and are cared for by both adults until they are able to fly. They are tropical to cool temperate, with those species breeding in colder areas migrating to warmer regions for the winter. Many species of herons and egrets had been intensively hunted for their courtship plumes; some were almost extinct before fashions of apparel changed and the birds received protection. The numbers of many species have been drastically reduced, and several are threatened mainly because of lack of the needed wetland habitat. The white stork of Europe, which nests readily on human structures and is a symbol of fertility, has been reduced greatly in much of its range because of accidents with wires and loss of wetlands.

Cathartae. The New World vultures appear to be typical hawks and had been placed in the Falconiformes since the beginnings of avian classification but with ever-increasing doubt. It has been shown rather convincingly that they should be placed in the Ciconiiformes and are closest to the storks. They are placed in a separate suborder to emphasize their specialization as scavengers. These vultures are large soaring birds; the Andean condor has the largest wing span of any living land bird. (However, their wings are shorter than the largest members of the fossil teratornithids.) Vultures locate their food from the air either by sight or by smell; these abilities differ in the several species, with the Turkey vulture (*Cathartes aura*) finding its food in forested areas by smell. Vultures may be solitary or hunt in loose flocks; larger concentrations may exist during the winter. They nest solitarily, with the nest placed on the ground or on a cliff ledge. The one to three young remain in the nest until they can fly. Most species are common, but the California condor (*Gymnogyps californianus*) has decreased steadily in numbers and became extinct in the wild. Survival of this species will depend on captive breeding and reintroduction of birds to the wild, which appears to have been successful following releases in California and in the Grand Canyon of Arizona.

The fossil history of the New World vultures is excellent. It suggests that the Cathartidae had their early evolution in the Old World and invaded the New World only in the Neogene. More interesting are the closely related Teratornithidae known from North and South America, which include the birds with the largest wing spans. The relatively small *Teratornis merriami* had a wing spread of up to 3.8 m (12 ft), and the larger *T. incredibilis* had an estimated wing span of up to 5.9 m (19 ft). However, *Argentavis magnificens* from the Late Miocene of Argentina had an estimated wing span of 7–7.6 m (22.5–24 ft) and a weight of about 120 kg (264 lb), making it the largest flying bird known by far. *See* AVES.

Walter J. Bock

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Cilia and flagella

Centriole-based, motile cell extensions. These organelles are usually indistinguishable in fine structure as seen with the electron microscope, but quantitatively there are many (several hundred) cilia and few or fewer (usually one or two) flagella, on one cell. Bacterial or prokaryotic flagella are entirely different organelles that are not considered in this article, which concerns only eukaryotic (higher-cell) flagella. *See* BACTERIA.

Characteristics and occurrence. Flagella move with undulatory motion in which successive bending waves progress along the length of the organelle (**Fig. 1**), whereas cilia move with flexural motion consisting of a planar effective stroke, with the organelle extended perpendicular to the cell body, followed by a nonplanar curving recovery stroke, with the organelle pulled parallel to the cell body. Cilia and flagella are low-Reynolds-number systems, which implies that viscous forces are more important to the motion of the organelles than inertial forces are. On a macroscopic scale, this is equivalent to swimming in molasses, and the fluid can be thought of as being clawed forward by the effective stroke of the cilium or as being pushed away by the propagating undulatory wave of the flagellum. Beat frequencies of cilia and flagella in different organisms range from about 2 to more than 50 per second. During a beat, bends usually originate and grow in restricted regions at the base of the organelle in the form of circular arcs. They then propagate toward the tip at rates of several

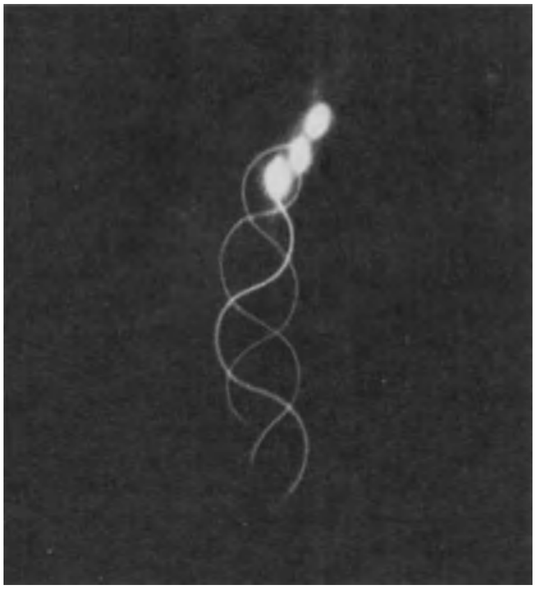

Fig. 1. Sea urchin sperm shown in three positions by dark-field microscopy. Note undulatory waveform as it swims. (*From C. J. Brokaw, Nonsinusoidal bending waves of sperm, J. Exp. Biol., 43:155–169, 1965*)

hundred micrometers per second without changing amplitude or form. On sperm tails, bends of equal magnitude but of opposite direction are separated by straight regions of uniform length to give a symmetrical waveform that is superficially sinusoidal. A similar but asymmetrical waveform on a shorter cilium produces one typical form of flexural motion. Both organelles function to move water past the cell. Their action may bring food and oxygen into an animal, or it may propel the cell to a new environment. Cilia often move sheets of mucus at velocities of about 0.008 in. (0.2 mm) per second, either in water or over surfaces exposed to humid air, as in the human respiratory tract. Particles trapped in such sheets are effectively cleared from the epithelial surface. *See* CELL MOTILITY.

Distribution. Cilia were first described by A. van Leeuwenhoek in 1676. The words cilium (eyelash) and flagellum (whip) are accurate descriptions of the appearance of these cell organelles when they are seen under the light microscope. Cilia are present on protozoa, such as *Paramecium*, and on metazoan cells of many different tissue types. For example, in humans, many cells lining the respiratory and reproductive tracts, the ear and the olfactory epithelium, as well as ependymal cells in the brain, have functioning cilia. A flagellum is present on human sperm; in fact, the sperm of most animals, and the male gametes of many lower plants are flagellated. Even the *Ginkgo* spermatozoon is ciliated. Derivatives that are similar to cilia but nonmotile are found on many sensory structures in a variety of animals and include insect pressure receptors and vertebrate photoreceptors. In addition, many ordinary types of cells of vertebrates, for example, from the thyroid, the kidney, or the pituitary gland, also possess modified nonmotile derivatives that resemble cilia, and other cell lines can be induced to grow them in tissue culture. *See* CILIOPHORA; EPITHELIUM; SPERM CELL; TISSUE CULTURE.

Size. Relative to cell size, both cilia and flagella are very long organelles. Flagella may be more than 50 micrometers long and, in sperm, may be four or more times the cell length. Certain compound cilia, such as the comb plates of ctenophores, are truly macroscopic structures, visible to the naked eye. In these structures, many thousands of individual cilia are joined together laterally, and the length of each cilium runs to a few millimeters. Usually, however, cilia range from 5 to 15 μm in length.

Metachronism. Fields of cilia or flagella such as those in invertebrate flame cells can beat synchronously. Often, however, even on a single cell, cilia beat so that coordinated waves of bending appear to cross the field. Originally, these waves were described as the sort that are seen rippling across a wheat field when the wind is blowing. The phenomenon of beating slightly out of phase is known as metachronism. Several types of metachronism are recognized, since the plane of ciliary beat may be either perpendicular (diaplectic) or parallel (orthoplectic) to the direction of the metachronal wave. Metachronal coordination is usually effected by purely mechanical means; that is, viscoelastic coupling establishes a phase difference between individual cilia so that there is minimal mechanical interference between one beating cilium and its neighbors. In a ciliated epithelium the cells can be functionally linked together so that metachronal waves pass smoothly from cell to cell.

Behavior. Under normal conditions, most cilia and flagella beat continuously, although some cilia (for example, mammalian respiratory cilia and mammalian sperm) require special activation for beating. Many organisms are able to alter properties of ciliary beat, including form, frequency, the direction of the effective stroke, or the direction of bend propagation; sometimes, the ciliary stroke can be arrested. Cells usually alter beat properties by common mechanisms leading to increases in second messengers, including internal calcium ion (Ca^{2+}) or cyclic nucleotide concentrations. For example, in *Paramecium*, depolarization of the cell membrane opens voltage-sensitive calcium channels in the ciliary membrane, which leads to an increase in calcium ion concentration in the cilium above $10^{-7}\,M$. This in turn leads to slowed and then to backward swimming at concentrations above $10^{-6}\,M$. When calcium ion is pumped out of the cilium, the normal beat resumes. Different second messengers may have different effects. Cyclic adenosine monophosphate (cAMP) increases normal beat frequency in *Paramecium* cilia, leading to faster forward swimming. Such processes allow the cell to respond to various stimuli and form the basis of behavioral responses of free-swimming ciliated cells. The same messenger may have different modes of action in different cilia; for example, calcium ion activates and increases beat frequency in mammalian respiratory cilia.

Ultrastructure. The electron microscope reveals that the cilium or flagellum is really an internal organelle since it is bounded by the cell membrane and enclosed at the tip. The main internal structure of the cilium is the axoneme. Under the electron microscope a single axoneme contains a fixed pattern of microtubules. The microtubules are not simple single units; rather, nine doublet microtubules are found on the periphery of the axoneme surrounding two central elements. This is the so-called 9 + 2 pattern (**Fig. 2**).

Microtubule arrangement. Each peripheral doublet is composed of one complete and one partial microtubule. The microtubules are themselves composed of subunits arranged into microfibers or protofilaments. The complete microtubule, labeled subfiber A, consists of a ring of 13 protofilaments. The incomplete microtubule, subfiber B, is a C-shaped structure of 10 or 11 protofilaments. In a transverse section the doublets appear as figure eights, with two short arms and several linkages extending from one end. The doublets form a ring around the central pair. The diameter of this ring is very constant, about 0.2 μm, even in different types of cilia or in cilia of different species.

Microtubule pattern variation. The 9 + 2 pattern is present in all known motile cilia. Motile flagella, especially sperm tails, sometimes possess altered

Fig. 2. Electron micrograph of mussel gill cilia cross sections showing 9 + 2 pattern of axoneme. At the left are cross sections through tips at various levels. (*From P. Satir, Studies on cilia, II: Examination of the distal region of the ciliary shaft and the role of the filaments in motility, J. Cell Biol., 26:805–834, 1965*)

patterns, although these are usually simple variations upon the basic array. Flatworm sperm, for example, show a 9 + 1 pattern (one central element instead of two), although somatic cilia of the same animal are 9 + 2. Insect sperm show even greater divergences. Mammalian sperm have the 9 + 2 pattern, but in addition have a set of thick fibers alongside the axoneme. The most simply organized motile flagella in eukaryotes are the 6 + 0 and 3 + 0 forms present in male gametes of certain gregarine protozoa. In these flagella, the doublet tubules appear to possess normal arms, but the spokes and central pair are lacking. Nonmotile flagellar derivatives usually have 9 + 0 patterns and lack both the arms and the central pair. All these patterns are constant within any one species of animal or plant, with the exception of certain very rare variants that are probably mistakes in assembly.

Symmetry. If the arms are disregarded, there is a plane of bilateral symmetry in the normal cilium which passes between two peripheral doublets, through the central pair, and through one doublet on the side opposite. This doublet is numbered 1, and the plane of bilateral symmetry is also the plane of the effective stroke. By looking from the cell surface and outward along the axoneme, looking clockwise from subfiber B of doublet number 1, the sequence is subfiber B, subfiber A, arms of doublet number 1, subfiber B, subfiber A, arms of doublet number 2, and so on. The arms always extend from subfiber A of any doublet N toward subfiber B of the adjacent doublet. In this manner the doublets can be numbered unequivocally. The two peripheral doublets between which the plane of bilateral symmetry passes are the numbers 5 and 6, and these may be specially distinguished in some cases by being connected by a distinctive bridge.

Axonemal linkages. The axonemal microtubules are interconnected into a functional whole by groups of projections extending in different directions from each subfiber A (**Fig. 3**). These include the two circumferentially oriented rows of dynein arms. The outer arms repeat at spacings of about 24 nanometers. The outer arms are uniform, but the inner arms are sometimes of two or three types with a more complicated spacing. There are also several types of circumferentially oriented links, some of which form elastic connections, some inelastic connections, between doublets. The periodicity of these links is about 96 nm. Radially oriented spoke groups project toward the central sheath with a major period of 96 nm; the spoke groups often comprise three individual spokes, each of which ends in an expanded spoke head. The spokes are spaced at intervals of 32, 24, and 40 nm, with the first spoke of each group in alignment with a set of dynein arms. There are six central sheath projections per spoke group. Such vernier alignments may prove to be important in the regulation of beat form.

Morphogenesis. At the base of the cilium or flagellum there is a basal body, or kinetosome, that is similar to, and sometimes derived from, a centriole. The basal body may have extensions of various sorts attached to it, notably a basal foot that indicates effective stroke direction and prominent striated rootlet fibers in many cilia. Ordinarily, the ciliary axoneme originates and grows in a membrane protrusion which forms just above the basal body, either at the cell surface or deeper inside the cytoplasm. The basal body remains attached to the cell membrane throughout morphogenesis by a structure that extends from the microtubules to the membrane, where it is seen as a ciliary necklace. The necklace forms a barrier that segregates the ciliary membrane from the general cell membrane. As morphogenesis proceeds, from a pool of subunits, axonemal

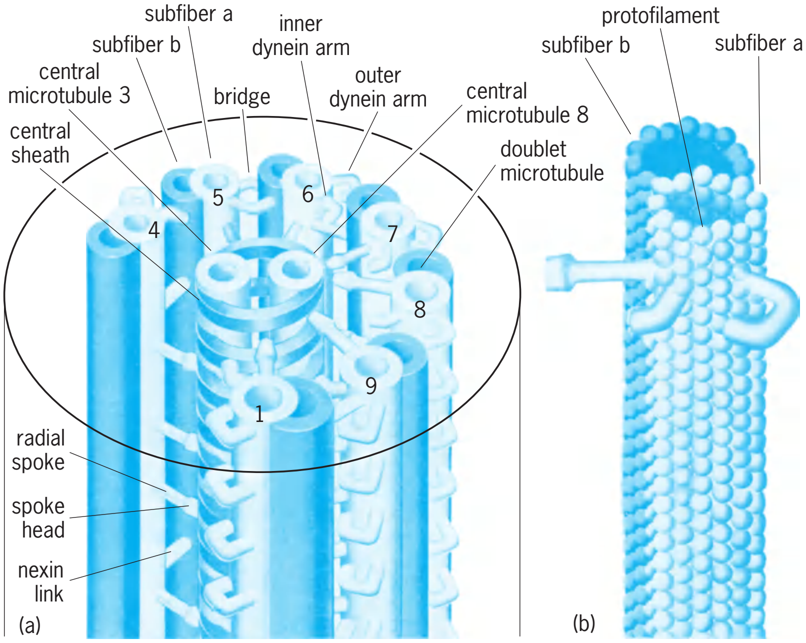

Fig. 3. Ultrastructure of a cilium. (*a*) Three-dimensional reconstruction with doublets 2 and 3 removed to show spoke periodicities more clearly. (*b*) Three-dimensional wall structure of a doublet showing tubulin subunits. (*After P. Satir, How cilia move, Sci. Amer., 231(4):44–52, 1974*)

microtubules polymerize above the basal body. Continuity of the microtubules between axoneme and basal body may be traced through a complex transition zone. Evidently, polymerization of the axonemal microtubules takes place at the growing tip of the cilium. Certain cells such as the ameboflagellate *Naegleria* can grow or resorb the cilia in response to internal programming during the cell cycle, or upon physiological stimulation. *See* CENTRIOLE.

Genetic control. Morphogenesis is under genetic controls, in part by nuclear genes. For example, certain nuclear mutants in *Chlamydomonas* fail to polymerize the central microtubules. Other mutants lack radial spokes or either the outer or the inner row of dynein arms. In these cases, the mutant flagella are partially or completely paralyzed, or the beat form or frequency is altered. Paralyzed and behavioral mutants have also been found in other species, ranging from *Paramecium* to humans. Approximately 1 in 40,000 people suffer from an inherited genetic defect originally known as Kartagener's syndrome, in which the cilia of the bronchial tract and the sperm flagella (in males) are paralyzed, in some instances because dynein arms are completely lacking on the doublet microtubules. People with this syndrome have considerable respiratory difficulty, and males are infertile. These people also have a 50% chance of their heart and other internal organs being on the opposite side of the body compared with normal anatomy, possibly as a result of ciliary immotility during embryonic development.

Growth parameters. The extent of each axonemal component is strictly determined. In mussel gill lateral cilia, all subfiber B's of the peripheral doublets end at the same level. Simultaneously the arms and the spokes also terminate. However, both the central pair and the subfiber A's of the doublets continue, the central pair to the exact end of the ciliary tip, where the elements are topped by a distinctive finial, the central pair cap. Every continuation of subfiber A is unique in length so that subfiber A's of doublets 3 and 8 are overall about 1 μm, or 10%, longer than subfiber A's of doublets 1, 4, and 5. A general reduction in axonemal diameter accompanies microtubule termination and gives the cilium a distinctive conical tip. These growth parameters and the shape of the tip are different for different kinds of cilia and flagella. In certain mammalian cilia the tip is blunt, and the membrane is decorated externally by a cell coat, the ciliary crown.

Chemical composition. Cilia may be isolated en masse from ciliated protozoa, such as *Tetrahymena*, and flagella may be isolated as sperm tails. Such preparations are suitable for chemical analysis, and reasonably pure preparations of axonemes and of membranes can be obtained in quantities adequate for study. The major protein component (70–80%) of the axoneme is tubulin, the structural protein of the microtubules. The second largest component (10–15%) is dynein, the axonemal adenosine triphosphatase protein (ATPase). The remaining 10–15% of the axonemal protein is distributed among approximately 250 distinct polypeptides that can be visualized by two-dimensional electrophoresis. Some of these polypeptides can be assigned to specific axonemal structures, but most have not yet been otherwise characterized. The molecular unit of tubulin is a heterodimer of α and β subunits, each a globular protein about 4 nm long and 5 nm wide. One $\alpha\beta$ tubulin heterodimer (molecular weight 100,000) contains one molecule of bound guanosine triphosphate and one more loosely bound guanosine diphosphate. Axonemal and cytoplasmic microtubules are similar in most properties, but they differ in their stability to depolymerization. In *Chlamydomonas*, axonemal tubulin is acetylated locally after synthesis, while tubulin in most other parts of the cell is not. Another difference is that the midwall of the doublet microtubules is not tubulin, but proteins related to intermediate filament proteins, termed tektins. This may account for the differential stability or other unique properties of the axonemal microtubules.

The axonemal adenosine triphosphatase (ATPase), dynein, consists of a group of related globular proteins of slightly different solubilities with high molecular weights in the range of 1–2 × 10^6. Isolated dynein (**Fig. 4**) resembles a bouquet of two or three globular masses attached to a common base by slender stalks. Analysis after brief protease digestion of the molecule shows that each head contains at least one distinctive heavy polypeptide chain (molecular weight 4–5 × 10^5) that has ATPase activity, and

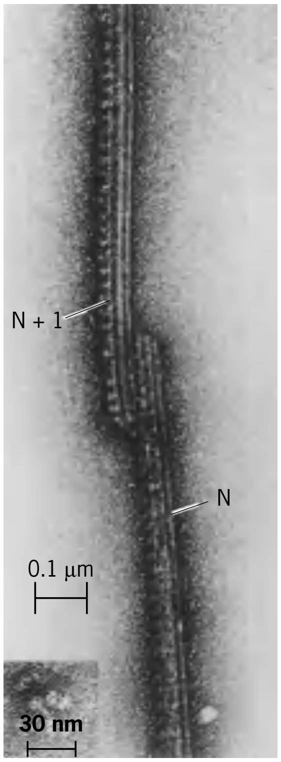

Fig. 4. Sliding of doublet microtubules from an axoneme after destruction of the control system. The dynein arms of the lower doublet (N) have interacted with subfiber B of the upper doublet (N + 1), displacing it toward the ciliary tip. Inset shows an isolated dynein molecule. (*After P. Satir, Structural analysis of the dynein cross bridge cycle, in F. D. Warner et al., eds., Cell Movement, vol. 1, Alan Liss, 1989*; *inset courtesy of K. Barkalow*)

each chain can be cleaved into two distinctive fragments by ultraviolet light in the presence of vanadate ions. In addition, purified dynein contains two or three intermediate-size chains (approximately 1×10^5) and several types of light chains (approximately $1–3 \times 10^4$). Outer and inner arm dyneins of the same axoneme may be different biochemically and structurally. Inner arm dyneins may be closely associated with other axonemal proteins, including small amounts of actin and centrin, in a so-called regulatory complex. The dynein genes of sea urchin and several other organisms have been cloned, and amino acid sequences of the heavy chains have been derived from the deoxyribonucleic acid (DNA) sequences. Each axonemal heavy chain is probably the product of a different gene. The sequences of the ATPase sites of the various dyneins seem highly conserved. Transcription of the axonemal dyneins, of tubulins and, other ciliary proteins, is increased after experimental deciliation of cells.

The membranes of flagella and cilia appear similar in structure, but they differ in composition, from the adjacent cell membranes. Like other membranes, the ciliary membrane is a phospholipid bilayer into which proteins are inserted. Some major membrane components of the cilia and flagella are glycoproteins, including immobilization antigens and other molecules involved in mating or cell recognition. Some ciliary membranes contain specific ion channels, including the voltage-sensitive calcium ion channel responsible for backward swimming in *Paramecium*.

Axonemes sometimes contain target proteins for the second messengers that control their behavior, including calmodulin which binds calcium and loosely or tightly bound protein kinases that may phosphorylate other axonemal proteins in the presence of cyclic nucleotides. A small polypeptide that copurifies with the outer arm dynein is phosphorylated in a cAMP-dependent manner and might act as a regulatory light chain of this dynein.

Mechanism of movement. Cilia and flagella are active structures, and the energy for their motion is provided by the dephosphorylation of adenosine triphosphate (ATP) at the dynein arms distributed along most of the length of the organelle. The membranes of cilia and flagella can be removed selectively by treatment with a nonionic detergent, such as Triton X-100. The motile mechanism in the resulting demembranated cilia and flagella is undamaged, so that when placed in an appropriate saline medium containing added ATP, the organelles regain motility and their pattern of beating closely resembles that of the same organelles in the living organism. An abrupt decrease in ATP concentration causes beating axonemes to set into a rigor state in which the stationary axonemes maintain the bent waveforms that they had at the moment the ATP concentration was lowered. The preservation of these rigor bends results from the dynein arms forming fixed cross-bridges between adjacent doublets in the absence of ATP. Movements between doublets can be regenerated by local addition of ATP; they are the result of a cyclic process in which the binding and hydrolysis of a molecule of ATP at a dynein arm from subfiber A of one doublet (N) causes it to release its cross-bridge attachment to the B subfiber of the adjacent doublet (N+1), change its angle, reattach to a new site closer to the basal end of the B subfiber, and then pull. This paradigm is known as the sliding microtubule model of ciliary motility. Both inner and outer dynein arms operate to produce sliding with the same polarity. Microtubule sliding can be seen in a beating axoneme by attaching gold beads to different parts of the structure and observing their periodic motion in the light microscope.

The outer dynein arms can be quantitatively extracted from certain axonemes. This causes the beat frequency to fall. The beat frequency also decreases in mutants of *Chlamydomonas* where the outer dynein arms or specific portions of them are missing. When corresponding mutants lack a specific type of inner arm, the beat frequency is largely unchanged but the bending pattern of the beat is altered. The suggestion is that sliding produced by the outer dynein arms is a primary determinant of beat frequency, while the inner arms primarily regulate beat form.

Active sliding of the doublet tubules can be demonstrated directly by brief treatment of demembranated axonemes with the protease trypsin. Trypsin rapidly destroys most of the spokes and circumferential links while leaving the arms and doublet tubules relatively intact. When ATP is then added, the treated axonemes no longer generate bending waves, but elongate and grow thinner as the doublets slide apart (Fig. 4). Isolated dynein arms will rebind to axonemal or other microtubules and slide them across glass surfaces in the presence of ATP. Dynein and tubulin are the only proteins necessary to produce sliding. This sliding microtubule mechanism is applicable to other microtubule-based forms of cell motility.

Since all dynein arms operate in the same way, the normal development and propagation of bends in the axoneme requires the presence of a suitable control system to generate appropriately phased localized sliding movements between the axonemal doublets. Trypsin damages this control system that normally limits sliding, leading to an uncoupling of sliding from bending.

The control system permits sliding to be asynchronous; one possibility is that sliding switches back and forth between the two bilaterally symmetrical halves of the axoneme and the other, during each stroke cycle. Inhibitors that act on the switches cause beating to cease abruptly at one particular stroke position. Such arrested cilia can be moved from one position to another by replacing one inhibitor with another, and microtubules from about half of each axoneme prepared from the arrested cilia will slide normally after trypsin treatment. This indicates that arrest is an active state in which the dynein arms producing bending to one side remain potentiated, while those producing bending to the reverse side are inhibited.

The main elements thought to convert the fundamental ATP-powered sliding interaction into local bending are the spokes. The spoke heads appear to be attached to the central sheath at points where bends develop, so as to provide the needed resistance to sliding, while the central tubules and sheath act as a fulcrum around which bending occurs. The presence of spokes affects the behavior of the inner dynein arms. Flagellar mutants of motile *Chlamydomonas* that possess axonemes lacking spokes appear capable of tubule sliding but not of bending. The 3 + 0 flagella in sperm of certain gregarines mentioned above lack both spokes and central tubules, yet generate helical bending waves of low frequency, which indicates that spokes and central tubules are not absolutely required for bending. However, their interactions may play a critical role in generating the asymmetric bending waves characteristic of normal ciliary motion and in the control of heat parameters. *See* ADENOSINE TRIPHOSPHATE (ATP). Peter Satir

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Ciliatea

The single class of the subphylum Ciliophora. This group has the characteristics of those defined for the subphylum. This protozoan class is divided into the subclasses Holotrichia, Peritrichia, Suctoria, and Spirotrichia. *See* CILIOPHORA; HOLOTRICHIA; PERITRICHIA; SPIROTRICHIA; SUCTORIA. John O. Corliss

Ciliophora

A subphylum of the Protozoa. The ciliates are a fairly homogeneous group of highly differentiated, unicellular organisms. Over 5000 species have been described, and many more surely exist but remain to be discovered. Typically, ciliates are larger than most other protozoa, ranging from 10 to 3000 micrometers or about 0.004 to 0.12 in. Some larger species are easily visible to the naked eye. The majority of them are free-living forms, found abundantly in a variety of fresh- and salt-water habitats, although a few entire groups live in association with other organisms, generally as harmless ecto- or endocommensals. Their principal value to humans is as experimental animals in a host of investigations concerned with fundamental problems of biology.

Systematics. Classification of ciliates followed here is that published in the "Honigberg Report," which appeared in 1964. That classification scheme, of the entire phylum Protozoa, was determined by an international committee of distinguished protozoologists. It is a reasonable and useful classification. Separate articles appear on each group included in the classification listed below. Subordinal divisions of some orders are commonly recognized by protozoologists, but such taxa are not considered here.

- Subphylum Ciliophora
  - Class Ciliatea
    - Subclass Holotrichia
      - Order: Gymnostomatida
        - Trichostomatida
        - Chonotrichida
        - Apostomatida
        - Astomatida
        - Hymenostomatida
        - Thigmotrichida
    - Subclass Peritrichia
      - Order Peritrichida
    - Subclass Suctoria
      - Order Suctorida
    - Subclass Spirotrichia
      - Order: Heterotrichida
        - Oligotrichida
        - Tintinnida
        - Entodiniomorphida
        - Odontostomatida
        - Hypotrichida

Protociliata or opalinids (**Fig. 1**) are entirely excluded. They are considered members of the subphylum Sarcomastigophora, because they possess only one type of nucleus, a symmetrogenic rather than a homothetogenic type of binary fission, and true syngamy, or sexual reproduction with anisogamous gametes, rather than conjugation. There are four genera of opalinids which are large, mouthless, multiflagellated forms found almost exclusively as saprozoic commensals in the posterior end of the alimentary tract of frogs and toads. *See* SARCOMASTIGOPHORA.

Major subdivisions of the ciliates are reduced to the four subclasses named above. Within the Holotrichia are included the Chonotrichida, a group formerly accorded a high-level, independent taxonomic status. *See* HOLOTRICHIA.

Characteristics. The usual ciliate life cycle is fairly simple. An individual feeds and undergoes binary

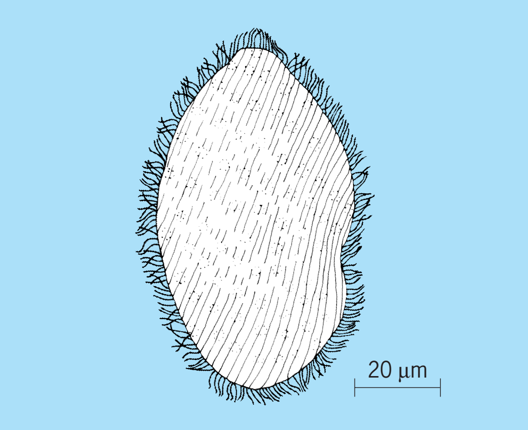

Fig. 1. *Opaline ranarum*, an opalinid; not considered a ciliate by many protozoologists.

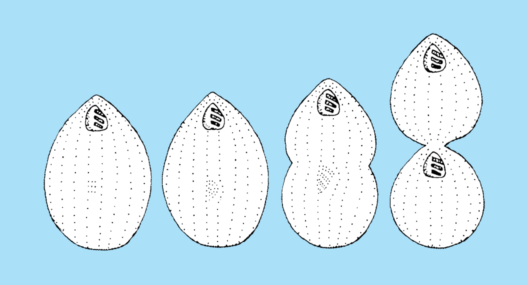

Fig. 2. Binary fission and stomatogenesis in ciliate *Tetrahymena*. Argentophilic basal bodies form part of silverline system and infraciliature.

fission, and the resulting filial products repeat the process. Some commensal or parasitic forms have a more complicated life history, but it is never as involved as the malarial species of the subphylum Sporozoa. Some ciliates, including free-living species, have a cystic stage in their cycle. As in other kinds of Protozoa this stage often serves as a protective phase during adverse environmental conditions, such as desiccation or lack of food. It also may be important in distribution, and thus possibly in preservation, of the species. *See* EUCOCCIDA.

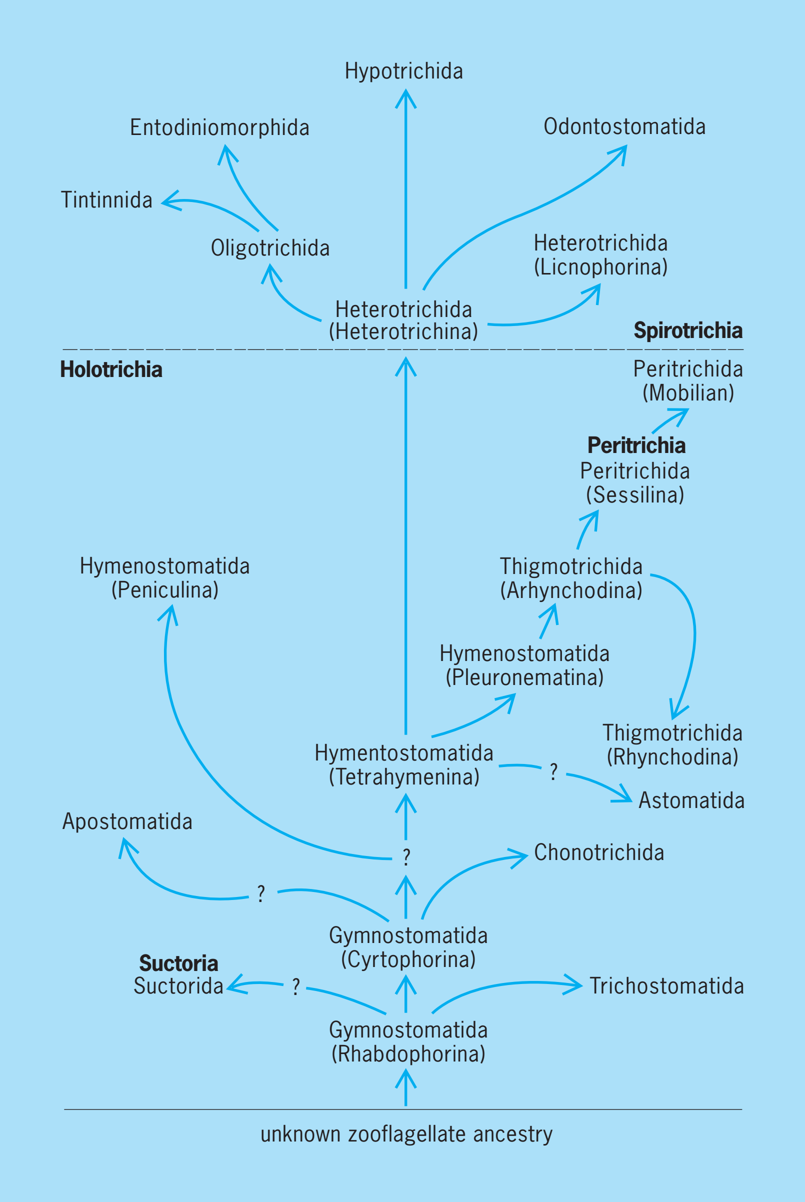

Fig. 3. Phylogenetic tree showing orders of the Ciliophora (names in boldface are of subclasses, and in parentheses of suborders).

Six major characteristics aid in distinguishing the Ciliophora from other protozoan groups. Not all of these are entirely unique, but when taken together they are definitely distinctive of ciliates.

Mouth. Most Ciliophora possess a true mouth or cytostome often associated with a buccal cavity containing compound ciliary organelles. However, some ciliates are completely astomatous, that is, mouthless. Nutrition is heterotrophic in ciliates. Some species are solely or primarily herbivorous since they eat bacteria or algae; some are carnivorous, eating other Protozoa or occasionally small aquatic invertebrate Metazoa; some are omnivorous; and still others live a saprozoic, or saprobic, existence, obtaining all their nutritive needs from materials dissolved in the medium. The process of stomatogenesis, or new mouth formation, which must take place before the completion of binary fission, is a morphogenetic phenomenon of great interest to students of Protozoa. Various modes of stomatogenesis exist in different ciliate groups. Their study helps in postulation of phylogenetic and evolutionary interrelationships within this subphylum of highly differentiated unicellular animals, as well as in throwing light on the important and not yet solved biological process of cell division and its control.

Ciliation. The Ciliophora possess simple cilia or compound ciliary organelles, often in abundance, in at least one stage of their life cycle. Morphologically, cilia are relatively short and slender hairlike structures, whose ultrastructure is known, from electron microscope studies, to be composed of nine peripheral and two central fibrils. Compound ciliary organelles include the undulating membrane, which is essentially a single sheet of fused cilia; the membranelle, a more or less fused block of cilia, typically two to four rows wide and of greater length; and the cirrus, a tuft of closely opposed cilia which is approximately circular in cross section near its base or proximal end but tapered or even fimbriate at its distal end. Functionally, cilia and cirri serve principally as locomotor organelles. Membranes and membranelles are characteristically associated with the mouth or buccal areas and serve to bring food into the oral opening, although they sometimes aid in locomotion as well. Membranelles are typically arranged as an adoral zone. *See* CILIA AND FLAGELLA.

Infraciliature. The presence, without exception, of some sort of infraciliature located at a subpellicular level in the cortex is another characteristic of Ciliophora. The infraciliature consists essentially of basal bodies, or kinetosomes, associated with cilia and ciliary organelles at their bases, plus certain more or less interconnecting fibrils. The basal bodies are argentophilic, that is, they readily stain with silver stains, and are the most important components of the so-called silverline system present in all ciliates (**Fig. 2**). Various argentophilic fibrils, the contractile vacuole pores, and the cell anus (cytoproct or cytopyge) are included in this system. The controversial neuromotor apparatus of ciliates, best known in hypotrichs, is not well understood. Anatomically, it appears to embrace certain parts of the silverline system, although parts of it are definitely not argentophilic. Much remains to be learned of its function.

Nuclear apparatus. Ciliophora possess two kinds of nuclei, and at least one of each is usually present. The smaller, or micronucleus, contains recognizable chromosomes and behaves much as the single nucleus in cells of metazoan organisms. Its mitotic divisions, however, appear to be acentric (without centrioles). The larger, or macronucleus, does not show mitosis but is considered indispensable in controlling metabolic functions, and is recognized as having genic control over all phenotypic characteristics of ciliates. Micronuclei are typically spherical or ovoid and show little variety in shape. Macronuclei vary in different species from compact bodies to C- or E-shaped forms, or from nodulated chains, which look like a string of tiny linked sausages, to bizarre dendritic configurations. Both nuclei divide in fission, but in sexual phenomena new macronuclei arise from what may be considered micronuclear origin. *See* GENETICS.

Fission. Ciliophora exhibit a type of binary fission commonly known as transverse division. In ciliates the splitting results in two filial organisms, the anterior or proter and the posterior or opisthe which, geometrically speaking, show homothety with respect to identical structures possessed by each (Fig. 2). Thus, homothetogenic is both a broader and more exact descriptive term. Indeed, in a number of groups the fission is more nearly longitudinal than transverse. Some ciliates show a budding type of asexual reproduction; some regularly reproduce within a cystic membrane.

Reproduction. Ciliophora lack true sexual reproduction. Ciliates do not show syngamy, with fusion of free gametes. Processes such as conjugation are considered to be sexual phenomena, since meiosis and chromosome recombination are involved, but not sexual reproduction. In addition to conjugation, certain ciliates exhibit forms of sexual phenomena known as autogamy and cytogamy. *See* REPRODUCTION (ANIMAL).

Evolution of ciliates. Ciliated protozoa, by virtue of their universal possession of an infraciliature and relatable patterns of somatic and buccal ciliature, appear to be the most taxonomically compact group in the phylum Protozoa. They also seem to lend themselves most readily to interpretation of their own phylogenetic interrelationships, that is, their own evolutionary history from the conjectured time of the first recognizable ciliate on the phylogenetic tree of the animal kingdom. Handicaps to study include lack of a usable fossil record, the usually microscopic size, and the very unicellularity which places all complexities of organization of necessity at a subcellular level. However, the student of the ciliated protozoa may still recognize, with a certain amount of reasonable, if indirect, supporting evidence, certain evolutionary lines or trends among the several orders. Most fruitful lines of such investigation have involved comparative study of life cycles, infraciliature, mouthparts, and the morphogenetic phenomenon of stomatogenesis. A possible genealogical tree of Ciliophora is given in **Fig. 3**. The change in somatic and buccal ciliature in the evolution of ciliates is emphasized in three present-day forms which, allegedly, are representative of the most primitive, intermediate, and most highly evolved orders (**Fig. 4**). *See* PROTOZOA.

John O. Corliss

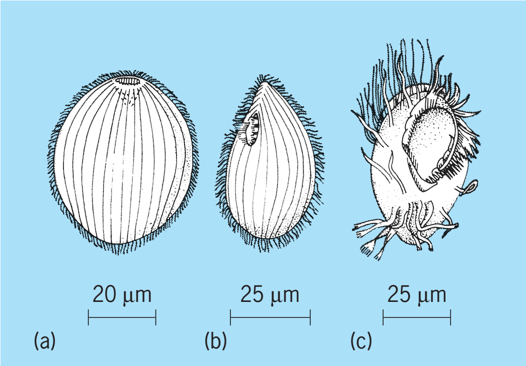

Fig. 4. Ciliates (not drawn to same scale). (*a*) Primitive form. *Holophyra*. (*b*) Intermediate form, *Tetrahymena*. (*c*) Highly complex form, *Diophrys*.

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Cinchona

A genus of trees belonging to the madder family (Rubiaceae), occurring indigenously in the cool, cloud forests of the Andes from Colombia to Peru. Many species have been described, most of which may be variants of *Cinchona pubescens* or *C. officinalis*. The bark contains several alkaloids, the most important of which is quinine. This bitter substance is the most specific drug used in the treatment of malaria. The great demand for quinine and the wasteful methods used in collecting the materials threatened extinction of the plants; therefore cultivation was begun. Now there are extensive cinchona plantations in India, Java, Sri Lanka, Australia, and Jamaica. *See* QUININE; RUBIALES.

Perry D. Strausbaugh; Earl L. Core

Cinematography

The process of producing the illusion of a moving picture. Cinematography includes two phases: taking the picture with a camera and showing the picture with a projector. The camera captures the action by taking a series of still pictures at regular intervals; the projector flashes these pictures on a screen at the same frequency, thus producing an image on the screen that appears to move. This illusion is possible because of the persistence of vision of the human eye. The still pictures appear on the screen many times a second, and although the screen is dark equally as long as it is lighted by the projected image, they do not seem to be a series of pictures but appear to the viewer to be one continuous picture.

Traditional Cinematography

This section discusses motion picture cameras, motion picture projectors, and wide-screen processes. For related information *see* CAMERA; MAGNETIC RECORDING; OPTICAL PROJECTION SYSTEMS; OPTICAL RECORDING; PHOTOGRAPHIC MATERIALS; PHOTOGRAPHY; STEREOPHONIC SOUND.

Cameras. Still photographs are taken by motion picture cameras (movie cameras) at the rate of 24 per second, even faster at times. The photographs are sharp and clear, and if they were superimposed on one another would be found to be extremely uniform with respect to position. This last feature is essential in order to have the image appear steady on the screen. A motion picture camera consists of five basic parts: lens, shutter, gate, film chamber, and pull-down mechanism.

Lens. The lens on a motion picture camera collects the light from the scene being photographed and focuses it on the photographic emulsion in the camera aperture. Lenses vary in focal length. The focal lengths most often used on 35mm cameras are between 30 and 50 mm. Other lenses in common use vary from wide-angle (14.5–25 mm), through long-focal-length (60–250 mm), to telephoto (300–1000 mm). Lenses of shorter focal length have a wider angle of view; those of longer focal length give a larger image size on the film. Lenses for the 16mm camera which give the same angle of view and the same relative image size are approximately one-half the focal length of those used on a 35mm camera. Variable-focal-length lenses (zoom lenses) are useful to cinematographers and directors and are used extensively not only for filming sporting events but also in making feature films, documentaries, and television films. *See* FOCAL LENGTH; TELEPHOTO LENS; ZOOM LENS.

To protect the lens from extraneous light and prevent lens flare, a lens shade must be used. On a motion picture camera this shade is called a matte box. It completely surrounds the lens and acts as a lens shade, but it also has slots to hold various types of filters (such as diffusion, fog, color correcting, and polarizing), and optically flat glass for use when needed. These items are used by cinematographers for the many effects required in making a professional motion picture.

Lenses for motion picture cameras have focusing mounts and can be focused on objects as close as 2 or 3 ft (0.6 to 0.9 m). They are fastened to the camera with threaded or bayonet mounts and can be changed when a lens of a different focal length is needed. Although some older cameras have turrets on the front which hold three or four lenses at one time, making it a simple matter to change from one lens to another, all modern professional cameras have solid fronts because of the size and weight of the zoom lens, and because the faster lenses now used require closer tolerances in the positional accuracy of the lens mount relative to the film plane.

The lens has an iris diaphragm which can be opened and closed to control the amount of light reaching the film, thus controlling the exposure. The *f*-number is a ratio of the focal length of the lens to the diameter of the lens opening, and a lens with a given *f*-number will always allow the same amount of light per unit area to strike the film regardless of the focal length of the lens. The *T*-system used in cinematography takes into account all of the light losses encountered in a lens, such as the number of reflecting surfaces inside the lens and the various types of coating on the surfaces. *T*-stops are determined by the amount of light transmitted through the lens, while *f*-stops are determined by a mathematical formula of the focal length of the lens divided by the diameter of the iris diaphragm opening. Since the *T*-stops system is more accurate as far as light transmission is concerned, this is usually used for exposure, while the *f*-number is used to determine the depth of field, that is, a range of subject distances between which all objects will be in sharp focus on the film. *See* LENS (OPTICS).

Shutter. The shutter in a motion picture camera rotates and exposes the film according to its angle of opening. When the shutter is open to its widest angle, the film receives its maximum exposure. Many cameras have variable shutters; that is, the angle of opening can be changed while the camera is running. Such shutter openings usually vary from 180° when the shutter is wide open to 0° when it is closed. The shutter in a motion picture camera is almost always located between the lens and the film.

Gate. The aperture called the gate is the passageway through which the film is channeled while it is being exposed. It consists of the aperture plate, which is in front of the film and masks the frame, or picture; the pressure plate, which is in back of the film and holds it firmly against the aperture plate; and the edge guides, which keep the film stable laterally.

Film chamber. This holds the unexposed film at one end and collects the exposed film at the other. Although some motion picture cameras have an interior film chamber, it is usually a separate piece of equipment called the film magazine. Magazines come in 400-ft (120-m) and 1000-ft (300-m) capacities. One thousand feet of 35mm film, exposed at the normal speed of 24 frames per second, and with a four-perforation pull-down, lasts slightly more than

11 min. The magazines are loaded with film in a darkroom or in a lightproof changing bag and are fitted on the camera as needed, making camera loading easy and rapid.

Pull-down mechanism. The part of the pull-down mechanism called the intermittent movement pulls the film down through the gate of the camera one frame at a time; in a conventional 35mm camera, each frame is four perforations high. Some wide-screen cameras have frames five or six perforations high. The pull-down claw engages the perforations and pulls the film down into place to be exposed. At the bottom of its stroke, the claw remains stationary for a moment to position the film and then disengages itself and returns to the upper portion of the stroke to pull another frame into place. During the time the claw is returning to the top of its stroke, the film is stationary and the shutter opens and exposes the film. Most modern cameras have registration pins which engage the film while the picture is being taken. This ensures that the film is perfectly still and is in exactly the same position as each frame is being exposed. This feature is especially important in special-effects photography where independently photographed images are superimposed.

Mobile cameras. When sound is being recorded, cameras must be absolutely quiet. In the early days of sound, cameras were put in enclosures called blimps. Almost all modern cameras are self-blimped, which enhances their portability. The Mitchell BNC (Blimped News Camera), introduced in 1935, was the first such camera (**Fig. 1**), and remained the worldwide industry standard for 35 years. Although this camera was portable, at approximately 125 lb (55 kg), fully loaded, it was not hand-holdable. In 1968 Arriflex introduced the first hand-held self-blimped camera, the 35 BL. The current model is the 535 (**Fig. 2***a*). In 1972 Panavision introduced the lightweight, silent Panaflex camera, the current version of which is the Millennium (Fig. 2*b*); and in 1979 the silent Moviecam camera was introduced, the current model of which is the lightweight SL (Fig. 2*c*). These later cameras range in weight from 15 to 30 lb (7 to 14 kg), including the lens and a 400-ft (120-m) load of film.

These smaller and lighter cameras have enabled production companies to achieve more mobility and to shoot many pictures on actual locations away from studios, using hotels, cafes, and even private homes in small towns as sets to give the pictures more authenticity. Most feature films, as well as those made for television, are made by independent producers who take advantage of these realistic backgrounds and at the same time save money on stage rentals.

When they go on location, most companies use mobile units which are complete with all the equipment necessary to make a professional motion picture. These vehicles can carry two or three complete camera packages, two or more sound outfits which have been reduced in size even more than the cameras, grip equipment which is used for construction where necessary, camera supports and dollies, and lightweight lamps and cables which feed from a gasoline-powered generator built into the vehicle. Some of these conveyances include space for makeup and wardrobe, although these two departments are usually housed in a separate unit.

Motors. Up until 1970 most sound cameras were driven by 220-VAC (volts alternating current) three-phase synchronous motors, while the sound film, 35mm perforated iron oxide-coated film running over a sprocket, was driven by a similar synchronous motor. After 1970, however, almost all professional

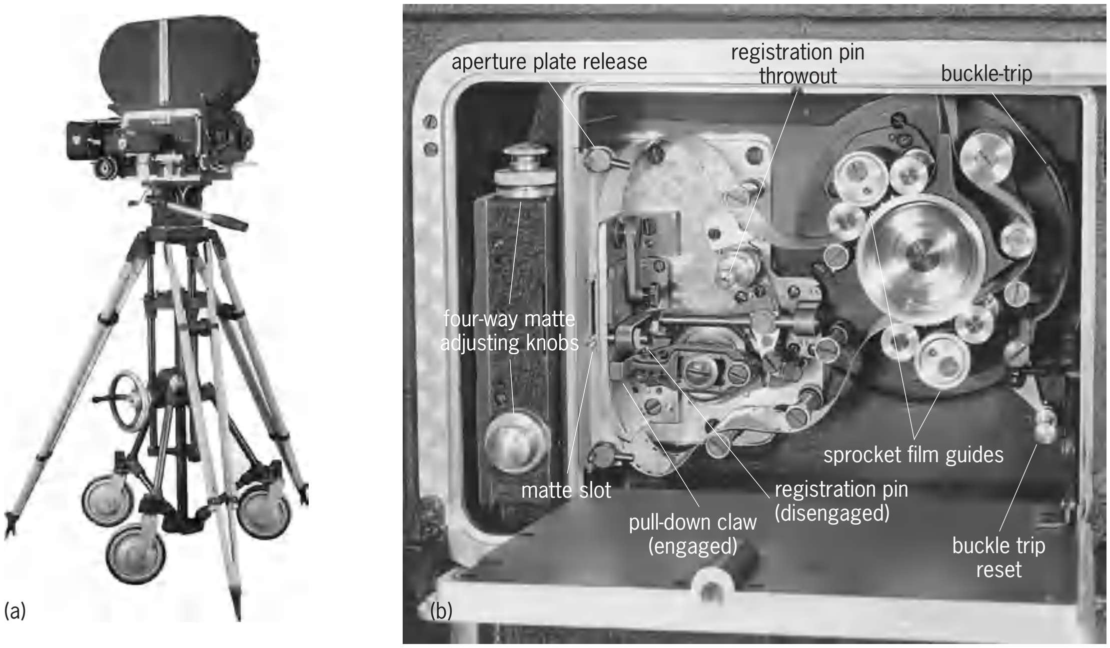

Fig. 1. Mitchell studio camera (BNC). (*a*) Overall view. (*b*) Film-moving mechanism. (*Mitchell Camera Corp.*)

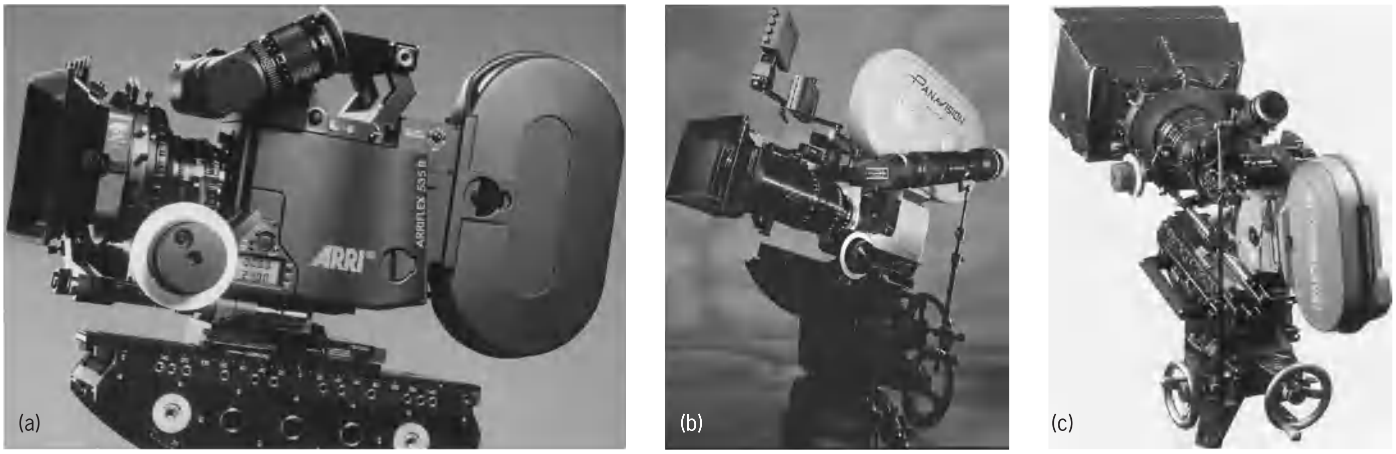

Fig. 2. **Hand-held silent cameras. (*a*) Arriflex 535B with 400-ft (120-m) magazine (*Arnold and Richter, Gmbh*). (*b*) Panaflex Millennium camera system with 1000-ft (300-m) magazine and zoom lens (*Panavision*). (*c*) Moviecam SL camera with 400-ft (120-m) magazine and zoom lens (*Moviecam*).**

35mm productions in the United States, and many 16mm sound films as well, changed to a new type of motor for driving the camera and a new method of recording synchronous sound, both of which have many advantages over the older system. The motor used on the camera is a direct-current motor, which runs off batteries (12 to 36 V) at a synchronous speed. The speed of the motor is controlled by a crystal oscillator which is so precise that the speed of the motor varies less than one-half a frame of picture in 1000 ft (300 m) of film. All modern cameras (16mm as well as 35mm) use these "crystal motors."

Sound. All sound is recorded on sprocketless 0.25-in. (6-mm) tape. Since tape is an elastic medium, some sort of "sync" pulse must be put on the tape in order to synchronize the recorded sound with the picture when they are put together in a "married" print. The sync pulse is usually an inaudible 1-V, 60-Hz (in Europe, 50-Hz) pulse put on the tape at the time of recording. This pulse can be one generated at the camera and sent to the sound recorder, which is exactly 60 Hz when the camera is running precisely 24 frames/s; or a similar pulse from a crystal oscillator either built into or attached to the tape recorder on which the sound is being recorded. The latter method is the one most commonly used on professional motion picture productions. It is the only system in which there is no physical or electrical connection between sound and camera. Without this connection the camera is completely free; it can be in a separate vehicle, car, boat, or aircraft, while the sound-recording equipment is in another. The only thing required to make a synchronous sound picture with this system is that a sync stick, or clap stick, be used so that sound can have an audible point of reference and the camera can have a visible point of reference.

After the sound is recorded on the 0.25-in. (6-mm) tape, it is put through a resolver, which transfers the sound from the tape to 16mm or 35mm perforated iron oxide–coated film. The resolver corrects for the aforementioned variations in sound-track recording by using the sync pulse as a reference. With the sound on the perforated film it can be precisely synchronized with the picture, using sync-stick marks when the picture is printed for release.

There are two types of sound tracks, optical and magnetic, on release prints, the prints seen by the audience. All 35mm and practically all 16mm release prints have optical sound tracks. A 16mm film may have a magnetic sound track if only one or two prints are to be made, but this is seldom the case. An optical sound track is printed photographically on the film; a magnetic sound track is printed in the same manner as on a tape recorder, after the film is coated with an iron oxide stripe in the area reserved for the sound track. All Super 8 films have magnetic sound tracks.

Until the late 1990s, all 65mm–70mm films, those shot on 65mm film in the camera and printed on 70mm film for release, had magnetic sound tracks. The 70mm prints have six-track sound, one track on each side inside the perforations and two tracks on each side outside the perforations. The space for the tracks outside the perforations is made possible by the additional width of 2.5 mm on each side.

Until the mid-1990s, all sound tracks, both optical and magnetic, were recorded in analog fashion. Developments in the technology, however, have enabled optical sound tracks to be recorded digitally as well, permitting optical sound tracks to provide sound quality comparable to a digital compact disk. For this reason, and for cost savings, the digital-optical sound track has rapidly replaced magnetic-stripe analog sound tracks on 70mm release prints. *See* COMPACT DISK.

Slate. In any motion picture a slate with all pertinent information is of utmost importance (**Fig. 3**). The slate is fastened to the sync stick, and the information is photographed at the beginning of each take. The slate has places for all information relating to the production, such as the name of the picture and its production number for identification at the laboratory, where the film is processed, and the name of the director and the camera operator. In addition, there are spaces for the scene number and the take number, and places to indicate whether the

Fig. 3. Time-code slate. (*Denecke Inc.*)

shot is an interior or exterior, a day or night shot, or sound or MOS (silent); MOS comes from the early European director's pronunciation of "mit-out sound." The term "MOS" is still used extensively throughout the motion picture industry instead of the expression "silent."

Time code. Current practice makes increasing use of some method of coding the film and sound track to facilitate postproduction, especially by permitting transfer to videotape for highly automated editing. Methods have been developed for optically printing time code along the edge of the film beside every frame. The code is machine-readable, and is also human-readable in some systems. A method has also been introduced for printing the human-readable key number, which normally appears as a latent image along the edge of the film, as a machine-readable latent-image bar code. All these schemes facilitate the task of conforming the edit decisions, made in the video domain, back to film for final cutting and assembly. A typical slate (Fig. 3) displays a continuously running time code that is simultaneously recorded as a synchronizing track on the sound recorder. When the clapstick closes, the displayed time stops, providing a visual reference for automatically synchronizing picture and sound in postproduction.

Camera support equipment. A number of devices have been developed to take advantage of the increased mobility of cameras. Their purpose is to give the camera a smooth fluid motion to follow the cinematic action in ever more difficult situations and in ever more ingenious ways. All of these devices are designed to move in such a manner that the film viewer is drawn into the illusion of the scene. A bumpy or jerky camera motion would make the viewer aware of the camera's presence and destroy the illusion.

Crab dolly. One of the first devices developed to permit camera movement was the crab dolly (**Fig. 4**). This dolly can be steered in the usual manner by turning the wheels for curves, and it can be put in a mode where all four wheels turn in the same direction so that it can go forward and backward and also crab across the stage sideways. The camera can be raised or lowered while the dolly is in motion, making it possible to get interesting and creative camera movements.

Cranes and boom arms. A crane (**Fig. 5**) is a larger and more versatile version of the crab dolly. Available in a wide range of sizes, some cranes are slightly larger than a dolly, similar in configuration to a dolly equipped with a boom arm; others extend to 30 ft (9 m) in the air. Cranes are used extensively to achieve large sweeping moves for dramatic effects.

Camera cars. Trucks specially fitted to provide a smooth-moving platform for motion picture cameras (**Fig. 6**) are extremely useful in photographing fast-moving action such as a car chase. These vehicles have become extremely sophisticated. They can support a camera smoothly at highway speeds, in conventional or crab mode, on a boom arm with battery or generator power to satisfy lighting needs.

Steadicam. This is a unique device to support cameras in a mobile situation (**Fig. 7**). It provides a stable platform for a handheld camera supported by the camera operator by means of a vest and supporting spring arm. The mass of the camera and its supporting structure is balanced about a gimbal. The operator guides the camera by gently grasping the system at the gimbal, and is able to walk, run, or go up or down stairs, and still provide totally smooth camera motion.

Film. The film used in the standard motion-picture camera is 35mm (wide) and is perforated along both edges. There are 64 perforations (or sprocket holes) to each foot of film.

Fig. 4. Chapman/PeeWee crab dolly. (*Chapman/Leonard Inc.*)

Fig. 5. Louma crane. (*Panavision Remote Systems*)

Motion-picture film consists of a cellulose acetate base approximately 0.006 in. (0.15 mm) thick and coated with a light-sensitive emulsion. In color film, several layers of emulsion are applied; each of three of the layers is sensitive to one of the three primary colors of light: blue, green, and red. The film is made in large rolls about 54 in. (1.37 m) wide and as long as several thousand feet. It is slit into 35mm strips, perforated, and packed in lightproof bags and cans in rolls 100, 200, 400, and 1000 ft (30, 60, 120, and 300 m) in length.

Smaller widths such as 16 and 8 mm are also made from these wide rolls if they are of the same emulsion type. These sizes are seldom used for feature films but are used extensively by professionals in the audiovisual field and for news and low-budget films for television. The kinds of motion picture film are numerous and varied to meet the needs of a many-faceted industry: black and white, color, high and low speed, fine and coarse grain, high and low contrast, and wide and narrow exposure latitude. These film characteristics describe a particular type of film emulsion.

Fig. 6. Camera car. (*Shotmaker Co.*)

Fig. 7. Steadicam. (*Cinema Products Corp.*)

Film types. There are two different types of film: negative film, from which a print is made in order to see the original subject in its true likeness (for example, Kodacolor, used in amateur photography), and reversal film, in which a negative is first formed in the original film and from this a positive is formed in the same piece of film (for example, Kodachrome, a film familiar to amateurs). In the negative film two pieces of film are necessary to get a picture that can be projected; in the reversal film only one piece of film is required, making it a much less expensive process. In Super 8, as well as regular 8, the reversal film is generally used because of the cost factor. In 16mm and 35mm professional work, the original, that is, the film used in the camera, is never used for projection. A work print is made in order to edit the film and the original negative is assembled to conform to the edited work print. Master positives are then struck from the original negative, and the master positives are used, in turn, to produce duplicate negatives. The release prints are made from the duplicate negatives, and during this process the sound tracks are added. The original film is all-important and is kept in a vault at the laboratory; it is used only for making prints.

Aspect ratio. The picture taken in standard 35mm motion picture cameras is masked by the aperture plate, which varies according to the camera. The silent aperture, that is, the aperture used on cameras that do not leave room on the film for a sound track, is almost the entire width of the film between perforations, slightly less than 1 in. (25 mm) and approximately 0.75 in. (19 mm) high. This gives an aspect ratio (the ratio of its width to its height) of 1.33:1 (4/3). Sound apertures are masked down to a width of 0.868 in. (22 mm), to allow room for the sound track, and a height of 0.631 in. (16 mm), which gives an aspect ratio of 1.37:1.

Projectors. The projector system in a modern motion picture theater has five main assemblies: the optical sound head, which reproduces optical (photographically recorded) sound; the projector head, which projects the image onto the screen; the lamphouse, which furnishes the illumination for the picture; the shutter; and the platter system, which feeds the film through the projector head. On some projectors, there is a second sound head for the reproduction of magnetic (magnetically recorded) sound.

With the development of digital optical sound, most projectors are now equipped with a charge-coupled-device (CCD) line array to read the digital track. The analog optical track, which is still present as a backup system, is now read by a light-emitting diode (LED) array in lieu of the traditional exciter lamp. An alternate dual-system approach has a time-code track on the film that is read to synchronize the picture with the sound track played back from a compact disk machine. *See* CHARGE-COUPLED DEVICES; LIGHT-EMITTING DIODE.

Optical sound head. This consists of an exciter lamp and a photoelectric cell. The optical sound track is 20 frames ahead of the picture on 35mm film (26 frames ahead on 16mm film). If the film has a magnetic sound track in addition to the optical one, it is first threaded over the magnetic sound head, which is above the projector head (**Fig. 8**). The magnetic sound track is 28 frames behind the picture on 35mm film and 23 frames behind on 70mm film (26 frames ahead on 16mm film, the same as optical sound).

Projector head. This consists of the projection lens and the projector intermittent. The projection lens is located in the front of the projector head between the aperture and the screen. The film is put in the projector aperture upside down and with the sound track on the right. The image is inverted by the lens and appears right side up on the screen. The sound track, if it were visible, would appear on the left side of the screen. The focal length of the lens is determined by the size of the image desired on the screen and the distance between projector and screen. The lens usually has a fixed speed of *f*/2 and has no iris diaphragm.

The projector intermittent uses a Geneva movement to pull the film through the gate. This movement drives a 16-toothed sprocket one-quarter of a revolution at a time. With each movement a new frame is pulled into place. The film is wrapped around this sprocket wheel and its perforations on both sides engage four or five teeth on the wheel at all times. This distributes the stress caused by the acceleration and deceleration over many perforations and results in less wear and tear on the film, substantially increasing its life. A framing device is incorporated in the projector head so that the frame can be moved up or down to position the picture correctly and put the frame lines at the top and bottom of the screen.

Lamphouse. All modern projectors employ xenon arc lamps in place of the previously used carbon arc lamps. The xenon arc lamps form a small plasma arc in a sealed glass bulb. A concave reflector behind the lamp collects the light and concentrates it on the film in the projector aperture. Depending on the size of the screen, the lamps generally range from 1 to 7 kW in power input. *See* ARC LAMP.

Platter system. Most modern theaters use a platter system (**Fig. 9**) rather than the conventional 2000-ft (600-m) reels used in older theaters. Conventional reels are labor-intensive and require two projectors to achieve a smooth transition (changeover) between subsequent reels of a motion picture. In the platter system, only one projector is needed. All reels of a motion picture are spliced together and loaded onto one of the platters with the start of the picture at the center of the reel. The film is then threaded from the center of the reel, through the projector, and onto a second platter. When the show is over, it is

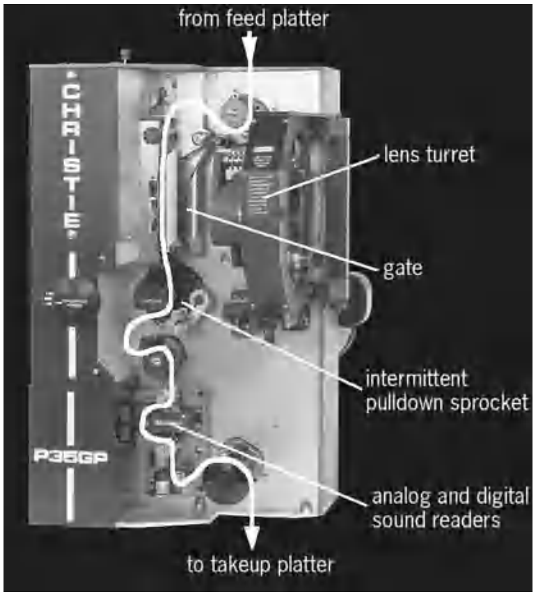

Fig. 8. Motion picture projector. The white ribbon shows the path of film from feed platter down through the projector head gate, over the intermittent pulldown sprocket, over analog and digital sound reader heads, and on the way to the take-up platter. (*Christie Inc.*)

Fig. 9. Nonrewind platter system. (*Kinotone*)

only necessary to rethread the projector, but starting from the second platter.

Shutter. A projector has a two-bladed shutter located between the lamphouse and the gate in the projector head. The shutter cuts off the light to the screen while the film is being moved down from one frame to the next and opens when the new frame has been moved into place. It then closes and opens a second time before another frame has been brought into position. This makes two exposures per frame, or 48 light impulses hitting the screen in 1 s, even though the picture was shot at 24 frames per second. This reduces the flickering effect that would be noticeable if only 24 light impulses per second were flashed on the screen.

Universal types. Universal projectors can show 35mm prints, both normal and anamorphic, with optical sound, four-track magnetic sound, or both. They can also show 70mm normal and anamorphic with six-track magnetic sound. The 35mm sprockets are between and below the 70mm sprockets, and either film can be run by selecting the correct lens and threading the film through the gate and through the appropriate sound head. *See* OPTICAL PROJECTION SYSTEMS.

Wide-screen processes. Until 1952 the motion picture industry as a whole used film and equipment that was well standardized. Film was 35 mm wide, the aspect ratio was 1.33:1, and the camera had a four-perforation pull-down mechanism. These standards had been in effect since early in the twentieth century. With the advent of sound in 1926, standard camera speed became established at 24 frames per second, and most sound tracks were reproduced optically. Beginning in 1952, however, many new processes were introduced which departed from these standards and utilized a multiplicity of film sizes, aspect ratios, and types of sound tracks. Some processes which employ 35mm film use a means of getting more picture on the film. The 1.85:1 ratio has practically become a standard when referring to wide screen. Multitrack digital-optical sound has become fairly common.

Cinerama. The first commercially successful wide-screen process was Cinerama, developed by F. Waller. First shown in 1952, the system employed three separate, matched film strips projected by three separate projectors. The projected image height was equivalent to six perforations, and the width the equivalent of three full 35-mm apertures. The deeply curved screen consisted of 1200 overlapping strips, arranged in such a manner as to minimize lateral reflections. A fourth 35mm film strip carried seven sound tracks for full stereophonic reproduction. The complexities of running these projectors in exact synchronism, in addition to jitter problems between the three panels, caused the system to be simplified some years later to a single 70-mm-wide film with multiple sound tracks and a 1.25:1 anamorphic "squeeze." The first picture made in this manner was *Mad Mad Mad Mad World* (1964).

Cinemascope. The single-film approach was anticipated by Cinemascope, developed by twentieth Century Fox, based on earlier work of the physicist H. Chrétien. Special lens adapters were designed that produced a linear 2:1 anamorphic squeeze when attached to conventional lenses. Integral anamorphic lenses were subsequently developed which were simpler to use. A special projector lens was used to unsqueeze the picture (**Fig. 10**). The first feature

Fig. 10. Action of Cinemascope anamorphic lens. (*a*) Image "squeezed" onto the film by an anamorphic lens. (*b*) "Unsqueezed" image as it appears on the screen. (*Twentieth Century Fox*)

filmed in Cinemascope was *The Robe* (1953). The format continues to be used.

VistaVision. This process, developed by Paramount, utilized an eight-perforation–pull-down, 35mm movement, operating from left to right rather than top to bottom. Conventional spherical lenses were used, and the resulting format was 37.7 mm wide by 25 mm high. *White Christmas* (1954) was the first picture produced by this process. The need for special projection equipment eventually caused VistaVision to be discontinued. It is still used, however, for shooting background plates for process photography since it provides a large format that will not degrade as much as a 35mm format during the duplicating process.

Todd-AO. In the mid-1950s B. O'Brien in cooperation with promoter M. Todd developed the Todd-AO wide-screen process. This process used a 70mm print derived directly from a 65mm negative, five perforations high, with six magnetic sound tracks arrayed as previously noted. A series of special lenses was developed to provide from 37 to 128° of angular coverage. The first picture produced in Todd-AO was *Oklahoma* (1955). As originally presented, Todd-AO used a deeply curved screen, but it was subsequently converted to flat-screen projection. Super Panavision, similar to Todd-AO in format, has been widely used. Mitchell 35mm and 65mm cameras have been used for these processes, as well as cameras specially designed and built for the process.

Screen formats. Films for theatrical release have now been standardized in two basic formats in the United States, as contrasted with the plethora of wide-screen and multiscreen formats that appeared and disappeared during the 1950s and 1960s. With rare exceptions all films for theatrical presentation are now shot either (1) in the 2.35:1 aspect ratio, using the 35mm anamorphic system that was originated by Cinemascope but that now exists largely through the use of Panavision anamorphic lenses and those developed by others, or (2) in the 1.85:1 aspect ratio, which is achieved by cropping the standard 35mm frame top and bottom. In Europe, the popular aspect ratio is 1.66:1.

The 1.85:1 format is extremely wasteful of film, and there have been several attempts to introduce a system involving three-perforation pull-down in the camera as well as in the projector to eliminate this waste.

Techniscope. This was a promising format that has now virtually disappeared in the United States. It was developed in the Technicolor Laboratories in Rome, Italy. The process involves shooting the original camera negative with the camera modified to pull down two perforations, rather than four, in a standard 35mm camera. The taking lenses are the normal complement of spherical lenses. In the laboratory the negative is optically printed through an anamorphic lens which stretches the image vertically by a factor of 2:1 so that the print is identical to one which would have resulted from a negative shot in the Cinemascope anamorphic process. A number of films were shot in this process, but it fell into disfavor in the United States because the increase in granularity and the decrease in resolution due to using a negative area one-half that of the standard 35mm size resulted in a film that was not of acceptable quality when compared with the 1.85:1 format or the anamorphic format. However, in Europe and elsewhere Techniscope is still an acceptable and frequently used process.

Super 16. An alternative means of arriving at current theatrical formats, called Super 16, was pioneered by R. Ericson in Sweden. This process involves photographing with a 16mm camera that is modified so that the full width of the negative is photographed, including that area reserved for sound track in the final release print. The negative is then enlarged, usually through liquid-gate optical printing, to a 35mm format with a 1.65:1 aspect ratio.

70mm presentation. Until the introduction of digital-optical sound, there had been a major move back to theatrical presentation in 70mm film. This was motivated by the ability to provide six magnetic sound tracks on the 70mm print. Original photography was typically on 35mm film and blown up to 70mm. Digital-optical sound technology permits full multichannel surround sound to be recorded on a standard 35mm print, obviating the need to produce very expensive 70mm magnetic-striped prints. However, there has been a growing trend in the use of 70mm prints from 65mm negatives for special-venue presentations such as theme parks, studio tours, dynamic motion simulator rides, and 3D (three-dimensional). To meet this growing need, new 65mm cameras have been developed (**Fig. 11**).

Imax. Epitomizing this trend to larger formats, the Imax process films on a 65mm negative moving

Fig. 11. CP-65 65mm camera system. (*Cinema Products Corp.*)

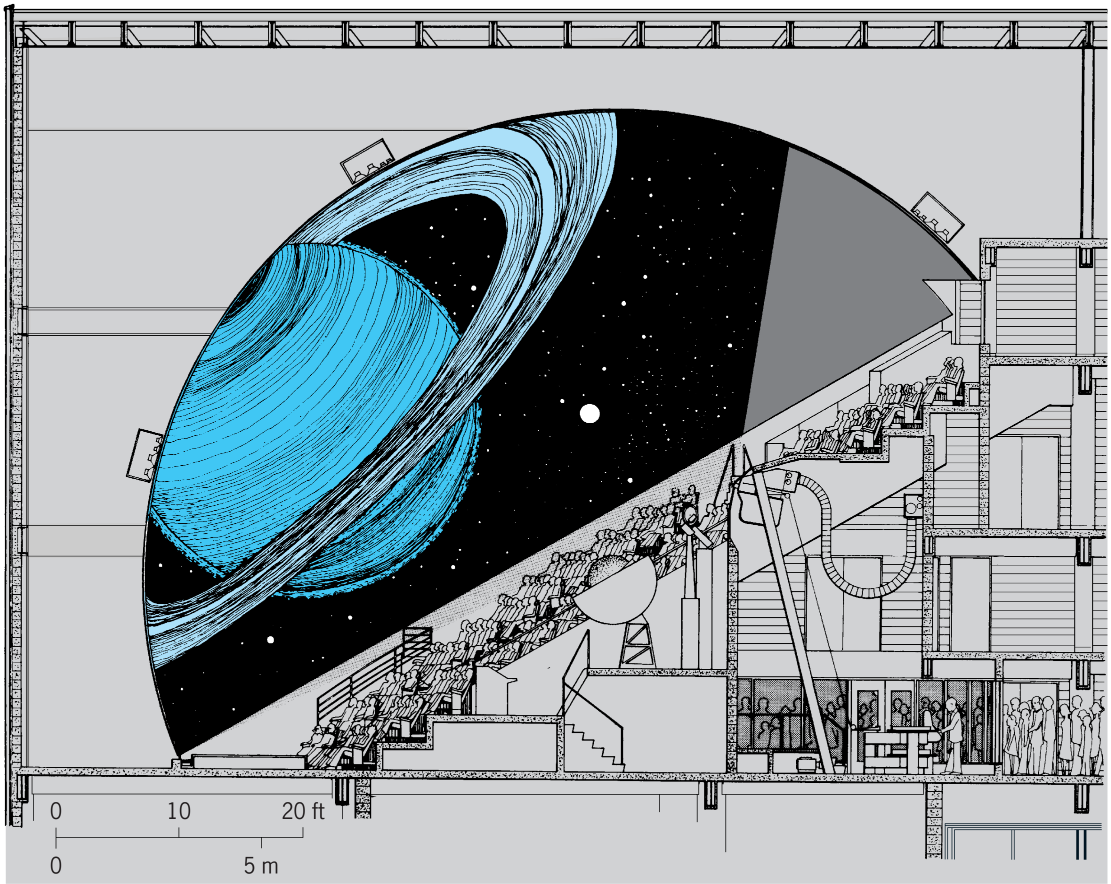

Fig. 12. Cross-sectional view of typical Omnimax theater.

horizontally through the camera, 15 perforations per frame. The resulting aspect ratio is 1.33:1. The 70mm prints are projected on a large flat screen. They can also be photographed and projected with a fisheye lens on a hemispheric dome in a process called Omnimax (**Fig. 12**). The projector is of a unique design that utilizes a rolling loop to rapidly advance the film with no damage and absolute flatness in the film gate. *See* PLANETARIUM.

A less expensive alternative to the Imax format is provided by the Iwerks system of recording eight perforations per frame on 65mm film moving vertically through the camera. This provides essentially the same format, but on a smaller negative area.

Showscan. This process uses the conventional 70mm, five-perforation format, but is filmed and projected at 60 frames per second. This frame rate virtually eliminates all filmic artifacts, such as strobe and flicker, to provide a heightened sense of reality. Edmund M. DiGiulio

Digital Cinematography

Like other forms of media, cinematography is undergoing a transition from photomechanical to digital processes, which offer greater flexibility, consume fewer resources, offer significant time saving, and allow electronic (versus physical) delivery of products. In cinematography, this transition involves three distinct operations: image capture, image editing, and image display. The complete transition will result in an all-digital workflow for the production of motion pictures. Although the implementation of an all-digital workflow is under way, the use of digital methods in the image editing or “postproduction” processes is far more widespread than in image capture or display.

Image capture. The image-capture process involves filming the scenes that will be edited together to make a movie. In this operation, the switch to digital involves capturing the scenes with a high-definition digital camera instead of traditional cinemagraphic 35mm film cameras.

There are several weaknesses in the traditional approach, such as the high cost of the film and the environmental impact of chemical film processing, which are alleviated by digital image capture. In addition, color negative film cannot be evaluated directly (even after processing), so the creative team cannot get immediate feedback on the success of a filming session; film is easily scratched and susceptible to dust; and in order to use digital editing techniques, film images must be scanned to create digital files. Still, cinematographers have been reluctant to give up film cameras because 35mm film captures a higher-resolution image with greater dynamic range than high-definition digital cameras.

Motion pictures in which digital image capture was used include *Sin City* and *Star Wars: Episode III Revenge of the Sith*. In both of these films, digitally generated backgrounds were extensively used. Thus, the limited resolution of the digital camera did not limit the detail that was evident in the background.

For *Sin City*, Sony HDC-F950 digital cameras were used, capturing red, green, and blue images at 1920 × 1080 pixels of resolution with 10-bit color depth at 24 frames per second. Scenes were viewed on a calibrated monitor immediately after shooting, which benefited the production team by avoiding multiple shoots of some scenes.

Star Wars: Episode III Revenge of the Sith used an all-digital workflow, including image capture. The production cost of $100 million is estimated to be half the amount required for a comparable movie shot on film. The savings came from the increased productivity gained by having immediate feedback during shooting and from doing much of the special-effects work before the shooting took place. This enabled the director to make decisions about which angles and perspectives were needed before (rather than after) the filming of a scene.

Over time, digital image capture should replace film because of the creative flexibility and cost savings it offers. Digital cinema cameras are improving steadily, as are data transport, storage, and compression techniques.

Film digitizing. Scanning rolls of film for digital editing has become a lucrative business because an increasing number of films are doing all the post-production processes digitally. The scanners used for rolls of film were initially developed for converting finished films to DVD format. Ideally, each frame would be scanned at 4K (4100 pixels wide by 3000 pixels high) for optimum quality, but the resulting files were too large and it would take days to scan a feature length film. Scanners now are capable of performing 2K scans in real time and 4K scans at 7.5 frames per second, or about 6 h for a feature-length film, with 4K scanning resolution reserved for critical projects and 2K (2048 pixels wide by 1556 pixels high) scanning is used for most applications.

Image editing. Nearly all special effects are achieved through digital means, making image editing the area with the greatest penetration of digital processes. Traditional film-editing methods involved cutting apart scenes from the developed film reels and taping them back together to form the desired sequence. After the taped-together master was made, it was duplicated with color adjustments to form a new master on a continuous piece of film. This process was extremely time-consuming and not easily reversible.

Digital editing offers significant advantages over film editing. It is faster, more precise, and more readily reedited. It also allows the easy integration of digital special effects into the shot sequences and the individual frames of the film.

Digital editing offers color effects that are not obtainable with photomechanical processes. For example, the film *O Brother Where Art Thou* used a restricted color palette for the background scenery that evoked the Dust Bowl era in the American South. This palette could have been achieved on film with the judicious use of lighting and filters, but it could not have been restricted to background elements only.

Image display. In June 1999, the first two films released for display in digital format were *Star Wars Episode I and An Ideal Husband*. There were two competing projectors in use: the Texas Instruments digital light processor (DLP) projector and Hughes/JVC ILA-12K liquid crystal on silicon (LCOS) projector. The DLP projectors were preferred for their larger color gamut and greater contrast range.

DLP projectors use optical semiconductors, called digital micromirror devices (DMD), to modulate the light and form images. Each DMD is an array of 1.3 million microscopic mirrors, which can be individually pivoted in and out of the projector's light path thousands of times per second. The individual mirrors are spaced 1 micrometer apart, so the device exhibits a high fill factor with good brightness and contrast. Cinema projectors are equipped with three DMD arrays (one for each primary color) to produce an image. Early projectors were limited to 1024 × 768 pixel resolution but current equipment offer 2K pixel resolution, 15-bit color depth, and sufficient brightness for a 75-ft-wide screen. In 2004, Sony released the SXRD 4K projector, which uses a variant of LCD technology. Its improved image resolution (4096 × 2160 pixels) offers a more lifelike image to the viewer.

Standards. The digital cinematography industry is developing standards for file format, compression technology, color display, and encryption needed for interoperability for the rapidly developing projector and hardware industries. Several groups are contributing to this effort, including the Motion Picture Association of America (MPAA) and the Digital Cinema Initiatives (DCI) consortium, a group of seven studios. The Society of Motion Picture and Television Engineering (SMPTE) has a technical committee for digital cinema (DC28) that has recommended specifications for file format, compression, and encryption technologies. The American Society of Cinematographers (ASC) has a technical committee to produce standardized evaluation materials for all aspects of digital cinema.

There has been steady development of encryption and digital rights management strategies for digital cinema. Currently, files are encrypted all the way into the projector, where the display files are extracted. This is of great importance to the industry in thwarting the piracy of intellectual property. It reduces the need for high security on the server since it will only receive and distribute encrypted files.

Anthony Stanton

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Cinnamon

An evergreen shrub or small tree, *Cinnamomum zeylanicum*, of the laurel family (Lauraceae). A native of Sri Lanka, the plant (see **illus.**) is now in cultivation in southern India, Burma, parts of Malaya, West Indies, and South America. In cultivation the trees are cut back and long, slender suckers grow up from the roots. The bark is removed from these suckers, dried and packaged for shipping. Cinnamon is a very important spice for flavoring foods. It is used in confectionery, gums, incense, dentifrices, and perfumes. Cinnamon oil is used in medicine and as a source of cinnamon extract. *See* MAGNOLIALES; SPICE AND FLAVORING. Perry D. Strausbaugh; Earl L. Core

Cinnamon (*Cinnamomum zeylanicum*). (*USDA*)

Circle

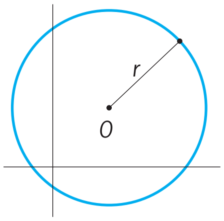

Fig. 1. Circle of radius *r* and center *O*.

The curve that is the locus of points in a plane with equal distance (radius) from a fixed point (center) (**Fig. 1**). In elementary mathematics, circle often refers to the finite portion of the plane bounded by a curve (circumference) all points of which are equidistant from a fixed point of the plane, that is, a circular disk. Circles are conic sections and are defined analytically by certain second-degree equations in cartesian coordinates. They were extensively studied by the ancient Greeks, who formulated the famous problem of "squaring the circle," that is, to construct, with compasses and unmarked straightedge only, a square whose area is equal to that of a given circle. It was not until 1882 that this was shown to be impossible, when F. Lindemann proved that the ratio of the length of a circle to its diameter (denoted by π) is not the root of any algebraic equation with integer coefficients. That π is irrational (that is, not the quotient of two integers) was shown by A. M. Legendre in 1794. Numerous approximations of π appeared quite early; for example, 3 (*Book of Kings*); $3\,{}^1/_7 > \pi > 3\,{}^{10}/_{71}$ (Archimedes); $\sqrt{10}$ (*Ch'ang Höng*, A.D. 78–139); and 3.1416 (Aryabhata, A.D. 476–550). Electronic computers have calculated π to over 10^{12} decimal places. Interesting expressions are

$$\pi = 4(1 - {}^1/_3 + {}^1/_5 - {}^1/_7 + \cdots)$$
$$\pi = 2 \cdot 2(2 \cdot 4/3 \cdot 3)(4 \cdot 6/5 \cdot 5)(6 \cdot 8/7 \cdot 7) \cdots$$

The area of a circle (circular disk) with radius r is πr^2; the length (circumference) is $2\pi r$. The area enclosed by a circle is greater than that bounded by any other curve of the same length. If a circular disk can cover each three points of an arbitrary plane set, then the disk can cover the whole set. It is, moreover, the only disk that has this property. *See* ANALYTIC GEOMETRY; CONIC SECTION. Leonard M. Blumenthal

A great many properties of the circle are in relation to a given triangle. Such, for example, is the nine-point circle theorem. Let the altitudes of any triangle *ABC* intersect each other in the orthocenter *H*, and intersect the opposite sides in *D*, *E*, and *F*, respectively. Then the circle *DEF* passes through the midpoints of each of the six segments *AB*, *BC*, *CA*, *AH*, *BH*, *CH*. It is called the nine-point circle of the triangle *ABC*, and also of each of the triangles *HBC*,

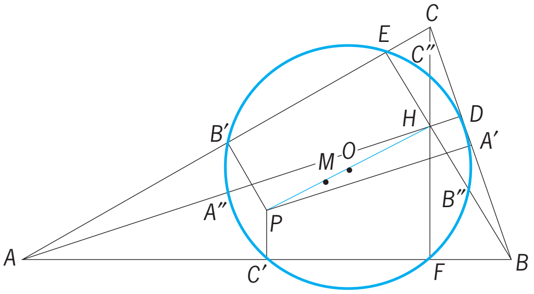

Fig. 2. Nine-point circle and Euler line *PMH*.

HCA, *HAB*, whose orthocenters are *A*, *B*, *C*, respectively. Feuerbach's theorem states that this nine-point circle is tangent both to the inscribed circle and to the three escribed circles of each of these triangles.

The center *O* of the nine-point circle (**Fig. 2**) of any triangle lies midway between the orthocenter *H* and the circumcenter *P* on the so-called Euler line that passes through these points and the centroid *M*. J. Sutherland Frame

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Circuit (electricity)

A general term referring to a system or part of a system of conducting parts and their interconnections through which an electric current is intended to flow. A circuit is made up of active and passive elements or parts and their interconnecting conducting paths. The active elements are the sources of electric energy for the circuit; they may be batteries, direct-current generators, or alternating-current generators. The passive elements are resistors, inductors, and capacitors. The electric circuit is described by a circuit diagram or map showing the active and passive elements and their connecting conducting paths.

Devices with an individual physical identity such as amplifiers, transistors, loudspeakers, and generators, are often represented by equivalent circuits for purposes of analysis. These equivalent circuits are made up of the basic passive and active elements listed above.

Electric circuits are used to transmit power as in high-voltage power lines and transformers or in low-voltage distribution circuits in factories and homes; to convert energy from or to its electrical form as in motors, generators, microphones, loudspeakers, and lamps; to communicate information as in telephone, telegraph, radio, and television systems; to process and store data and make logical decisions as in computers; and to form systems for automatic control of equipment.

Electric circuit theory. This includes the study of all aspects of electric circuits, including analysis, design, and application. In electric circuit theory the fundamental quantities are the potential differences (voltages) in volts between various points, the electric currents in amperes flowing in the several paths, and the parameters in ohms or mhos which describe the passive elements. Other important circuit quantities such as power, energy, and time constants may be calculated from the fundamental variables. For a discussion of these parameters *see* ADMITTANCE; CONDUCTANCE; ELECTRICAL IMPEDANCE; ELECTRICAL RESISTANCE; REACTANCE; SUSCEPTANCE; TIME CONSTANT.

Electric circuit theory is an extensive subject and is often divided into special topics. Division into topics may be made on the basis of how the voltages and currents in the circuit vary with time; examples are direct-current, alternating-current, nonsinusoidal, digital, and transient circuit thoery. Another method of classifying circuits is by the arrangement or configuration of the electric current paths; examples are series circuits, parallel circuits, series-parallel circuits, networks, coupled circuits, open circuits, and short circuits. Circuit theory can also be divided into special topics according to the physical devices forming the circuit, or the application and use of the circuit. Examples are power, communication, electronic, solid-state, integrated, computer, and control circuits. *See* CIRCUIT (ELECTRONICS); NEGATIVE-RESISTANCE CIRCUITS.

Direct-current circuits. In dc circuits the voltages and currents are constant in magnitude and do not vary with time (**Fig. 1**). Sources of direct current are batteries, dc generators, and rectifiers. Resistors are the principal passive element. For a discussion of direct-current circuits *see* DIRECT-CURRENT CIRCUIT THEORY

Magnetic circuits. Magnetic circuits are similar to electric circuits in their analysis and are often included in the general topic of circuit theory. Magnetic circuits are used in electromagnets, relays, magnetic brakes and clutches, computer memory devices, and many other devices. For a detailed treatment. *See* MAGNETIC CIRCUITS.

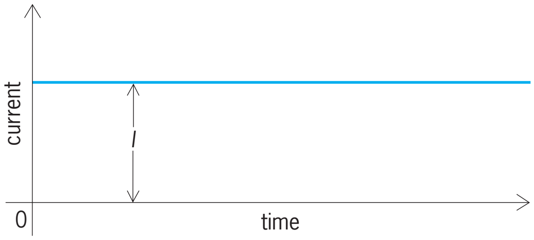

Fig. 1. Direct current, which is constant in magnitude and does not vary with time.

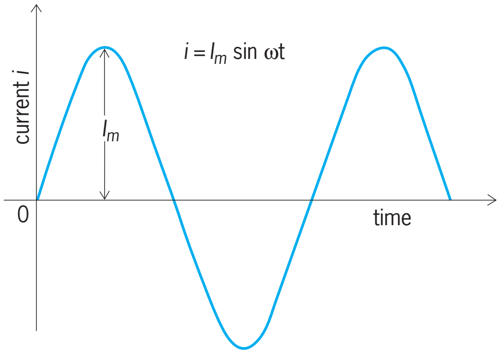

Fig. 2. Alternating current, which periodically reverses direction with time. In this example, the current varies sinusoidally with time.

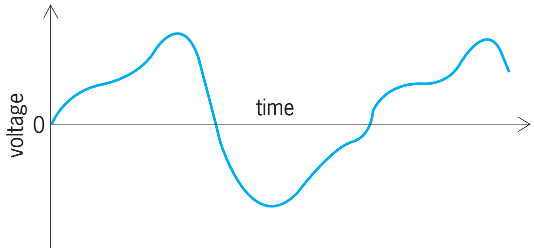

Fig. 3. Nonsinusoidal voltage wave.

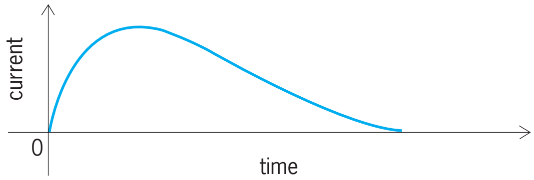

Fig. 4. Transient electric current.

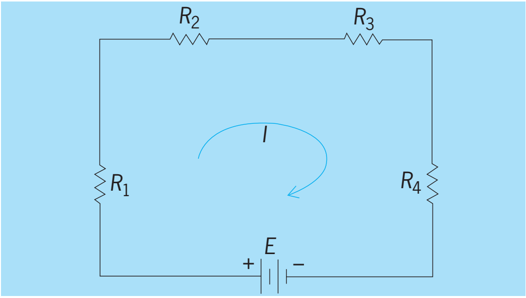

Fig. 5. Series circuit.

Alternating-current circuits. In ac circuits the voltage and current periodically reverse direction with time. The time for one complete variation is known as the period. The number of periods in 1 s is the frequency in cycles per second. A cycle per second was named a hertz (in honor of Heinrich Rudolf Hertz's work on electromagnetic waves).

Most often the term ac circuit refers to sinusoidal variations. For example, the alternating current in **Fig. 2** may be expressed by $i = I_m \sin \omega t$. Sinusoidal sources are ac generators and various types of electronic and solid-state oscillators; passive circuit elements include inductors and capacitors as well as resistors. The analysis of ac circuits requires a study of the phase relations between voltages and currents as well as their magnitudes. Complex numbers are often used for this purpose. For a detailed discussion. *See* ALTERNATING-CURRENT CIRCUIT THEORY.

Nonsinusoidal waveforms. These voltage and current variations vary with time but not sinusoidally (**Fig. 3**). Such nonsinusoidal variations are usually caused by nonlinear devices, such as saturated magnetic circuits, electron tubes, and transistors. Circuits with nonsinusoidal waveforms are analyzed by breaking the waveform into a series ofsinusoidal waves of different frequencies known as a Fourier series. Each frequency component is analyzed by ac circuit techniques. Results are combined by the principle of superposition to give the total response. *See* NONSINUSOIDAL WAVEFORM.

Electric transients. Transient voltage and current variations last for a short length of time and do not repeat continuously (**Fig. 4**). Transients occur when a change is made in the circuit, such as opening or closing a switch, or when a change is made in one of the sources or elements. For a discussion of dc and ac transients. *See* ELECTRIC TRANSIENT.

Series circuits. In a series circuit all the components or elements are connected end to end and carry the same current, as shown in **Fig. 5**. *See* SERIES CIRCUIT.

Parallel circuits. Parallel circuits are connected so that each component of the circuit has the same potential difference (voltage) across its terminals, as shown in **Fig. 6**. *See* PARALLEL CIRCUIT.

Series-parallel circuits. In a series-parallel circuit some of the components or elements are connected in parallel, and one or more of these parallel combinations are in series with other components of the circuit, as shown in **Fig. 7**.

Electric network. This is another term for electric circuit, but it is often reserved for the electric circuit that is more complicated than a simple series or parallel combination. A three-mesh electric network is shown in **Fig. 8**. *See* NETWORK THEORY.

Coupled circuits. A circuit is said to be coupled if two or more parts are related to each other through some common element. The coupling may be by means of a conducting path of resistors or capacitors or by a common magnetic linkage (inductive coupling), as shown in **Fig. 9**. *See* COUPLED CIRCUITS.

Open circuit. An open circuit is a condition in an electric circuit in which there is no path for current flow between two points that are normally connected. *See* OPEN CIRCUIT.

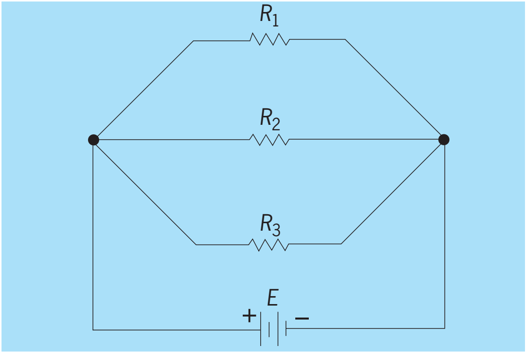

Fig. 6. Parallel circuit.

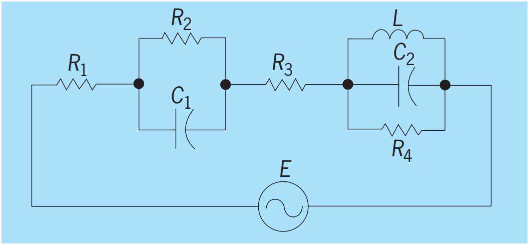

Fig. 7. Series-parallel circuit.

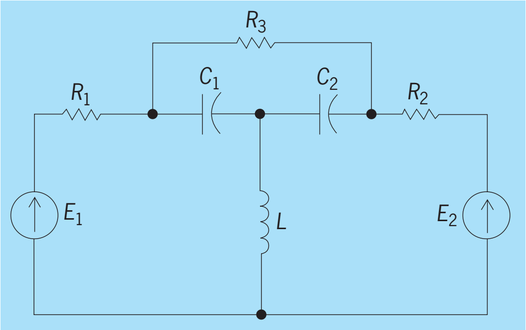

Fig. 8. A three-mesh electric network.

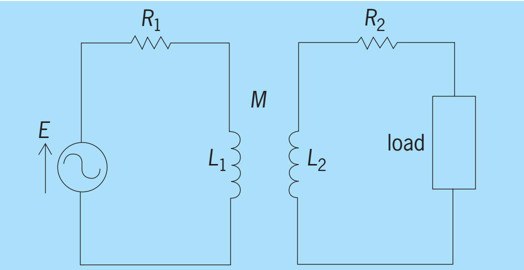

Fig. 9. Inductively coupled circuit.

Short circuit. This term applies to the existence of a zero-impedance or low-impedance path between two points of an electric circuit that are not intended to be connected. *See* SHORT CIRCUIT.

Integrated circuit. In the integrated circuit the entire circuit is contained in a single piece of semiconductor material. Sometimes the term is also applied to circuits made up of deposited thin films on an insulating substrate. *See* INTEGRATED CIRCUITS; SEMICONDUCTOR.

Clarence F. Goodheart

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Circuit (electronics)

An interconnection of electronic devices, an electronic device being an entity having terminals which is described at its terminals by electromagnetic laws. Most commonly these are voltage–current laws, but others, such as photovoltaic relationships, may occur.

Basic Concepts

Some typical electronic devices are represented as shown in **Fig. 1**, where a resistor, a capacitor, a diode, transistors, an operational amplifier, an inductor, a transformer, voltage and current sources, and a ground are indicated. Other devices (such as vacuum tubes, switches, and logic gates) exist, in some cases as combinations of the ones mentioned. The interconnection laws are (1) the Kirchhoff voltage law, which states that the sum of voltages around a closed loop is zero, and (2) the Kirchhoff current law, which states that the sum of the currents into a closed surface is zero (where often the surface is shrunk to a point, the node, where device terminals join). **Figure 2** represents an electronic circuit which is the interconnection of resistors (R, R_{B1}, R_{B2}, R_E, R_L), capacitors (C), a battery voltage source (V_{CC}), a current source (i_s), a bipolar transistor (T), and a switch (S). Functionally Fig. 2 represents a high-pass filter when S is open, and an oscillator when S is closed and the current source is removed. *See* AMPLIFIER; BATTERY; CAPACITOR; CURRENT SOURCES AND MIRRORS; DIODE; ELECTRIC FILTER; ELECTRONIC SWITCH; INDUCTOR; KIRCHHOFF'S LAWS OF ELECTRIC CIRCUITS; LOGIC CIRCUITS; OPERATIONAL AMPLIFIER; OSCILLATOR; RESISTOR; TRANSFORMER; TRANSISTOR; VACUUM TUBE.

Active and passive devices. The devices in an electronic circuit are classified as being either passive or active. The passive devices change signal energy, as is done dynamically by capacitors and statically by transformers, or absorb signal energy, as occurs in resistors, which also act to convert voltages to currents and vice versa. The active devices, such as batteries, transistors, operational amplifiers, and vacuum tubes, can supply signal energy to the circuit and in many cases amplify signal energy by transforming power supply energy into signal energy. Often, though, they are used for other purposes, such as to route signals in logic circuits. Transistors can be considered the workhorses of modern electronic circuits, and consequently many types of transistors have been developed, among which the most widely used are the bipolar junction transistor (BJT), the junction field-effect transistor (JFET), and the metal-oxide-silicon field-effect transistor (MOSFET). *See* ELECTRONIC POWER SUPPLY.

Fortunately, most of these transistors occur in pairs, such as the *npn* and the *pnp* bipolar junction transistors, or the *n*-channel and the *p*-channel MOSFETs, allowing designers to work symmetrically with positive and negative signals and sources. This statement may be clarified by noting that transistors can be characterized by graphs of output current i versus output voltage v that are parametrized by an input current (in the case of the bipolar junction transistor) or input voltage (in the MOSFET and JFET cases). Typically, the curves for an *npn* bipolar junction transistor or an *n*-channel field-effect transistor are used in the first quadrant of the output *i-v* plane, while for a *pnp* bipolar junction transistor or a *p*-channel field-effect transistor the same curves show up in the third quadrant. Mathematically, if $i = f(v)$ for an *npn* bipolar junction transistor or *n*-channel field-effect device, then $i = -f(-v)$ for a *pnp* bipolar junction transistor or *p*-channel field-effect device when the controlling parameters are also changed in sign.

Transistor properties. Because the transistors are so basic to the operation of electronic circuits, their performance will be briefly discussed.

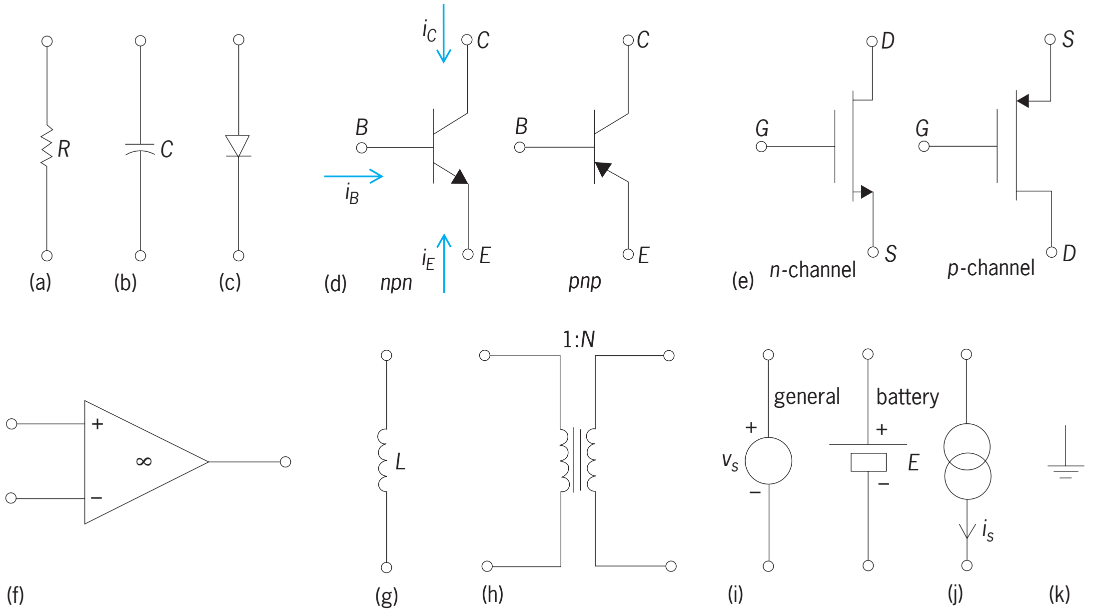

Fig. 1. Representation of some typical electronic devices. (*a*) Resistor. (*b*) Capacitor. (*c*) Diode. (*d*) Bipolar junction transistors (BJTs). (*e*) Metal-oxide-semiconductor field-effect transistors (MOSFETs). (*f*) Operational amplifier. (*g*) Inductor. (*h*) Transformer. (*i*) Voltage sources. (*j*) Current source. (*k*) Ground.

Bipolar transistors. These have three terminals, designated as the base *B*, the collector *C*, and the emitter *E*. These terminals connect to two diode junctions, *B-C* and *B-E*, these forming back-to-back diodes. The *B-E* junction is often forward-biased, in which case its voltage is about 0.7 V, while the *B-C* junction is reverse-biased for linear operation. In the case of linear operation, the bipolar junction transistor is much more than two back-to-back diodes because it has a very thin base which allows almost all of the current i_E entering the emitter to be collected by the collector. Thus, the collector current is nearly equal to the emitter current. This is expressed in Eq. (1), where

$$i_C = -\alpha i_E \tag{1}$$

the transistor parameter α is very close to 1. (The negative sign arises because the positive direction of current is assumed into the terminals, while one current must come out when the other goes in.) By Kirchhoff's current law for a sphere around the transistor ($i_B + i_C + i_E = 0$), the collector current can be expressed in terms of the base current to obtain Eq. (2), where the parameter β, given by Eq. (3), is

$$i_C = \beta i_B \tag{2}$$

$$\beta = \frac{\alpha}{1-\alpha} \tag{3}$$

very large. From this it follows that in linear operation the (bipolar junction) transistor acts like a current-controlled current source which, when used with base current as input and collector current as output, can have a high current gain β (typically 20 to 600). Because a current can be changed into a voltage via resistors, the transistor in its linear mode of operation also can be used to obtain a high voltage gain. For example, if the current source, the three capacitors, the two resistors labeled *R*, and the switch are replaced with a capacitor-coupled voltage source v_s between the point *B* and ground in Fig. 2 the voltage gain is given by Eq. (4), and can be chosen large

$$\frac{v_L}{v_s} = -\alpha \frac{R_L}{R_E} \tag{4}$$

in magnitude by appropriately choosing the ratio of the load resistance R_L to the emitter resistance R_E to be large.

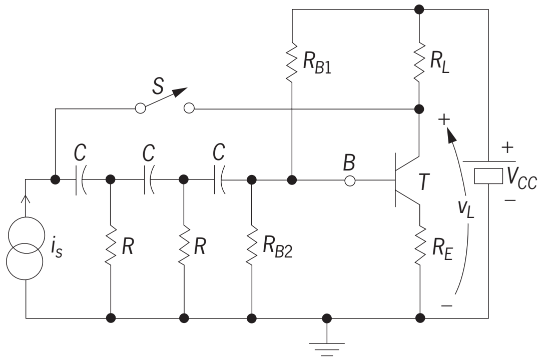

Fig. 2. Diagram of electronic circuit.

Besides biasing of the junctions for linear operation, any state of the two junctions can occur. For example, both junctions might be forward-biased, in which case the transistor is said to be in saturation and acts nearly as a short circuit between *E-C*, while if the junctions are simultaneously back-biased the transistor is said to be cut off and acts as an open circuit between all terminals. The transistor can be controlled between saturation and cutoff to make it act as an electronically controlled switch. This mode of operation is especially useful for binary arithmetic, as used by almost all digital computers, where 0 and 1 logic levels are represented by the saturation and cutoff transistor states.

MOSFET. These also have three regions of operation: cutoff, saturated, and resistive. The MOSFET also has three terminals, the gate *G*, the drain *D*, and the source *S*. A key parameter characterizing the MOSFET is a threshold voltage V_{th}. When the *G-S* voltage is below the threshold voltage, no drain current flows and the transistor is cut off. When the *G-S* voltage is above threshold, then for *D-S* voltages large in magnitude the MOSFET acts as a voltage-controlled current source, with the drain current given by Eq. (5), where *K* can conveniently be controlled by process parameters. Finally, for *D-S* voltages of small magnitude, the drain curent law is given by Eq. (6), in which case the MOSFET acts as a resistor between drain and source which can be varied by the *G-S* voltage v_{GS}. This resistor is nonlinear, because of the square term, but for very small values of v_{DS} can be considered linear [of conductance $K(v_{GS} - V_{th})$].

$$i_D = \frac{K(v_{GS} - V_{th})^2}{2} \tag{5}$$

$$i_D = K\left[(v_{GS} - V_{th})v_{DS} - \frac{v_{DS}^2}{2}\right] \tag{6}$$

The MOSFET is a versatile device, acting as a voltage-controlled current source in the saturation region and approximately as a voltage-controlled resistor in the resistive region. It can also be electronically controlled between cutoff and the resistive region to make it act as a switch, while for small signals around an operating point in the saturation region it acts as a linear amplifier. Another feature of the MOSFET is that, besides the categories of *n*-channel and *p*-channel devices, there are also enhancement- and depletion-mode devices of each category. In practice, for electronic circuit considerations, an *n*-channel device has $V_{th} > 0$ for enhancement-mode devices and $V_{th} < 0$ for depletion-mode devices, while the signs are reversed for *p*-channel devices.

Biasing of circuits. Since active devices usually supply signal energy to an electronic circuit, and since energy can only be transformed and not created, a source of energy is needed when active devices are present. This energy is usually obtained from batteries or through rectification of sinusoidal voltages supplied by power companies. When inserted into an electronic circuit, such a source of energy fixes the quiescent operation of the circuit; that is, it allows the circuit to be biased to a given operating point with no signal applied, so that when a signal is present it will be processed properly. To be useful, an electronic circuit produces one or more outputs; often inputs are applied to produce the outputs. These inputs and outputs are called the signals and, consequently, generally differ fromthe bias quantities, though often it is hard to separate signal and bias variables. For example, i_s in Fig. 2 would be an input signal, while V_{CC} would be a bias supply voltage. The voltage v_L would contain an output signal but would also include a bias component. The resistors R_{B1}, R_{B2}, R_E, and R_L are used to set the bias point of the transistor, but since they also affect the signal-handling capabilities, their choice is important in the design of the circuit. Biasing of electronic circuits is an important, nontrivial, and often overlooked aspect of their operation. *See* BIAS (ELECTRONICS).

Analog versus digital circuits. Electronic circuits are also classified as analog or digital. Analog circuits work with signals that span a full range of values of voltages and currents, while digital circuits work with signals that are at prescribed levels to represent numerical digits. Analog signals generally are used for continuous-time processes, while digital ones most frequently occur where transistions are synchronized via a clock. However, there are situations where it is desirable to transfer between these two classes of signals, that is, where analog signals are needed to excite a digital circuit or where a digital signal is needed to excite an analog circuit. For example, it may be desired to feed a biomedically recorded signal, such as an electrocardiogram into a digital computer, or it may be desired to feed a digital computer output into an analog circuit, such as a temperature controller. For such cases, there are special electronic circuits, called analog-to-digital and digital-to-analog converters. *See* ANALOG-TO-DIGITAL CONVERTER; DIGITAL-TO-ANALOG CONVERTER.

Feedback. An important concept in electronic circuits is that of feedback. Feedback occurs when an output signal is fed around a device to contribute to the input of the device. For example, in Fig. 2, when the switch *S* is closed, the voltage v_L is fed around the transistor *T* back to the input point; removal of i_s then allows v_L to contribute to its own generation, resulting in oscillations if the proper conditions are met. Consequently, when positive feedback occurs, that is, when the output signal returns to reinforce itself upon being fed back, it can lead to the generation of signals which may or may not be wanted. Circuit designers need to be conscious of all possible feedback paths that are present in their circuits so that they can ensure that unwanted oscillations do not occur. In the case of negative feedback, that is, when the output signal returns to weaken itself, then a number of improvements in circuit performance often ensue; for example, the circuit can be made less sensitive to changes in the environment or element variations, and deleterious nonlinear effects can be minimized. *See* CONTROL SYSTEMS; FEEDBACK CIRCUIT.

Specific Circuits

In designing integrated electronic circuits, one of the most useful tools is the current mirror. Two basic current mirrors are that shown in **Fig. 3*a*** for taking current out of a terminal attached to point A, and that shown in Fig. 3*b* for sending current into a terminal attached to point B. In Fig. 3*a*, the base-to-emitter

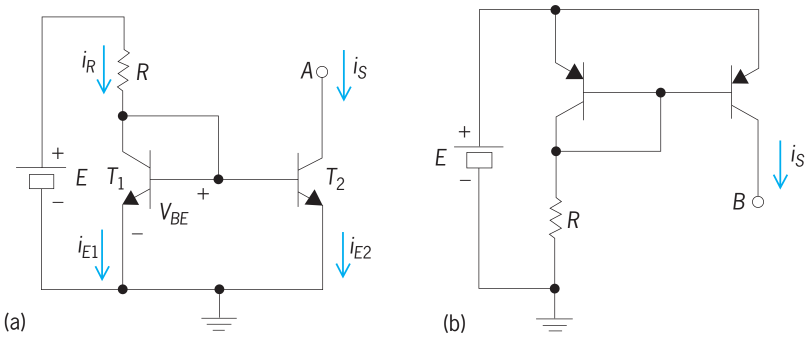

Fig. 3. Basic current mirrors. (*a*) Sink. (*b*) Source.

voltages of both transistors are identical and given by V_{BE}, with typically $V_{BE} = 0.7$ V (since the base-to-emitter junction of T_1 is a forward-biased diode). The current in the resistor i_R is then given by Ohm's law as Eq. (7) since the short circuit between collector

$$i_R = \frac{E - V_{BE}}{R} \tag{7}$$

and base makes T_1 a diode-connected transistor that forces the voltage $E - V_{BE}$ to be across R. From Kirchhoff's current law applied to a sphere encircling T_1, it follows that this current is about equal to the emitter current i_{E1} of T_1 (since the current into the base of transistor T_2 is very small). If the two transistors are identical, then $i_{E2} = i_{E1}$ (because the base-to-emitter voltages are the same). Finally, the collector current i_s of T_2 is about equal to its emitter current [by the construction and characteristics of transistors so that this current is given by Eq. (8)], mirroring the current i_R.

$$i_s = i_R \tag{8}$$

One of the most versatile circuits is the differential pair, since it finds increasing use in both analog and digital circuits. A bipolar-junction-transistor differential pair is shown in **Fig. 4**, where the dc bias current source I_E can be constructed from the output of a current mirror of the type of Fig. 3*a*. If the differential input voltage v_{id} is defined by Eq. (9), then it

$$v_{id} = v_{i1} - v_{i2} \tag{9}$$

can be shown that the differential output voltage v_{od} is given by Eq. (10), where V_T is the thermal voltage

$$v_{od} = \alpha R I_E \tanh \frac{v_{id}}{2V_T} \tag{10}$$

($V_T = 25$ mV at room temperature), α is the parameter alpha (defined above) for the two transistors (which are assumed identical), and tanh[·] is the hyperbolic tangent function. As Eq. (10) shows, the differential pair performs as a differential voltage-controlled voltage source. An MOS differential pair is obtained simply by replacing the bipolar junction transistors in Fig. 4 by MOSFETs, although a somewhat more complicated input-output law results. *See* DIFFERENTIAL AMPLIFIER.

Analog circuits. By replacing the resistive loads of the differential amplifier of Fig. 4 with the current mirror of Fig. 3*b*, a differential voltage-controlled current source (DVCCS) is generated, as shown in **Fig. 5**, where from the above Eq. (11) follows. Since

$$i_o = i_{c2} - i_{c1} = aI_E \tanh \frac{v_{id}}{2V_T} \tag{11}$$

tanh (x) $\simeq x$ when x is very small in magnitude, for small differential inputs the linear law (12) holds.

$$i_0 = \frac{\alpha I_E v_{id}}{2V_T} \tag{12}$$

An application of the differential voltage-controlled current source is seen by connecting its output to a capacitor, in which case an integrator results. Connecting the output of a differential voltage-controlled current source to its input can result in a resistor.

Operational amplifiers. The differential pair forms the input stage to the operational amplifier (op amp), an

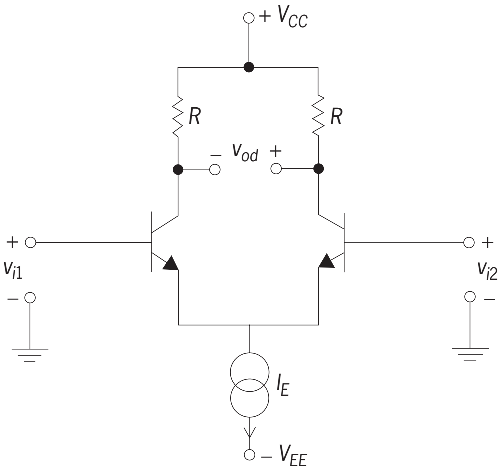

Fig. 4. Differential pair based on bipolar junction transistors.

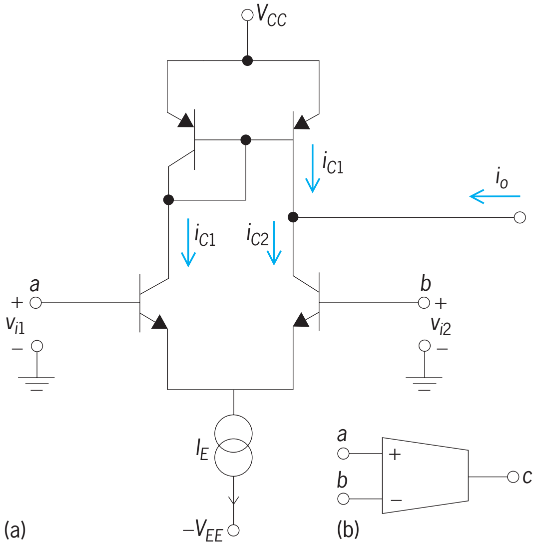

Fig. 5. Differential voltage-to-current converter. (*a*) Circuit. (*b*) Symbol.

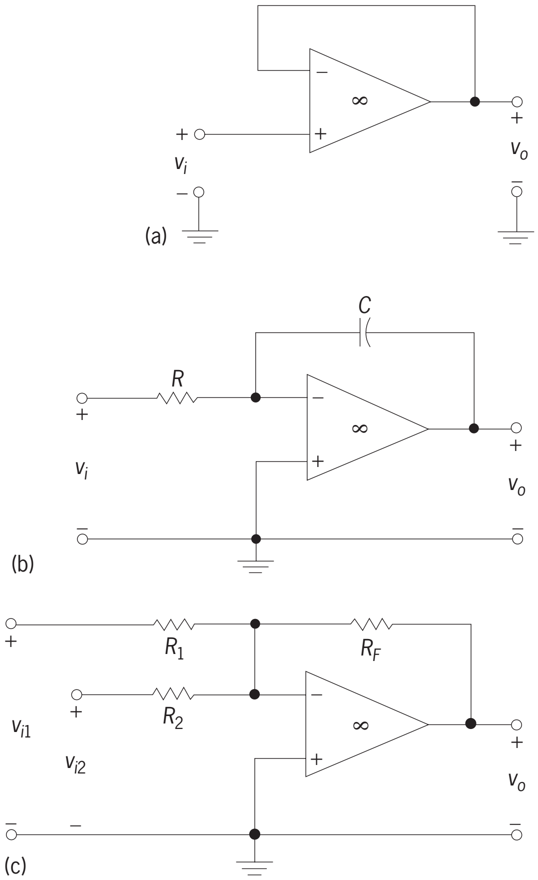

Fig. 6. **Basic operational amplifier circuits. (*a*) Unity-gain (isolation) amplifier. (*b*) Integrator. (*c*) Summer.**

extremely important electronic circuit device. The operational amplifier is typically realized by taking v_{od} of Fig. 4, greatly amplifying it, terminating with an output stage that allows for loading, and improving the input terminals so that miniscule input current is drawn. From this description, it follows that an operational amplifier in the linear region is characterized by the input-output voltage relationship given by Eq. (13), with K tending to infinity. Since v_o is

$$v_o = Kv_{id} \tag{13}$$

finite, this means that either $v_{id} \simeq 0$ or the output is saturated at a bias voltage of the operational amplifier. In either case, for most practical purposes the input current can be assumed to be zero. Therefore, in the linear region the operational amplifier has the very interesting description given by Eq. (14),

$$v_{id} = 0, \quad i_{\text{input}} = 0 \tag{14}$$

in which case its input looks like a simultaneous short and open circuit (while its output can be "anything").

By applying feedback through a direct connection of the output to the negative input, the unity-gain buffer amplifier satisfying Eq. (15) results. The buffer amplifier is shown in **Fig. 6*a***. If the positive input is grounded and negative feedback is applied, then the negative input must be also at ground potential and, since the operational amplifier draws no current, the negative input terminal is said to be a virtual ground. Using the concept of the virtual ground, it is readily seen that the circuit of Fig. 6*b* functions as an integrator, given by Eq. (16), where *s* is the derivative operator (and hence its inverse, 1/*s*, is the integral operator). The circuit of Fig. 6*c* functions as a summer, given by Eq. (17). Using the three circuits of Fig. 6, any set of linear differential equations with constant coefficients can be simulated, and arbitrary transfer functions realized. The operational amplifier is one of the most useful of the electronic circuit devices. *See* ANALOG COMPUTER.

$$v_o = v_i \tag{15}$$

$$v_o = \frac{-v_i}{RCs} \tag{16}$$

$$v_o = -R_F\left(\frac{v_{i1}}{R_1} + \frac{v_{i2}}{R_2}\right) \tag{17}$$

Applying positive feedback in operational amplifier circuits, some interesting results can also be obtained. For example, the circuit of **Fig. 7*a*** is a practical way to obtain a negative resistance; its operation depends on Eq. (18). When the operational amplifier is in its linear region, that is, when notation (19) is valid, Eq. (20) holds, giving the negative resistor equation (21). When the operational amplifier is forced into saturation the behavior of the circuit

$$i = \frac{v - v_o}{R} \tag{18}$$

$$-V_{EE} < v_o < V_{CC} \tag{19}$$

$$v_o = \left(1 + \frac{R_F}{R_1}\right)v \tag{20}$$

$$i = -\left(\frac{R_F}{R_1 R}\right)v \tag{21}$$

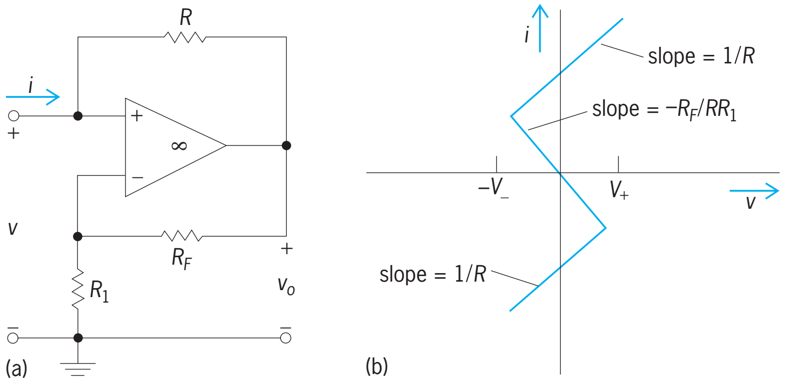

Fig. 7. **Negative resistor circuit. (*a*) Diagram. (*b*) Voltage-current characteristic.**

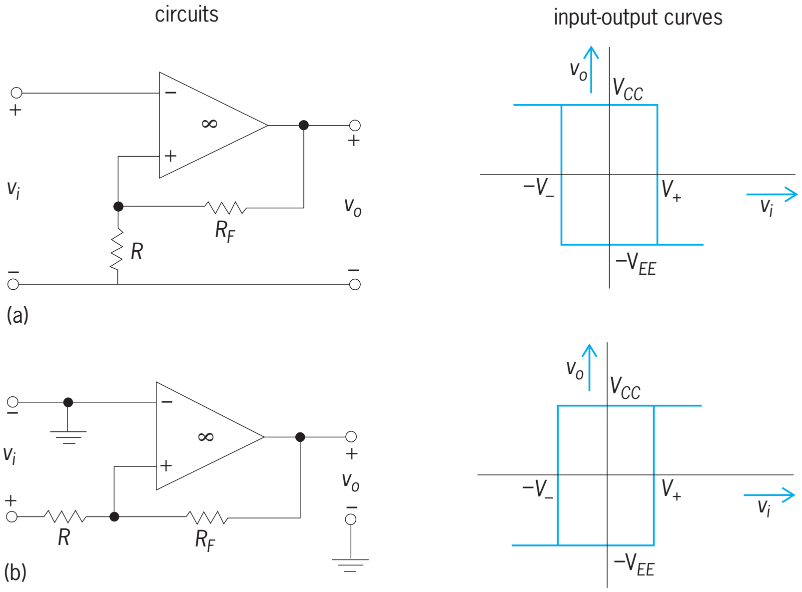

Fig. 8. Schmitt trigger circuits and their input-output curves. (*a*) Circuit with isolated input (negative gain). $V_+ = V_{CC}/[1 + (R_F R)]$; $V_- = V_{EE}/[1 + (R_F R)]$. (*b*) Circuit with coupled input (positive gain). $V_+ = RV_{CC}R_F$; $V_- = RV_{EE}/R_F$.

is given by Eqs. (22) and (23) [Fig. 5]. The resulting

$$i = \frac{v - V_{CC}}{R} \quad \text{when } v < V_+ = \frac{V_{CC}}{1 + (R_F/R_1)} \tag{22}$$

$$i = \frac{v + V_{EE}}{R} \quad \text{when } v > -V_- = -\frac{V_{EE}}{1 + (R_F/R_1)} \tag{23}$$

transfer characteristic is shown in Fig. 7*b*. This negative resistor is multiple-valued when the input voltage v is used as the independent (that is, control) variable. Hence, an attempt to use it as a voltage-controlled device will result in its exhibiting hysteresis, since a switch onto the upper curve occurs at $v = V_+$ whereas a switch off the upper curve occurs at $-V_-$. *See* HYSTERESIS; NEGATIVE-RESISTANCE CIRCUITS; OPERATIONAL AMPLIFIER.

Schmitt triggers. Other circuits exhibiting hysteresis are Schmitt trigger circuits (**Fig. 8**), where positive feedback is again used. In these circuits the output is taken as the operational amplifier output voltage, which saturates at the bias voltages. As shown in the input-output curves of Fig. 8, the Schmitt triggers give binary-valued hysteresis, which makes them useful for storage of binary information or for maintaining a constant output in the presence of noise.

Role of nonlinearity. Since the characteristics of the circuits of Figs. 7 and 8 are very nonlinear, they serve as examples to illustrate that nonlinear theory plays an important role in the area of electronic circuits. There are many other instances where nonlinearities are important, for example, in the construction of analog multipliers where the output is the product of two inputs. (Such a multiplier can be obtained via the differential pair of Fig. 5 if I_E is made to vary with an input. This is achievable by using the current sink of Fig. 3*a* to generate I_E. With this circuit the voltage E becomes the second input.) Likewise, nonlinearities are required in the modern theories of neural networks, where so-called sigmoid-type nonlinearities are used to obtain convergence toward set patterns. (The hyperbolic tangent function realized by the differential pair is a sigmoid-type of nonlinearity.) *See* NEURAL NETWORK.

Filters. One of the most common uses of analog active circuits is in the construction of electrical filters. Electrical filters are circuits whose input-output characteristics allow signals at certain frequencies (called the passband) to pass through unattenuated while signals at unwanted frequencies (called the stopband) are eliminated. By appropriately positioning the passband and the stopband, various filter types such as low-pass, band-pass, and high-pass can be attained. Filter design often concentrates on low-pass filters, since through relatively elementary transformations the band-pass and high-pass responses can be obtained from the low-pass transfer function. The transfer function, $H(s)$, is the ratio of the output v_o to the input v_i as a function of the complex frequency variable s.

Maximally flat filters are common with these resulting from using the Butterworth polynomials, $B_n(s)$, to obtain the low-pass transfer function given by Eq. (24). Here, $B_n(s)$ is given by Eq. (25), where

$$H(s) = 1/B_n(s) \tag{24}$$

$$B_n(s) = (s - s_1) \cdot \ldots \cdot (s - s_n) \tag{25}$$

$s_1, \ldots, s_n$ are the 2nth roots of $(-1)^{n+1}$ with negative real parts. As a function of frequency, f, the magnitude of the transfer function satisfies Eq. (26), so

$$|H(j2\pi f)| = \frac{1}{[1 + (2\pi f)^{2n}]^{1/2}} \tag{26}$$

that it is equal to 1 at dc and to $1/\sqrt{2}$ at $f = 1/2\pi$ [termed the 3-decibel attenuation point]. The substitution of Eq. (27) shifts the 3-dB point to the frequency $\Omega/(2\pi)$; the substitution of Eq. (28) changes

$$s = \frac{S}{\Omega} \tag{27}$$

$$s = \frac{\Omega}{S} \tag{28}$$

the low-pass characteristic to high-pass. The substitution of Eq. (29) leads to a band-pass characteristic

$$s = \Omega_o \left(\frac{S}{\Omega} + \frac{\Omega}{S} \right) \tag{29}$$

(with Ω_o adjusting the bandwidth and Ω adjusting the center frequency).

Since the complex frequency variable s also serves as the derivative operator, a description of the filter in terms of differential equations can be obtained from the transfer function. One way these differential equations can be realized is with the electronic circuits of Fig. 6. Alternatively, the transfer function can be realized by specialized circuits created for the purpose of filtering. Indeed, because of the importance of filters to technology, their theory is extensive, and vast tables of filter transfer functions and circuits to realize them have been compiled. *See* ELECTRIC FILTER.

Digital circuits. The digital computer is based on digital electronic circuits. Although some of the circuits are quite sophisticated, such as the microprocessors integrated on a single chip, the concepts behind most of the circuits involved in digital computers are quite simple compared to the circuits used for analog signal processing. The most basic circuit is the inverter; a simple realization based upon the MOS transistor is shown in **Fig. 9***a*. The upper (depletion-mode) transistor acts as a load "resistor" for the lower (enhancement-mode) transistor, which acts as a switch, turning on (into its resistive region) when the voltage at point *A* is above threshold to lower the voltage at point *B*. Adding the output currents of several of these together into the same load resistor gives a NOR gate, a two-input version of which is shown in Fig. 9*b*; that is, the output is high, with voltage at V_{DD}, if and only if the two inputs are low. Placing the drains of several of the enhancement-mode switches in series yields the NAND gate, a two-input version of which is shown in Fig. 9*c*; that is, the output is low if and only if both inputs are high. From the circuits of Fig. 9, the most commonly used digital logic circuits can be constructed. Because these circuits are so simple, digital circuits and digital computers are usually designed on the basis of negation logic, that is, with NOR and NAND rather than OR and AND circuits. *See* DIGITAL COMPUTER; INTEGRATED CIRCUITS; MICROPROCESSOR.

Conversion. Because most signals in the real world are analog but digital computers work on discretizations, it is necessary to convert between digital and analog signals. As mentioned above, this is done through digital-to-analog and analog-to-digital converters. Most approaches to digital-to-analog conversion use summers of the type shown in Fig. 6*c*, where the voltages representing the digital bits are applied to input resistors, either directly or indirectly through switches gated on by the digital bits which change the input resistance fed by a dc source (as is the case in the R-to-2R type of analog-to-digital converters).

One means of doing analog-to-digital conversion is to use a clocked counter that feeds a digital-to-analog converter, whose output is compared with the analog signal to stop the count when the digital-to-analog output exceeds the analog signal. The counter output is then the analog-to-digital output. The comparator for such an analog-to-digital converter is similar to an open-loop operational amplifier (which changes saturation level when one of the differential input levels crosses the other). Other types of analog-to-digital converters, called flash converters, can do the conversion in a shorter time by use of parallel operations, but they are more expensive.

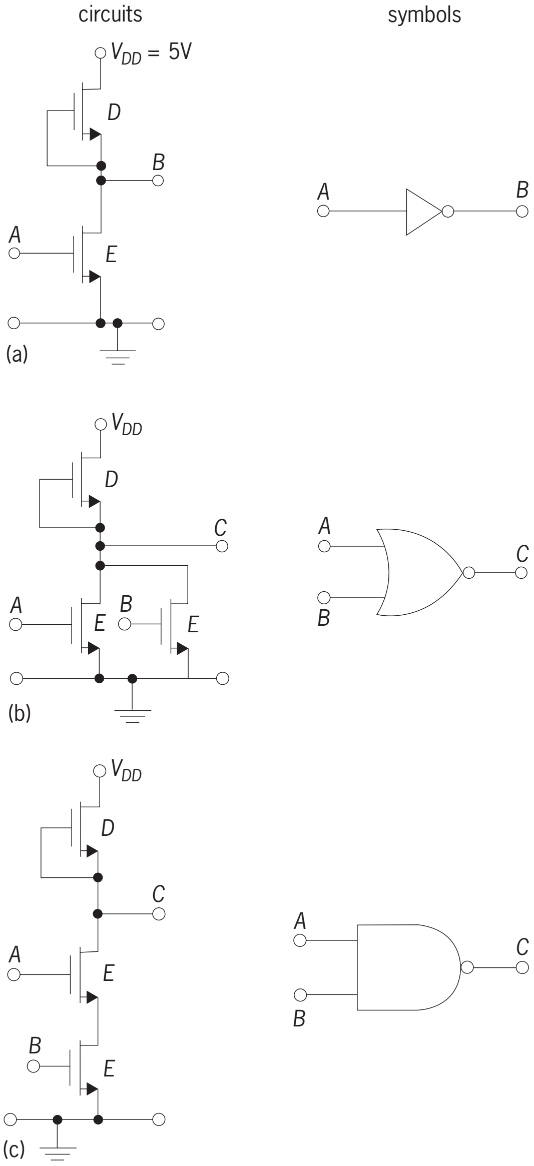

Fig. 9. Digital logic gates and their symbols. *D* = depletion-mode transistor; *E* = enhancement-mode transistor. (*a*) Inverter. (*b*) NOR gate. (*c*) NAND gate.

Other circuits. The field of electronic circuits is very broad and there are a very large number of other circuits besides those discussed above. For example, the differential is a key element in operational amplifier design and in biomedical data acquisition devices which must also be interfaced with specialized electronic sensors. Light-emitting and -detecting diodes allow for signals to be transmitted and received at optical frequencies. Liquid crystals are controlled by electronic circuits and are useful in digital watches, flat-panel color television displays, and electronic shutters. *See* BIOMEDICAL ENGINEERING; ELECTRONIC DISPLAY; LIGHT-EMITTING DIODE; LIQUID CRYSTALS; OPTICAL DETECTORS; TRANSDUCER.

Design

Because some circuits can be very complicated, and since even the simplest circuits may have complicated behavior, the area of computer-aided design

(CAD) of electronic circuits has been extensively developed. A number of circuit simulation programs are available, some of which can be run on personal computers with good results. These programs rely heavily upon good mathematical models of the electronic devices. Fortunately, the area of modeling of electronic devices is well developed, and for many devices there are models that are adequate for most purposes. But new devices are constantly being conceived and fabricated, and in some cases no adequate models for them exist. Thus, many of the commerical programs allow the designer to read in experimentally obtained data for a device from which curve fitting techniques are used to allow an engineer to proceed with the design of circuits incorporating the device. Reproducibility and acceptability of parts with tolerances are required for the commerical use of electronic circuits. Consequently, theories of the reliability of electronic circuits have been developed, and most of the computer-aided design programs allow the designer to specify component tolerances to check out designs over wide ranges of values of the elements. Finally, when electronic circuits are manufactured they can be automatically tested with computer-controlled test equipment. Indeed, an area that will be of increasing importance is design for testability, in which decisions on what to test are made by a computer using knowledge-based routines, including expert systems. Such tests can be carried out automatically with computer-controlled data-acquisition and display systems. *See* CIRCUIT (ELECTRICITY); COMPUTER-AIDED DESIGN AND MANUFACTURING; EXPERT SYSTEMS; RELIABILITY, AVAILABILITY, AND MAINTAINABILITY; ROBOTICS. Robert W. Newcomb

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Circuit breaker

A device to open or close an electric power circuit either during normal power system operation or during abnormal conditions. A circuit breaker serves in the course of normal system operation to energize or deenergize loads. During abnormal conditions, when excessive current develops, a circuit breaker opens to protect equipment and surroundings from possible damage due to excess current. These currents are usually the result of short circuits created by lightning, accidents, deterioration of equipment, or sustained overloads. *See* CIRCUIT (ELECTRICITY); LIGHTNING AND SURGE PROTECTION.

Formerly, all circuit breakers were electromechanical devices. In these breakers a mechanism operates one or more pairs of contacts to make or break the circuit. The mechanism is powered either electromagnetically, pneumatically, or hydraulically. The contacts are located in a part termed the interrupter. When the contacts are parted, opening the metallic conductive circuit, an electric arc is created between the contacts. This arc is a high-temperature ionized gas with an electrical conductivity comparable to graphite. Thus the current continues to flow through the arc. The function of the interrupter is to extinguish the arc, completing circuit-breaking action.

Current interruption. In alternating-current circuits, arcs are usually extinguished at a natural current zero, when the ac voltage applied across the arcing contacts reverses polarity. Within a short period around a natural current zero, the power input to the arc, equal to the product of the instantaneous current and voltage, is quite low. There is an opportunity to remove more energy from the arc than is applied to it, thus allowing the gas to cool and change from a conductor into an insulator. *See* ALTERNATING CURRENT.

In direct-current circuits, absence of natural current zero necessitates the interrupter to convert the initial arc into one that could only be maintained by an arc voltage higher than the system voltage, thus forcing the current to zero. To accomplish this, the interrupter must also be able to remove energy from the arc at a rapid rate. *See* DIRECT CURRENT.

Different interrupting mediums are used for the purpose of extinguishing an arc. In low- and medium-voltage circuits (1110–15,000 V) the arc is driven by the magnetic field produced by the arc current into an arc chute (**Fig. 1**). In the arc chute the arc is either split into several small arcs between metal plates or driven tightly against a solid insulating material. In the former case the splitting of the arc increases the total arc voltage, thus increasing the rate of energy dissipation. In the latter case the insulating material is heated to boiling temperatures, and the evaporated material flows through the arc, carrying a great deal of energy with it.

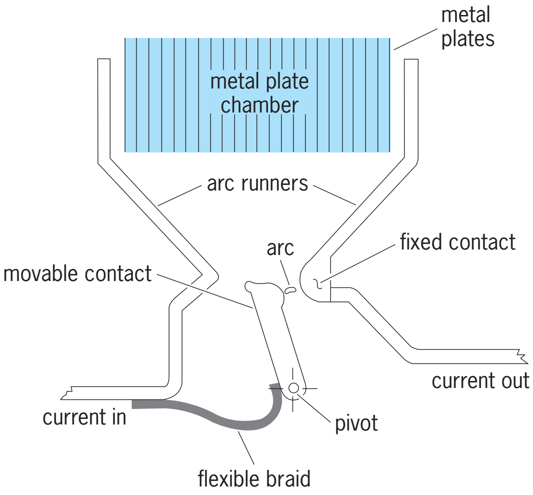

Fig. 1. Cross section of interrupter for a typical medium-voltage circuit breaker.

Oil and gas-blast circuits. For outdoor applications at distribution and subtransmission voltage (10 kV and above), oil breakers are widely used. In the United States, bulk oil breakers are used (**Fig. 2**), and in European and many other countries, "low-oil-content" breakers are quite popular. The principles of operation of both kinds of oil breakers are basically the same. Only the amount of oil used and the detailed engineering design differ. In oil breakers, the arc is drawn in oil. The intense heat of the arc decomposes the oil, generating high pressure that produces a fluid flow through the arc to carry energy away. At transmission voltages below 345 kV, oil breakers used to be popular. They were, however, increasingly replaced by gas-blast circuit breakers such as air-blast breakers (**Fig. 3**) and sulfur hexafluoride (SF_6) circuit breakers (**Fig. 4**).

In air-blast circuit breakers, air is compressed to high pressures (approximately 50 atm $= 5 \times 10^6$ pascals). When the contacts part, a blast valve is opened to discharge the high-pressure air to ambient, thus creating a very high-velocity flow near the arc to dissipate the energy. In SF_6 circuit breakers, the same principle is employed, with SF_6 as the medium instead of air. In the "puffer" SF_6 breaker, the motion of the contacts compresses the gas and forces it to flow through an orifice into the neighborhood of the arc. Both types of SF_6 breakershave been developed

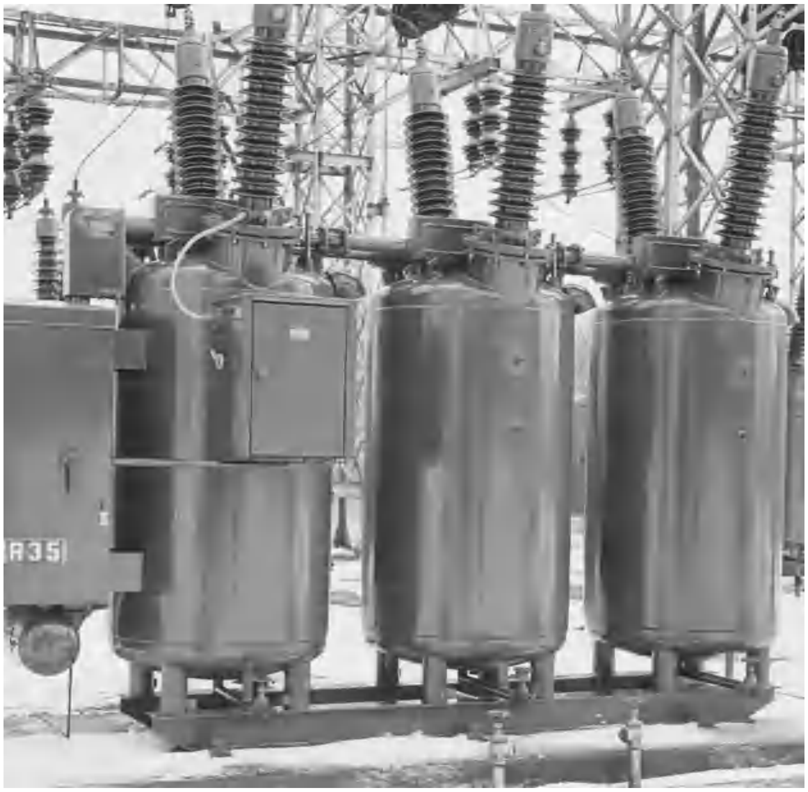

Fig. 2. Bulk oil circuit breaker for 138-kV application.

Fig. 3. Air blast circuit breaker rated for 500 kV.

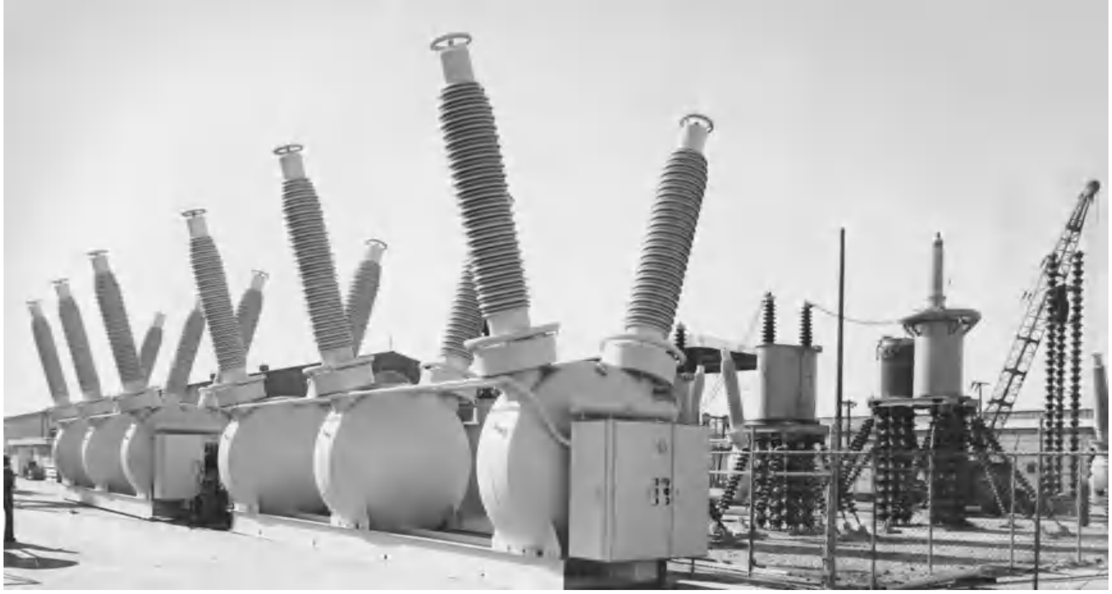

Fig. 4. Sulfur hexafluoride circuit breakers, 500-kV, 3-kA.

for EHV (extra-high-voltage) transmission systems.

For EHV systems, it was discovered that closing of a circuit breaker may cause a switching surge which may be excessive for the insulation of the system. The basic principle is easy to understand. If a breaker is closed at the peak of the voltage wave to energize a single-phase transmission line which is open-circuited at the far end, reflection can cause the transient voltage on the line to reach twice the peak of the system voltage. If there are trapped charges on the line, and if it happens that at the moment of breaker-closing the system voltage is at its peak, equal in magnitude to but opposite to the polarity of the voltage due to the trapped charges left on the line, the switching surge on the line can reach a theoretical maximum of three times the system voltage peak.

One way to reduce the switching surge is to insert a resistor in series with the line (**Fig. 5**) for a short time. When switch A in Fig. 5 is closed, the voltage is divided between the resistance and the surge impedance Z of the line by the simple relationship $V_L = V[Z/(R + Z)]$, where V is voltage impressed, V_L is voltage across the transmission line, R is resistance of the resistor, and Z is surge impedance of the line. Only V_L will travel down the line and be reflected at the other end. The magnitude of the switching surge is thus considerably reduced.

Vacuum breakers. The vacuum breaker, another electromechanical device, uses the rapid dielectric recovery and high dielectric strength of vacuum. A pair of contacts is hermetically sealed in a vacuum envelope (**Fig. 6**). Actuating motion is transmitted through bellows to the movable contact. When the contacts are parted, an arc is produced and supported by metallic vapor boiled from the electrodes. Vapor particles expand into the vacuum and condense on solid surfaces. At a natural current zero the vapor particles disappear, and the arc is extinguished. Vacuum breakers of up to 242 kV have been built (**Fig. 7**).

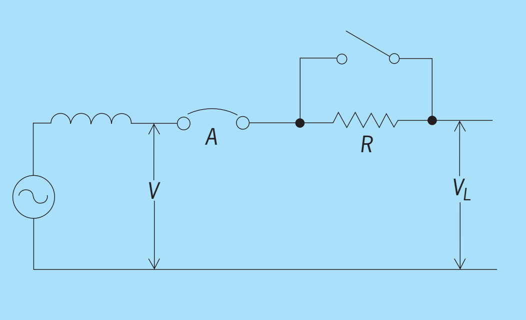

Fig. 5. Resistor insertion to reduce switching surge.

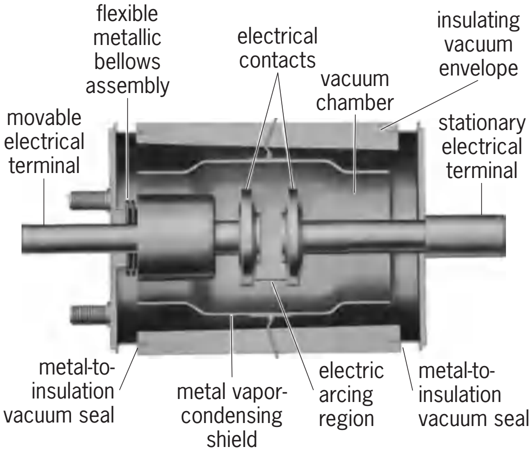

Fig. 6. Cutaway view of vacuum interrupter.

Solid-state breakers. The other type of breaker uses a thyristor, a semiconductor device which in the off state prevents current from flowing but

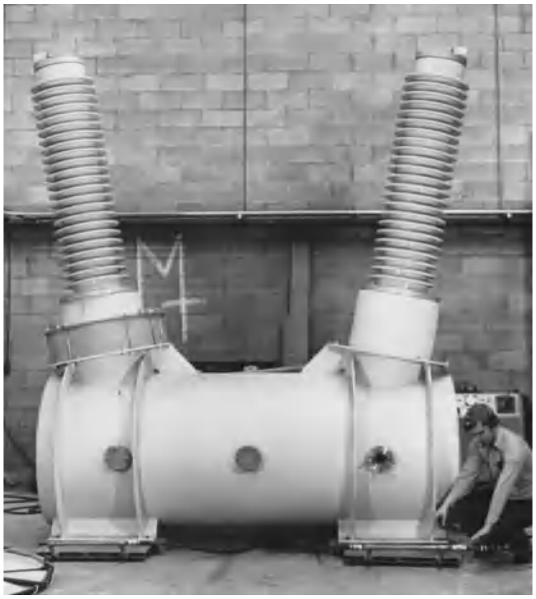

Fig. 7. Vacuum circuit breaker, 242-kV, 40-kA.

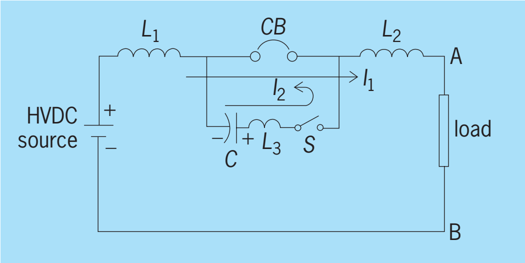

Fig. 8. Commutation principles of circuit interruption.

which can be turned on with a small electric current through a third electrode, the gate. At the natural current zero, conduction ceases, as it does in arc interrupters. This type of breaker does not require a mechanism. Semiconductor breakers have been built to carry continuous currents up to 10,000 A.

Semiconductor circuit breakers can be made to operate in microseconds if the commutation principle is applied. **Figure 8** illustrates the commutation principle for an hvdc (high-voltage direct-current) circuit, but it can easily be extended to ac circuits. During normal operation, the circuit breaker (CB in the diagram) would be closed from the hvdc source. In this diagram, inductances L_1 and L_2 represent the circuit inductance on either side of the breaker. Suppose that a fault occurs which applies a short circuit between points A and B. The current will commence to increase, its rate being determined by L_1 and L_2. When the increased current is detected, the contacts of the circuit breakers are opened, drawing an arc, and the switch (S in the diagram) is closed, causing the precharged capacitors C to discharge through the circuit breaker. The current I_2 so produced is traveling in such a direction as to oppose I_1 and drive it to zero, thereby giving the circuit breaker an opportunity to interrupt.

Thyristors can be used for both circuit breakers and switches. The closing and opening operations are, of course, not mechanical but are controlled by the gates. Such a circuit breaker was built for very special switching applications, such as thermonuclear fusion research. Thomas H. Lee

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Circulation

Those processes by which metabolic materials are transported from one region of an organism to another. Ultimately, the essential gases, nutrients, and waste products of metabolism are exchanged across cell membranes by diffusion. Diffusion is the movement of material, by random motion of molecules, from a region of high concentration to one of low concentration. The amount of material moved from one place to another depends on the difference in concentrations and on the distance between the two points. The greater the distance, the less movement of material per unit time for a given difference in concentration. Consequently, in all but the smallest animals, convection (or bulk circulation) of materials to the cell must be employed to supplement diffusion.

Protoplasmic movement aids diffusion at the intracellular level. In multicellular animals, however, either the external medium or extracellular body fluids, or both, are circulated. In sponges and coelenterates (**Fig. 1***a* and *b*), water is pumped through definite body channels by muscular activity or, more often, by cilia or flagella on the cells lining the channels. Even external water currents can be tapped for this purpose. It is generally assumed that flows driven by these mechanisms will be slow. However, this may not be the case.

In sponges, flow driven by flagella in flagellated chambers enters through pores in the body wall and exits through the large central osculum. The cross-sectional area of all the flagellated chambers is approximately 6000 times that of the osculum. Hence, the exceptionally low flow velocity in the flagellated chambers increases markedly as the total volume of water is forced out through the osculum. In fact, water may flow through the osculum at velocities of 5 cm · s^{-1}, approaching those attained in major arterial vessels in vertebrates. This is an example of the principle of continuity, which states that the total volume of fluid moving past any point in a circulation (providing it has no major leaks) must be the same as that flowing past any other point. In regions of large cross-sectional area, the velocity of flow is low, whereas when cross-sectional area is small the flow velocity will be high.

Coelenterates have a body wall derived from two cell layers; an outer ectoderm is separated from an inner endoderm by a noncellular gelatinous

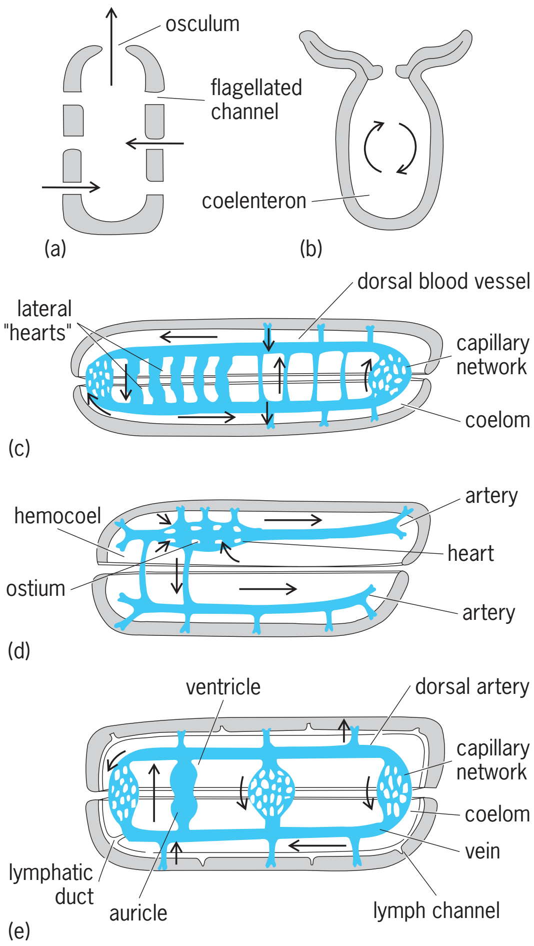


Fig. 1. Systems of internal transport. (*a*) Sponge type, with flagellated channels. (*b*) Coelenterate type. (c) Oligochaete type, with coelom and closed blood system. (*d*) Crustacean-molluscan type, with blood system open to hemocoel which is derived from primary cavity or blastocoel. (*e*) Vertebrate type, with coelom, closed vascular system, and lymphatic channels. (*After C. L. Prosser*, *Comparative Animal Physiology*, 3d ed., *W. B. Saunders*, *1973*)

material (mesoglea). All higher animals have bodies consisting of three cell layers, with the ectoderm being separated from the endoderm by a cellular layer of mesoderm. The mesoderm proliferates and separates to develop a fluid-filled body cavity or coelom. The coelom separates the ectoderm (together with an outer layer of mesoderm) from the endoderm (which has an inner layer of mesoderm). Coelomic fluid is moved around by body movements or ciliary activity, but in larger animals this movement is usually inadequate to supply the metabolic requirements of the organs contained within the coelom. These needs are provided for by pumping a fluid, blood, to them through vessels, the blood vascular system (Fig. 1*c*–*e*).

Open and Closed Circulatory Systems

When the blood is in a separate compartment from the rest of the extracellular fluid, the vascular system is described as closed. In such a system, the blood is circulated by a pump, the heart, through special channels, blood vessels; it comes into close association with the tissues only in the capillaries, fine vessels with walls only one cell thick. In some tissues or regions, larger blood spaces may exist, called sinuses. A closed vascular system is found in most annelids (segmented worms and leeches), cephalopod mollusks (squids and octopods), holothurian echinoderms (sea cucumbers), and vertebrates (Fig. 1*c* and *e*).

In most vertebrates, a functional but anatomically closed connection exists between the extracellular spaces (between the cells) and the blood vascular system in the form of lymph channels. Lymph is derived from the noncellular component of blood (plasma), modified in its passage through the tissues, and is picked up by blind-ending lymphatic vessels, which conduct the lymph to the veins (Fig. 1*e*). The presence of a lymphatic system in fish is controversial. In many fishes, a secondary circulation exists which parallels the primary circulation in extent and connects to it by narrow channels, which are small enough to exclude most red blood cells from the secondary circulation. It is unlikely that the secondary circulation is the evolutionary forerunner of a true lymphatic system, which is first observed in lungfishes, or that the secondary circulation subserves the same function as a true lymphatic system.

In most arthropods (crustaceans, insects), most mollusks (shellfish), and many ascidians (sea squirts), the extracellular spaces are confluent with the blood system. In these animals, blood is pumped through a limited network of vessels into a body cavity called a hemocoel (Fig. 1*d*). After bathing the tissues, blood (called hemolymph in these organisms) collects in sinuses and returns to the heart. This is the open vascular system. In animals with open circulatory systems, the coelom is much reduced.

Dynamics

A pump is required to circulate the blood in animals. The pump (usually called a heart) imparts propulsive energy to the blood, which flows from regions of high fluid energy to regions of low fluid energy (or down an energy gradient). The total energy of flowing blood consists of pressure energy, imparted by the pump, and energy contained in blood due to its motion (kinetic energy). Even in mammals, where blood flows very rapidly, the kinetic energy component is small compared with pressure energy and is usually ignored. Consequently, it is usual to refer to blood flow as taking place down a pressure gradient rather than energy gradient.

As the blood courses around the circulatory system, pressure energy is lost as heat. This loss of energy is described as resistance to flow. In closed circulations, flow resistance is concentrated in short narrow regions of blood vessels, known as resistance vessels. These are fine vessels (diameter of 0.02 mm), and since they have a muscular coat they are able to change their diameter to regulate flow. However, it is not the friction between the wall and blood that causes energy dissipation but rather friction between the various layers of the flowing blood (internal friction or viscosity). Blood flow in tubes is streamlined; the layer of blood at the wall is stationary while that in the middle flows fastest. Hence, slower-moving layers close to the wall tend to slow down and stop faster-moving layers, while they, in turn, will try to speed up slower-flowing layers. It is this internal friction which must be overcome by flowing blood, and the higher the viscosity of the fluid, the more energy will be dissipated in doing this. For instance, it takes much more effort to force treacle (a high-viscosity fluid) than water, at the same flow rate, through the same-diameter pipe. Blood is also much thicker (or more viscous) than water.

In a closed circulation, the total peripheral resistance (*R*) can be expressed by the equation below,

$$R = \frac{P_1 - P_2}{Q}$$

in which P_1 = pressure in the outflow vessels of the heart, P_2 = pressure in the inflow vessels, and Q = the output of a single propulsive chamber (ventricle). This equation is a simplified form of a formula used to describe flow in tubes (Poiseuille's law) and is a direct analog of Ohm's law for the relationship between electrical potential difference (pressure gradient), current (flow), and resistance. The resistance of the vascular system will depend on its geometry, as well as the viscosity of the fluid. Of the geometric factors, the radius of the tubes is far more important than length because only the radius is a variable in the circulation. In fact, flow per unit time changes in proportion to the fourth power of the radius for a given fall in pressure along the vessel. Hence, in the resistance vessels, halving the radius by muscular contraction will reduce flow to one-sixteenth of what it was before for the same pressure gradient.

In open circulations, the concept of total peripheral resistance cannot apply. Certainly, the pump imparts propulsive energy to the blood which is dissipated, due to viscous losses, as the blood courses through the hemocoel. But a pressure difference between the outflow and inflow vessels of the heart can, at best, indicate only the resistance of the major shunts in the circulation. A shunt is a short circuit between the outflow and inflow vessels. In the simplest possible case, when the pump sits in the hemocoel and there are no blood vessels, the heart activity only stirs the blood, and pressure differences across the heart are mostly a reflection of its filling and emptying mechanisms.

Physiology of Open and Closed Systems

In open blood systems, there is no separation between extracellular fluid and blood, so the total volume of hemolymph in these animals is large (up to 40% of the body weight). In closed circulations, blood is separated from fluid around the cells, and blood volume is much smaller, about 5–10% of the body weight. In both open and closed systems, blood is conveyed directly to the organs, but only in closed systems can its distribution be regulated with any precision. The best that can be done to facilitate the normal functioning of open circulations is to regulate hemolymph flow to a particular region by opening or closing valves of the junction of the major arteries and the heart.

On the outflow side of the pump (arterial side), closed vascular systems are effectively overfilled with blood, and the elastic blood vessel walls bear down on their contained volume and maintain a high pressure, even when the pump is in the filling phase (diastole). The arterial system is "topped up" again with each ejection of the pump (systole). Obviously, blood pressure can be maintained only if rapid escape of blood from the arteries is prevented by having a high resistance to flow in the periphery of the circulation. As a consequence, almost continuous blood flow is provided to the tissues by the elastic recoil of the stretched arterial walls during diastole. In open systems, peripheral flow resistance is low, as are the pressures generated in these systems. Furthermore, pressures in the outflow vessels of the pump will be highly pulsatile, reaching a peak in systole (the pump-ejection phase) and perhaps falling to zero in diastole (the pump-filling phase). Likewise, flow will be extremely pulsatile, often stopping between heartbeats.

In both open and closed circulatory systems, the volume of blood pumped by the heart must be the same volume as returns to the heart in any given time period. However, only in closed circulations does this have important consequences with regard to the rate at which blood flows through the vessels in the various regions of the vascular system. The velocity of blood flow at any part of a closed system depends on the cross-sectional area of the vessels in that part. Since the vessels that arise from or join to the heart must necessarily be about the same size, flow velocity in the veins is almost as rapid as in the arteries. Furthermore, since the cross-sectional area of the vessels within all the tissues is many times greater than vessels leaving the heart, the flow in the tissue vessels is very slow (usually less than $1\ \mathrm{mm} \cdot \mathrm{s}^{-1}$), allowing plenty of time for exchange across cell walls.

Components of Circulatory Systems

The two principal components of all circulatory systems are hearts and blood vessels.

Hearts. The circulatory pumps are the hearts, all of which operate by causing a wave of muscular contraction followed by a wave of relaxation (peristaltic wave) to travel over the walls of a tube. When the muscle contracts, the volume is reduced and fluid contents are expelled.

Tubular heart. If the heart persists in adult animals as a tube, such as the dorsal vessel of annelids or the dorsal heart of insects (**Fig. 2*b***), it is called a tubular heart. The peristaltic wave passes along the tube in an anterior direction, pushing the blood before it in the same way the air in a balloon is squeezed down to one end by pulling the balloon through a cupped hand. Therfore, valves are unnecessary to ensure unidirectional flow of blood. In earthworms, the peristaltic waves travel up the dorsal vessel at

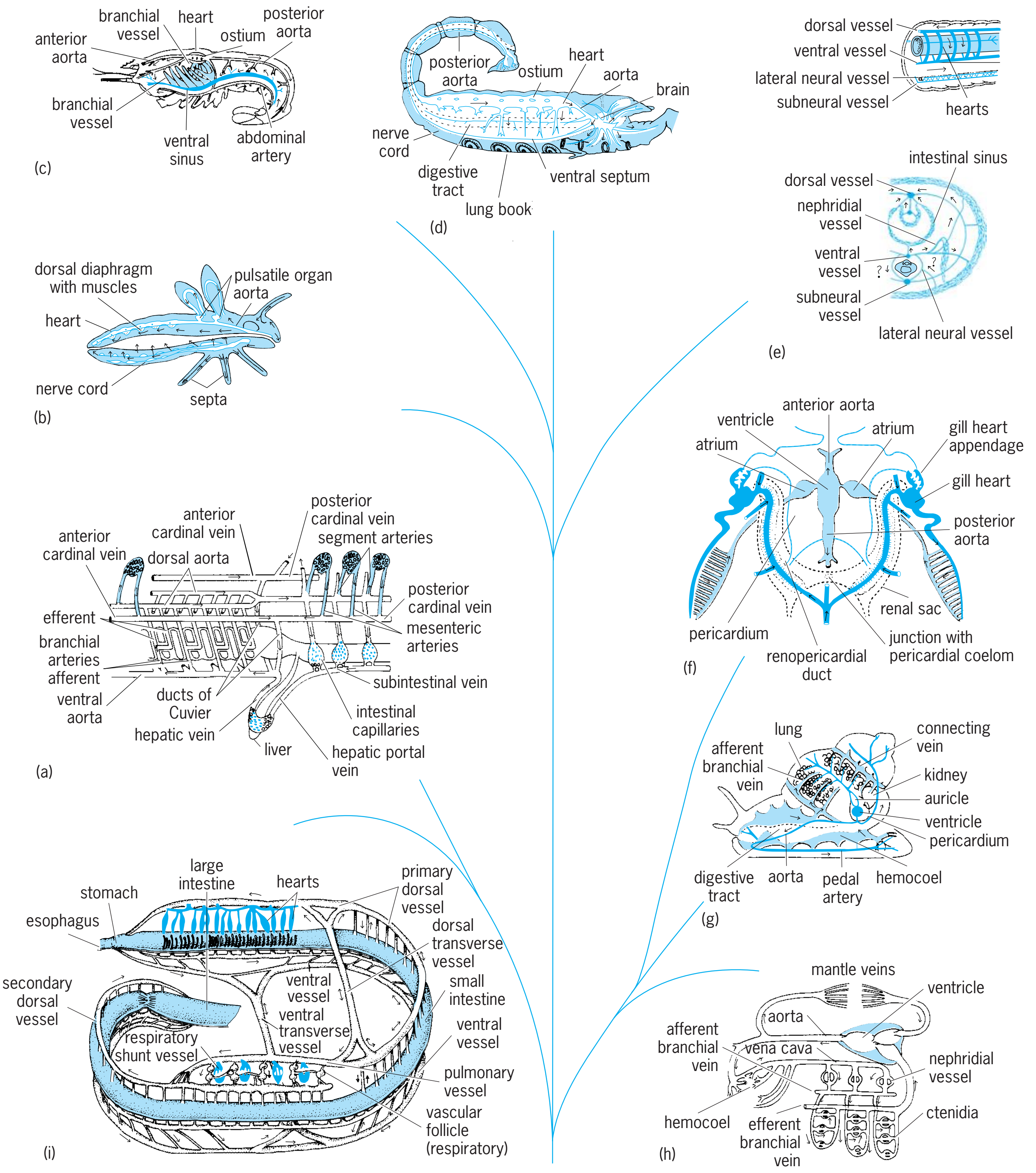


Fig. 2. Representative invertebrate and ancestral vertebrate circulatory systems on a schematic evolutionary tree. In all diagrams the arrows indicate the direction of blood flow. (*a*) Ancestral vertebrate, represented by *Amphioxus*. (*b*) Insect: a main dorsal vessel carries blood from the heart. (*c*) Crustacean: circulation in the lobster. (*d*) Arachnid, represented by the scorpion *Bathus*. (*e*) Annelid: cross section and longitudinal section. (*f*) Cephalopod mollusk, represented by the closed circulation in the octopus. (*g*) Gastropod mollusk: an open circulation represented by the snail *Helix*. (*h*) Bivalve mollusk: an open circulation represented by the fresh-water mussel *Anodonta*. (*i*) Echinoderm represented by the sea cucumber, *Stichopus*. (*Part a after A. J. Waterman et al., Chordate Structure and Function, MacMillan, 1971; b, c, e after K. Schmidt-Nielsen, Animal Physiology, 2d ed., Cambridge University Press, 1979; d, g, h after W. F. Hamilton and P. Dow, eds., Handbook of Physiology, Sec. 2, Circulation, vol. 3, American Physiological Society, 1965; f after E. Florey, An Introduction to General and Comparative Animal Physiology, W. B. Saunders, 1966; i after C. F. Herreid et al., Blood vascular system of the sea cucumber, Stichopus moebi, J. Morphol., 150:423, 1976*)

rates of 2–4 cm · s^{-1} about 10 times each minute. Vessels in the gills of hagfishes and octopods also contract rhythmically and propel the blood.

Multiple and chambered hearts. In the majority of animals, the zone of propulsive activity is restricted to a localized region. Some animals have many hearts: earthworms have five pairs of lateral hearts connecting the dorsal and ventral vessels (Fig. 2*e*); octopods and squids have hearts which boost blood flow through the gas exchanger (gills) in addition to a main or central heart (Fig. 2*f*); sea cucumbers may have over 150 hearts between dorsal and ventral vessels (Fig. 2*i*). However, many animals have only one heart, and in order to pump a volume equivalent to that pumped by a long contractile vessel, the lumen is greatly enlarged and usually divided into a number of chambers (chambered heart). To ensure undirectional flow of blood, chambered hearts require one-way valves. Valves are flaps of tissue situated around the edges of orifices between heart chambers or in vessels.

Contractile chambers. The more powerful the heart muscle becomes, the faster the blood can be driven into the outflow vessels, but filling the heart then requires a greater force. In vertebrates, there is often enough energy in the fast-flowing venous blood to do this, but other chambers may be necessary to fill the main propulsive chamber (or ventricle) in stages. These chambers are auricles and must have sufficiently thin walls to be expanded by the energy of the inflowing blood, yet must be powerful enough to fill the ventricle when they contract.

Most animals with chambered hearts have a single auricle, but in mollusks there is one for each pair of gills, so there may be from one to four (Fig. 2*f* and *h*). Fishes have a single auricle, but in amphibians the auricle is divided into two atria. In birds and mammals, the ventricle is divided, giving two separate circulations: one to the body and the other to the lungs. Fishes and amphibians have an extra contractile chamber, the sinus venosus, which fills the auricle when it contracts. Elasmobranchs and amphibians also have an extra contractile chamber on the ventricular outflow pathway, the conus arteriosus. Its role has not been established, but it could be in actively closing the outflow valves of the heart.

All vertebrate hearts, and many in invertebrates (such as mollusks and arthropods; Fig. 2*f* and *g*), are enclosed in a small portion of the coelom called the pericardial cavity. This cavity is fluid-filled and serves to prevent the heart from being buffeted by other body organs, but it can also aid in returning blood to the heart. If the pericardial wall is rigid, as in elasmobranchs and most mollusks and crustaceans, one chamber of the heart cannot contract unless another is expanding. If the ventricle starts to contract, the reduction in volume will tend to increase the volume of the pericardial cavity, and since it has rigid walls, the pressure inside it will be reduced. This suction pressure is transmitted through the thin auricular wall and draws blood in from outside the pericardium. This mechanism ensures successful filling of the heart even in open blood systems.

In tubular hearts, blood will tend to be sucked into the lumen when the muscle relaxes behind the wave of contraction. It has even been suggested that the major function of the dorsal contractile vessel in annelids is to prime the lateral hearts with blood. In insects, the tubular heart is suspended by alary or aliform muscles attached to the external skeleton, and when these contract the expansion of the lumen sucks blood through valved openings (ostia) into the heart (Fig. 2*b*).

Electrophysiology. The wave of contraction which passes across the heart is driven by an electrical impulse (action potential) which arises spontaneously, either in modified heart muscle cells, or in special nerve cells located on or near the heart. These cells form the pacemaker, which sets the heart rhythm. When nerve cells initiate the heartbeat, the pacemaker is called neurogenic. A pacemaker of muscle cells is called myogenic. Myogenic pacemakers are found in vertebrates, mollusks, echinoderms, and perhaps in some annelids. Neurogenic pacemakers are found in most arthropods. Many hearts have more than one pacemaker. In tunicates, the tubular heart pumps into the open circulation in two directions. After several hundred beats the rhythm slows and stops, and the direction of the wave of contraction reverses when the heart starts up again. Consequently, the tunicate heart must have at least two pacemakers. In frogs, heart contraction can be driven by electrical impulses arising in the sinus venosus, atria, or ventricle. Usually the sinus pacemaker beats fastest and drives all the others.

In birds and mammals, the heart is large and generates high pressures. To prevent the pressure set up by the contraction of one part of the heart from stretching, and perhaps rupturing, the relaxed part, all of the ventricular muscle must be activated simultaneously. This is achieved by conveying the electrical impulse to all parts of the ventricle through specialized conduction pathways composed of modified muscle cells. *See* CARDIAC ELECTROPHYSIOLOGY.

Chemical and mechanical excitation. Many hearts are innervated by nerves which regulate the beat. When these nerves are active, they liberate chemicals such as noradrenalin or acetylcholine from their terminals, and these neurotransmitters affect the cardiac muscles directly. In general, the pacemaker of myogenic hearts is inhibited by acetylcholine; excitation is produced by noradrenaline (vertebrates) or serotonin (mollusks). In neurogenic hearts, gamma aminobutyric acid (GABA) is inhibitory, whereas glutamic acid is excitatory. Neurotransmitters affect not only the rate but also the strength of cardiac contraction. For example, noradrenaline increases the amount of blood pumped by a single ventricle (stroke volume) while acetylcholine decreases stroke volume. *See* ACETYLCHOLINE; ENDOCRINE MECHANISMS.

Mechanical factors may also affect rate and strength of heart contraction. In earthworms, mollusks, and some fishes, stretching the pacemaker region of the myocardium increases its rhythm. Moreover, in all vertebrates, and probably in all mollusks as well, the length of the muscle fibers in the heart at the end of diastole is directly proportional to the strength of the next muscle contraction (Starling's law of the heart).

Many animals, both vertebrate and invertebrate, take advantage of muscular activity in the body, such as during exercise, as an aid to circulation of the blood. In vertebrates, valved thin-walled veins run through blocks of skeletal muscle and are compressed when the muscle contracts, squeezing blood toward the heart (muscle pump). In other animals, the blood functions directly in locomotion. Spiders have no leg extensor muscles, so leg extension is brought about by forcing hemolymph into the leg at high pressure (50 kilopascals), which is generated by the contraction of lateral cephalothoracic muscles depressing the carapace. Backflow into the abdominal heart (which can generate pressures of only 13 kPa) is prevented by valves on the outflow vessels at the junction of the cephalothorax and abdomen. But there are no valves in the veins, and blood returns rapidly to the abdomen.

Caudal heart. Hagfishes have a unique caudal heart. A longitudinal rod of cartilage separates two chambers, and when body muscles on one side contract, the rod is bent to that side. The bend in the rod causes the volume of the chamber on the actively contracting side to expand so that it fills with blood, while the volume of the chamber on the other side is decreased, expelling blood. Valves at the inflow and outflow ends of the chambers ensure unidirectional flow of blood. *See* HEART (INVERTEBRATE); HEART (VERTEBRATE).

Blood vessels. Blood ejected from the heart is conveyed by vessels which are usually called arteries or aortas. In some animals, structural differences between outflow and inflow vessels are not obvious, and they are usually referred to simply as blood vessels. In closed systems, the arteries (outflow vessels) divide and subdivide so that ultimately tubes only a few micrometers thick (capillaries) run between the cells of each organ.

Capillaries. In vertebrates, each capillary consists of a single layer of endothelial cells surrounded by a basement membrane. In some echinoderms with well-developed circulatory systems (such as holothurians; Fig. 2*i*) capillary structure is similar to that in vertebrates, while in cephalopods (such as the octopus) capillaries are extremely small (1 micrometer in diameter) but are usually more than one cell thick. The total number of capillaries in a vertebrate is large, and in humans it is enormous: over 50 billion in the whole body. Therefore, although each capillary is small the total cross-sectional area of all capillaries is perhaps a thousand times greater than that of the main arterial vessels. Consequently, blood flows very slowly in the capillaries, about one-thousandth of the velocity in the aorta, allowing lots of time for exchange of materials with the cells.

In open circulations, after a greater or lesser number of branchings blood vessels ultimately open to the spaces between the cells. Even so, networks of fine blood pathways may occur, especially in gas-exchange organs, nephridia, and masses of nervous tissue (such as brains or ganglia). In animals with closed circulatory systems, a plexus of fine capillaries brings blood close to the external environment in skin (annelids, frogs), respiratory trees (holothurians), gills (fishes), and lungs. Similar close associations between blood and external media are seen in animals with open circulatory systems (Fig. 2*c* and *d*). For instance, gills of shrimp look similar to those of fish in all but the finest morphological details. Book lungs of spiders are unique structures in which blood is moved across rows of fine air tubes, stacked one on the other, in channels only a few micrometers in width. In insects, air is distributed directly to the body cells by way of the trachea, a system of tubes independent of the circulation. Fine blood channels are lacking in these animals. Nevertheless, the circulation in insects reduces the diffusion distances for metabolites, nutrients, and hormones. Furthermore, in large flying insects it plays an important role in controlling body temperature, particularly in the thoracic region where the large flight muscles are located.

Veins and portal systems. After traversing the capillaries, blood is collected into large vessels which return it to the heart. In cephalopods and vertebrates, these collecting vessels are called veins. In open circulations, channels returning blood to the heart exist, but the pattern of blood flow is less precise than in closed systems. In insects and arachnids, longitudinal membranes impose some direction on blood movement (Fig. 2*b* and *d*).

In many vertebrates, venous blood is transported to another organ (such as the liver or kidney) on its way back to the heart. In these organs the veins divide into a capillary network supplying blood to the tissues at low pressure. This is a portal blood supply, and there are a large number of these in vertebrates. The hepatic portal system occurs in all vertebrates and serves to transport materials from the intestine, where they are absorbed, to the liver, where they are stored (Fig. 2*a*). Another prominent portal system is the renal portal system. It occurs in all vertebrates except mammals, and transports blood from the caudal parts of the body to the kidneys. The function of the renal portal system is not known. *See* KIDNEY; LIVER.

Contraction. Many blood vessels have muscular coats, the muscle cells being rhythmically contractile (myogenic rhythm). Contraction of blood vessels is found in the dorsal and ventral vessels and some capillaries of annelids, in the gill vessels of cephalopods and cyclostomes, and also in the fine vessels leading to the capillary beds in higher vertebrates. In these small vertebrate vessels (called arterioles, with a diameter of 50–200 μm), the muscles are in a continual state of activity, modulating the radius of the vessel and therefore the blood flow. This activity can be altered by nerves, by blood-borne agents such as adrenaline, and also at the local level by changes in the level of tissue metabolites (a fall in oxygen tension in the body tissues causes the muscles to relax).

Aortic elasticity. The aortas (or arteries leaving the heart) are fairly elastic in nearly all animals. In closed circulations, the stroke volume is stored by the elastic distension of the arteries and is fed to the periphery between cardiac ejections. This elastic reservoir (or Windkessel effect) is exemplified by the arterial vessels of vertebrates. In humans, the whole arterial tree participates in producing a Windkessel effect. In contrast, fishes have a very short ventral aorta, and only a very elastic bulb (bulbus cordis) just outside the ventricle provides a pressure reservoir, which smooths blood flow through the gills. Many mollusks with open circulatory systems have a similar elastic expansion of the aortic wall just beyond the ventricle. *See* BLOOD VESSELS.

Evolution of Vertebrate Circulation

The evolution of an organ system which is not preserved in fossils can only be inferred from investigations of extant species. Thus, understanding must always be clouded by uncertainty. For example, a major pattern of increasing complexity, which emerges from comparative studies of circulatory systems, is related in vertebrates to life on land. More promising are investigations of the early stages of development of the heart and circulation. These show that all types of vertebrate circulations can be related to a common ancestral pattern (Fig. 2*a*). The ancestral pattern of circulation in vertebrates is for a ventral heart to pump blood anteriorly in a ventral vessel, connecting to the dorsal vessel through the gas exchanger (gills; Fig. 1*e*). The gills are situated on the high-pressure side of the circulation, and blood flows posteriorly in the dorsal vessel.

Annelid worms exhibit a superficial resemblance to the circulation in the ancestral vertebrate in the pattern of dorsal and ventral vessels (Fig. 1*c*), except that the heart is dorsal, flow in the dorsal vessels is anteriorly directed, and flow in the ventral vessel is posteriorly directed. More important, in most invertebrates the gas exchanger, when it exists as a discrete entity, is on the low-pressure side of the circulation. This arrangement limits metabolic scope, a problem which is solved in large, active invertebrates (such as cephalopods) by the development of high-pressure, prebranchial hearts.

Apparently, the chordate stock arose from ancestors in common with primitive echinoderms, a group with a very poorly developed circulation. Hence, the apparent similarities between the circulations in vertebrates and invertebrates are superficial and presumably arose as an evolutionary response to similar physiological demands. This is an example of convergent evolution due to common selection pressures, the circulatory systems in vertebrate and invertebrate groups being analogous rather than homologous. *See* CARDIOVASCULAR SYSTEM. David R. Jones

Circulation disorders

Circulation disorders include both localized disturbances of circulation and diseases of the circulatory system.

Circulatory system. The function of the circulatory system is to transport and distribute substances either used or produced by cells or both. Excluded are those materials that are discharged directly from sweat glands, digestive glands, and renal tubule cells. Included, however, are nutritive and metabolic substances, hormones, waste products, water, and heat.

The circulating fluids are distributed between the heart, blood vessels, capillaries, intercellular spaces and lymphatics and within the cells. The blood and body fluids are in a constant state of dynamic equilibrium (see **illus.**). Blood flows through the vessels to the capillaries where some fluid passes through the endothelium to the intercellular spaces to bathe the cells. Fluid with contained electrolytes and metabolic substances can then pass into and out of the cells. At the distal end of the capillaries most of this fluid passes back into the vascular compartment. A portion of this fluid is returned to the circulation by way of the lymphatics. *See* CARDIOVASCULAR SYSTEM; LYMPHATIC SYSTEM.

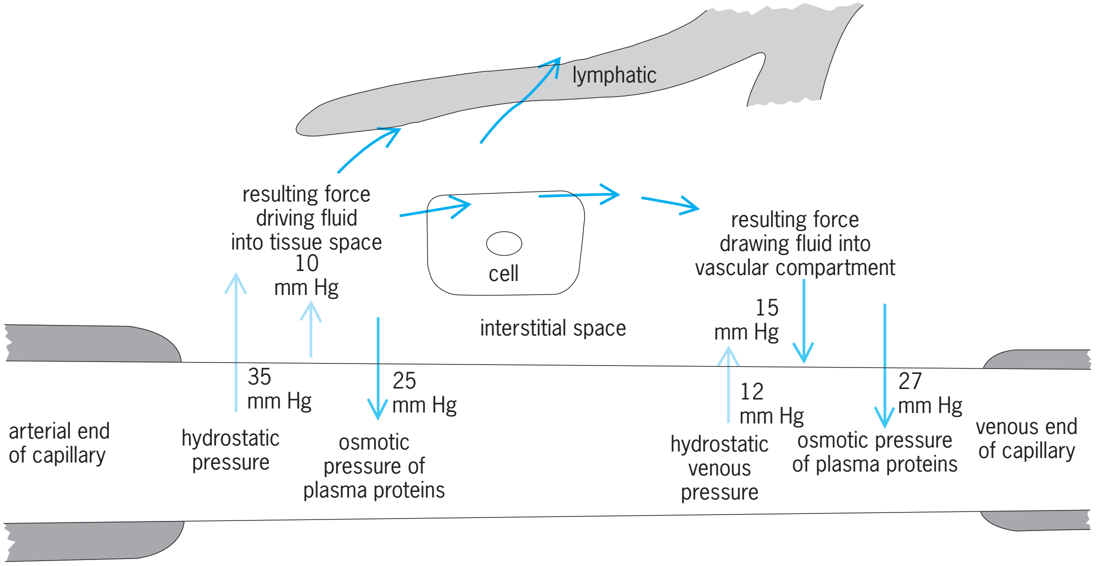
Vascular disturbances. Disturbances in this pattern can either result in or from disease conditions. An example is edema, which is an abnormal accumulation of fluid in the cells, tissue spaces, or cavities of the body. There are three main factors in the formation of generalized edema and a fourth which plays a role in the formation of local edema. They are the permeability of the capillary wall, the colloid osmotic pressure of the plasma proteins, and the hydrostatic pressure in the capillaries. The fourth factor, which is of importance in local edema formation, is lymphatic obstruction.

An example of edema formation secondary to a decrease in the colloid osmotic pressure of the plasma proteins is nephrotic edema. In chronic Bright's disease there is a marked loss of urine albumin and the plasma protein level drops as a result.

Cardiac edema follows the generalized venous congestion of cardiac failure and is an example of edema formation resulting from increased hydrostatic pressure in the capillaries.

Increased permeability of the capillary walls plays an important role in the formation of inflammatory edema, the edema of severe infections, metabolic intoxications, asphyxia, anaphylactic reactions, secondary shock, and acute nephritis. *See* EDEMA; HYPERTENSION.

Deficiencies. A deficiency of circulating blood volume, both cellular elements and fluid, is called oligemia. This may be the result of an acute blood loss or it may be of a chronic nature, such as an anemia combined with dehydration. Anemia, or oligochromemia, is a deficiency of circulating red cell volume or, more specifically, hemoglobin content. This is the oxygen-carrying component of the circulating red blood cell. The normal value for the adult human is 14–16 g/100 ml of blood. The norm for most domestic animals is 10–12 g/100 ml of blood, except for the dog with a norm of 13 g. *See* ANEMIA; HEMOGLOBIN.



arterial end of capillary		venous end of capillary	
hydrostatic pressure (force tending to drive fluid out)	= 35 mm Hg	hydrostatic pressure	= 12 mm Hg
osmotic pressure of proteins (force tending to draw fluid into vascular compartment)	= 25 mm Hg	osmotic pressure of proteins	= 27 mm Hg
resulting force pushing fluid out of vascular compartment into interstitial space	= 10 mm Hg	resulting force drawing fluid back into vascular compartment	= 15 mm Hg

Fluid movements and resulting pressures at the capillary level of circulating blood.

Anemia can result from a variety of causes. It may be secondary to a chronic nutritional deficiency with an inadequate intake of iron. Iron is a necessary substance used by the blood-forming tissue to make hemoglobin. Anemia can also result from a defect in the blood-forming tissue (the bone marrow) so that it is unable to use the materials available to make red blood cells. It can also be the result of a displacement of blood-forming tissue, as from a tumor. It may also follow periods of acute blood loss. These are just a few examples of the causes of anemia. *See* BLOOD; HEMATOPOIESIS.

Pancytopenia, or oligocythemia, is a deficiency of all circulating blood cellular elements. This is usually the result of a deficiency of the blood-forming tissue, the bone marrow.

Ischemia. The decrease of blood flow to an organ or tissue is known as ischemia. This can be sudden as when a vessel is ligated, when a thrombus or blood clot forms, or when an embolus comes to lodge in the vessel. A gradual occlusion can follow arteriosclerotic changes in the vessel wall with resulting diminution of the lumen and blood-carrying capacity of the vessel. The effect of a sudden occlusion depends to a great extent on the collateral circulation to the organ or tissue involved. If an adequate collateral circulation comes to be established, the tissue survives; it not, it dies and an infarct results.

An infarct is a region of necrosis resulting from a vascular obstruction. The usual cause is occlusion of an artery or vein by a thrombus or embolus. If the vessel is the sole source of blood supply, the tissue dies. *See* ARTERIOSCLEROSIS; EMBOLISM; INFARCTION; THROMBOSIS.

Plethora. An excess of blood is referred to as plethora. This increase may be the result of an increase in the size or the number of red blood cells. The increase in red cell volume may be a polycythemia vera, or true polycythemia, which is a primary increase in the number of red blood cells with no regard to the needs of the organism. Polycythemia, or erythrocytosis, is usually a secondary increase in red cells following conditions of chronic hypoxia, such as congenital heart disease, emphysema, or residence at high altitudes. Serous plethora is an increase in the watery part of the blood.

Hyperemia. Hyperemia, or congestion, refers to an excess of blood within an organ or tissue. This condition may be localized or generalized. Active hyperemia is congestion which is caused by an active dilatation of arterioles and capillaries. This occurs under certain physiological conditions, such as in the muscle when there is an increased need for blood during exercise. It also occurs in pathological states such as inflammation. *See* INFLAMMATION.

Passive hyperemia is a condition which results in an accumulation of blood in the venous system. It may be generalized or localized and can result from any obstruction or hindrance to the outflow of blood from the venous circuit. The generalized form can result from valvular diseases of the heart, such as mitral or aortic stenosis or insufficiency, or myocardial failure from any cause. Tricuspid valvular disease is slightly more frequent in animals. *See* HEART DISORDERS.

Diseases of the lungs such as emphysema, fibrosis, or pulmonary hypertension of any origin can result in right ventricular failure and generalized venous congestion. The late stages of these conditions can result in cor pulmonale, which is a hypertrophy and dilatation of the right ventricle secondary to an obstruction to the pulmonary blood flow associated with a generalized venous congestion.

Localized venous congestion results when a main vein from a region is occluded either by a thrombus or some extrinsic pressure such as a tumor or enlarged lymph nodes.

In congestion the organ is usually wet and bloody. Microscopically there is an enlargement of the veins and capillaries associated with edema formation.

Hemorrhage. The escape of blood from within the vascular system is hemorrhage. This process can be the result of trauma to, or disease of, the vessel wall. Diapedesis is the passage of the corpuscular elements of the blood through an intact vessel wall.

The trauma which results in hemorrhage may be direct, such as a cut from a knife, or it may be indirect, such as a blow to the head, resulting in a tearing of cerebral or meningeal vessels.

The causes of hemorrhage other than trauma can be divided into three main groups. In the first group are those conditions in which there is a disease process affecting the vessel wall, such as arteriosclerosis or aneurysm formation. An infarct, or tissue death from any case, can result in hemorrhage.

In the second group are conditions in which there is an acute process affecting the vessel wall, as in septicemia, poisoning by heavy metals, or even anoxia.

The third and last group consists of those conditions in which there is a defect in the blood itself, which results in hemorrhage. Under this heading are included the blood-clotting disorders, thrombocytopenia, leukemia, and pernicious anemia.

Apoplexy, or stroke, is an acute vascular lesion of the brain. This can be the result of hemorrhage of, thrombosis in, or embolism to a cerebral vessel. *See* HEMORRHAGE.

Thrombosis. Thrombosis is the formation of a thrombus, which is a solid body formed during life and composed of the elements of the blood: platelets, fibrin, red cells, and leukocytes.

Thrombosis is essentially platelet deposition and may occur on a vessel wall anywhere that the endothelium is damaged. However, because the platelets release thromboplastinogen, which activates the clotting mechanism, thrombosis and blood coagulation may occur together. Platelets normally exhibit a tendency to stick together. This tendency is increased if the number of platelets is increased, as in thrombocytosis, if the velocity of the stream is decreased below a certain speed, or if the endothelium is roughened. These are the same factors which promote thrombus formation.

Thrombi may form in the veins, arteries, capillaries, or within the heart. The most common sites for the formation of thrombi are in the veins.

The venous thromboses can be divided into two groups: venous thrombosis (phlebothrombosis) and thrombophlebitis. Phlebothrombosis is the more important and is often a sequela of generalized circulatory failure, trauma, or prolonged bed rest from any cause.

Thrombophlebitis is the formation of a thrombus secondary to inflammation in the wall of the vein. Arterial thrombosis is usually the result of local causes, for example, arteriosclerosis of the vessel wall.

Embolism. The sudden blocking of an artery or vein by a clot or other substance which has been brought to its place by the blood current is an embolism. The material carried in the circulation in this process is an embolus. Emboli may be composed of thrombi, fat, air, tumor cells, masses of bacteria or parasites, bone marrow, amniotic fluid, or atheromatous material from the vessel wall.

Emboli originating in the right side of the heart or the great venous system of the body come to lodge in the lungs, those from the portal system in the liver, and those from the pulmonary veins or left side of the heart in some segment of the peripheral arterial tree.

One of the dire consequences of an embolus is infarction or death of the tissue supplied by the occluded vessel. This occurs if the collateral circulation is inadequate to supply the tissue with blood. *See* DEATH; VASCULAR DISORDERS.

Romeo A. Vidone

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Cirrhosis

Severe scarring of the liver due to a marked increase in fibrous connective tissue, resulting in a firm, nodular, distorted liver. Cirrhosis is the eighth most common cause of death in the United States and the fourth leading cause of death among Americans between the ages of 30 and 60.

Etiology. Cirrhosis is the end product of any one of a number of different liver diseases. Regardless of the cause, the potential consequences of cirrhosis are the same. Whereas a healthy liver typically repairs and regenerates itself when injured, once cirrhosis has occurred, the damage may never be undone. Not all liver diseases cause cirrhosis—only those that cause chronic, ongoing damage to the liver. Alcoholic liver disease and chronic hepatitis C are the two most common causes of cirrhosis in the United States. However, there are numerous causes of cirrhosis as listed below.

Viral hepatitis—hepatitis B, C, and D
Autoimmune hepatitis (a disease in which the body's immune system attacks liver cells)

Primary biliary cirrhosis (a liver disease that slowly destroys the bile ducts in the liver)
Nonalcoholic fatty liver disease [a range of liver diseases that commonly affect people who have type 2 diabetes (adult onset diabetes), with hypertriglyceridemia (high level of fats, or triglycerides, in the blood), and who are obese but drink little or no alcohol)]
Excessive alcohol consumption
Hemochromatosis (excessive deposition of iron in the body that may be genetic or acquired)
Excessive intake of vitamins, such as vitamin A
Certain herbal remedies, such as comfrey
Certain medications, such as methotrexate, isoniazid, methyldopa (hypertension)
Primary sclerosing cholangitis (a liver disease characterized by inflammation, narrowing, and scarring of the bile ducts inside and outside the liver)
Vascular anomalies (for example, Budd-Chiari syndrome)
Congestive heart failure
Wilson's disease (a genetic disorder of copper overload)

See ALCOHOLISM; HEPATITIS; LIVER DISORDERS.

Symptoms and complications. The symptoms of cirrhosis are essentially uniform regardless of its cause. Some people with cirrhosis feel perfectly normal or have nonspecific symptoms, such as fatigue, decreased appetite, and loss of libido. These individuals are said to have compensated cirrhosis. People with compensated cirrhosis often live a normal life span with relatively few health-related consequences. However, they remain at risk for developing many life-threatening complications such as portal hypertension, ascites, encephalopathy, jaundice, hepatorenal syndrome, and hepatocellular carcinoma. When one of these complications has occurred, individuals are said to have decompensated cirrhosis.

Portal hypertension. Due to extensive scarring of the liver that occurs in cirrhosis, the vessels associated with blood flow to and from the liver may become obstructed. This, in combination with increased blood flow to the liver, leads to elevated pressure in the portal circulation, a condition known as portal hypertension. The liver attempts to adapt to this situation by creating alternative routes that bypass this obstruction. These alternative passageways for blood flow are known as collateral shunts or simply "collaterals." These shunts enable blood to be rerouted to and circulated within the rest of the body. Unfortunately, the formation of these shunts has its drawbacks, as they can give rise to serious and even life-threatening complications. When any one of the complications associated with portal hypertension (for example, ascites, esophageal varices, and/or encephalopathy) has occurred, the body can no longer "compensate" for the extensive scarring that has occurred in the liver, and the patient has decompensated cirrhosis. People with any form of portal hypertension should be evaluated for liver transplantation.

Portal hypertension can result in congestion of the spleen, leading to a markedly enlarged spleen (splenomegaly).

Esophageal varices portal hypertension may result in the formation of new collateral venous channels that bypass the liver. The most important collateral channels are those in the region of the lower esophagus, called esophageal varices. When varices become dilated, they can erode through the lining of the esophagus, resulting in life-threatening bleeding.

Ascites is the most common complication of portal hypertension. It is characterized by massive accumulation of fluid in the peritoneal cavity (the space between the abdominal organs and the skin). A fever in a person with ascites may indicate that this fluid is infected and constitutes a serious condition known as spontaneous bacterial peritonitis.

Encephalopathy. Encephalopathy is a disorder of brain function, typically leading to a coma that can occur in people with cirrhosis. It is mainly associated with poor coordination, fetor hepaticus (foul-smelling breath), and asterixis (uncontrollable flapping of the hands). The exact cause of encephalopathy is unknown; most researchers believe that it is mainly associated with the ailing liver's inability to clear toxins, primarily ammonia, from the body.

Jaundice. In addition to obstruction of blood flow, the bile ducts within the liver may become distorted and partially obstructed. This results in jaundice, a yellow discoloration of the skin and eyes. *See* JAUNDICE.

Hepatorenal syndrome. Some individuals with cirrhosis develop hepatorenal syndrome, a progressive deterioration of kidney function associated with lack of urination. This may lead to renal failure, and kidney dialysis may become necessary. Hepatorenal syndrome can result in death unless a liver transplantation is performed. *See* KIDNEY DISORDERS.

Hepatocellular carcinoma. Anyone who has cirrhosis, whether compensated or decompensated, is at risk for developing liver cancer—also known as hepatocellular carcinoma or hepatoma. Risk varies with the cause of liver disease. *See* CANCER (MEDICINE).

Morphological changes. In general, cirrhosis results in similar physical damage to the liver, regardless of which type of liver disease caused it. The liver may be slightly enlarged, but as the disease progresses it usually becomes smaller due to progressive loss of liver cells. In the final stage the liver may weigh as little as 14–18 oz (400–500 g; normal is 50–60 oz or 1400–1700 g). Microscopic examination reveals that liver cells of varying size and shape are surrounded by dense fibrous connective tissue that contains inflammatory cells and distorted bile ducts. Fibrosis, or scar tissue, is the liver's effort to keep contained the damage done by alcohol or hepatitis C virus, for example. But scar tissue can block the blood flow through the liver, resulting in an inability to perform its normal duties. *See* LIVER.

Diagnosis. A liver biopsy, the removal of a tiny piece of liver tissue using a special needle, continues to be the “the gold standard” to determine the presence or absence of cirrhosis. However, signs of cirrhosis such as muscle wasting, a hard and bumpy liver, and splenomegaly may be detected on a physical exam. Some laboratory test results (such as a low albumin level, an abnormally low cholesterol level, an elevated or prolonged prothrombin time, a decreased platelet count, and/or an elevated alpha-fetoprotein level) may also suggest cirrhosis. Imaging studies such as a sonogram or computerized tomography (CT) scan of the liver may suggest, but cannot confirm, cirrhosis. Once cirrhosis has occurred, a physician will not be able to definitively identify which liver disorder caused it, even from a liver biopsy specimen.

Treatment. Recent studies have shown that with removal of the cause of the underlying liver disease (for example, alcohol or the hepatitis C virus), and with effective treatment (such as interferon and ribavirin for hepatitis C virus), cirrhosis can be reversed—at least in its very early stages, when scarring is minimal. The point at which cirrhosis becomes irreversible is not clear. However, there is a broad consensus among liver disease experts that once decompensated cirrhosis has occurred, it can never be reversed. Much research is being conducted on drugs (known as antifibrotic agents) and drug combinations that can potentially reverse cirrhosis. Examples of promising antifibrotic agents include interferon, pentoxifylline, prostaglandins, antioxidants, pioglitazone, and angiogenesis inhibitors. Currently, therapy of cirrhosis is aimed primarily at preventing or reducing complications. However, while the complications of decompensated cirrhosis can be controlled, the liver is beyond the point of any possible repair, and a liver transplant must be considered. *See* CARDIOVASCULAR SYSTEM; LIVER DISORDERS.

Melissa Palmer

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Cirripedia

An order of the crustacean class Maxillopoda. The cirripedes, particularly the organisms known as barnacles, are the most well-known and easily recognized members of the subclass Thecostraca. The thecostracans are characterized by two features. First, all exhibit a distinctive and unique larva, called the cypris (**Fig. 1***b*). Second, when they have a carapace, it generally envelops the entire body, which typically is composed of a five-segment head, a seven-segment thorax, and a short or rudimentary limbless abdomen. In addition to the cirripedes, the thecostracans include the enigmatic Facetotecta, or “y-larvae,” as well as Ascothoracica, a group of parasites of echinoderms and anthozoan cnidarians. *See* ASCOTHORACICA; CRUSTACEA; MAXILLOPODA.

The Cirripedia sensu stricto are composed of three infraorders: Thoracica (the goose and acorn barnacles), Acrothoracica (the burrowing barnacles), and Rhizocephala (internal parasites of shrimp and crabs) [see **table**].

Thoracica and Acrothoracica

Generally, the two free-living cirripede infraorders bear long, setose, filtering thoracic limbs called cirri. In addition, cirripedes have nauplius larvae that bear peculiar structures called frontolateral horns (Fig. 1*a*), whose function is still not certain. As adults, the free-living cirripedes are permanently attached and commonly referred to as barnacles.

Morphology. The carapace forms a complete cover of the body, and it is usually strengthened by calcareous shell plates (**Fig. 2**). In principle, the head bears the usual five pairs of limbs. However, the antennules and antennae are seen only in the larvae (Fig. 1). The antennules form the points of attachment of the adult barnacle but persist only in adult goose barnacles as the peduncular stalk (Fig. 1*d*). The mouth appendages include the paired mandibles with palps, maxillules, and maxillae. The thorax bears up to six pairs of biramous appendages (cirri) composed of numerous segments, each with a considerable number of setae (Fig. 2*b*). A rostral vessel and/or sinus (Fig. 2*b*) serve as a heart that pumps blood through a virtually closed circulatory system. Naupliar and compound eyes occur only in the larvae (Fig. 1*b*).

Reproduction and development. Thoracican adults are typically hermaphrodites, whereas acrothoracicans have separate sexes. The female genital pore is on the first thoracic segment at the base of cirrus I,

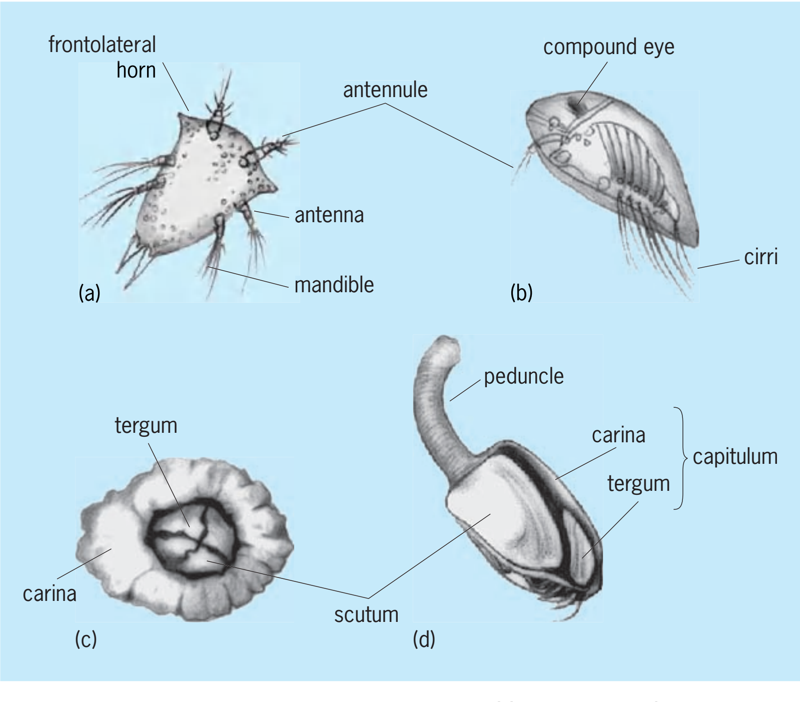

Fig. 1. Larval and adult stages of thoracican barnacles. (*a*) Nauplius larva (note diagnostic frontolateral horns). (*b*) Cypris larva. (*c*) *Balanus*, a typical acorn barnacle (top view). (*d*) *Lepas*, the goose barnacle (lateral view).

Characteristics and some genera of Cirripedia

Infraorder	Characteristics	Some genera
Thoracica	Permanently attached, stalked or sessile, independent or commensal barnacles; with filtering thoracic limbs as long setose cirri; typically with carapace developed as calcareous plates; hermaphroditic	*Lepas, Scalpellum, Conchoderma, Heteralepas, Balanus, Coronula, Verruca*
Acrothoracica	Burrowing barnacles living in shells, coral, or limestone; cirri modified or often reduced in number; carapace without calcareous plates; bisexual with dwarf males	*Trypetesa, Lithoglyptes, Kochlorine*
Rhizocephala	Internal parasites of decapod crustaceans; adult body is a formless ramifying mass among the host tissues; no gut; eggs and larvae produced in an external sac on host's body; bisexual with dwarf males	*Sacculina, Loxothylacus, Thompsonia*

while the male genital pore is on an elongated penis lying medially on the segment posterior to cirrus VI. Cross-fertilization of the hermaphrodites is normal. The extremely long penis is extended out of the shell to grope around for a receptive neighbor. The eggs are incubated in the shell cavity and hatch into free-swimming nauplius larvae (Fig. 1*a*). Thoracicans pass through six successive naupliar stages, whereas acrothoracicans have four. The final nauplius molts into an entirely different form with a bivalved carapace, the cypris larva (Fig. 1*b*), so named because it resembles the ostracode genus *Cypris*. The cypris has prominent antennules and well-developed, though short, cirri. The cypris seeks a suitable substrate or host and attaches by the antennules. Thereafter, an extremely strong cement is secreted from glands in the antennules, and the animal is permanently anchored.

The attached cyprid then undergoes metamorphosis, and a minute replica of the adult (only without calcified shell plates) is produced. By differential growth and elongation of the preoral region, the free body of the animal within the body cavity comes to lie parallel to the substrate with the ventral side uppermost. The thoracic appendages, or cirri, face away from the substrate and are immediately below the opening of the shell, which is uppermost (Fig. 2*b*). Through this aperture, the cirri are extended and unfolded into a fanlike array. The cirri sweep through the water in the manner of a cast net and withdrawn back into the shell with whatever has been netted. Edible particles are then removed from the cirri by the mouthparts and passed to the mouth to be swallowed.

Stalked thoracicans. In the stalked thoracican, or goose barnacles, the antennular region elongates and forms a stalk, or peduncle. At the distal end is the capitulum with the rest of the animal's body inside. In *Lepas* (Fig. 1*d*) the penduncle may be up to 1 ft (30 cm) long and the capitulum only 2–3 in. (5–8 cm). The capitulum in *Lepas* is strengthened by five calcareous plates: thecarina, or keel, extends

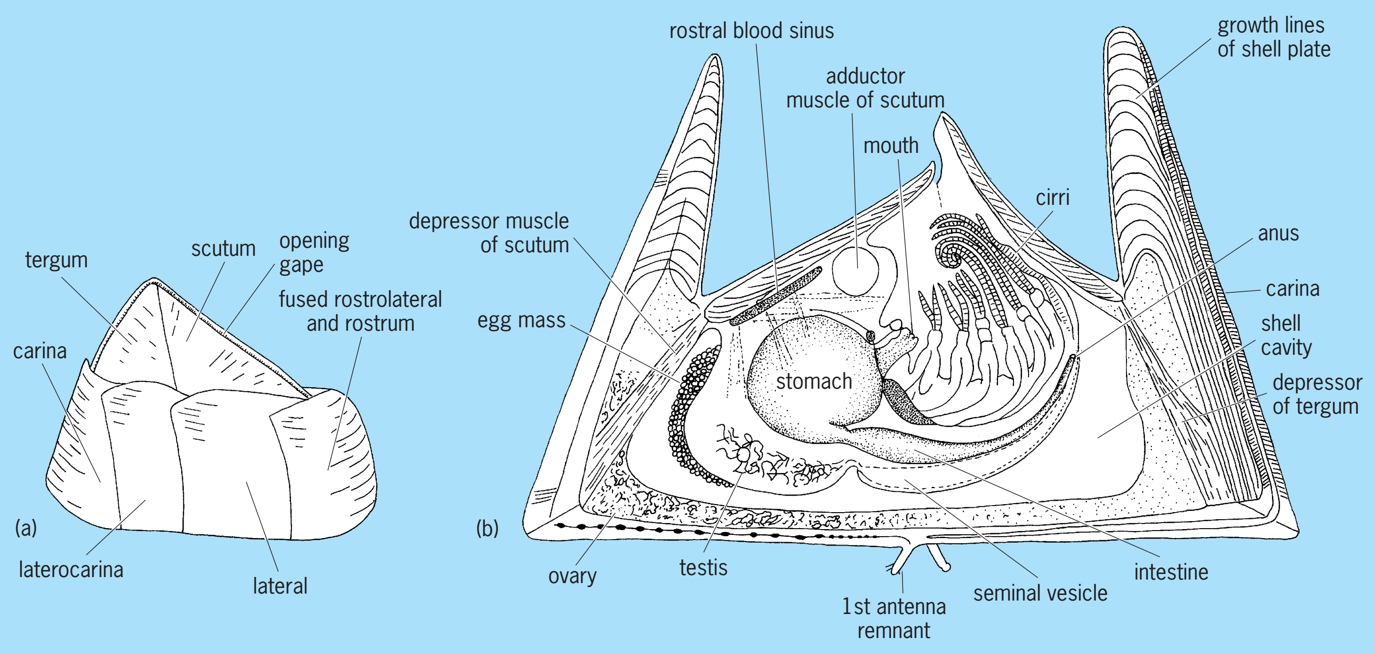

Fig. 2. Diagrams of the anatomy of *Balanus*, a sessile acorn barnacle. (Note the lack of a stalk.) (*a*) Lateral view. (*b*) Vertical cross section. (*After E. R. Ruppert, R. S. Fox, and R. D. Barnes, Invertebrate Zoology: A Functional Evolutionary Approach, 7th ed., Brooks Cole, 2003*)

down the posterior or morphologically dorsal side of the capitulum; and paired scuta and terga lie on either side of the capitulum. Calcification occurs from centers all over the capitulum and peduncle, giving rise to small oval or triangular scales. In many species of *Scalpellum* (sensu lato), in which these peduncular scales are present, there is a ring of larger scales around the base of the capitulum.

The number of capitular plates can be variable both within and between species. However, forms such as the fouling barnacle *Conchoderma* and the commensal of sea urchins *Heteralepas* are protected by the spines of its host and have both lost most of the capitular plates. *Lepas* and *Conchoderma* are found on floating debris in the ocean. *Lepas fascicularis* actually secretes a horny float that supports a cluster of individuals. The more heavily armored species of scalpellids are found on the bottom of the ocean and extend into very deep waters.

The peduculate goose barnacles are not a single monophyletic group. Rather, they form a transition series of distinct lineages leading to the sessile acorn barnacles.

Sessile thoracicans. Most of the sessile thoracicans, or acorn barnacles, live in shallow waters or between the tide marks, where they can be present in immense numbers. They lack any stalk and can be thought of as composed only of a capitulum (Figs. 1*c* and 2). These intertidal forms have economic importance. They settle on any suitable immersed surface, including the hulls of ships and submerged equipment. Their presence interferes with efficient operation and increases running costs. Large sums have been spent devising antifouling paints, principally using tributyl tin, and other techniques to discourage settlement of barnacles. Typically, the shell is formed of six to eight plates and a basal membrane, which may be calcified. The opening of the shell is closed by strong depressor muscles of a pair of movable lids (Fig. 2*a*), each composed of two articulated plates homologous with the scutum and tergum seen in the *Lepas* capitulum. Apart from ship bottoms, rocks, docks, pilings, and shells, acorn barnacles also cling to turtles (*Chelonibia*) and whales (*Cornonula*, *Tubincinella*). *See* THORACICA.

Acrothoracicans. The burrowing acrothoracicans are cryptic forms, millimeters in size. The settled cypris does not develop shell plates on the carapace during metamorphosis. Rather, the carapace bears chitinous teeth that assist in excavating the adult's burrow in the calcarous substrates on which they settle. Although some chemical action in this process has been suspected, apparently most of the burrow excavation is achieved by mechanical abrasion. Once properly housed, virtually little of the adult body ever extends beyond the burrow entrance, with all life processes taking place within the adults snug little home. *See* ACROTHORACICA.

Rhizocephala

The parasitic rhizocephalans can be identified as cirripedes only because of their nauplius larva, which bears frontolateral horns, and the possession of the thecostracan cypris larva. The cypris injects a wormlike stage into a decapod crustacean host, and this grows into an entangling network of female parasitic tissue that effectively takes over the host body. When the time comes to reproduce, an external gonad sac is protruded under the pleon (limbed abdomen) of the host. This attracts a male cypris that settles on the externa and becomes a hyperparasite on the female. Since they do not have an adult body form that can be compared with that of any other crustacean, let alone a thecostracan, the relationship of the rhizocephalans to the barnacles was unclear for a century or more, and until recently most researchers thought they were a group quite separate from the barnacles. However, analysis of DNA sequence data has shown that the rhizocephalans are closely related as a sister group to the thoracicans within Cirripedia. *See* RHIZOCEPHALA.

Fossil Record

Unquestioned fossil remains of Cirripedia are known from the Silurian, but there are also possible plateless forms that occurred earlier in the Cambrian Burgess Shale of Canada. Proper stalked barnacles are known from the Late Paleozoic onward. In Mesozoic and Cenozoic deposits, disarticulated shell plates occur, but only a few intact capitular shells are recognized. *See* FOSSIL; GEOLOGIC TIME SCALE.

Frederick R. Schram

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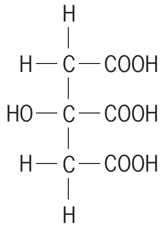
Citric acid

A hydroxytricarboxylic acid, general formula $C_6H_8O_7$, with the structure shown below. It is



$$\begin{array}{ccccc} & & \text{H} & & \\ & & | & & \\ & \text{H}- & \text{C} & -\text{COOH} \\ & & | & & \\ & \text{HO}- & \text{C} & -\text{COOH} \\ & & | & & \\ & \text{H}- & \text{C} & -\text{COOH} \\ & & | & & \\ & & \text{H} & & \end{array}$$

also available primarily as anhydrous material but as the monohydrate. The major commercial salts are sodium and potassium, with calcium, diammonium, and ferric ammonium (complex) also available. *See* ACID AND BASE.

Citric acid and its salts are widely used because they are nontoxic, safe to handle, and easily biodegraded. They are universally accepted, without

TABLE 1. Citrate content of natural products

Product	Percent citric acid
Lemon juice	4.0–8.0
Orange juice	0.6–1.0
Tangerine juice	0.9–1.2
Grapefruit juice	1.2–2.1
Strawberry	0.65–0.82
Raspberry	1.1–1.3
Black currant	1.5–3.0
Red currant	0.7–1.4
Gooseberry	0.98–0.99
Tomato	0.25
Cabbage	0.05–0.07
Corn	0.02
Eggplant	0.01
Peas	0.05
Cow milk	0.08–0.23
Human milk	0.35–1.25
Chicken organs	0.01–0.07

restriction on level, as food ingredients, including acceptance by the Joint FAO/WHO Expert Committee on Food Additives and the U.S. Food and Drug Administration. Because of their food use, specifications for purity are included in the *Food Chemicals Codex* (except diammonium citrate). In addition, specifications for citric acid, sodium citrate, and potassium citrate are included in the *U.S Pharmacopeia* and many pharmacopeia throughout the world.

Occurrence. Citric acid occurs in relatively large quantities in citrus fruits. It also occurs in other fruits, in vegetables, and in animal tissues and fluids either as the free acid or as citrate ion (**Table 1**). It is an integral part of the Krebs (citric acid) cycle involving the metabolic conversion of carbohydrates, fats, and proteins in most living organisms. *See* CITRIC ACID CYCLE.

Manufacture. Prior to World War I, all of the world's citric acid was produced by extraction from cull citrus fruit. Today, essentially all of the commercial citric acid is produced by fermentation. Processes employed are surface or submerged fermentation by mold (*Aspergillus niger*) and submerged fermentation by yeast (*Candida guilliermondii, C. lipolytica*), using a variety of substrates including sucrose, molasses, corn syrup, enzyme-treated starch, and normal paraffins. Citric acid is recovered from the fermentation broth by solvent extraction or more commonly by precipitation as calcium citrate, followed by treatment with sulfuric acid to convert the calcium citrate to calcium sulfate and citric acid. The calcium sulfate is removed by filtration, and the citric acid solution is further purified. Crystallization of citric acid from a hot aqueous solution (above the transition temperature of 36.6°C or 97.9°F) yields anhydrous citric acid; crystallization from a cold solution yields the monohydrate. Although total chemical syntheses for citric acid have been published, they have never achieved commercial success. *See* FERMENTATION; INDUSTRIAL MICROBIOLOGY.

Properties. Key properties of anhydrous citric acid are summarized in **Table 2**. Citric acid is a relatively strong organic acid (see dissociation constants), and is very soluble in water.

Uses. Citric acid is widely used in the food and pharmaceutical industries. In foods it is used primarily to produce a tart taste and to complement fruit flavors in carbonated beverages, beverage powders, fruit-flavored drinks, jams and jellies, candy, sherbets, water ices, and wine. It is also used to reduce pH in certain canned foods to make heat treatment more effective, and in conjunction with antioxidants to chelate trace metals and retard enzymatic activity. *See* FOOD MANUFACTURING.

In pharmaceuticals, citric acid provides the acid source in effervescent tablets in addition to being used to adjust pH, impart a tart taste, and chelate trace metals. It is also used as a blood anticoagulant. *See* PHARMACEUTICAL CHEMISTRY.

Citric acid, because of its low toxicity, relative noncorrosiveness, and biodegradability, is also being used for applications normally reserved for the strong mineral acids. These include preoperational and operational cleaning of iron and copper oxides from boilers, nuclear reactors, and heat exchangers; passivation of stainless steel tanks and equipment; and etching of concrete floors prior to coating. It is also used as a dispersant to retard settling of titanium dioxide slurries and as a sequestering and pH control agent in the textile industry. *See* TEXTILE CHEMISTRY.

Salts. Since citric acid is a tribasic acid, it can form acid and neutral salts, and will buffer over a broad pH range. The salts which are readily available commercially are trisodium citrate (dihydrate and anhydrous), tripotassium citrate (monohydrate), calcium citrate (tetrahydrate), diammonium citrate (anhydrous), and ferric ammonium citrate. *See* BUFFERS (CHEMISTRY); PH.

Trisodium citrate dihydrate, the salt which is most widely used, is a stable white crystal or granule. It is used as an emulsifier in processed cheese products where it prevents fat separation, imparts good meltdown properties, and produces slices with proper flexibility. In other dairy products, such as ice cream, whipping cream, and evaporated milk, it acts as a stabilizer and viscosity control agent. The sharpness of high-acid beverages is mellowed with sodium citrate, and it is used as a buffer to control pH in jams and jellies, gelatin desserts, and many pharmaceutical preparations. It is also used as a blood anticoagulant. Its largest single industrial use is as a detergent builder since it is rapidly biodegradable, environmentally acceptable, and can chelate

TABLE 2. Properties of anhydrous citric acid

Property	Value
Formula	$H_3C_6H_5O_7$
Molecular weight	192.13
Dissociation constants	K_1 8.2×10^{-4}
	K_2 1.8×10^{-5}
	K_3 3.9×10^{-7}
Melting point	153°C (307°F)
Solubility, g/100 ml at 25°C (77°F)	
Water	181
Ethanol	59
Ether	0.75

calcium, magnesium, and other metal ions. Sodium citrate is also used as a water conditioner, set-retardant for cement, buffer, and scrubbing agent to remove sulfur dioxide from stack gases or process tail gases. In most applications the dihydrate is used since it is less expensive. Occasionally, certain dry formulations require the use of the anhydrous salt. *See* CHEESE; DETERGENT.

Potassium citrate is a white crystalline granule or powder which readily absorbs moisture from the air. It is often used as a substitute for sodium citrate in special food products where sodium ion is undesirable. Calcium citrate is a stable, white, free-flowing powder used as a source of calcium either for nutritional purposes or for functional purposes (that is, as a firming agent). Ferric ammonium citrate is a complex salt, of undetermined structure, composed of iron, ammonia, and citric acid. Product containing 14.5–16% iron is green in color, and product containing 14.5–18.5% iron is brown. Both absorb moisture readily and are affected by light. They are used as a nutrient source of iron in food and in pharmaceutical syrups and elixirs. Diammonium citrate is a white granule or powder which is stable in air and used in dry formulations for metal cleaning. Fred Sauer

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Citric acid cycle

In aerobic cells from animal and certain other species, the major pathway for the complete oxidation of acetyl coenzyme A (the thioester of acetic acid with coenzyme A); also known as the Krebs cycle or tricarboxylic acid cycle. Reduced electron carriers generated in the cycle are reoxidized by oxygen via the electron transport system; water is formed, and the energy liberated is conserved by the phosphorylation of adenosine diphosphate (ADP) to adenosine triphosphate (ATP). Reactions of the cycle also function in metabolic processes other than energy generation. The role of the cycle in mammalian tissues will be emphasized in this article. *See* ADENOSINE DIPHOSPHATE (ADP); ADENOSINE TRIPHOSPHATE (ATP); COENZYME; ENZYME.

Reactions. The first step in the cycle involves the condensation of the acetyl portion of acetyl coenzyme A (CoA) with the four-carbon compound oxaloacetate to form citrate, a tricarboxylate containing six carbons (see **illus.**). A shift of the hydroxyl group of citrate to an adjacent carbon results in the formation of D-threo-isocitrate, which in turn is oxidized to the five-carbon compound α-ketoglutarate and carbon dioxide (CO_2). In a second oxidative decarboxylation reaction, α-ketoglutarate, in the presence of CoA, is converted to succinyl CoA and another molecule of CO_2. In the subsequent formation of the four-carbon compound succinate and CoA, the energy in the thioester bond of succinyl CoA is conserved by the formation of guanosine triphosphate (GTP) from guanosine diphosphate (GDP) and inorganic phosphate. Fumarate is formed from succinate by the removal of two atoms of hydrogen, and the unsaturated compound is then hydrated to L-malate. The dehydrogenation of malate forms oxaloacetate, the starting four-carbon compound of the metabolic cycle. Thus, beginning with the two-carbon acetyl group, one completion of the cycle results in the formation of two molecules of carbon dioxide. The obligatory role of the intact cycle for the complete oxidation of acetyl CoA has been demonstrated by inhibiting enzymes required for specific reactions (for example, inhibition of succinate dehydrogenase by the substrate analog malonate) or by altering the regeneration or depletion of an intermediate of the cycle.

Electron transport and oxidative phosphorylation. The oxidation of acetyl CoA to CO_2 in the cycle occurs without direct reaction with molecular oxygen. The oxidations occur at dehydrogenation reactions in which hydrogen atoms and electrons are transferred from intermediates of the cycle to the electron carriers nicotinamide adenine dinucleotide (NAD^+) and flavin adenine dinucleotide (FAD). The NAD-specific dehydrogenase reactions are isocitrate dehydrogenase [reaction (1)], α-ketoglutarate dehydrogenase (2), and malate dehydrogenase (3). FAD is the coenzyme for succinate dehydrogenase, (4). The electrons from NADH and $FADH_2$ are transferred to molecular oxygen via a series of electron transport carriers, with regeneration of NAD^+ and FAD. The energy liberated in the electron transport chain is partially conserved by the formation of ATP from ADP and inorganic phosphate, by a process called oxidative phosphorylation. The energy generated as oxygen accepts electrons from the reduced coenzymes generated in one turn of the cycle results in the maximal formation of 11 molecules of ATP. Because GTP obtained by phosphorylation of GDP at the succinyl CoA to succinate step of the cycle is readily converted to ATP by nucleotide diphosphokinase, as in reaction (5), the yield is 12 molecules of ATP per molecule of acetyl CoA metabolized. *See* NICOTINAMIDE ADENINE DINUCLEOTIDE (NAD).

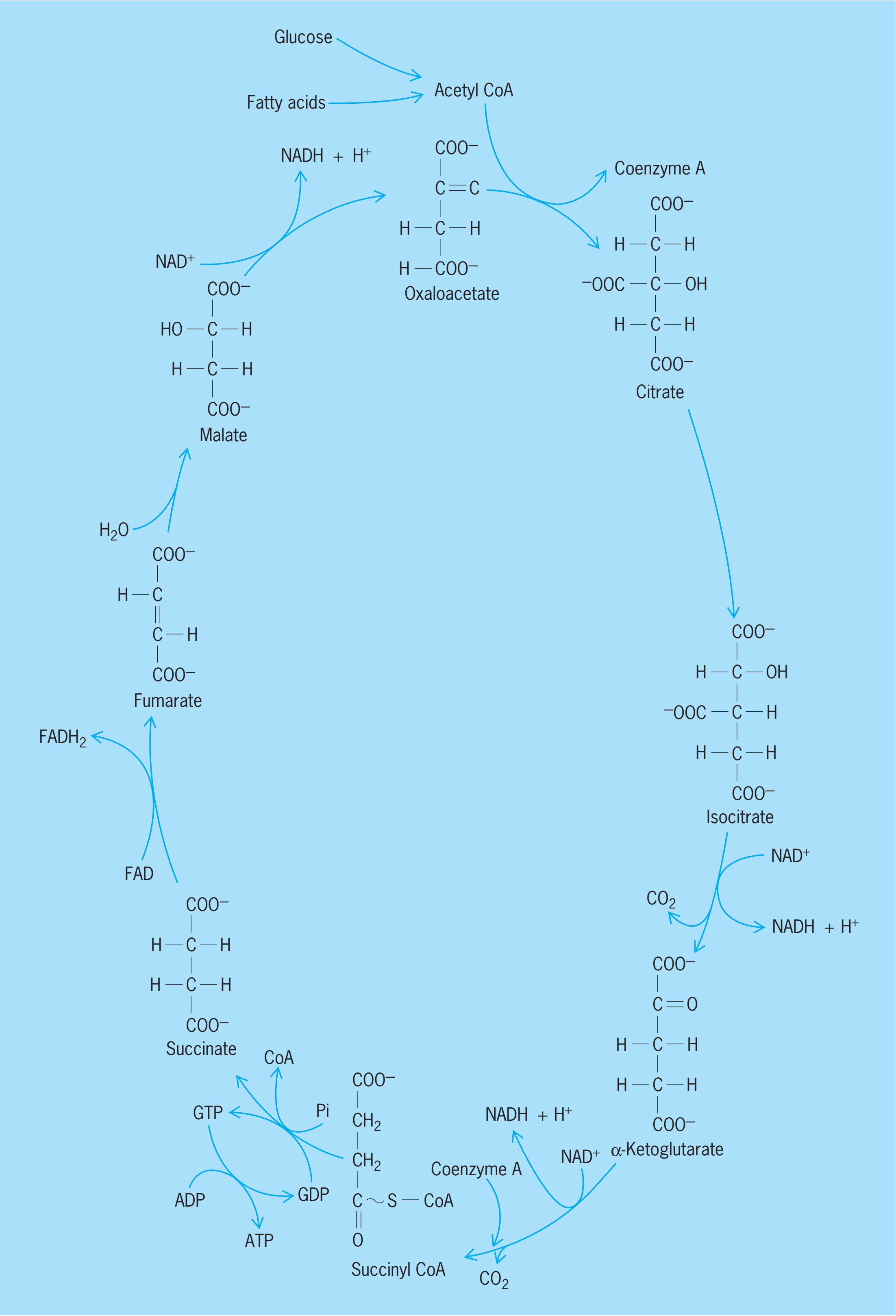
$$\begin{aligned}&\text{Isocitrate} + \text{NAD}^+ \longrightarrow\\&\qquad \alpha\text{-ketoglutarate} + \text{CO}_2 + \text{NADH} + \text{H}^+ \qquad (1)\end{aligned}$$

$$\begin{aligned}&\alpha\text{-Ketoglutarate} + \text{CoA} + \text{NAD}^+ \longrightarrow\\&\qquad \text{succinyl CoA} + \text{CO}_2 + \text{NADH} + \text{H}^+ \qquad (2)\end{aligned}$$

$$\text{Malate} + \text{NAD}^+ \longleftrightarrow \text{oxaloacetate} + \text{NADH} + \text{H}^+ \qquad (3)$$

$$\text{Succinate} + \text{FAD} \longleftrightarrow \text{fumarate} + \text{FADH}_2 \qquad (4)$$

$$\text{GTP} + \text{ADP} \longleftrightarrow \text{GDP} + \text{ATP} \qquad (5)$$



Citric acid cycle.

The electron transport and oxidative phosphorylation systems and the enzymes required for the citric acid cycle are located in the mitochondria of cells. These mitochondrial systems are the major source of ATP for energy-consuming reactions in most tissues. The citric acid cycle does not occur in all cells. For example, mature human red blood cells do not contain mitochondria and the cycle is absent. In these cells, ATP is formed by the anaerobic conversion of glucose to lactate (anaerobic glycolysis). *See* MITOCHONDRIA; PHOSPHATE METABOLISM.

Regulation. A major rate-limiting step of the citric acid cycle in aerobic mammalian tissues (for example, heart) is at NAD-specific isocitrate dehydrogenase [reaction (1)]. The activity of the enzyme is dependent on the concentration of the substrate (magnesium isocitrate): it is activated by ADP, calcium (Ca^{2+}), and citrate, and it is inhibited by NADH and reduced nicotinamide adenine dinucleotide phosphate (NADPH). Differences in energy demand affect the rate of citric acid flux and concentrations of modulators of NAD-dependent isocitrate dehydrogenase. At rest, the flux through the cycle is slowed, the cellular concentration of the isocitrate dehydrogenase inhibitor NADH is raised; and the activator ADP is lowered; the opposite occurs during high energy demand. The rate of cycle oxidation in liver mitochondria increases with decreased NADPH concentration; increased mitochondrial free Ca^{2+} enhances cycle flux. *See* NICOTINAMIDE ADENINE DINUCLEOTIDE PHOSPHATE (NADP).

Formation of acetyl CoA and intermediates. Acetyl CoA is formed from carbohydrates, fats, and the carbon skeleton of amino acids. The origin of a precursor and the extent of its utilization depend on the metabolic capability of a specific tissue and on the physiological state of the organism. For example, most mammalian tissues have the capacity to convert glucose to pyruvate in a reaction called glycolysis. Pyruvate is then taken up from cellular cytosol by mitochondria and oxidatively decarboxylated to acetyl CoA and carbon dioxide by pyruvate dehydrogenase, as in reaction (6). Acetyl CoA is also the end product of fatty acid oxidation in mitochondria. However, the fatty acid oxidation pathway occurs in fewer tissues than does glycolysis or the citric acid cycle. For example, nervous tissue utilizes the complete oxidation of glucose but not of fatty acids to maintain energy needs. In prolonged starvation, the level of blood glucose declines to a concentration inadequate to support the optimal energy needs of brain, whereas the level of blood ketone bodies (formed from fatty acids in liver) rises. In this case, the oxidation of ketone bodies (acetoacetate and 3-hydroxybutyrate) via acetyl CoA supplements the diminished oxidation of glucose to fulfill the energy requirements of the brain.

$$\text{Pyruvate} + \text{NAD}^+ + \text{CoA} \longrightarrow \text{acetyl CoA} + \text{CO}_2 + \text{NADH} + \text{H}^+ \quad (6)$$

The amino acids follow varied pathways for forming compounds that can enter the citric acid cycle. For example, the paths of degradation of leucine and lysine lead directly to formation of acetyl CoA; only part of the carbons of aromatic amino acids and of isoleucine are converted to acetyl CoA. Pyruvate, formed bytransamination of alanine with the citric acid cycle intermediate α-ketoglutarate [reaction (7)], can be oxidatively decarboxylated to acetyl CoA by pyruvate dehydrogenase [reaction (6)] or carboxylated to the cycle intermediate oxaloacetate by pyruvate carboxylase [reaction (8)]. Oxaloacetate can also be formed by aspartate aminotransferase [reaction (9)]. Portions of the carbon skeletons of valine, isoleucine, methionine, and threonine are converted to methylmalonyl CoA, which rearranges to the citric acid cycle intermediate succinyl CoA. *See* AMINO ACIDS.

$$\text{Alanine} + \alpha\text{-ketoglutarate} \longleftrightarrow \text{pyruvate} + \text{glutamate} \quad (7)$$

$$\text{Pyruvate} + \text{CO}_2 + \text{ATP} \longrightarrow \text{oxaloacetate} + \text{ADP} + \text{P}_1 \quad (8)$$

$$\text{Aspartate} + \alpha\text{-ketoglutarate} \longleftrightarrow \text{oxaloacetate} + \text{glutamate} \quad (9)$$

Role in lipogenesis and gluconeogenesis. In addition to the cycle's role in yielding catabolic energy, portions of it can supply intermediates for synthetic processes, such as the synthesis of the fatty acid moiety of triglycerides from glucose (lipogenesis), and formation of glucose from the carbon skeletons of certain amino acids, lactate, or glycerol (gluconeogenesis).

Lipogenesis. When dietary intake exceeds the energy needs of the body, the excess calories are deposited as body fat. Under these conditions in humans, the synthesis of fatty acids from glucose occurs mainly in the liver. It is favored by metabolic changes resulting principally from a rise in blood insulin: (1) The rate of pyruvate formation increases because of the rise in tissue glucose and enhancement of glycolysis. (2) Increases in enzyme activities catalyzing the conversion of pyruvate to acetyl CoA at pyruvate dehydrogenase [reaction (6)] and to oxaloacetate at pyruvate carboxylase [reaction (8)] raise the concentrations of both of these substrates for citrate synthesis. When this occurs at a rate exceeding that of the citric acid cycle, the citrate concentration rises and citrate exits from the mitochondria to the cytosol. (3) In the cytosol, citrate is cleaved to oxaloacetate and acetyl CoA in a reaction requiring CoA and ATP. The acetyl CoA is converted to palmitate and other long-chain fatty acids in a series of condensation steps requiring CO_2, ATP as energy source, and NADPH as reductant. *See* LIPID METABOLISM.

Gluconeogenesis. Dietary deprivation of an adult human for more than 2–3 days results in the depletion of liver glycogen stores supporting blood glucose, and the oxidation of fatty acids derived from body triglyceride depots becomes the principal body energy source. However, certain tissues, such as brain and red and white blood cells, remain partially or wholly dependent on glucose as the energy source. In the starved state, where blood insulin decreases and glucagon increases, increased mobilization of amino acids from skeletal muscle proteins occurs, and carbons from some of these amino acids become available for glucose synthesis. The interactions of degradation pathways of individual amino acids in various tissues result in markedly increased blood alanine, an important substrate for gluconeogenesis.

Some of the steps in the conversion of alanine to glucose are as follows: (1) Alanine is taken up from the bloodstream by the liver and converted to pyruvate by transamination [reaction (7)]. (2) The further metabolism of pyruvate in liver mitochondria is affected by the increase in the rate of fatty acid oxidation in the starved state, which raises the levels of acetyl CoA and NADH. Since NADH inhibits pyruvate dehydrogenase [reaction (6)], and acetyl CoA activates pyruvate carboxylase [reaction (8)], the conversion of pyruvate to oxaloacetate rather than acetyl CoA is favored. The increased NADH displaces the malate dehydrogenase reaction [reaction (3)] from oxaloacetate toward malate. Malate is transported from the mitochondria to the cytosol, where it is reoxidized by NAD^+ to oxaloacetate by cytosolic malate dehydrogenase. (3) Oxaloacetate is converted to phosphoenolpyruvate (PEP) by the PEP-carboxykinase reaction [reaction (10)].

$$\text{Oxaloacetate} + \text{GTP} \longrightarrow \text{PEP} + \text{CO}_2 + \text{GDP} \qquad (10)$$

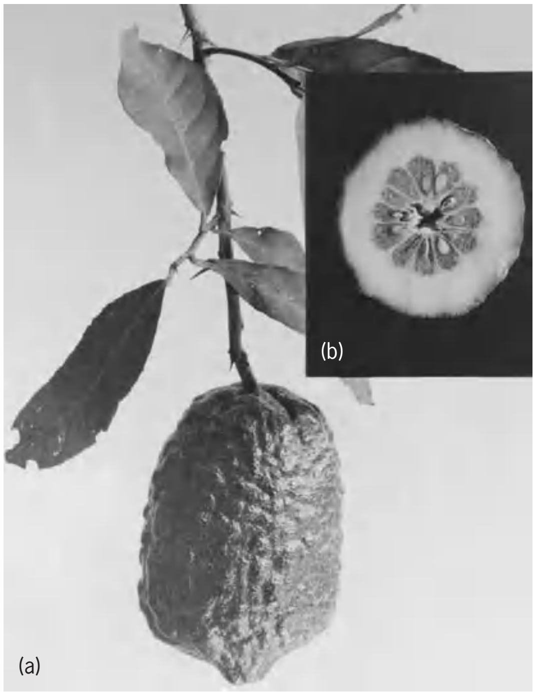
Phosphoenolpyruvate is an intermediate of both gluconeogenesis and glycolysis. In the starved state, the levels of modulators, metabolites, and so forth activate certain rate-limiting steps favoring the formation of glucose from PEP, and also inhibit key enzyme activities facilitating glycolysis. The net effect of these opposing trends is to funnel the flux of carbons from amino acids toward glucose synthesis. *See* BIOLOGICAL OXIDATION; CARBOHYDRATE METABOLISM; CELL (BIOLOGY); GLUCOSE; GLYCOGEN; METABOLISM. Gerhard W. E. Plaut

Citron

Citrus medica, a species of true citrus. The plant has a long and interesting history, being the first contact between citrus, which came from the Far East, and western Judaeo-Christian civilization. A citron, the Etrog, was the "hadar" or "goodly fruit" offering at the ancient Jewish Feast of the Tabernacles. At the time of the first Jewish revolt against Rome in A.D. 66–70, the rebels minted their own coins with the Etrog substituting for Nero's imperial visage.

Commercially, citrons are still grown almost exclusively in the Mediterranean area, principally in Italy, Sicily, Corsica, Greece, and Israel. The tree is evergreen, as are all citrus, and frost-tender. It is thorny, straggly, shrubby, and tends to be short-lived.

The fruit is scarcely edible fresh, having a very thick skin with little flesh and that lacking in juice (see **illus.**). However, it is very fragrant and was valued in ancient times for its aroma and its fragrant peel oil, used in perfumes and as a moth repellent. Later, when the citron was the only known citrus fruit, it was very highly valued. Today, it is grown commercially only as a source of candied peel for use in cakes and confections. The actual candying is usually done in the importing country, the citron peel being exported in brine. Traditionally the fruit was halved and held in large unsealed casks in seawater, a mild fermentation taking place for a week or more, after which additional coarse salt was added and the casks sealed. Today brining is more typically done in a 15% salt solution to which about 2000 parts per million of SO_2 has been added as a preservative and 1% $CaCl_2$ to firm the tissues. The candying process involves first leaching out the brine with boiling water and then transfers through successive syrups of increasing strength up to about 75%.



Commercial citron (*Citrus medica*), approximately one-half natural size. (*a*) Foliage and fruit. (*b*) Cross section of fruit. (*From J. Horace McFarland Co.*)

Confusion sometimes arises due to the name "citron" also being used for a small, wild, inedible melon in the United States and for lemons (*C. limon*) in France. *See* FRUIT; FRUIT, TREE. William Grierson

Citronella

A tropical grass, *Cymbopogon nardus,* from the leaves of which oil of citronella is distilled. This essential oil is pale yellow, inexpensive, and much used in cheap perfumes and soaps. It is perhaps best known as an insect repellent. A large acreage is devoted to the cultivation of this grass in Java and Ceylon. *See* CYPERALES; ESSENTIAL OILS.

Perry D. Strausbaugh; Earl L. Core

Civet

The common name for any of various carnivorous catlike mammals of the family Viverridae of Africa and Asia. These small and medium-sized carnivores are often called “weasel cats” because of their long, slender weasel-like body with short limbs and their long, bushy tail and catlike disposition. They inhabit the warmer parts of the Old World, including southern Asia, the East Indies, portions of Africa, and Madagascar.

Classification. The family Viverridae includes 35 species divided among the following genera: genets (*Genetta*, *Osbornictis*), linsangs (*Poiana*, *Prionodon*), binturongs (*Arctictis*), Oriental civets (*Viverra*), the African civet (*Civettictis*), lesser Oriental civet (*Viverricula*), African palm civet (*Nandinia*), small-toothed palm civet (*Arctogalidia*), masked palm civet (*Paradoxurus*, *Paguma*), Sulawesian palm civet (*Macrogalidia*), banded palm civet (*Hemigalus*), Hose’s palm civet (*Diplogale*), Owston’s palm civet (*Chrotogale*; see **illustration**), otter civets (*Cynogale*), Malagasy civet (*Fossa*), and falanoucs (*Eupleres*).

Morphology. The civet’s head is elongate and the muzzle is pointed. Civets have five toes on each foot, with each toe ending in a sharp claw. Claws may be retractile, semiretractile, or nonretractile. Like cats, civets walk softly and spring swiftly upon their prey. Like skunks, civet cats are strikingly marked so that they are easily recognized, remembered and avoided by potential enemies. They may be striped, spotted, or have a uniform color pattern. In some species the tail is banded or ringed. Females usually have two or three pairs of abdominal mammae. There are between 32 and 40 teeth, with the carnassial teeth being well developed. The senses of slight, hearing, and smell are well developed. Head-body length is 350–950 mm (13.5–37 in.), tail length is 130–900 mm (5–35 in.), and adult weight is 0.6–20 kg (1.3–44 lb).

Habitat. Viverrids are primarily forest dwellers, although they also inhabit dense brush and thick grass. Most species are terrestrial, although many are skillful climbers and spend most of their lives in trees. Shelters include burrows, caves, crevices, tree cavities, or thick brush. Some civets are solitary, whereas others live in pairs or groups. They may be diurnal or nocturnal.

Otter civets (*Cynogale*) are semiaquatic. They have the flat head, broad toes and feet, and thick, dense fur of an aquatic animal. They swim and fish like otters and are as much at home in the water as on dry land.

Diet. Civets are omnivorous. Food consists of small vertebrates and invertebrates and occasionally some vegetable matter such as fruits, bulbs, and nuts. Carrion is taken by some species. Since civets do not digest the seeds of fruits and berries, they distribute the seeds over a considerable distance where they germinate and eventually grow into trees and shrubs.

Owston’s palm civet (*Chrotogale owston*). (*Photo © by Mark Kostich*)

Breeding and longevity. Breeding may occur seasonally or throughout the year. Some species produce two litters of one to six young annually. Newborn civets are blind but covered with hair. Potential longevity ranges from 5 to 15 years.

Economic importance. Members of the family Viverridae are valued for their musk, fur, and meat.

Civet musk. Most members of this family possess scent, or musk, glands in the anal region that secrete a fluid with a musky odor, known as civet, as a defensive measure. This thick yellowish substance is composed of ammonia, resin, fat, and volatile oil. When rubbed on tree trunks, the ground, and similar objects, the secretion is probably used as a means of communication between individuals of the same species. Civet is obtained from several genera (*Civettictis*, *Viverra*, and *Viverricula*) for use in perfumes and medicine, primarily in the Orient. Some civets are tamed and kept in captivity specifically for their musk, which is extracted every 14 to 20 days. Many perfume manufacturers now use civetone, a synthetic alternative.

One excellent producer of civet is the Oriental civet (*Viverra*), as its musk glands are greatly enlarged. It typically has a head-body length of 60 cm (2 ft), a 45-cm (18-in.) tail, and a weight of 11 kg (25 lb). The Oriental civet has a full, black-and-white ringed tail, many ill-defined markings on its grizzled body, and a broad black band set off by areas of white across the throat. A prominent crest of long erectile hairs extends down the middle of the back. The feet are black, and the fur is soft and thick, making it of considerable importance to the fur trade. *See* SCENT GLAND.

Fur and meat. Besides their importance to the perfume industry, civets are prized for their fur and meat. The civet cat is considered a delicacy in southern China. It has been suggested that the practice of eating civets may have resulted in the severe acute respiratory disease (SARS) virus outbreak of 2003. SARS, a type of atypical pneumonia, first broke out in Guangdong province in southern China in November 2002. In January 2004, Guangdong province banned sales of civet cats and ordered the slaughter of all captive civets. In January 2004, the United States announced an embargo on the importation of civets.

Status. Several species are listed as either vulnerable or endangered by the International Union for the Conservation of Nature and Natural Resources (IUCN) and/or the U.S. Department of the Interior. The Malabar civet (*Viverra civettina*) is one of the world's rarest mammals and is listed as critically endangered. It is known only from an isolated belt of rainforests in the Western Ghats of southwestern India. Extensive deforestation has reduced the forests it inhabits to a series of isolated patches. Habitat loss continues. Cashew plantations, which probably hold most of the surviving populations of this species, are now threatened by large-scale clearing for planting rubber. *See* CARNIVORA; ENDANGERED SPECIES; MAMMALIA. Donald W. Linzey

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Civil engineering

A branch of engineering that encompasses the conception, design, construction, and management of residential and commercial buildings and structures, water supply facilities, transportation systems for goods and people, as well as control of the environment for the maintenance and improvement of the quality of life. Civil engineering is a people-serving profession; it includes planning and design professionals in both the public and private sectors, contractors, builders, educators, and researchers who strive to meet the needs and desires of the community.

The civil engineer holds the safety, health, and welfare of the public paramount. Civil engineering projects and systems should conform to governmental regulations and statutes; should be built economically to function properly for a reasonable period of time with a minimum of maintenance and repair while withstanding anticipated usage and weather; and should conserve energy and allow hazard-free construction while providing healthful, safe, and environmentally sound utilization by society.

Because the desired objectives are so broad and encompass an orderly progression of interrelated components and information to arrive at the visually pleasing, environmentally satisfactory, and energy-frugal end point, civil engineering projects are actually systems requiring the skills and inputs of many diverse technical specialties, all of which are subsets of the overall civil engineering profession.

The infrastructure is the foundation of the modern industrialized urban society. The infrastructure includes roads; mass transit; railroads; bridges; airports; storage buildings; terminals; communication and control towers; water supply and treatment systems; storm water control systems; wastewater collection, treatment and disposal systems; as well as living and working areas, recreational buildings, and ancillary structures for civil and civic needs. Without a well-maintained and functioning infrastructure, the urban area, and society, cannot stay healthy, grow, and prosper. Civil engineers, with their various technical specialties, play a major role in developing workable solutions to construct, renovate, repair, maintain, and upgrade this infrastructure. The civil engineer works with other professionals in developing functional projects, arriving at realistic cost estimates, and advocating reasonable investment strategies.

Civil engineers who move into management combine their technical training and skills with the ability to organize and properly employ the four basics of any project—personnel, time, materials, and money. Civil engineers in management may work for private engineering firms, for industries, for the military, for governmental agencies, or for regional authorities. The civil engineer may also choose a career in education. The teaching civil engineer educates students in technical specialties, inculcates engineering ethics and standards of safety, and engages in research and scholarly endeavors. Civil engineering faculty members are frequently involved as consultants or specialists on boards or commissions for standards, planning, or educational certification.

Photogrammetry, surveying, and mapping. The civil engineer in this specialty precisely measures the Earth's surface to obtain reliable information for locating, planning, and designing engineering projects. This specialty involves everything from traditional land surveying to high-technology methods using aerial surveying, satellites, and computer-processing of photographic imagery. The information obtained by optical sighting, radio signal, laser scan, or sonic beam is converted to maps to provide accurate locations for designing planned developments, boring tunnels, building highways or pipelines, plotting flood control, irrigation or hydroelectric projects with dams and other structures, delimiting subsurface geologic formations that may affect construction projects, and aiding many other building uses. *See* AERIAL PHOTOGRAPH; PHOTOMETRY; REMOTE SENSING; SURVEYING; TOPOGRAPHIC SURVEYING AND MAPPING.

Community and urban planning. Those engaged in this segment of civil engineering evaluate environmental, social, and economic factors in affecting the use and development of land and natural resources as they plan to establish planned developments, recreational park areas, or industrial complexes for regions, cities, or portions of a community. They work with other professionals to coordinate required infrastructure to ensure social, economic, and environmental well-being. *See* LAND-USE PLANNING.

Geotechnical engineering. Civil engineers in this specialty analyze and evaluate the behavior of earth materials and the ability of these materials to support structures on or below the ground. They design and establish procedures to prevent the pressure or weight of structures from compressing the supporting earth and causing settlement. They are also concerned with methods to stabilize slopes and fills, to protect structures and infrastructure from earthquakes, and to mitigate the unwanted effects of ground water. *See* ENGINEERING GEOLOGY; FOUNDATIONS; PERMAFROST; PILE FOUNDATION; ROCK MECHANICS; SOIL MECHANICS.

Construction engineering. Civil engineers in this area manage and direct the physical construction of a project from start to finish; this field is also known as construction management. Construction engineers apply the knowledge of construction methods and equipment along with principles of financing, scheduling, planning, organization, and coordination to convert the paper designs into completed usable facilities. They maintain a continuous record of the personnel, time, materials, and costs expended and prepare periodic reports depicting the project's progress to completion. *See* CONSTRUCTION ENGINEERING; CONSTRUCTION METHODS; ENGINEERING AND ARCHITECTURAL CONTRACTS.

Structural engineering. In this specialty, civil engineers plan, design, and evaluate a wide variety of structures, including buildings, bridges, offshore platforms, space platforms, amusement park rides, towers, and any other construction that must support its own weight and the loads it must carry. These structures must be designed for, and capable of withstanding, the loads due to rain, snow, or ice; the forces due to wind, hurricanes, and earthquakes; the effects of temperature changes and the like. The structural engineer must determine which construction materials or combinations of them such as steel, concrete, stone, brick, aluminum, plastics, and glass are most economical, safe, and appropriate for the project under the site-specific conditions. *See* BRIDGE; BUILDINGS; STRUCTURAL ANALYSIS; STRUCTURAL DESIGN; STRUCTURAL MATERIALS; STRUCTURE (ENGINEERING).

Environmental engineering. In this branch of the profession, civil engineers plan, design, construct, operate, and supervise systems to protect human health and the ecological balances necessary for environmental quality in both natural and humanmade environments. These systems include development and treatment of drinking water; collection and treatment of sanitary and industrial wastes to prevent contamination of the land and water; containment of hazardous and toxic materials; safe disposal of garbage, refuse, and other solid wastes; minimization or elimination of air pollution caused by industrial manufacturing or combustion processes; and design for containment of radioactive discharges. The environmental engineer is involved, either personally or through a team effort, to reduce, mitigate, or eliminate the hazards and risks associated with air, food, and water contaminants, radiation, toxic chemicals, solid wastes, disease vectors, safety hazards, and habitat alterations to preserve or conserve ecological biomes. *See* AIR POLLUTION; HAZARDOUS WASTE; INDUSTRIAL WASTEWATER TREATMENT; LAND RECLAMATION; SEWAGE TREATMENT; WATER POLLUTION; WETLANDS.

Water resources engineering. Civil engineers who specialize in this area deal with all aspects of the physical control of water. They plan, evaluate, design, construct, supervise, and operate systems to control floods; to supply water for cities; to develop irrigation; to manage and control river navigation, locks, and banks; to prevent beach erosion; and to maintain waterfront facilities. They are also involved in the planning and design of harbors, docks, wharfs, port facilities, canals, and offshore platforms and systems. They are involved with other civil engineers in planning and designing flood control dikes, dams, and hydroelectric power impoundments. *See* CANAL; COASTAL ENGINEERING; DAM; HARBORS AND PORTS; RESERVOIR; REVETMENT; RIVER ENGINEERING; WATER SUPPLY ENGINEERING.

Waste management and risk assessment. Civil engineers involved in this area must function as a part of a team. The improper disposal of hazardous or toxic wastes, as well as the indiscriminate dumping of wastes in landfills, has created a situation that impacts on the land and subsurface water supplies. A subset of environmental engineering has evolved that is specifically concerned with the management of these sites. At the same time it is imperative that the available time, money, and personnel be utilized to treat these existing sites in a systematic and cost-effective manner. One method of establishing the hierarchy for treating the existing sites is to perform a risk assessment and establish which areas pose the greatest threat to people and natural resources. The civil engineers in this area of work must develop treatability procedures and estimate costs needed to reduce the risk. The data must then be presented to the public to explain the trade-offs of potential risk and the costs necessary to reduce them, since the locally affected community must be willing to expend time, effort, and money to clean up and manage the site. *See* RISK ASSESSMENT AND MANAGEMENT.

Transportation engineering. Civil engineers working in this specialty plan, design, construct, and maintain facilities to safely and efficiently move people and goods. Accomplishing this task involves modal system planning for pedestrians, bikeways, streets, roads, highways, mass transit, railroads, airports, ports, and harbors. The ancillary structures to the vehicles and the travel way, which includes parking areas and terminals as the transfer facilities between the various modes of traffic, must be considered. Transportation engineers must apply technological acumen and consider the economic, social, and political factors that impact on each system. It is essential that transportation planning be done in conjunction with community and urban planners. The goal is an acceptable means of enhancing the movement of goods and people from residence to place of employment or entertainment, to shopping areas, and to health care facilities while always permitting quick response of emergency vehicles. The prosperity and quality of life of a community are intimately tied up with the transportation system. *See* AIRPORT ENGINEERING; HIGHWAY ENGINEERING; RAILROAD ENGINEERING; TRANSPORTATION ENGINEERING.

Pipeline engineering. Civil engineers in this highly specialized task of transporting liquids, gases, or slurries plan, design, maintain, and operate the pipelines in which these various types of noncombustible to highly combustible materials are moved from one location to another. The engineers determine pipeline design, location, and the environmental and economic impacts on the region that the line traverses. They select the material for constructing the line based on the qualities of durability and safety. Further, they specify installation techniques, methods of testing, and controls for maintaining proper pressure and rate of flow of the material within the line. When a hazardous or toxic material is to be carried, safety is a major concern. *See* ENGINEERING; PIPELINE.

Kenneth Lazuruk; Gerald Palevsky

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Cladding

An old jewelry art, now employed on an industrial scale to add the desirable surface properties of an expensive metal to a low-cost or strong base metal. In the process a clad metal sheet is made by bonding or welding a thick facing to a slab of base metal; the composite plate is then rolled to the desired thickness. The relative thickness of the layers does not change during rolling. Cladding thickness is usually specified as a percentage of the total thickness, commonly 10%.

Uses. Gold-filled jewelry has long been made by this process; the surface is gold, the base metal bronze or brass with the cladding thickness usually 5%. The process is used to add corrosion resistance to steel and to add electrical or thermal conductivity, or good bearing properties, to strong metals. One of the first industrial applications, about 1930, was the use of a nickel-clad steel plate for a railroad tank car to transport caustic soda; by 1947 stainless-clad steels were being used for food and pharmaceutical equipment. Corrosion-resistant pure aluminum is clad to a strong duralumin base, and many other combinations of metals are widely used in cladding; a development includes a technique for cladding titanium to steel for jet-engine parts.

Fig. 1. Rolls of copper clad with copper-nickel facing for minting composite coins.

Today's coinage uses clad metals as a replacement for rare silver. Since 1965 dimes and quarters have been minted from composite sheet consisting of a copper core with copper-nickel facing. The proportion of core and facing used duplicates the weight and electrical conductivity of silver so the composite coins are acceptable in vending machines (**Fig. 1**).

A three-metal composite sole plate for domestic steam irons provides a thin layer of stainless steel on the outside to resist wear and corrosion. A thick core of aluminum contributes thermal conductivity and reduces weight, and a thin zinc layer on the inside aids in bonding the sole plate to the body of the iron during casting.

Cladding supplies a combination of desired properties not found in any one metal. A base metal can be selected for cost or structural properties, and another metal added for surface protection or some special property such as electrical conductivity. Thickness of the cladding can be made much heavier and more durable than obtainable by electroplating.

Combinations. The following clad materials are in common use.

Stainless steel on steel. Provides corrosion resistance and attractive surface at low cost for food display cases, chemical processing equipment, sterilizers, and decorative trim.

Stainless steel on copper. Combines surface protection and high thermal conductivity for pots and pans, and for heat exchangers for chemical processes.

Copper on aluminum. Reduces cost of electrical conductors and saves copper on appliance wiring.

Copper on steel. Adds electrical conductivity and corrosion resistance needed in immersion heaters and electrical switch parts; facilitates soldering.

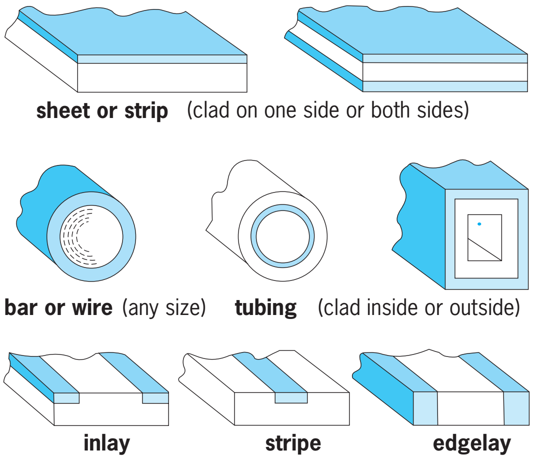


Fig. 2. Types of cladding.

Nickel or monel on steel. Provides resistance to corrosion and erosion for furnace parts, blowers, chemical equipment, toys, brush ferrules, and many mechanical parts in industrial and business machines; more durable than electroplating.

Titanium on steel. Supplies high-temperature corrosion resistance. Bonding requires a thin sheet of vanadium between titanium and steel.

Bronze on copper. Usually clad on both sides, for current-carrying springs and switch blades; combines good electrical conductivity and good spring properties.

Silver on copper. Provides oxidation resistance to surface of conductors, for high-frequency electrical coils, conductors, and braiding.

Silver on bronze or nickel. Adds current-carrying capacity to low-conductivity spring material; cladding sometimes is in form of stripes or inlays with silver areas serving as built-in electrical contacts.

Gold on copper. Supplies chemical resistance to a low-cost base metal for chemical processing equipment.

Gold on nickel or brass. Adds chemical resistance to a stronger base metal than copper; also used for jewelry, wristbands, and watchcases.

Types. Cladding can be added to both sides of a sheet or strip of base metal. Tubing can be supplied with a clad surface on inside or outside; round and rectangular wire can be clad similarly (**Fig. 2**).

For some forms of electrical contact, the composite materials are bonded side by side, or silver is inset as a stripe on one side or along the edges. This construction can place solid silver just where it is needed to form an electrical contact with no waste of costly metal.

Another related form of cladding is found in thermostatic bimetals in which equal thicknesses of low- and high-expansion metals are bonded together. With a change in temperature, differing expansion rates of the two metals cause the composite material to bend and thus operate valves in automobile cooling systems, or electrical contacts in room thermostats.

Clad wires with properly chosen proportions of materials of different thermal-expansion rates can match the thermal expansion of types of glass used for vacuum-tight seals for conductors in lamp bulbs and hermetically sealed enclosures.

In making parts from clad metal, the composite material can be bent, drawn, spun, or otherwise formed just the same as the base metal without breaking the bond. The maximum service temperature is limited by the melting point of the material at the juncture of the two metals; annealing temperatures during manufacturing are similarly limited.

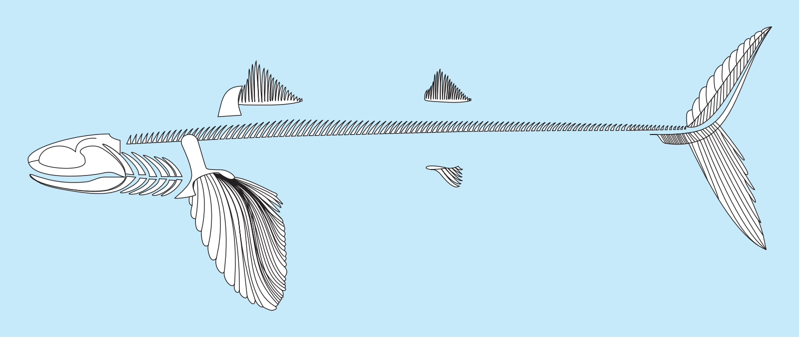
Cut edges of clad sheets expose the base metal and thus may require special protection. Welding of thick clad sheets sometimes offers special problems in maintaining the integrity of the protective surface, but joining methods are generally the same as for the base metal. *See* ELECTROPLATING OF METALS; METAL COATINGS.

Robert W. Carson

Cladoselache

A genus of Paleozoic chondrichthyan "sharks," characterized by broad-based paired fins, a short stout bony spine preceding the first of the two dorsal fins, and a large lunate tail-fin. Often cited as among the best known, earliest, and/or most primitive of the early chondrichthyans (cartilaginous fishes including modern chimaeroids, sharks and rays), *Cladoselache* now appears ill defined and poorly diagnosed. Most of the best fossil specimens of *Cladoselache* are from the Upper Devonian Cleveland Shales, and include complete individuals of around 1 m (3.3 ft) in length. Several of these have mineralized traces of soft tissues, including much of the superficial jaw and gill musculature, and even apparent traces of internal organs such as the kidneys. The dentition consists of small tricuspid teeth in which the central cusp is largest; the body is mostly naked except for compound scales on the head and fins. No specimens of *Cladoselache* are known to have claspers—the sex organs of male chondrichthyans used for internal fertilization (otherwise preserved as skeletal rods extending from the rear of the hind set of paired fins). *See* CHONDRICHTHYES.

In the context of more recent discoveries of early sharklike fishes, *Cladoselache* is emerging as unusual and specialized in several respects. The high-aspect-ratio (tall and narrow) tail is like that of only a subset



***Cladoselache fyleri*, from the Upper Devonian of Cleveland. (*After S. E. Bendix-Algreen, 1975*)**

of Paleozoic sharks, all of which have a transformed stretch of the vertebral column supporting the upper lobe, but this is far from primitive and completely absent from most contemporaneous chondrichthyan and nonchondrichthyan fishes. The pectoral fins are remarkably large for the total body size, and are supported by a series of broad straplike cartilages—most of which extend directly from the shoulder girdle. This pattern was once considered primitive because it resembled a hypothesized archetypical fin condition (the continuous lateral fin-fold model) for which there is now little fossil and embryological support. Comparisons with paired fins among other early fishes now highlight the cladoselachian pattern as unusual. The braincase (neurocranium) is known in outline only; it is peculiarly wide, although this might result from postmortem compression.

Few other aspects of the paleobiology of *Cladoselache* are known. The Cleveland Shale was deposited in a shallow inland sea covering what is now northeastern Ohio. *Cladoselache* was probably a medium-sized pelagic member of the fauna, dwarfed by large arthrodire placoderms (such as *Dunkleosteus*) known from the same fossil localities. Stomach contents of *Cladoselache* include the intact remains of small ray-finned (actinopterygian) fishes (*Kentuckia*), preserved with heads directed toward the front of the enclosing gut-trace. This rare detail from a fossil fish suggests that they (the ray-finned prey) were engulfed from the rear, tail-first, implying that in this instance *Cladoselache* behaved as an active, pursuit predator. *See* ACTINOPTERYGII; PLACODERMI.

Michael Coates

Bibliography. J. A. Long, *The Rise of Fishes*, Johns Hopkins University Press, Baltimore, 1995; J. G. Maisey, *Discovering Fossil Fishes*, Westview Press, New York, 1996.

Clarification

The removal of small amounts of fine, particulate solids from liquids. The purpose is almost invariably to improve the quality of the liquid, and the removed solids often are discarded. The particles removed by a clarifier may be as large as 100 micrometers or as small as 2 micrometers. Clarification is used in the manufacture of pharmaceuticals, beverages, rayon, nylon, and other fiber and film polymers; in the reconditioning of electroplating solutions; in the recovery of dry-cleaning solvent; and for the purification of drinking water and wastewater. The filters in the feed line and lubricating oil system of an internal combustion engine are clarifiers.

The methods of clarification include gravity sedimentation, centrifugal sedimentation, filtration, and magnetic separation. Clarification differs from other applications of these mechanical separation techniques by the low solid content of the suspension to be clarified (usually less than 0.2%) and the substantial completion of the particle removal.

Gravity sedimentation is employed, usually in continuous settling tanks of simple construction, to concentrate the solid fraction and to clarify the liquid fraction of suspensions amenable to separation by this method. Gravity clarifiers differ from thickeners only in the concentration of solids in the feed and in the demand that the overflow be practically particle free. *See* SEDIMENTATION (INDUSTRY); THICKENING.

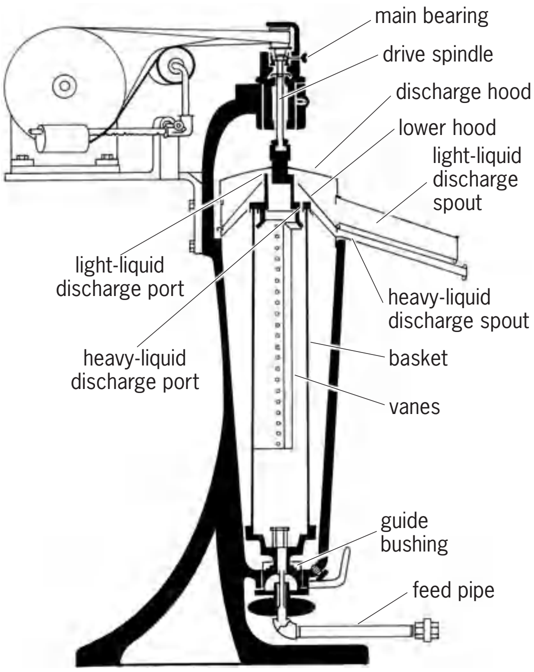


Fig. 1. Continuous high-speed clarifying centrifuge. (*After W. L. Bader and J. T. Banchero, Introduction to Chemical Engineering, McGraw-Hill, 1955*)

When the settling rate is too slow for gravity sedimentation to be feasible, centrifugal force up to approximately 100,000 times the force of gravity may be employed to clarify a suspension. In a separator called a centrifuge the suspension is passed through a rapidly rotating tube or basket (**Fig. 1**). The relatively dense solids are forced to the walls of the rotor, and the clarified liquid overflows a dam in the end of the centrifuge. *See* CENTRIFUGATION; ULTRACENTRIFUGE.

Clarifying filters comprise a versatile class of mechanical separators that are effective over the entire range of particle sizes encountered in clarification (from 0.1 mm down to molecules with a molecular weight on the order of 1000), regardless of relative densities and in spite of high viscosities. Sand or coal filters are used extensively for potable and industrial water clarification. Precoat filters are used for water and suspensions carrying slimy, amorphous impurities. Disk and plate filters (**Fig. 2**) service a wide variety of clarifying demands, removing particles over a range of 0.1 to 5 μm. Cartridge filters are in-line units with cleanable or replaceable elements that can remove particles in the range of 0.5 to 50 μm. Ultrafilters (also called microfilters and hyperfilters) contain fibrous sheets or porous membranes with carefully sized pores. These can remove particles as small as 0.002 μm. *See* FILTRATION; STERILIZATION; ULTRAFILTRATION.

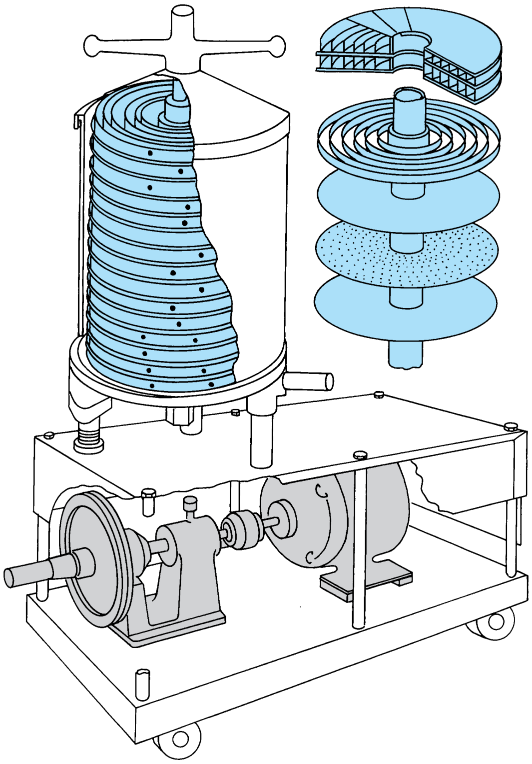


Fig. 2. Disk-and-plate clarifying filter. (*After R. H. Perry and D. Green, eds., Perry's Chemical Engineers' Handbook, 6th ed., McGraw-Hill, 1984*)

Magnetic separators are effective for the removal of ferrous particles. *See* MAGNETIC SEPARATION METHODS.

Clarification processes often depend on flocculating agents for their success. These are additives that cause the suspended solids to agglomerate into flocs that settle more rapidly or are more readily filtered than their smaller components. **Shelby A. Miller**

Bibliography. C. O. Bennett and J. E. Myers, *Momentum, Heat and Mass Transfer*, 3d ed., 1993; R. H. Perry and D. Green (eds.), *Perry's Chemical Engineer's Handbook*, 7th ed., 1991; W. L. McCabe, J. C. Smith, and P. Harriot, *Unit Operations of Chemical Engineering*, 5th ed., 1993.

Classical field theory

The mathematical discipline that studies the behavior of distributions of matter and energy when their discrete nature can be ignored; also known as continuum physics or continuum mechanics. The discrete nature of matter refers to its molecular nature, and that of energy to the quantum nature of force fields and of the mechanical vibrations that exist in any sample of matter. The theory is normally valid when the sample is of laboratory size or larger, and when the number of quanta present is also very large. *See* PHONON; PHOTON; QUANTUM MECHANICS.

Classical field theories can be formulated by the molecular approach, which seeks to derive the macroscopic (bulk) properties by taking local averages of microscopic quantities, or by the phenomenological approach, which ignores the microscopic nature of the sample and uses properties directly measurable with laboratory equipment. This article follows the phenomenological course, although the microscopic treatment sometimes yields profounder insights. The problems considered below illustrate a selection of classical field theories without long mathematical discussions. Partial differential equations are used because the neglect of microscopic structure allows quantities like density and pressure to be expressed by continuously varying numbers.

Bending of a beam. A first example, leading to an ordinary differential equation, is the bending of a solid beam. To calculate the bending, isolate a segment of length dx (see **illus.**), and take account of the conditions that produce a mechanical equilibrium. The forces exerted up and down on the beam must balance, as well as the moments or torques tending to turn it. These conditions, combined with some geometry, lead to an equation from which the curvature of the beam can be calculated.

The quantity $M(x)$ is defined to be the moment or torque exerted by the part of the beam to the right of point x on the part to the left, and similarly $S(x)$ is the shear force exerted from right to left. If $\rho(x)$ is the beam's linear density, it follows from definitions that S and M change as in Eqs. (1) and (2), where g is

$$dS = -\rho g dx \qquad \frac{dS}{dx} = -\rho g \tag{1}$$

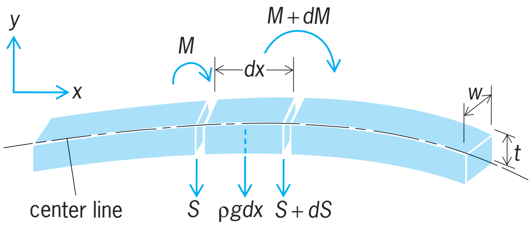
$$dM = S dx \qquad \frac{dM}{dx} = S \tag{2}$$

the acceleration of gravity. To find the bending, the beam is assumed to consist of parallel fibers; those above the center line are in tension and those below in compression. It is easy to see that at any point x, M is as given in Eq. (3), where R is the beam's

$$M = \frac{E}{R} I \qquad I = \int y^2 dA \tag{3}$$

radius of curvature, E is Young's modulus of elasticity for the material, dA is an element of area, and I is the moment of inertia of the cross section. If the beam is nearly horizontal, Eq. (4) relates R to the second derivative of y. For the rectangular cross section

$$\frac{d^2y}{dx^2} = \frac{1}{R} \tag{4}$$



Portion of a rectangular solid beam, showing quantities used in calculating the bending of the beam.

shown, I is evaluated around the center line and is given by Eq. (5).

$$I = {}^{1}/_{12}\omega t^{3} \tag{5}$$

See MOMENT OF INERTIA; SHEAR; STATICS.

Combining Eqs. (1)–(4) gives Eq. (6) for the shape

$$\frac{d^{4}y}{dx^{4}} = -\frac{pg}{EI} \tag{6}$$

of the beam. It can be integrated, requiring four boundary conditions, to find the curve under different conditions of loading; for example, if the beam is of length l and is supported horizontally at one end, the sag Y at the other end, given in Eq. (7), varies as

$$Y = -\frac{pg}{EI}\frac{l^{4}}{8t^{3}} \tag{7}$$

l^4/t^3. Historically, the analysis in terms of the moment of inertia I was begun by G. W. Leibniz in 1694, and results equivalent to the foregoing were obtained by C. Coulomb in 1773. The representation of the beam as a sheaf of fibers of infinitesimal thickness leads to the field equation (6), which is extremely simple in form and involves only the bulk properties of the material. *See* LOADS, TRANSVERSE.

Diffusion. In a vessel of fluid (liquid or gas) a small quantity of a different fluid is released and spreads slowly (in the absence of convection) through the vessel. To calculate the rate at which it spreads, let $n(x)$ be the number of molecules of the new fluid per unit volume, and $\mathbf{j}(x)$ be the flow (molecules per unit area per unit time) produced by any nonuniform distribution of n. This current has the direction in which n changes most rapidly, and the simplest assumption is that it is given approximately by Eq. (8),

$$\mathbf{j}(x) = -D\nabla n(x) \tag{8}$$

proposed by A. Fick in 1855, where D is the diffusivity, a coefficient which for simplicity is here assumed independent of x. If the molecules of the new fluid are neither created nor destroyed, $\mathbf{j}$ satisfies the conservation equation (9), and Fick's law becomes the

$$\nabla \cdot \mathbf{j} + \frac{\partial n}{\partial t} = 0 \tag{9}$$

field equation (10) giving the variation of n with po-

$$\frac{\partial n}{\partial t} = D\nabla^{2}n \tag{10}$$

sition and time. *See* CALCULUS OF VECTORS.

If the initial distribution of n is $n_0(x)$ and the region is so large that its boundaries are far away, this equation is easy to solve. Let $\tilde{n}(k)$ be the Fourier transform of $n_0(x)$, so that Eq. (9) is solved by Eq. (11) where

$$n(x, t) = \int \tilde{n}(k)\exp(i\mathbf{k}\cdot\mathbf{x} - k^{2}Dt)d^{3}k \tag{11}$$

the integration is over all values of k; this expression satisfies Eq. (9) whatever the function $\tilde{n}$ may be. If $t = 0$, the value of the integral is n_0, and if $t > 0$, Eq. (11) shows what happens as time goes on. For any $\tilde{n}$, as t becomes large, the distribution spreads and becomes uniform. (If $t < 0$, the integral shows correctly only in exceptional cases what happened earlier.)

The diffusion equation contains a single parameter, the diffusivity D. It can be determined from experiment and also in other ways, for diffusion can be analyzed as a random molecular process. The drag β that a diffusing particle experiences as it moves through the fluid is defined by Eq. (12), where v is

$$F = -\beta v \tag{12}$$

the particle velocity. Then the diffusivity can be calculated as in Eq. (13), where k is Boltzmann's con-

$$D = \frac{kT}{\beta} \tag{13}$$

stant and T is the absolute temperature. Evidently the warmer the environment and the less the resistance, the faster the diffusion. Equation (13) was first given by A. Einstein in 1905. *See* DIFFUSION.

Temperature, T, is another field quantity in classical physics, and the argument used for diffusion makes it plausible that heat diffusing through a solid follows the same law. Equation (14) duplicates the

$$\frac{\partial T}{\partial t} = \alpha^{2}\nabla^{2}T \tag{14}$$

diffusion equation and has the same solutions. The coefficient α is calculated in the theory of solids by methods that differ according to the physical properties of the solid. *See* CONDUCTION (HEAT).

Hydrodynamics. The calculation of the flow of a fluid presents great mathematical difficulties; in fact, the essentially chaotic nature of turbulence often makes it impossible to represent flow in terms of a continuously varying field. The following discussion is therefore restricted to nonturbulent motion. *See* TURBULENT FLOW.

The basic equation of fluid flow was given by L. Euler in 1755. In modern notation, it can be derived as follows: A small volume of the fluid moves with velocity $\mathbf{v}$. The force exerted on it by the pressure p of the surrounding fluid is

$$-\oint p d\mathbf{A}$$

where dA is an outward-directed element of area, and this is transformed by a vector identity into

$$-\int \nabla p dV$$

that is to say, the force on the element of fluid is $-\nabla p$ per unit volume. If p is the density of the fluid, Newton's law gives the equation of motion, Eq. (15), where the gravitational force on the element is included. It is more convenient mathematically to study changes in velocity at a given point in space than to follow an element of fluid as it moves.

$$\frac{\rho d\mathbf{v}}{dt} = -\nabla p + p\mathbf{g} \tag{15}$$

It is easy to show that Eq. (16) is valid, which gives Euler's equation (17).

$$\frac{d\mathbf{v}}{dt} = \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{v} \qquad (16)$$

$$\frac{\partial \mathbf{v}}{\partial t} = -(\mathbf{v}\cdot\nabla)\mathbf{v} - \frac{1}{\rho\nabla}p + \mathbf{g} \qquad (17)$$

Solutions of Euler's equation are as varied as the conditions under which fluids flow; to see what it does and does not contain let us look at a very simple case, the propagation of sound through a fluid. Let $p = p_0 + p'$ and $\rho = \rho_0 + \rho'$, where p_0 and ρ_0 are the ambient values, and assume that the amplitude is so small that second-order terms in p, ρ, and $\mathbf{v}$ can be neglected, as well as $\mathbf{g}$. In addition, $\mathbf{v}$ can be represented as $\nabla\phi$, where ϕ is called the velocity potential. Then Euler's equation gives Eqs. (18). Equations (19) compare the time derivative of Eqs. (18) with the conservation equation (9) expressed in terms of ϕ. An equation for ϕ is possible if p' can be expressed in terms of ρ'. To do this requires a hypothesis that is not included in either Euler's equation or the conservation law, namely, an equation of state for the fluid. If $(\partial p/\partial\rho)_0$ is denoted by c^2, comparison of Eqs. (18) and (19) gives Eq. (20),

$$\begin{aligned} \nabla\left(\frac{\partial\phi}{\partial t} + \frac{p'}{\rho_0}\right) &= 0 \\ \rho_0\frac{\partial\phi}{\partial t} + p' &= 0 \end{aligned} \qquad (18)$$

$$\begin{aligned} \rho_0\frac{\partial^2\phi}{\partial t^2} + \frac{\partial p'}{\partial t} &= 0 \\ \rho_0\nabla^2\phi + \frac{\partial\rho'}{\partial t} &= 0 \end{aligned} \qquad (19)$$

$$\nabla^2\phi - \frac{1}{c^2}\frac{\partial^2\phi}{\partial t^2} = 0 \qquad (20)$$

which is d'Alembert's equation for a wave traveling with velocity c.

The foregoing example shows how the equation of motion for the acoustical field arises from three hypotheses: Newton's second law, the conservation of the fluid, and its equation of state. Whereas the previous examples of field equations could have been derived by reasoning from the microscopic properties of matter, Eq. (20) would have been very difficult to derive in this way. *See* FLUID-FLOW PRINCIPLES; HYDRODYNAMICS; SOUND; WAVE EQUATION; WAVE MOTION.

Electromagnetic field. The theory of the electromagnetic field, which J. C. Maxwell developed during the 1860s, was intended as a phenomenological theory of the ether analogous to the theories outlined above. There is of course no ether, and therefore no phenomenological properties, but this was not known at the time, and to discover the properties of ether was generally considered the most important task of physics. Maxwell based his work on a microscopic model of the ether involving tiny whirling vortices, but when it was finished the model's phenomenological constants had almost entirely disappeared from the equations; only one remained. The electric current could be calculated from the theory in two ways, and the constant, now called c, is determined by the ratio of the two resulting numbers. During the succeeding 40 years Maxwell's equations were regarded as a clever device that gave correct answers while avoiding the important questions.

In terms ofthe electrodynamic potentials, using the modern International System of Units (SI), Maxwell's equations can be written in the form of Eqs. (21); here $\mathbf{A}(x)$ and $\varphi(x)$ are vector and scalar potentials, respectively, and $\mathbf{j}(x)$ and $\rho(x)$ are the current and charge densities, respectively, that produce them. They occur on the right sides multiplied by μ and $1/\epsilon$, respectively, and since $\mathbf{j}$ is simply the result of moving ρ, the units are effectively different in the two equations. Their ratio is $c^2 = 1/(\epsilon\mu)$; in Maxwell's day its value was approximately known. In empty space, $\mathbf{j} = \rho = 0$, and the equations are d'Alembert's for waves traveling at a speed c. The correspondence between this c and the measured speed of light was convincing evidence that light is an electromagnetic phenomenon.

$$\begin{aligned} \nabla^2\mathbf{A} - \epsilon\mu\frac{\partial^2\mathbf{A}}{\partial t^2} &= -\mu\mathbf{j} \\ \nabla^2\varphi - \epsilon\mu\frac{\partial^2\varphi}{\partial t^2} &= -\frac{1}{\epsilon}\rho \end{aligned} \qquad (21)$$

Maxwell's equations are still phenomenological in content, but they are now considered to describe the electromagnetic fields and potentials and not properties of the ether. They are fully relativistic and survive in form, though not exactly in content, in the modern theory of quantum electrodynamics. *See* ELECTROMAGNETIC RADIATION; MAXWELL'S EQUATIONS; QUANTUM ELECTRODYNAMICS; RELATIVISTIC ELECTRODYNAMICS.

Gravitational field. During the nineteenth century, tentative efforts were made to create a theory of gravity along the same lines as Maxwell's theory of electromagnetism. The results, however, were trivial, and the development of special relativity showed that they could not possibly be correct. Only with a reformulation of the entire problem in terms of curved space-time was Einstein able in 1915 to create a classical theory of the gravitational field. Like the classical theories mentioned above, it gives its results in terms of phenomenological constants: the speed of light and the force of attraction between two unit masses one unit distance apart. It is very successful in explaining not only the phenomena of gravitation known in 1915 but also various new facts that have been learned since. Unlike Maxwell's equations, however, Einstein's do not give reasonable results in the context of a quantum theory of gravity. They must represent some sort of approximation, but so far no successful quantum version has been developed with which they can be compared. *See* GRAVITATION; QUANTUM GRAVITATION; RELATIVITY.

Mathematical development. The foregoing examples illustrate some of the most important classical field theories. Solving the equations has produced a vast body of mathematics. Computers have aided in special calculations, but many mathematicians are working on the analytical theory of partial differential equations, and new results continue to be produced. *See* DIFFERENTIAL EQUATION. David Park

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Classical mechanics

The science dealing with the description of the positions of objects in space under the action of forces as a function of time. Some of the laws of mechanics were recognized at least as early as the time of Archimedes (287?–212 B.C.). In 1638, Galileo stated some of the fundamental concepts of mechanics, and in 1687, Isaac Newton published his *Principia*, which presents the basic laws of motion, the law of gravitation, the theory of tides, and the theory of the solar system. This monumental work and the writings of J. d'Alembert, J. L. Lagrange, P. S. Laplace, and others in the eighteenth century are recognized as classic works in the field of mechanics. Jointly they serve as the base of the broad field of study known as classical mechanics, or Newtonian mechanics. This field does not encompass the more recent developments in mechanics, such as statistical, relativistic, or quantum mechanics.

The general principles of classical mechanics are stated in mathematical form. With mathematical logic, one can deduce countless possible motions of bodies and then compare the predictions with experimental observations. Classical mechanics illustrates the essential nature of a physical theory, and it is usually an important ingredient in or a starting point for the various branches of modern physics. Its study offers one the opportunity to become acquainted with mathematical techniques and procedures which are useful in other fields.

In the broad sense, classical mechanics includes the study of motions of gases, liquids, and solids, but more commonly it is taken to refer only to solids. In the restricted reference to solids, classical mechanics is subdivided into statics, kinematics, and dynamics. Statics considers the action of forces that produce equilibrium or rest; kinematics deals with the description of motion without concern for the causes of motion; and dynamics involves the study of the motions of bodies under the actions of forces upon them. An important example of a force whose effect on bodies is often studied is the Earth's gravitational force. For some of the more important areas of classical mechanics *see* BALLISTICS; CANONICAL COORDINATES AND TRANSFORMATIONS; CELESTIAL MECHANICS; COLLISION (PHYSICS); DYNAMICS; ENERGY; FORCE; GRAVITATION; KINEMATICS; LAGRANGE'S EQUATIONS; MASS; MOTION; PRECESSION; RIGID-BODY DYNAMICS; STATICS; WORK.

The mathematical structure of classical mechanics is essential to understand both the historical development and the current status of relativity theory and of quantum mechanics. *See* QUANTUM MECHANICS; RELATIVITY. Newell S. Gingrich; John L. Safko

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Classical swine fever

A highly contagious epizootic disease of pigs, also known as hog cholera. The causative agent is a virus in the family Flaviviridae, genus *Pestivirus*. Due to its significant economic impact, this disease is the subject of statutory controls in a majority of countries. It has been eradicated from many areas, including the United States, Canada, Australasia, and most parts of Europe. Clinically and pathologically, it closely resembles African swine fever, which is caused by an unrelated virus.

Transmission. Classical swine fever affects domestic and feral pigs as well as European wild boar. Humans are not susceptible. The primary mode of transmission is by contact or proximity. Infected animals shed virus in all bodily secretions. The virus may also be spread by contact with contaminated equipment and vehicles. It can survive for many months in frozen or refrigerated meat from infected pigs, and is not inactivated by mild forms of curing. Most primary outbreaks of classical swine fever are attributable to the feeding of pigs with waste human foodstuffs containing uncooked pig meat. Pregnant sows that recover from classical swine fever infection may give birth to congenitally infected carrier piglets with or without clinical signs that are a source of infection for other pigs.

Clinical signs. Pigs of any age may be affected; however, clinical signs are more severe in young pigs. High fever, loss of appetite, and dullness are the most typical symptoms of the acute form of the disease. Other symptoms may include blotchy discoloration of the skin (particularly the extremities), incoordination and weakness of the hindquarters, constipation followed by diarrhea, conjunctivitis, and coughing. Death may occur within 4 to 7 days after onset of symptoms. Mortality is usually high among young animals. Older pigs often develop immunity and recover completely. Recovered sows may abort or may give birth to poor litters that experience congenital tremors and convulsions.

Some pigs develop chronic disease that is characterized by undulating fever, dullness, poor performance (such as decreased daily weight gain), capricious appetite, and variable degrees of coughing, diarrhea, and emaciation. There may be joint swellings and ulceration of the skin. These animals will die after 2 or 3 months.

Piglets that have been infected during pregnancy will develop the late-onset form of the disease, and death will occur within a few months after birth.

Strains vary in virulence, and classical swine fever may still be suspected when milder signs occur in epizootic form. Low-virulence strains may produce few signs apart from reproductive failure in sows or congenital tremors in their offspring.

Pathology. A few days after the infection, white blood cells and thrombocytes (platelets) are greatly reduced. Petechial (small, round) to confluent hemorrhages occur in the body, but particularly in the lymph nodes, kidneys, laryngeal mucosa, and urinary bladder. Infarcts are sometimes seen in the spleen. In chronic cases, a characteristic lesion is button ulceration of the large intestine. In cases of congenital infection, a proportion of piglets may show incomplete development of the cerebellum or other developmental abnormalities.

Microscopic and ultrastructural lesions include signs of microthrombosis (blood clot formation in the capillaries and other small blood vessels) and apoptosis (programmed cell death) as well as activation of macrophages and platelets. Damaged capillary endothelial cells lead to either obstruction or dilation of the vascular lumen and affect permeability. In addition, there is depletion of lymphocytes in the lymphoid tissues.

Diagnosis. The majority of outbreaks of classical swine fever are diagnosed on clinical grounds, especially in the severe acute form of disease; however, it is essential to carry out laboratory tests to confirm a presumptive diagnosis. Differential diagnoses include African swine fever, pseudorabies, porcine epidemic abortion and respiratory syndrome, porcine dermatitis and nephropathy syndrome, parvovirosis, bacterial septicemias (for example, salmonellosis, leptospirosis, swine erysipelas), thrombocytopenic purpura (a bleeding disorder), and poisoning with the rodenticide warfarin. Infections of pigs with the related pestivirus from cattle (bovine viral diarrhea virus) can occasionally cause similar symptoms and cross-reactions in diagnostic laboratory tests. *See* LEPTOSPIROSIS; SALMONELLOSES.

Control and vaccination. There is no specific treatment for classical swine fever. In classical swine fever–free countries, disease outbreaks are controlled by a stamping-out policy; that is, once the disease has been confirmed all pigs on affected and suspected farms are slaughtered to prevent further spread. Vaccination is usually prohibited, as it interferes with international trade. In areas with dense pig populations this policy might be very costly. Vaccination programs are widely practiced in regions with enzootic infection. Vaccination can control the severe clinical effects of the disease but cannot completely prevent infection and spread of the virus. Recently marker vaccines have been licensed. These vaccines are promising tools in the control of the infection, since they allow the distinction between vaccinated and infected animals. (Serological tests can be performed that detect the presence of antibodies to viral proteins that are produced only by the infected animals.) Thus, they can prevent the unnecessary slaughter of healthy animals. Epidemics of classical swine fever in wild boar populations may be long lasting and difficult to control. They are a threat to any local domestic pig holding. Specific hunting measures and oral vaccination campaigns are suitable tools to shorten the duration of these epidemics. *See* ANIMAL VIRUS; SWINE PRODUCTION; VACCINATION.

Volker Moennig; Steven Edwards

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Classification, biological

Arrangements of the names of species and groups of species meant to convey how these organisms are related to one another. The purposes of biological classifications are to organize the known biodiversity, provide a framework that will incorporate newly discovered biodiversity, and provide a predictive framework for studying biodiversity. Systematics focuses on studies of biodiversity and relationships among organisms. Taxonomy is a subdiscipline of systematics that focuses on formal classifications of organisms. *See* ANIMAL SYSTEMATICS; BIODIVERSITY; TAXONOMY.

Hierarchy of Ranks

Most, but not all, biological classifications are hierarchical, group-within-group arrangements in which a larger group will include one to many smaller groups within it. A group, or taxon, is given a formal name. The name refers to the organisms that are classified in the group. For example, *Homo sapiens* is the taxon name for all of the organisms classified as living humans, whereas Eukaryota is the taxon name for all plants, animals (including humans), and fungi. The place within a hierarchy is traditionally indicated using ranks. *See* TAXON; TAXONOMIC CATEGORIES.

Domain Eukaryota (organisms with organelles)
    Kingdom Metazoa (multicellular animals)
        Phylum Chordata (vertebrate animals and kin)
            Class Mammalia (mammals)
                Order Primates (primate mammals)
                    Family Hominidae (fossil and living humans)
                        Genus *Homo* (living humans and close relatives)
                            Species *Homo sapiens* (living humans)

Purposes and Applications of Modern Biological Classifications

Most systematists now agree that modern biological classifications must serve two purposes. First, they must serve the primary biological function of expressing the common ancestry relationships (phylogenies) of organisms when possible, that is, when we have reliable information from which we can infer these relationships. One of the major activities of systematists is discovering these phylogenies using the characters of organisms (from DNA to behavior) and building from their studies the Tree of Life. Second, biological classifications must serve as systems from which information about the relationships of organisms can be reliably obtained. This requires that the classifications be consistent with the Tree of Life for groups of organisms with reliable phylogenies. It also requires that names be used consistently so that all biologists understand their meaning.

Classifications have very important applications. For example, the manner in which bacteria are classified forms the basis for predicting the pathogenesis of newly discovered or unknown bacteria. The entire genomes of organisms, such as the mouse and roundworm, are used as model systems to understand the development and causes of disease. Where these organisms fit into a classification has great value in predicting how generalizable the results of this research might be and to which other organisms the findings might apply.

Medical researchers frequently use rats and mice as the first subjects of studies, but it is understood that research using monkeys and great apes is critical if the findings are to be applied to humans. This is because our biological classifications show a close evolutionary relationship between humans and chimps, and we know that the more a medical breakthrough applies to species closely related to humans, the better the chances that they are applicable to humans.

Development of Modern Biological Classifications

The history of the development of the purposes and uses of modern biological classifications has two major themes: (1) how biologists have agreed to name taxa in a way that the use of names is consistent across international borders and over generations and (2) how the function of classifications to serve the needs of modern evolutionary biology emerged with increasing understanding of the nature of taxa.

Use of consistent names. Our modern biological classifications date to classifications published by the eighteenth-century Swedish botanist Carol Linnaeus (1707–1778). Linnaeus gathered both his work and the works of others into volumes outlining his system for organizing plant (*Species Plantarum*, 1753) and animal diversity (*Systema Naturae*, 1758). Linnaeus was by no means the first person to classify plants and animals, but his system of binomial nomenclature (that is, giving each species a two-part name, such as *Homo sapiens*) was widely adopted.

Three International Codes of Nomenclature. By the midnineteenth century, the chaos caused by individual taxonomists proposing different names for the same groups resulted in international efforts to propose rules that govern both the way that names were formed and what names should be used for any particular group. These rules have evolved into the three International Codes of Nomenclature, one each for plants, animals, and prokaryotes (bacteria). Each code specified when the official nomenclature of a particular group begins. For example, animal names proposed before 1758 (that is, before publication of the 10th edition of *Systema Naturae*) cannot be used; only names proposed in the *Systema Naturae* or after the publication of this work are permissible. Other works were selected for other groups as the starting point for names. Further, when possible, the oldest name that was proposed for a group is the official name of the group (Principle of Priority). Finally, each code includes a principle of typification.

Typification signals the intention of the person who names a group, usually by pointing to an actual specimen (for species names) or species (for group names) that the original author meant to include in the taxon. For example, the commercially important Indo-Pacific tuna commonly known as the kawakawa tuna was first described in 1849 by T. E. Cantor. The current name of this species is *Euthynnus affinis* (Cantor, 1849) and a dry skin of the fish used by cantor in his description can be found in the Natural History Museum, London. We understand that Cantor's intention was to apply this name to this specimen because he made reference to the specimen and it still exists and can be studied. We infer that this is the same fish that Cantor named by comparing the skin to specimens that we continue to collect and harvest for commercial purposes, taking into consideration modern concepts of how species in nature can vary and how the specimens we collect might differ from the type specimen as a result of this variation.

Naming is also regulated by the various Codes. For example, all Codes require that species have two names, the name of a genus and a specific epitaph. *Homo sapiens* is the name for living humans, not "*sapiens*." *Pinus ponderosa* is the name of the ponderosa pine tree, not "*ponderosa*." The genus name is always capitalized and the specific epitaph is never capitalized. And, the name is always set apart from the rest of the text, usually by using italics. The names of higher taxa (those that have ranks higher than species) may have specific endings and are frequently formed using the names of lower taxa. For example, in zoological nomenclature, priority and typification extends to the level of the rank family. Family names take on the root of a genus name and end in "idea." Subfamilies take on the name of a type genus and carry the ending "inae." The names of Tribes take on a genus name and end with "ini." Using this knowledge, we can actually "decode" the classification of the kawakawa tuna:

Kingdom Animalia (animals)
- Phylum Chordata (animals with notochords)
  - Subphylum Vertebrata (animals with backbones)
    - Superclass Gnathostomata (vertebrates with jaws)
      - Class Osteichthyes (ray-fin fishes and tetrapods)
        - Subclass Actinopterygii (ray-fin fishes)
          - Order Perciformes (fishes related to perches)
            - Suborder Scombroidei (mackerels, billfishes, and tunas)
              - Family Scombridae (mackerels and tunas, but not billfishes)
                - Subfamily Scombrinae (tunas, mackerels)
                  - Tribe Thunni (tunas but not mackerels)
                    - Genus *Euthynnus* (lesser tunas, but not the larger tunas)
                      - Species *Euthynnus affinis* (Cantor, 1849)

These efforts to regulate the names of organisms were designed to result in an international language of classification; biologists in China would use the same name for the same organisms as biologists in Sweden. Since Latin was the unofficial language of western scientists when Linnaeus formed his systems of classification, Latin continued to be used. Although cumbersome for the layperson, this has effect of producing a "neutral" language for international communication, setting aside national or regional preferences.

Zoological Code. From Kingdom to Suborder, the rules of priority and typification do not apply in the Zoological Code, so zoologists are free to use the names they wish, subject to general community consensus. However, some names are traditionally derived from lower group names. For example, Perciformes is a name formed around the genus name *Perca*, to which the common yellow perches of Europe and North American belong. At the rank level Family, the rules begin to apply. Scombridae and Scombrinae refer to all fishes of the family that includes the genus *Scomber* (mackerels), Thunni refers to a tribe that includes the large tunas of the genus *Thunnus* and relatives, including *Euthynnus; E. affinis* is one of three species of that genus. The form of the name is subject to the grammatical rules of Latin, thus "Scombridae" rather than "Scomberidae." *See* ZOOLOGICAL NOMENCLATURE.

Botanical and Bacteriological Codes. The rules for plants and prokaryotes (bacteria) work a bit differently and are independent of zoological rules. The names of prokaryotes names must be registered in the approved Lists of Prokaryotic Names, but no such requirement exists for zoological or botanical names. Name endings of plant and prokaryote groups are mostly similar, but they differ from the endings for animal groups. In botany, typification is applied to all ranks, whereas in prokaryotes, it is applied only to ranks below class, and thus naming is more rigid. For example, the classification of the ponderosa pine tree is as follows:

Kingdom Plantae
- Division Pinophyta (the conifers)
  - Class Pinopsida (the conifers again)
    - Order Pinales (living conifers)
      - Family Pinaceae (pines but not yews or cypresses, etc.)
        - Genus *Pinus* (pines but not spruces, etc.)
          - Species *Pinus ponderosa*

This classification is very simple to decode because each name after Plantae refers to conifers, and *Pinus* is the type name of the entire Division, so all names leading to *Pinus* are formed around this name. Note that some names refer to the same group. For example, Pinophyta contains only one class, so Pinophyta and Pinopsida refer to exactly the same group of organisms. This redundancy is one of the quaint features of nomenclature when the rules state that each category rank be associated with a name. The first name, Pinophyta, serves a purpose, which is to classify conifers relative to other plants. The second name is redundant (and thus biologically unnecessary) but was retained to present a complete hierarchy of ranks. *See* BACTERIAL TAXONOMY; PLANT TAXONOMY.

Changing ideas of taxa. The International Codes have largely achieved their goal of promoting the consistent and regular use of taxon names. However, from the eighteenth century to the middle of the twentieth century, there was no general agreement on what constituted a "natural" classification. There were many ideas. Some of them, such as grouping in fives, seem quite quaint to modern readers. As late as the 1960s, there were three general "schools" competing for the attention of systematists (the others having faded into history). The evolutionary taxonomists, who emerged during the 1930s with the rise of the Neo-Darwinian Revolution, asserted that classifications should be based on phylogeny and similarity. The pheneticists, who emerged with the Computer Revolution of the 1950s, asserted that ideas of phylogeny were speculative and that taxonomic classification should be based on similarity alone. The phylogeneticists (cladists), led by the German entomologist Willi Hennig, emerged in the 1960s and asserted that there was a rigorous method for building phylogenies and that classifications should be based on phylogeny (common ancestry) alone, letting similarity fall where it may.

The pheneticists lost, in spite of sophisticated computer algorithms for calculating similarity, because there were too many ways to calculate similarity. Similarity, it seems is in the eyes of the beholder, and each beholder has a different idea. In addition, classification based purely on similarity mixes up the different types of similarities. That is, some similarities may be due to descent from a common ancestor (the evolutionary concept of homology), whereas other similarities may be gained independently, perhaps due to similar environmental selection pressures (the evolutionary concept of convergence). Classifications that mix the two kinds of similarity might miss some important phenomena. The evolutionary taxonomists also lost because their idea of basing classifications on a combination of phylogeny and similarity would make it difficult to determine whether a particular classification was based on phylogeny or on similarity (the use of which had already been rejected).

The phylogeneticists won for two reasons. First, they demonstrated rigorous methods for the reliable reconstruction of common ancestry relationships. Second, they demonstrated that their classifications had predictive power. However, there are costs; for example, many traditional taxonomic groups (such as Reptilia) are no longer recognized, and some groups traditionally ranked at very high levels (such as Aves) have been demoted. The group Reptilia has been abandoned because birds are more closely related to crocodiles than crocodiles are to lizards. Reptilia was what Hennig called a "paraphyletic group," a group that did not include all the descendants of a common ancestor. Only "monophyletic groups," groups that include all the descendants of a common ancestral species, are permitted. Otherwise, the classification becomes inconsistent with the phylogeny, and efficient retrieval systems cannot be based on inconsistency. Thus, groups such as Reptilia no longer appear in the most modern classifications even if they persist in introductory and general-interest publications. Further, there is no longer a "Class" Aves. Birds and crocodiles are classified along with dinosaurs in the taxon Archosauria. If ranks were applied (they are not in the National Center for Biotechnology Information, NCBI, taxonomy system), Aves would probably be a suborder (as would Mammalia), not a class. Further, certain questions simply disappear. For example, the question of whether *Archaeopteryx lithographica*, the famous "missing link" between birds and reptiles, is a bird or a reptile disappears if "Reptilia" is not a natural group and is thus unrecognized in taxonomy. Rather, two new questions appear: What is the relationship of *A. lithographica* to Aves and other archosaurs? Is this species more closely related to birds than to, for example, dromaeosaur dinosaurs (the raptors made famous in the movie "Jurassic Park")?

Biological meaning of classifications. The Codes of Nomenclature are designed to stabilize the names applied to organisms and regulate how names are formed. However, the modern rules are not meant to impose a particular view of what the names mean biologically. The debate over the biological meaning of classifications is significant because classifications form the framework for comparing organisms.

From the time of Linnaeus to the middle of the twentieth century, taxonomists generally thought that the rank of a taxon had some biological meaning. Exactly what was meant varied from taxonomist to taxonomist and from system to system, but generally the fact that a taxon was classified at the rank "Family" as opposed to the rank "Subfamily" was thought to confer some significance on the taxon that made it comparable to other taxa of the same rank. In one system this might take on the significance of some perceived perfection, echoing "the great chain of being," with classifications arranged from "lower" forms of life to "higher" forms of life, with humans at the pinnacle, an idea quite popular with medieval philosophers. In other cases, it might have signified the uniqueness of form or adaptation; this approach treated the arrangement of organisms as a form of strict classification in which the ranks formed classes and the classes had biological significance quite apart from the taxa. Thus, a group of fishes classified at the level in the hierarchy of Family (for example, mackerels and tunas in Scomberidae) was considered comparable to a group of frogs placed at the same Family level (for example, toads in Bufonidae).

Classification to systematization. Today, systematists are moving away from this old idea of classification. Linnaean ranks are meant only to place taxon names in the hierarchy. A family of frogs and a family of fishes are no longer considered equivalent in terms of some biological attributes; they are ranked as families only because that is where they happen to fit in the classification hierarchy relative to other fishes or other frogs. The exception is the species category. Species are hypothesized units of process (species give rise to other species through various evolutionary processes) and thus all recognized species are thought to be comparable. Monophyletic groups of species are not units of process, but they are units of history.

Using ranks to show relationships rather than to express a biological level of organization is referred to as systematization rather than classification. As biological classifications change to reflect strictly evolutionary/common ancestry relationships rather than grades or levels of organization, they no longer reflect ancient and outmoded ideas reflected in older notions of "classification." This is because we have come to understand that taxa, groups of organisms in nature, are not the static classes of Aristotle but the dynamic evolutionary units of Darwin. We can express the evolutionary relationships of these groups through the use of Linnaean ranks (such as family, order, genus) because the Linnaean system is a hierarchical system easily adapted to express the relationships that result from evolutionary descent. But, the ranks no longer have the same meanings; they are simply placeholders for which we could substitute any number of alternative systems, such as numerical codes or even simply the phylogeny. For example, the Tree of Life Project uses taxon names and tree graphs to express the relationships among taxa, dispensing with Linnaean ranks (but not Linnaean names) entirely. The NCBI, a repository for all the genetic information known for most organisms, is very consistent in following the various Codes in naming taxa but dispenses with ranking in favor of a linked indented list that can be used to navigate within and between taxa.

In the modern era, classifications are meant to convey specific information as to the evolutionary relationships of organisms to form predictive systems for comparison. Given this, is there any use for the seemingly outmoded, eighteenth-century systems of nomenclature represented by the various Linnaean Codes of Nomenclature? Interestingly, the answer is "yes." The major functions of the codes are to promote stability and correct use of the names of taxa. That these names now refer to groups of evolutionary significance rather than to static classes of preevolutionary taxonomists does not mean that the need for stable and universally understood names has disappeared. In fact, it means just the opposite: Natural taxa are the result of evolutionary descent and thus have biological significance and biological predictability. The need to have international codes that govern the use of these names is as important now as in the past. E. O. Wiley

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Clathrate compounds

Well-defined addition compounds formed by inclusion of molecules in cavities existing in crystal lattices or present in large molecules. The constituents are bound in definite ratios, but these are not necessarily integral. The components are not held together by primary valence forces, but are the consequence of a tight fit preventing the smaller partner, the guest, from escaping from the cavity of the host. Thus, the geometry of the molecules is the decisive factor.

Clathrate compounds are of theoretical interest because they represent a special type of bonding. In practice they can be used for separation of hydrocarbons, for stablization of drugs or pesticides, and as enzyme models.

Inclusion compounds can be subdivided into (1) lattice inclusion compounds (inclusion within a lattice which, as such, is built up from smaller single molecules); (2) molecular inclusion compounds (inclusion into larger ring molecules with holes); and (3) inclusion compounds of macromolecules (see **table**).

The best-known lattice inclusion compounds are the urea and thiourea channel inclusion compounds, which are formed by mixing hydrocarbons, carboxylic acids, or long-chain fatty alcohols with solutions of urea. Urea, in this case the host lattice, crystallizes in the presence of the other molecules in a particular crystal structure which contains long channels or tubes 0.4–0.5 nanometer in diameter. The hydrocarbons are accommodated in these channels, but only unbranched molecules find enough space to fit into the urea channel. The molar ratio of urea to hydrocarbon is simply determined by the lengths of the hydrocarbon molecule, not by any functional group. The longer the paraffin chain, the

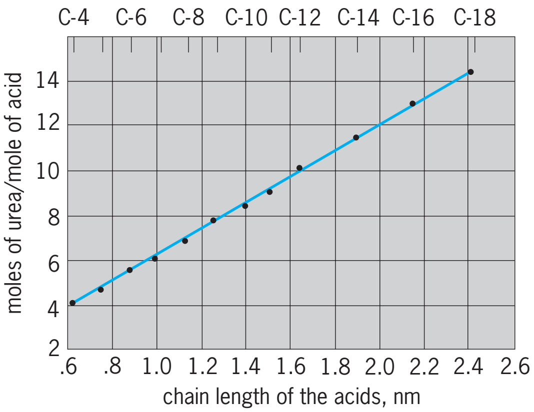

Fig. 1. Dependence of the urea/fatty acid composition of the inclusion compound on the chain length of the fatty acid. (*After W. Schlenk, Jr., Organic occlusion compounds, Fortschr. Chem. Forschg., 2:92–145, 1951*)

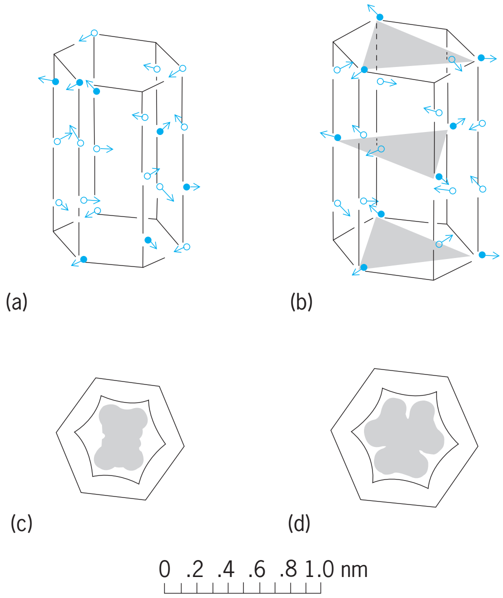

Fig. 2. Schematic drawing of the lattices of (*a*, *c*) urea and (*b*, *d*) thiourea; *c* and *d* show accommodation of unbranched and branched paraffin chains, respectively.

Inclusion compounds

Host substance	Shape of cavity	Guest substance examples
Lattice inclusion compounds		
Urea	Channel	Derivatives of straight-chain hydrocarbons
Thiourea	Channel	Branched-chain hydrocarbons
Deoxycholic acid	Channel	Paraffins, fatty acids, aromatic hydrocarbons
Dinitrodiphenyl	Channel	Diphenyl derivatives
Hydroquinone, phenol	Cage	Hydrogen chloride, sulfur dioxide, acetylene
Gas hydrates	Cage	Halogens, inert gases, hydrocarbons
Trithymotide	Cage	Benzene, chloroform
Nickel dicyanobenzene	Cage	Benzene, chloroform
Cyclodextrins	Channel or cage	Hydrocarbons, iodine, aromats
Molecular inclusion compounds		
Cyclodextrins	Cage	Hydrocarbons, iodine, aromats
Bis(*N,N′*-alkyl benzidines)	Cage	Benzene, dioxane
Crown ether compounds	Cage	Inorganic cations
Ionophore antibiotics	Cage	Inorganic cations
Inclusion compounds of macromolecular substances		
Clay minerals	Channel or sheet	Hydrophilic substances
Graphite	Sheet	Oxygen, bisulfate ion, alkali metals
Cellulose, starch	Channel	Hydrocarbons, dyes, iodine

more urea is necessary in order to envelop the paraffin (**Fig. 1**). Thiourea has a similar lattice structure, but a larger diameter of the channel. Therefore, only branched paraffins are included; the unbranched ones are too small, and cannot be held tightly (principle of closest packing), as shown in **Fig. 2**.

Other representatives of lattice inclusion compounds are the choleic acids, which are adducts of deoxycholic acid with fatty acids, and other lipoic substances. Most likely, these compounds play a role in the digestion process by emulsifying or dissolving fat and fat-soluble substances. Hydroquinone and phenol, cyclic anhydrides of phenol carboxylic acids, such as *o*-trithymotide and tetrasalicylide, as well as some other aromatic compounds, form an open crystal lattice which can accommodate smaller gas and solvent molecules (clathrates in the stricter sense of the word). The gas hydrates, which have been known since about 1810 (for example, $Cl_2 \cdot 6H_2O$), are inclusion compounds of gases in a somewhat expanded ice lattice. The gas or solvent molecules are inserted into definite places within the ice lattice and are surrounded by water molecules on all sides.

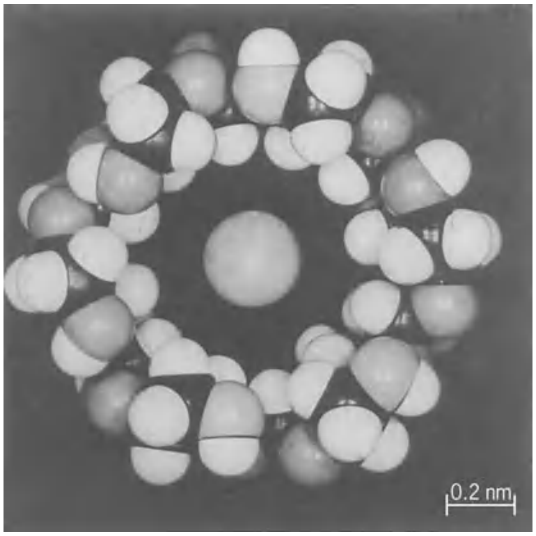

Fig. 3. Molecular model of α-dextrin–iodine compound seen in the direction of the *c* axis, that is, in the direction of the iodine chains, which lie in channels.

The cyclodextrins (cycloamyloses) are cyclic degradation products of starch which contain six, seven, or eight glucose residues (α-, β-, γ-cyclodextrin) and have the shape of large-ring molecules, the cavity diameters being 0.6–1.0 nm. Here, a great number of inclusion compounds in solution or in the crystalline state can be prepared with various kinds of molecules, the only requirement being the fit of the guest within the cyclodextrin cavity. α-Cyclodextrin forms blue iodine inclusion compounds in which the host molecules are stacked to form a cylinder reminiscent of the starch helix (**Fig. 3**). Polyiodide, located within the thus formed channellike cavity, consists of I_2, I_3^-, or I_5^- units in α-cyclodextrin, as well as in starch. A similar structure is likely for the blue iodine poly(vinyl alcohol) inclusion compound which exhibits a strong dichroism when stretched. This is used technically to prepare (light) polarizing sheets and spectacles.

Crown ether compounds are cyclic or polycyclic polyether compounds (for example, with the repeating unit . . . $O—CH_2—CH_2$. . .) capable of including another atom in the center of the ring. In this way, sodium or potassium compounds can be solubilized in organic solvents. Similarly, a series of ionophore antibiotics can complex inorganic cations. *See* MACROCYCLIC COMPOUND.

Some clay minerals are made up of distinct silicate layers. Between these layers some free space may exist in the shape of channels. Smaller hydrocarbon molecules can be accommodated reversibly within these channels. This phenomenon is used in some technical separation processes for separating hydrocarbons (molecular sieves). Furthermore, ion-exchange processes used for water deionization are based on similar minerals. *See* CLAY MINERALS; MOLECULAR SIEVE; ZEOLITE.

Enzymes are believed to accommodate their substrates in active sites, pockets, or clefts prior to the chemical reaction which then changes the chemical structures of the substrates. These binding processes are identical to those of low-molecular-weight inclusion compounds. On the other hand, some low-molecular-weight inclusion compounds can mimic enzyme action, such as ester hydrolysis, but only with modest efficiency.

Friedrich Cramer; Wolfram Saenge; D. Gauss

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Clay

A term used to refer to the finest-grain particles in a sediment, soil, or rock. According to the Wentworth scale (see **table**), clay is finer than silt, characterized by a grain size of less than approximately 4 micrometers. However, the term clay can also refer to a rock or a deposit containing a large component of clay-size material. Thus clay can be composed of any inorganic materials, such as clay minerals, allophane, quartz, feldspar, zeolites, and iron hydroxides, that possess a sufficiently fine grain size. Most clays, however, are composed primarily of clay minerals. *See* CLAY MINERALS; FELDSPAR; QUARTZ; ZEOLITE.

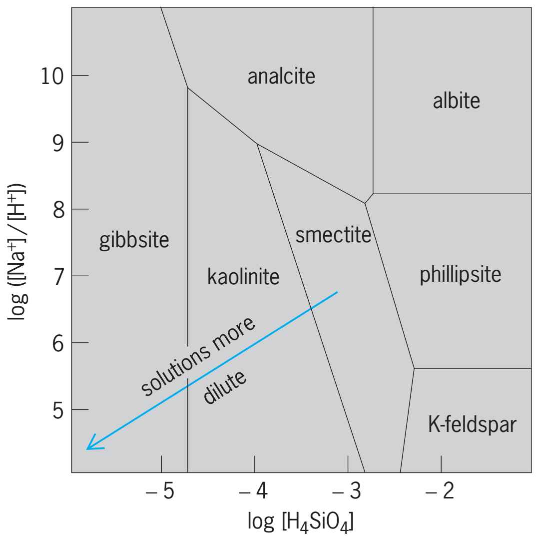
Although the composition of clays can vary, clays can share several properties that result from their fine particle size. These properties include plasticity when wet, the ability to form colloidal suspensions when dispersed in water, and the tendency to flocculate (clump together) and settle out in saline water. *See* COLLOID.

Origin and occurrence. Clays occur most abundantly in nature in soils, sediments, sedimentary rocks, and hydrothermal deposits.

Clays, together with organic matter, water, and air, are one of the four main components of soil. Clays can form directly in a soil by precipitation from solution (neoformed clays); they can form from the partial alteration of clays already present in the soil (transformed clays); or they can be inherited from the underlying bedrock or from sediments transported into the soil by wind, water, or ice (inherited clays). *See* SOIL.

Wentworth scale for size classification of sediment particles

Particle	Grain size, mm
Boulder	>256
Cobble	64–256
Pebble	4–64
Granule	2–4
Sand	1/16–2
Silt	1/256–1/16
Clay	<1/256



Example of a stability diagram for the system Na_2O-K_2O-Al_2O_3-SiO_2-H_2O drawn for log ($[K^+]/[H^+]$) = 4. The soluble species in brackets are in activity units. (*After J. I. Drever, The Geochemistry of Natural Waters, Prentice-Hall, 1982*)

The type of clays neoformed in a soil depends on the composition of the soil solution, which in turn is a function of climate, drainage, original rock type, vegetation, and time. Generally, neoformed clays that have undergone intense leaching, such as soils formed under wet, tropical climates, are composed of the least soluble elements, such as ferric iron, aluminum, and silicon. These soils contain clays such as gibbsite, kaolinite, goethite, and amorphous oxides and hydroxides of aluminum and iron. Clays formed in soils that are found in dry climates or in soils that are poorly drained can contain more soluble elements, such as sodium, potassium, calcium, and magnesium, in addition to the least soluble elements. These soils contain clays such as smectite, chlorite, and illite, and generally are more fertile than those formed under intense leaching conditions. The importance of the composition of soil solution to the type of clay neoformed at equilibrium can be shown quantitatively in mineral stability diagrams, such as that given in the **illustration**. *See* CHLORITE; GOETHITE; ILLITE; KAOLINITE.

Examples of clays formed by the transformation of other clays in a soil include soil chlorite and soil vermiculite, the first formed by the precipitation of aluminum hydroxide in smectite interlayers, and the second formed by the leaching of interlayer potassium from illite. Examples of inherited clays in a soil are illite and chlorite-containing soils formed on shales composed of these minerals. *See* SHALE.

Clays also occur abundantly in sediments and sedimentary rocks. For example, clays are a major component of many marine sediments. These clays generally are inherited from adjacent continents, and are carried to the ocean by rivers and wind, although some clays (such as smectite and glauconite) are neoformed abundantly in the ocean. Clays also are a chief constituent of shale, are found in pore spaces in sandstones, and are found dispersed in limestones, dolomites, and coals. The ashes that remain after coal is burned, for example, are the residue of clays and silts washed into coal swamps and later incorporated into the coal. Hydrothermal clays can form abundantly where rock has been in contact with hot water or steam. Illite and chlorite, for example, form during the deep burial of sediments, and smectite and chlorite form by the reaction of hot, circulating waters at ocean ridges. Kaolinite can form hydrothermally where hot springs invade volcanic ash, given proper solution chemistries. *See* COAL; DOLOMITE; GLAUCONITE; LIMESTONE; MARINE SEDIMENTS; SANDSTONE; SEDIMENTARY ROCKS.

Properties and uses. Various clays possess special properties which make them important industrially. Bentonite, a smectite formed primarily from the alteration of volcanic ash, swells; is readily dispersible in water; and possesses strong absorptive powers, including a high cation exchange capacity. These properties lead to uses in drilling muds, as catalysts and ion exchangers, as fillers and absorbents in food and cosmetics, and as binders for taxonite and fertilizers. Swelling clays also must be taken into account in building design. In agriculture, swelling clays in a soil may lead to undesirable tilth and water runoff characteristics, and to unexpected reactions with soil additives, such as the catalytic conversion of pesticides into other compounds, or the fixation of ammonia fertilizer. *See* BENTONITE; CATALYSIS; ION EXCHANGE; SOIL CHEMISTRY.

Kaolinite-rich clays are used as paper-coating materials because they are white and show desirable rheological properties; as additives to rubber because they can bind with organic compounds; and as refractory materials due to their high melting point. Other important uses for clays include the manufacture of brick, ceramics, molding sands, decolorizers, detergents and soaps, medicines, adhesives, liners for ponds and landfills, lightweight aggregate, desiccants, molecular sieves, pigments, greases, paints, plasticizing agents, emulsifying, suspending, and stabilizing agents, and many other products. Ore deposits sometimes are composed of clays (for example, lateritic nickel and bauxites), and clay in shale may play an important role in the generation of petroleum. *See* CLAY, COMMERCIAL; REFRACTORY.

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Clay, commercial

Commercial clays, or clays utilized as raw material in manufacturing, are among the most important nonmetallic mineral resources. The value of clays is related to their mineralogical and chemical composition, particularly the clay mineral constituents kaolinite, montmorillonite, illite, chlorite, and attapulgite. The presence of minor amounts of mineral or soluble salt impurities in clays can restrict their use. The more common mineral impurities are quartz, mica, carbonates, iron oxides and sulfides, and feldspar. In addition, many clays contain some organic material. *See* CLAY MINERALS.

Clay is an abundant raw material; however, certain high-grade types of clay deposits are limited in geographic occurrence and extent. Examples are the white kaolin clays found in abundance only in Georgia and South Carolina; the high-quality bentonites found in Wyoming, South Dakota, California, Texas, and Mississippi; and the attapulgite clays found in Georgia and Florida.

Kaolinitic clays. Clays containing a preponderance of the clay mineral kaolinite are known as kaolinitic clays. Several commercial clays are composed predominantly of kaolinite. These are china clays, kaolins, ball clays, fireclays, and flint clays. The terms china clay and kaolin are used interchangeably in industry. *See* KAOLINITE.

China clay. China clays are high-grade white kaolins found in the southeastern United States, England, Brazil, and many other countries. In Georgia and South Carolina, the largest producing states, the deposits are composed almost wholly of the mineral kaolinite and occur as lenticular-shaped bodies generally 6–25 ft (1.8–7.5 m) in thickness. Many grades of kaolin are used in the manufacture of ceramics (whitewares, refractories, and porcelain), paper, rubber, paint, plastics, insecticides, adhesives, catalysts, and ink. They are also used for many other industrial purposes.

Kaolin has the desirable properties of being white in color, very fine in particle size, nonabrasive (hardness 2–2.5 on Mohs scale), and chemically inert in most uses. The individual kaolin particle is a thin, flat, pseudohexagonal platelet, so tiny that approximately 10,000,000 spread on a postage stamp would form a layer thinner than the thickness of a human hair. This thin, flat particle shape is a distinct advantage in many uses. The grades of kaolin that are commercially available generally are based on particle size, color, and brightness.

By far the largest consumer of white kaolins is the paper industry, which uses them to make paper products smoother, whiter, and more printable. The kaolin is used both as a filler in the sheet to enhance opacity and receptivity to ink and as a thin coating (about 0.005 in. or 0.013 cm) on the surface of the sheet to make it smoother and whiter for printing. The clay coating makes possible sharp photographic illustrations and brilliant color printing. Other important properties of kaolin for paper manufacture are softness of texture, ease of dispersion in the coating formulation, and ability to produce a high-gloss finish.

Because of the trend toward whiter coatings and lighter-weight paper (to minimize postal charges), the kaolin producers have developed new products. The colorant in kaolin is generally iron and titanium minerals; through flotation procedures, selective flocculation, and high intensity magnetic separation, a portion of the iron and titanium can be removed, making a significantly whiter product. To aid in the development of lighter-weight coatings, a delaminated kaolin is produced. The thicker kaolin particles are separated by force to produce thin, white particles which give excellent coated-sheet properties with lighter coat weights.

In ceramics the kaolin clays are used in whitewares, sanitary ware, special refractories, and porcelain insulators. In whitewares and sanitary ware the kaolin provides a white body, gives easy molding properties, and adds strength, dimensional stability, and smooth surfaces to the finished product. Refractoriness, dimensional stability, and chemical inertness make the kaolins uniquely suitable for special refractories. In addition, the excellent dielectric properties of kaolin are very suitable for porcelain electric insulators. *See* CERAMICS; PORCELAIN.

In the manufacture of both natural and synthetic rubber, kaolin clays are used as a functional filler. The kaolin adds strength, abrasion resistance, rigidity, and whiteness. It costs less than most other fillers used in rubber.

In paint and ink kaolins are used as extenders because of their chemical inertness, smooth flow properties, ease of dispersion, nonabrasiveness, relatively low cost, and the high pigment volume concentrations that can be attained.

In plastics kaolin is used to provide smooth surfaces, dimensional stability, and better resistance to chemical attack, and to improve physical and electrical properties, to minimize water absorption, to reduce brittleness, and to lower costs.

In insecticides the inertness, low abrasiveness, and good adsorption and flow properties of kaolin make it an effective carrying agent in dust and spray forms.

A relatively new field is the chemical modification of kaolinite to make it an effective catalyst for use in petroleum refining. The kaolin is treated and calcined to produce zeolites, which are used as molecular sieves. Molecular sieves are widely used in petroleum refining.

Because the United States has very small reserves of bauxite, kaolin, which contains 38% Al_2O_3, has been studied as a source of alumina. Many patents utilizing either bases or acids to extract the alumina have been issued. Some companies which are basic producers of aluminum metal have acquired large reserves of kaolin, but to date no processing plants have been constructed.

Calcined clay is another commercial product of the kaolins. It is used in paint, ceramics, plastics, paper, and other materials. The calcined kaolins have the advantage of increased opacity and brightness. The kaolinite is changed during the calcination to the minerals mullite and cristobalite. The hardness after calcination is about 6.5 to 7 on Mohs scale, and therefore the calcined kaolin makes an exceptional, very fine polishing agent. This product is used in toothpaste, automobile polishes, and silver and brass polishes. High-temperature calcined kaolins (1803–2703°F or 984–1484°C) are used as grog by the refractory industry.

Ball clay. Ball clays are composed mainly of the mineral kaolinite but usually are much darker in color than kaolin. The term ball clay is used for a fine-grained, very plastic, refractory bond clay. Most ball clays contain minor amounts of organic material and the clay mineral montmorillonite. Usually ball clays are finer grained than china clays. This fineness, together with the montmorillonite and organic material, gives ball clays excellent plasticity and strength. For these reasons and because they fire to a light-cream color, ball clays are commonly used in whitewares and sanitary ware. Commercial deposits of ball clay are located in western Kentucky, western Tennessee, northern Mississippi, and northeastern Texas.

Fireclay. This term is used for clays that will withstand temperatures of 2730°F (1500°C) or higher. Such clays are composed primarily of the mineral kaolinite. The most common fireclays are the underclays, which occur directly under coal seams. Not all under-clays are fireclays because many contain materials that lower the fusion point to below 2730°F (1500°C). Fireclays are generally light to dark gray in color, contain minor amounts of mineral impurities such as illite and quartz, and fire to a cream or buff color. Most fireclays are plastic, but some are nonplastic and very hard; the latter are known as flint clays.

Fireclays are used primarily by the refractories industry. The refractoriness of fireclays is proportional to the amount of alumina present in the clay and is reduced by impurities such as calcium carbonate and iron compounds. The foundry industry uses fireclay to bind sands into shapes in which metals can be cast. From 10 to 15% fireclay is necessary to bind the sand grains together. Fireclay-bonded sands give the metal a smoother surface than when other clays, such as bentonite, are used, but equivalent or higher mold strengths can be attained with approximately one-third as much bentonite. In many cases even though the strength properties of bentonite-bonded sands are higher, fireclays are used if the cost of clay and transportation is lower. Large quantities of fireclay are mined in Pennsylvania, West Virginia, Kentucky, Ohio, and Missouri.

Flint clay. This term is used for a special type of fireclay. Flint clays are composed essentially of kaolinite and are also refractory but are nonplastic and very hard.

Diaspore clay. This clay is composed of the minerals diaspore and kaolinite. Diaspore is a hydrated aluminum oxide with an Al_2O_3 content of 85% and a water content of 15%. This mineral is quite hard (6.5–7 on Mohs scale) and very refractory. Diaspore clay is used almost exclusively by the refractories industry in making refractory brick. However, after calcination, it is sometimes used as an abrasive material. Diaspore clay is produced commercially in Missouri and Pennsylvania. It is found in nature mixed with flint and plastic fireclays. High-grade diaspore clay contains 65–70% Al_2O_3. When its Al_2O_3 content is 50–65%, this material is called burley clay.

Mullite. Mullite is a high-temperature conversion product of many aluminum silicate minerals, including kaolinite, pinite, topaz, dumortierite, pyrophyllite, sericite, andalusite, kyanite, and sillimanite. Mullite is used in refractories to produce materials of high strength and great refractoriness. Mullite does not spall, withstands the shock of heating and cooling exceptionally well, and is resistant to slag erosion. It is used in making spark plugs, laboratory crucibles, kiln furniture, saggars, and other special refractories. Mullite crystals occur as long needlelike or lathlike forms. The intermeshing of these crystals produces high-strength bodies. The only natural occurrence of mullite is on the island of Mull in the Western Isles of Scotland, and here it is found in such small quantities that it has no commercial significance.

Bentonites. Those clays that are composed mainly of the clay mineral montmorillonite and are formed by the alteration of volcanic ash are known as bentonites. They are used in many industries; the most important uses are as drilling muds, as bonding clays in foundries, as bonding agents for taconite pellets, and as adsorbents in many industries. *See* MONTMORILLONITE.

The largest producing areas of bentonite are Wyoming, western South Dakota, central and eastern Texas, and northeastern Mississippi. The Wyoming and South Dakota bentonites are known as sodium bentonites, because the montmorillonite has a relatively high sodium content. The Texas and Mississippi bentonites are known as calcium bentonites, because the montmorillonite has a relatively high calcium content. Sodium montmorillonite and calcium montmorillonite have significantly different physical properties which regulate their use and acceptance by many industries.

The term bentonite is a rock term, but in industrial usage it has become almost synonymous with swelling clay. Bentonite contains minor amounts of other clay minerals, particularly illite, chlorite, and kaolinite, and up to approximately 30% opal C-T, a partially amorphous form of silicon dioxide. The properties of the bentonites are largely dependent on the type and amount of montmorillonite present.

Drilling mud. Drilling mud consists of bentonite, water, a weighting material such as barite, and various electrolytes. This mud is circulated in the hole at all times while the drilling is progressing. The functions of the drilling mud are to remove the drill cuttings from the drill hole, to form a filter cake on the wall of the drill hole to keep the drilling fluid in the hole and prevent water in the rock formations from entering, to cool and lubricate the bit, and to prevent blowouts. Bentonite, especially the sodium variety, imparts high viscosity and shear strength to the mud and also imparts a property called thixotropy. A thixotropic body acts as a fluid when agitated and as a thick gel when standing. Because the properties imparted by the bentonites to the drilling fluid are so important to the success of the oil industry, these clays are an extremely important mineral commodity.

Bonding clay. Bentonites are used in the foundry industry to bind sands into desired shapes in which metals can be cast. Only 3–5% bentonite is needed to bond the sand grains together. Because of their fine particle size and their nature of their water adsorption, bentonites give the mold a higher green, dry, and hot strength than does any other type of clay.

Another use of bentonite as a bonding agent is in the taconite industry. Taconite, low-grade iron ore, is crushed into a fine powder and the iron particles are separated from silica and other rock particles magnetically or by flotation. The fine iron particles are pelletized with the aid of bentonite, of which 12–18 lb (5.4–7.2 kg) is used to pelletize a ton of ore.

Other uses. Bentonites are also used as bleaching clays to remove coloring matter from oils, and as clarifying agents for products such as wines and beers. Bentonite is used as an adsorbent for oils, insecticides, alkaloids, vitamins, proteins, and many other materials. Calcium montmorillonites generally have better decolorizing and adsorbent properties than the sodium variety. Bentonite suspensions in water are widely used in industry, in addition to that suspension used as a drilling mud by the petroleum industry. Some applications are as fire retardants, as media for suspending materials for medicinal purposes, and as media for suspending lumps of coal to separate them from heavier impurities. Sodium bentonites are the better suspending agents because of their higher viscosities. Large quantities of sodium bentonite are used to line irrigation ditches and to seal leaks in dams, because it forms an impermeable cake or film by swelling and filling the pores. Sodium montmorillonite swells in water to many times its original size. Other uses are as catalysts, emulsion stabilizers, deinking agents, suspending agents in enamels, plasticizers in ceramics and pastes, and ingredients in cosmetics. *See* BENTONITE.

Attapulgite clays. Attapulgite is a hydrated magnesium aluminum silicate with a needlelike shape. It is commercially produced from a small area in southwestern Georgia and northwestern Florida. The needlelike shape gives attapulgite its unusual properties; each individual needle is exceedingly small, about 1 micrometer in length and approximately 0.01 micrometer across. Attapulgite is used as a suspending agent, and gives high viscosity because of the interaction of the needles. Some commercial uses are as an oil well drilling fluid, in adhesives as a viscosity control, in oil base foundry sand binders, as thickeners in latex paints, in liquid suspension fertilizers, and as a suspending agent and thickener in pharmaceuticals. Other uses are as adsorbent beds for pets, floor adsorbents, carriers for agricultural chemicals, catalyst, flatting agent in paint, and anticaking agent. An unusual use is as a coating on paper used in NCR (no carbon required) multicopy business forms. The attapulgite acts as a catalyst to convert the dye intermediates to the colored dyes when the encapsulated intermediates are released by pressure. The names attapulgite and palygurskite are synonymous.

Miscellaneous clays. Most of these clays and shales contain mixtures of differing proportions of illite, chlorite, kaolinite, and montmorillonite, plus a variety of nonclay minerals. By far the largest user of these miscellaneous clays is the structural clay products industry. This industry manufactures brick, drain tile, sewer pipe, conduit tile, glazed tile, terra cotta, and other items.

The clays that can be used for the different structural clay products necessarily have wide variations in properties. For example, a clay that can be used for conduit tile must be very plastic and have high green and dry strength and uniform shrinkage; for drain tile or common brick, these properties do not have to be controlled so closely. In general, however, the properties of clays that are important in the manufacture of structural clay products are plasticity, green strength, dry strength, drying and firing shrinkage, vitrification range, and fired color. These properties are largely dependent on the composition of the clay and the particle size of the constituents.

Mining and processing. Almost all the commercial clays are mined by open-pit methods, with overburden-to-clay ratios ranging as high as 10 to 1. The overburden is removed by motorized scrapers, bulldozers, shovels, or draglines. The clay is won with draglines, shovels, or bucket loaders, and transported to the processing plants by truck, rail, aerial tramways, or belt conveyors, or as slurry in pipelines.

The clay is processed dry or in some cases, wet. The dry process usually consists of crushing, drying, and pulverizing. The clay is crushed to egg or fist size or smaller and dried usually in rotary driers. After drying, it is pulverized to a specified mesh size, such as 90% retained on a 200-mesh screen with the largest particle passing a 30-mesh screen. In other cases, the material may have to be pulverized to 99.9% finer than 325 mesh. The material is shipped in bulk or in bags. All clays are produced by this method.

Where more exacting products must be produced, as in the case of kaolins for the paper industry and bentonites for certain pharmaceutical uses, wet processing is used. In the case of kaolins, the material is slurried in water at the mine face at about 35–40% solids with the aid of a dispersant. The slurry is pumped to a degritting station, where the very coarse impurities are removed, and then through pipelines to the processing plant. The general processing steps are particle size fractionation, that is, separation into coarse and fine particles; magnetic separation and/or flotation to remove titanium and iron minerals, leaching out colloidal iron impurities; dewatering by filtration; and drying and pulverization. Fractionation is done by centrifuging or by gravity settling; dewatering by centrifuges, filter presses, or rotary vacuum drum filters; and drying by rotary, apron, drum, or spray driers. Most of the kaolin is shipped dry bulk by rail, but about 20% is bagged and shipped by rail or truck. Some kaolin is shipped in slurry form in tank cars at 70% solids.

Properties. Most clays become plastic when mixed with varying proportions of water. Plasticity of a materal can be defined as the ability of the material to undergo permanent deformation in any direction without rupture under a stress beyond that of elastic yielding. Clays range from those which are very plastic, called fat clay, to those which are barely plastic, called lean clay. The type of clay mineral, particle size and shape, organic matter, soluble salts, adsorbed ions, and the amount and type of nonclay minerals all affect the plastic properties of a clay.

Strength. Green strength and dry strength properties are very important because most structural clay products are handled at least once and must be strong enough to maintain shape. Green strength is the strength of the clay material in the wet, plastic state. Dry strength is the strength of the clay after it has been dried. Plasticity and green strength are closely related and are affected largely by the same variables. Dry strength is dependent on the proportion of fine particles present, the degree of hydration of the colloidal fraction, the method of forming the ware, and the extent of drying. The presence of a small amount of montmorillonite, which is of very fine particle size and highly hydrated, generally increases the dry strength.

Shrinkage. Both drying and firing shrinkages are important properties of clay used for structural clay products. Shrinkage is the loss in volume of a clay when it dries or when it is fired. Drying shrinkage is dependent on the water content, the character of the clay minerals, and the particle size of the constituents. Drying shrinkage is high in most very plastic clays and tends to produce cracking and warping. It is low in sandy clays or clays of low plasticity and tends to produce a weak, porous body. Montmorillonite in relatively large amounts (10–25%) causes excessive shrinkage, cracking, and slow drying. Firing shrinkage depends on the volatile materials present, the types of crystalline phase changes that take place during firing, and the dehydration characteristics of the clay minerals.

Vitrification range. The temperature range of vitrification, or glass formation, is a very important property in structural products. Vitrification is due to a process of gradual fusion in which some of the more easily melted constituents begin to produce an increasing amount of liquid which makes up the glassy bonding material in the final fired product. Some clays have a short vitrification range so that the temperature of the kiln must be very closely regulated. Illites, montmorillonites, and chlorites all have lower vitrification temperatures than kaolinite. Some nonclay minerals such as calcite and feldspar lower the vitrification temperature of the body by acting as fluxes. The degree of vitrification developed depends on the duration of firing as well as on the temperature attained. Usually the degree of vitrification is regulated by the amount of shrinkage and porosity that is needed in the final product. There is, however, a practical limit as to the amount of shrinkage and reduction in porosity than can be attained at a given temperature.

Color. Color is important in most structural clay products, particularly the maintenance of uniform color. The color of a product is influenced by the state of oxidation of iron, the state of division of the iron minerals, the firing temperature and degree of vitrification, the proportion of alumina, lime, and magnesia in the clay material, and the composition of the fire gases during the burning operation. The best white-burning clays contain less than 1% Fe_2O_3. Buff-burning clays contain 1–5% Fe_2O_3 and red-burning clays contain 5% or more Fe_2O_3. Other constituents also affect the color, but finely divided iron-bearing minerals are considered to be the principal colorants.

Uses. All types of clay and shale are used in the structural products industry but, in general, the clays that are used are considered to be relatively low grade. Clays that are used for conduit tile, glazed tile, and sewer pipe are underclays and shales that contain large proportions of kaolinite and illite. The semirefractory plastic clays found directly beneath the coal seams make the best raw material for the above mentioned uses. Brick and drain tile can be made from a wide variety of clays depending on their location and the quality of product desired. Clays used for brick and drain tile must be plastic enough to be shaped. In addition, color and vitrification range are very important. For common brick, drain tile, and terra-cotta, shales and surface clays are usually suitable, but for high-quality face bricks, shales and underclays are used. Geographic location is a prime factor in the type of clay used for structural clay products because, in general, these products cannot be shipped great distances without excessive transportation costs. Many raw materials of questionable quality are utilized in certain areas because no better raw material is available nearby. *See* BRICK; TILE.

Lightweight aggregate is produced from many types of clays and shales. The raw material is heated very rapidly in rotary kilns or sintering machines to the temperature range between incipient and complete fusion. After fusion has developed a molten jacket around the particle, certain constituents, if present, release gas to produce bloating and vesiculation. The molten jacket must be viscous enough to retain the expanding gas. Shales containing illites, montmorillonites, or chlorites, plus nonclay materials such as carbonates, sulfates, and organic matter, are the best raw material for lightweight aggregate. Adequate testing of a clay or shale is the only way to determine whether or not it will make a suitable lightweight aggregate. Mineral and chemical composition, particle size distribution, fusion temperature, and final strength of the aggregate particles are all important factors which control the production of lightweight aggregate from a clay or shale. The presence of a high percentage of kaolinite causes the material to be too refractory and the presence of excess fluxing agents causes the material to melt much too rapidly to control the vesiculation necessary to make the material lightweight.

The cement industry uses large quantities of impure clays and shales. Clays are used to provide alumina and silica to the charge for the cement kiln. Generally, a suitable clay can be found in the area in which the cement is being manufactured. *See* CEMENT; POTTERY; REFRACTORY.

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Clay minerals

Fine-grained, hydrous, layer silicates that belong to the larger class of sheet silicates known as phyllosilicates. Their structure is composed of two basic units. (1) The tetrahedral sheet is composed of silicon-oxygen tetrahedra linked to neighboring tetrahedra by sharing three corners to form a hexagonal network (**Fig. 1**). The fourth corner of each tetrahedron (the apical oxygen) points into and forms a part of the adjacent octahedral sheet. (2) The octahedral sheet is usually composed of aluminum or magnesium in sixfold coordination with oxygen from the tetrahedral sheet and with hydroxyl. Individual octahedra are linked laterally by sharing edges (**Fig. 2**). Tetrahedral and octahedral sheets taken together form a layer, and individual layers may be joined to each other in a clay crystallite by interlayer cations, by van der Waals and electrostatic forces, or by hydrogen bonding.

Because clay minerals are nearly ubiquitous in the Earth's upper crust, they offer a unique record of earth processes and earth history. Thus, the study of clay minerals forms an important branch of the science of geology. It has been suggested also that clay minerals may have been a necessary precursor for the origin of life by providing protection for primitive organic molecules, and by catalyzing their transformation into more complex substances. *See* PREBIOTIC ORGANIC SYNTHESIS.

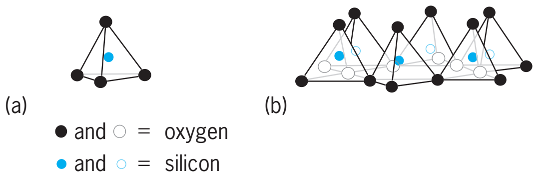


Fig. 1. Diagrammatic sketch showing (*a*) single silica tetrahedron and (*b*) sheet structure of silica tetrahedrons arranged in a hexagonal network. (*After R. E. Grim*, *Clay Mineralogy*, *McGraw-Hill*, *1953*)

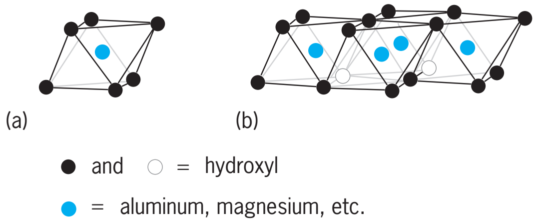


Fig. 2. Diagrammatic sketch showing (*a*) single octahedral unit and (*b*) sheet structure of octahedral units. (*After R. E. Grim*, *Clay Mineralogy*, *McGraw-Hill*, *1953*)

Classification. Clay minerals are classified by their arrangement of tetrahedral and octahedral sheets. Thus, 1:1 clay minerals contain one tetrahedral and one octahedral sheet per clay layer; 2:1 clay minerals contain two tetrahedral sheets with an octahedral sheet between them; and 2:1:1 clay minerals contain an octahedral sheet that is adjacent to a 2:1 layer (see **table**).

Ionic substitutions may occur in any of these sheets, thereby giving rise to a complex chemistry for many clay minerals. For example, cations small enough to enter into tetrahedral coordination with oxygen, cations such as Fe^{3+} and Al^{3+}, can substitute for Si^{4+} in the tetrahedral sheet. Cations such as Mg^{2+}, Fe^{2+}, Fe^{3+}, Li^{+}, Ni^{2+}, Cu^{2+}, and other medium-sized cations can substitute for Al^{3+} in the octahedral sheet. Still larger cations such as K^{+}, Na^{+}, and Cs^{+} can be located between layers and are called interlayer cations. F^{-} may substitute for $(OH)^{-}$ in some clay minerals. *See* COORDINATION CHEMISTRY.

Clay minerals and related phyllosilicates are classified further according to whether the octahedral sheet is dioctahedral or trioctahedral. In dioctahedral clays, two out of three cation positions in the octahedral sheet are filled, every third position being vacant. This type of octahedral sheet is sometimes known as the gibbsite sheet, with the ideal composition $Al_2(OH)_6$. In trioctahedral clay minerals, all three octahedral positions are occupied, and this sheet is called a brucite sheet, composed ideally of $Mg_3(OH)_6$. Some dioctahedral and trioctahedral clay minerals and related phyllosilicates are listed in the table.

Clay minerals can be classified further according to their polytype, that is, by the way in which adjacent 1:1, 2:1, or 2:1:1 layers are stacked on top of each other in a clay crystallite. For example, kaolinite shows at least four polytypes: *b*-axis ordered kaolinite, *b*-axis disordered kaolinite, nacrite, and dickite. Serpentine shows many polytypes, the best-known of which is chrysotile, a mineral that is used to manufacture asbestos products. *See* KAOLINITE; SERPENTINE.

Finally, clays are named on the basis of chemical composition. For example, two types of swelling clay minerals are the 2:1, dioctahedral smectites termed beidellite and montmorillonite. The important difference between them is in the location of ionic substitutions. In beidellite, charge-building substitutions are located in the tetrahedral sheet; in montmorillonite, the majority of these substitutions are located in the octahedral sheet. Other examples of chemistry used in classification are nontronite, an iron-rich beidellite, and sauconite, a zinc-containing beidellite.

Another family of clay minerals is the chain clays, which have a structural resemblance to the chainlike arrangement of silica tetrahedra in pyroxene. In sepiolite and palygorskite, 2:1 layers are joined at their corners to form long channels that can contain water, a few exchangeable cations, and other substances.

Because clay minerals are composed of only two types of structural units (octahedral and tetrahedral sheets), different types of clay minerals can articulate with each other, thereby giving rise to mixed-layer clays. The most common type of mixed-layer clay is mixed-layer illite/smectite, which is composed of an interstratification of various proportions of illite and smectite layers. The interstratification may be random or ordered. The ordered mixed-layer clays may be given separate names. For example, a dioctahedral mixed-layer clay containing equal proportions of illite and smectite layers that are regularly interstratified is termed potassium rectorite. A regularly interstratified trioctahedral mixed-layer clay mineral containing approximately equal proportions of chlorite and smectite layers is termed corrensite.

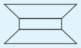
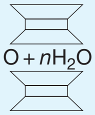
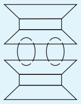
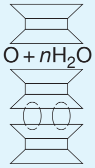
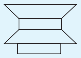
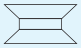
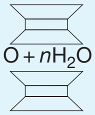
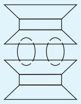
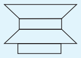
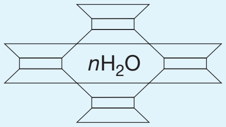
Properties. Many of the properties of clay minerals are related to their crystal structure. Some of these properties are discussed below.

Kaolinite-serpentine group. These 1:1 layer silicates possess a *c* dimension of approximately 0.7 nanometer. The dioctahedral clays include the polytypes of kaolinite mentioned previously. The trioctahedral minerals include varieties of serpentine such as chrysotile, antigorite, lizardite, and amesite. These clays are nonswelling in water, with the exception of halloysite, a variety of kaolinite which can swell to about 1.0 nm. Kaolinites, however, can be made to swell by using intercalation compounds. Kaolinites can be distinguished from serpentines in x-ray diffraction analysis by their smaller *b* dimension, and by heat treatment: the kaolinite structure will decompose at 550°C (1020°F), whereas the serpentine structure will not. Also, serpentines are more susceptible to acid attack and will not intercalate. The 1:1 clay minerals possess a cation exchange capacity of 3–15 milliequivalents per 100 g, this arising mainly from broken bonds on crystal edges. Kaolinites are used in the manufacture of ceramics, paper, rubber, and medicine. A variety of serpentine (chrysotile) is used to manufacture asbestos products such as fireproof cloth and brake linings. *See* HALLOYSITE.

Pyrophyllite-talc group. These 2:1 layer silicates possess a *c* dimension of slightly more than 0.9 nm and exist in several polytypes and chemical varieties. Talc generally shows a triclinic structure (lTc), but a disordered variety is called kerolite. Minnesotaite is an iron-rich variety of talc, and willemseite is a nickel-rich variety. Polytypes of pyrophyllite are monoclinic, triclinic, and disordered pyrophyllite. Generally, these 2:1 minerals possess a high thermal stability, have a low cation-exchange capacity, and do not swell in water or in intercalation agents. *See* PYROPHYLLITE; TALC.

Smectite group. These 2:1 clays possess a variable *c* dimension because of their ability to swell. It ranges generally from 1.2 to 1.5 nm in air, depending on the type of interlayer cation, on the layer charge, and on the relative humidity. When saturated with ethylene glycol, however, smectites will swell to approximately 1.7 nm regardless of these factors, and therefore this treatment is a commonly used test for smectite. The ability to swell and other unusual properties associated with this group arise from isomorphous

Some dioctahedral and trioctahedral clay minerals and related phyllosilicates

Type	Layer structure*	Mineral	Idealized formula
		DIOCTAHEDRAL	
1:1		Kaolinite	$Al_2Si_2O_5(OH)_4$
2:1		Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
		Dioctahedral smectite	
		Beidellite	$Al_2(Si_{3.7}Al_{.3})O_{10}(OH)_2Na_{.3} \cdot nH_2O$
		Montmorillonite	$(Al_{1.7}Mg_{.3})Si_4O_{10}(OH)_2Na_{.3} \cdot nH_2O$
		Dioctahedral vermiculite	$Al_2(S_{3.2}Al_{.8})O_{10}(OH)_2Mg_{.4} \cdot nH_2O$
		Illite	
		Muscovite	$Al_2(Si_{3.2}Al_{.8})O_{10}(OH)_2K_{.8}$
		Celadonite	$Al_2(Si_3Al)O_{10}(OH)_2K$
		Leucophyllite	$(Fe,Al,Mg)_2Si_4O_{10}(OH)_2K$
		Mixed-layer illite/smectite	
2:1:1		Dioctahedral chlorite	$Al_4Si_4O_{10}(OH)_8$
		TRIOCTAHEDRAL	
1:1		Serpentine	$Mg_3Si_2O_5(OH)_4$
2:1		Talc	$Mg_3Si_4O_{10}(OH)_2$
		Trioctahedral smectite	
		Saponite	$Mg_3(Si_{3.7}Al_{.3})O_{10}(OH)_2Na_{.3} . nH_2O$
		Hectorite	$(Mg_{2.7}Li_{.3})Si_4O_{10}(OH)_2Na_{.3} . nH_2O$
		Trioctahedral vermiculite	$Mg_3(Si_3Al)O_{10}(OH)_2Mg_{.5} . nH_2O$
		Phlogopite	$Mg_3(Si_3Al)O_{10}(OH)_2K$
2:1:1		Trioctahedral chlorite	$Mg_6Si_4O_{10}(OH)_8$
		Sepiolite	$Mg_8Si_{12}O_{30}(OH)_4(OHH)_4 \cdot 8H_2O$
Chain		Palygorskite (attapulgite)	$Mg_5Si_8O_{20}(OH)_2(OHH)_4 \cdot 4H_2O$

*Tetrahedral sheets are drawn as trapezoids, octahedral sheets as rectangles, and interlayer cations as circles. The *c* axis is approximately parallel to the table's columns.

substitutions in the tetrahedral and octahedral sheets which give rise to a negative charge on the 2:1 layers. This charge is balanced by interlayer cations which usually are hydrated.

The association of water with interlayer cations gives rise to crystalline (or first-stage) swelling for smectites. Smectities may undergo further osmotic (second-stage) swelling in wet environments if the interlayer cation is Na^+ or Li^+. In third-stage swelling, 2:1 layers are dispersed completely in water. An osmotically swelling smectite may be transformed into a smectite that undergoes only the more limited form of crystalline swelling by exchanging interlayer Na^+ for a divalent cation such as Ca^{2+}. Other properties related to the expanded interlayer region are a large cation-exchange capacity, a large surface area, and a Brönsted acidity related to a greater degree of dissociation for interlayer water. Many of these properties may be lost, either reversibly or irreversibly, by heating smectite in air to drive off interlayer water, thereby causing the 2:1 layers to collapse around interlayer cations. Water also can be driven out of the interlayer by increasing negative charge on 2:1 layers. This process happens spontaneously in nature during burial metamorphism, wherein layer charge is increased, leading to water expulsion and layer collapse around interlayer K^+, thereby transforming smectite into illite. The many industrial uses for smectite include drilling muds, binders, cation exchangers, and catalysts.

Vermiculite group. Clays in this group are similar to smectite, except that a larger layer charge leads to a decreased ability to swell, although some can swell osmotically under certain conditions. Their *c* dimension is about 1.4 nm, and generally, unlike smectite, they will not swell further in ethylene glycol. Many vermiculites will collapse to 1.0 nm on potassium exchange and on heating in air. Like smectite, these clays also possess special properties related to the expanding interlayer region, including a large cation-exchange capacity and surface area. Macroscopic vermiculite is exploded by heating in air for use in potting soil and insulation. Some micas and illites can be transformed into vermiculite by replacing interlayer K^+ with cations of greater hydration energy. *See* VERMICULITE.

Illite group. These clays possess a *c* dimension of about 1.0 nm. They are nonswelling and possess a small cation-exchange capacity, unless they are interlayered with smectite to form mixed-layer illite/smectite. Illite/smectites show properties intermediate between pure illite and smectite. Illite's layer charge and potassium content are less than those of a true mica. *See* ILLITE.

Chlorite group. Chlorites, like vermiculites, show a *c* dimension of about 1.4 nm, but unlike vermiculite, they will not collapse on heating or potassium saturation. Chlorites share many polytypes and chemical varieties. *See* CHLORITE.

Sepiolite and palygorskite. The structure of these minerals are similar, except that sepiolite shows a *b* dimension of about 1.21 nm, whereas that for palygorskite is about 1.04 nm. This difference arises from the fact that palygorskite incorporates only two linked pyroxenelike chains in each 2:1 layer rather than three. Both clays possess a fibrous morphology and channels which can accommodate water and a few cations. The ability of these channels to absorb organic substances gives rise to their use in clarification. Sepiolite also is used to manufacture meerschaum tobacco pipes. *See* SEPIOLITE; ZEOLITE.

Origin. A primary requirement for the formation of clay minerals is the presence of water, because clay minerals are hydrous silicates. Hence clay minerals are not expected to form on the Moon because there is no water on the Moon. Evidence for the presence of water on Mars, and the unusual catalytic properties of Martian soil, suggest that clay minerals may be present on this planet. Likewise, the presence of clay minerals in some meteorites suggests that these materials have been exposed to water during some part of their long and complex history.

Clay minerals form on Earth in many different environments, including the weathering environment, the sedimentary environment, and the diagenetic-hydrothermal environment. Clay minerals composed of the more soluble elements (for example, smectite and sepiolite) are formed in environments in which these ions can accumulate (for example, in a dry climate, in a poorly drained soil, in the ocean, or in saline lakes), whereas clay minerals composed of less soluble elements (for example, kaolinite and halloysite) form in more dilute water such as that found in environments that undergo severe leaching (for example, a hilltop in the wet tropics), where only sparingly soluble elements such as aluminum and silicon can remain. Illite and chlorite are known to form abundantly in the diagenetic-hydrothermal environment by reaction from smectite. *See* CLAY; CLAY, COMMERCIAL; LITHOSPHERE; SILICATE MINERALS.

Dennis D. Eberl

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Clear-air turbulence

Turbulence above the boundary layer but not associated with cumulus convection. The atmosphere is a fluid in turbulent motion. That turbulence of a scale sensed by humans in aircraft is primarily associated with the boundary layer within a kilometer or so of the Earth, where it is induced by the surface roughness, or in regions of deep convection such as cumulus cloud development or thunderstorms. However, aircraft occasionally encounter turbulence when flying at altitudes well above the surface and far from convective clouds. This phenomenon has been given the rather unsatisfactory name of clear-air turbulence (CAT).

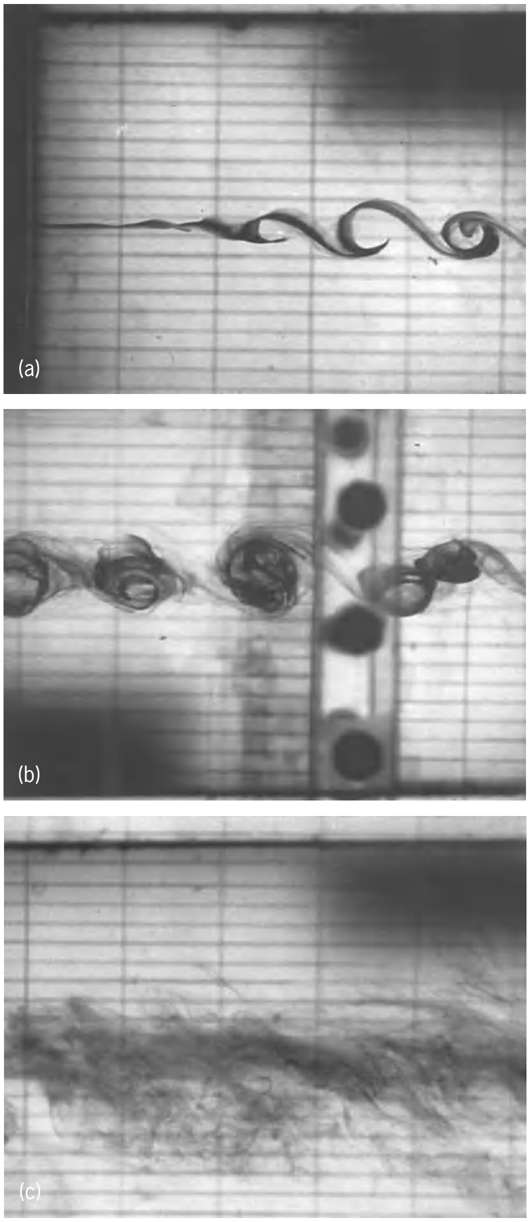
What is a primarily sensed in clear-air turbulence by the human is vertical acceleration. This acceleration will depend on the person's location in the plane, the speed of flight relative to the air, and the response characteristics of the airframe. A plane with a wing that generates aerodynamic lift more efficiently or an airframe with less weight per unit wing area will respond more strongly to a given gust magnitude. When allowances are made for different tolerance thresholds in different humans, a rough scale for subsonic aircraft has become accepted, with one-tenth the acceleration of gravity (*g*) as the threshold for light clear-air turbulence, 0.5 *g* for moderate, and 1 *g* for severe. *See* AEROELASTICITY.

Occurrence. Clear-air turbulence is encountered in the atmosphere with probability depending on flight altitude, geographical location, season of the year, and meteorological conditions. Given this variability and the small scale of the phenomenon, it is difficult to establish reliable statistics on the frequency of its occurrence. A number of extensive investigations have been carried out with this aim. One of these was a series of 90 flights by the National Aeronautics and Space Administration (NASA) supersonic aircraft YF-12A. At commercial-jet cruising levels (around 7.5 mi or 12 km), clear-air turbulence was encountered during approximately 12% of flight time in winter and 4% in summer. Above 11 mi (18 km) altitude (in the stratosphere) the frequency falls off rapidly. Other NASA studies have estimated clear-air turbulence frequency below 7.5 mi (12 km) to be somewhat increased, especially over mountainous terrain. The turbulent patches varied from 0.5 or 1.5 mi (1 or 2 km) in length to as large as 30 mi (50 km), although such large patches were very infrequent. The depth of the turbulent air was found to be almost always less than 0.6 mi (1 km).

Although clear-air turbulence may be encountered in unexpected meteorological contexts, there are highly favored locations for its occurrence. One is in the vicinity of the jet stream, particularly in ridges and troughs where the wind direction is turning sharply. A second and even more common location of occurrence is in the lee of a mountain range when a strong air flow is distorted by being forced over the range. In this situation a gravity lee wave is generated, which propagates to stratospheric heights. At various altitudes and distances from the mountain, this wave may break, and as many as a dozen or more patches of clear-air turbulence, light to severe, may be formed. *See* JET STREAM.

Forecasting and detection. Despite knowledge of these favored meteorological areas, it is not possible to forecast with confidence the precise location of a patch of clear-air turbulence. Warning forecasts for substantial portions of routes are typically given to pilots when conditions of clear-air turbulence prevail.

In view of this situation, effort has been expended to develop remote-sensing systems to give warning of a patch of clear-air turbulence with sufficient lead time to be avoided by minor diversions of flight path or at least to assure that all passengers are seated with safety belts fastened. Some ground-based techniques have the capability to produce a unique clear-air turbulence signature; of these, ultrasensitive radar probably has had the most demonstrable success. However, it is clearly impracticable to attempt to monitor any significant portion of commercial flight paths with costly ground-based instrumentation. Airborne infrared and microwave sensors, some using multiple frequencies, detect sharp temperature gradients or water-vapor concentration irregularities. The usefulness of these as clear-air turbulence warning systems is a subject of vigorous debate and investigation. *See* AERONAUTICAL METEOROLOGY; METEOROLOGY.



Laboratory realization of (*a*) Kelvin-Helmholtz instability, (*b*) the subsequent generation of turbulent eddies, and (*c*) mixing and dissipation. Fluid flow is left to right. (*Courtesy of Drs. G. G. Koop and F. K. Browand*)

Flight safety. Despite sophisticated design techniques applied to airframe response and despite pilot avoidance procedures, clear-air turbulence is still a factor in 10% of air transport accidents and safety incidents in the United States. Of all weather-related accidents, at least 20% may be associated with turbulence in flight.

Origin and explanation. The early observational documentations of clear-air turbulence excited much theoretical interest and speculation as to the fluid-dynamic explanation of this phenomenon. The consensus of researchers is that clear-air turbulence is the result of Kelvin-Helmholtz instability, a breakdown of smooth flow that occurs when the destabilizing velocity gradient of the fluid becomes large relative to the stabilizing density gradient.

It was initially obvious that this hypothesis was consistent with the occurrence of clear-air turbulence in the jet stream and in distorted flow downwind of mountain ranges where velocity gradients are large. Further quantitative experiments in the field identified a number of clear-air turbulence events precisely under the theoretically predicted conditions. In the laboratory it has been possible to reproduce the instability mechanism and follow its breakdown into turbulence (see **illus.**). This is the dynamic mechanism widely thought to be the fundamental one in clear-air turbulence.

One way of viewing clear-air turbulence is as an increase in energy of the smaller scales (30 ft to 0.6 mi, or 10 m to 1 km) of atmospheric motion. This is best presented in a spectral diagram, that is, a graph of energy versus wavelength.

Aside from the practical implications of clear-air turbulence for air transport, this phenomenon plays a role of undetermined magnitude in the dissipation of the kinetic energy of the atmosphere. *See* UPPER-ATMOSPHERE DYNAMICS.

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Cleavage (developmental biology)

The subdivision of fertilized eggs (zygotes) into progressively smaller cells called blastomeres. **Figure 1** shows the development of the frog *Xenopus laevis* from the fertilized egg to the stage of the hatched larva (tadpole). At an intermediate stage called blastula, the *Xenopus* embryo is a hollow sphere of blastomeres surrounding a fluid-filled cavity called the blastocoel. Cleavage covers the period from egg to midblastula, when the *Xenopus* embryos consists of about 1200 cells. *See* BLASTULATION.

Cleavage shares the basic characteristics of most cell divisions. First, the cell nucleus is duplicated in a process known as mitosis. Then the cytoplasmic body of the cell divides so that each daughter cell inherits part of the cytoplasm along with one nucleus. The division of cytoplasm, called cytokinesis, may be executed by a contractile ring of proteins that pinches the daughter cells apart. This mode of cytokinesis is typical of eggs that are cleaved in their entirety, as in *Xenopus* and many other species. Alternatively, cytokinesis may occur by folds growing out from the outer cell membrane. This mode is characteristic of large eggs that contain major amounts of yolk, as do the eggs of birds, reptiles, and fishes. Here, only a small disc of yolk-free cytoplasm is cleaved while the yolky part of the egg remains undivided. *See* CELL DIVISION; CYTOKINESIS; MITOSIS.

Nucleocytoplasmic ratio and midblastula transition. Cleavage differs from later cell divisions by its fast pace, which leaves little or no time for cell growth. Thus, blastomeres become smaller and smaller while the overall size of the embryo remains nearly constant. One advantage of this fast pace is the rapid increase of the nucleocytoplasmic ratio, that is, the number of gene copies (typically two) relative to the volume of cytoplasm. Most cells need nuclear DNA to maintain a healthy turnover of their RNA and protein molecules. Embryos can synthesize new proteins using an endowment of maternal RNA (stored while the egg was growing in the ovary) but only for a limited time. Another advantage of rapid cleavage is the shortening of embryonic development, a period during which organisms are especially vulnerable to parasites and predators.

Typically, cleavage divisions slow down during the blastula stage. The longer cell cycles leave time for blastomeres to transcribe their nuclear DNA into RNA, which then replaces the maternal RNA. Along with making their own RNA, blastomeres may synthesize more protein and begin to grow between cell divisions. As blastomeres use their own genetic information, they may drive their cell cycles at different speeds, causing them to fall out of synchrony. Around the same time, blastomeres may also start moving relative to one another in different ways. In *Xenopus*, all these changes occur simultaneously at the blastoderm stage and are known as the midblastula transition, or MBT. In other species, MBT events may occur at successive stages. It is thought that key MBT events are triggered when the nucleocytoplasmic ratio reaches a threshold level, possibly as some cytoplasmic component is titrated out by nuclear DNA. *See* CELL CYCLE; DEOXYRIBONUCLEIC ACID (DNA); RIBONUCLEIC ACID (RNA).

Role of cleavage in cell determination. Cleavage is the beginning of a developmental process that will lead to the formation of specialized cells, such as epidermal or blood cells. What becomes of a blastomere in the course of normal development is called its fate. However, in most species early blastomeres are not restricted to their fate but are pluripotent, meaning they are capable of forming multiple embryonic parts. For instance, when the blastomeres of a frog embryo are teased apart at the two-cell stage, each may give rise to a complete larva. Conversely, two complete mouse embryos, when stuck together experimentally and reinserted into the uterus of a foster mother, will give rise to one mouse consisting of a mosaic of cells derived from the two constituent embryos.

The stepwise process that restricts pluripotent blastomeres to their fate is known as cell

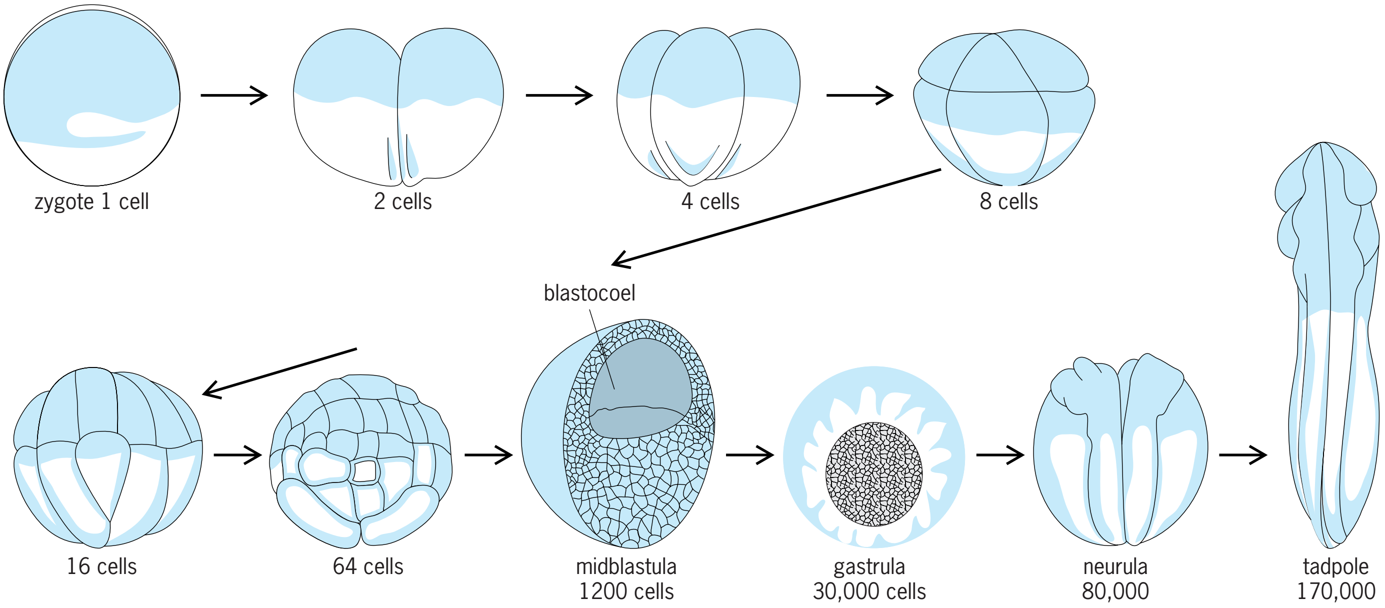

Fig. 1. Development of the African clawed frog, *Xenopus laevis*, from the fertilized egg to the tadpole stage. The midblastula stage is shown in section to reveal the blastocoel. (*Modified from K. Kalthoff, Analysis of Biological Development, 2d ed., McGraw-Hill, 2001*)

determination. In many embryos, such as amphibians, cell determination relies in part on asymmetrically distributed molecules in the egg cytoplasm, which are segregated into different blastomeres as the egg is cleaved. These cytoplasmic determinants elicit different patterns of gene activity in the enclosed cell nuclei. Blastomeres that have inherited different cytoplasmic determinants may later exchange signals that lead to increasingly complex patterns of cells with different determined states. In some species, the process of cell determination occurs early; their embryos cleave in stereotypical patterns that are virtually identical from one embryo to the next. In other species, cleavage patterns are more variable, and blastomere determination relies more on later adjustments by intercellular signals.

Cleavage of mammalian embryos. Cleavage of mammalian embryos is peculiar in several respects. The mammalian egg is unusually small (about 0.1 mm in diameter) and cleaves at a very leisurely pace. Embryonic RNA synthesis starts at the two-cell stage, and cell growth begins early on. All these traits are possible because the embryo develops in the uterus, which provides nutrients and protects the embryo from parasites and predators. The mammalian cleavage pattern produces a ball of cells, which secrete fluid to generate a blastocoel in an off-center position. This leads to the hallmark stage of mammalian development known as the blastocyst (**Fig. 2**). The blastocyst consists, in part, of an outer cell layer known as the trophoblast, which contributes to the formation of the placenta. Positioned excentrically within the trophoblast is the inner cell mass, or ICM, which gives rise to the embryo proper.

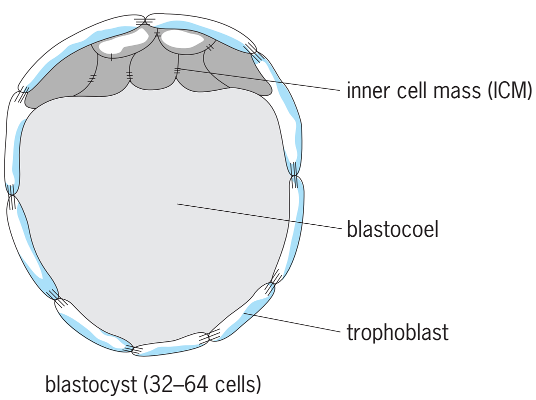

Fig. 2. Mammalian embryo at the blastocyst stage (about 50 cells). (*Reprinted with permission from K. Kalthoff, Analysis of Biological Development, 2d ed., McGraw-Hill, 2001*)

ICM cells are of medical interest because, if cultured under favorable conditions, they may give rise to embryonic stem cells, or ES cells. ES cells divide and grow indefinitely in an undifferentiated state, and they can divide asymmetrically, with one daughter being again an ES cell while its sister cell becomes a committed progenitor cell. The latter, depending on signal molecules in the culture medium, may give rise to all kinds of specialized cells, such as neurons or heart muscle cells. ES cells may, therefore, be used for cell replacement therapy for patients with diseases that leave certain cell lineages dysfunctional, such as Parkinson's disease or heart muscle failure. Cell replacement would be especially useful in conjunction with another technique known as nuclear transfer. Here, the nucleus of a cell from the patient is transferred into an enucleated human egg, which is grown in culture to the blastocyst stage. ICM cells are then harvested to raise ES cells that carry the patient's genetic information, so that their descendants will not be rejected by the patient's immune system. *See* EMBRYONIC DIFFERENTIATION; STEM CELLS.

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Cleft lip and cleft palate

Two of the most common congenital anomalies in humans, resulting from incomplete closure of the lip and palate during early embryonic life. During the first trimester of pregnancy, the face and mouth are formed by the fusion of several different parts. The lip is fully fused 6 or 7 weeks after fertilization. The palate, which forms the roof of the mouth and separates the oral cavity from the nasal cavity, is fully fused 10 weeks after fertilization. If fusion fails to occur or breaks down, an opening, or cleft, occurs in the lip, the palate, or both. Although cleft lip and cleft palate are associated with separate embryologic events, that is, are separated by a long time on the embryonic time scale, both often occur in an affected individual. Clefts vary in frequency among racial subgroups, with incidence ranging from 1 per 250 live births to 1 per 750 live births. *See* MOUTH.

Clefts of the lip may occur on one side (unilateral, **Fig. 1**) or both sides (bilateral). When they occur in the exact midline of the lip, they are often associated with severe anomalies of the brain. The cleft usually extends through the lip and nostril floor. The underlying dental arch is also typically involved.

The palate consists of an anterior bony portion (hard palate) and a posterior muscular portion (soft palate). The soft palate alone may be cleft, or both the soft and hard palate may be cleft (**Fig. 2**), but rarely is the hard palate cleft with the soft palate intact. A variant of cleft palate is the submucous cleft palate, in which the muscles of the palate are cleft but the overlying mucous membrane is intact.

Fig. 1. Unilateral, incomplete cleft lip in which the notch does not extend to the nose.

Fig. 2. Cleft palate, resulting in a fissure in the palate connecting the nasal and oral cavities.

Causes. Clefts are the only major abnormality in approximately half of newborns who have them. In the other half, they occur as a part of a pattern of multiple anomalies (a syndrome). It has been determined that most clefts are associated with genetic factors; the genetic patterns range from autosomal dominant inheritance (50% risk of inheritance) in many syndromes to a genetic predisposition for clefting (about 4% risk of inheritance). Clefting is often associated with chromosome abnormalities, intrauterine disturbances (such as tears in the amnion), and teratogenic (malformation-causing) substances, such as alcohol, anticonvulsant drugs, and excessive levels of retinoic acid (vitamin A). *See* HUMAN GENETICS.

Secondary complications. Cleft lip is both an esthetic and a functional problem because of the disruption of the lip musculature. The defect in the floor of the nose causes asymmetry of the nose. The cleft of the dental arch causes orthodontic and occlusal (bite) problems, including congenitally missing teeth. The palatal cleft may result in some minor difficulties with feeding in early life, but a more significant problem is abnormal speech, including excessive nasal resonance (hypernasality) and articulation disorders. Clefting is also associated with chronic middle-ear disease (ear infections) and mild hearing loss. Additional structural or functional disorders can be associated with other features of a syndrome that includes cleft lip or cleft palate. *See* HEARING (HUMAN); SPEECH.

Management. Because of the combination of esthetic, structural, and functional requirements for total repair of clefts, that is, surgical, dental, ear, hearing, and speech, the care of children with clefts has usually been managed by comprehensive teams of specialists, including plastic surgeons, speech pathologists, audiologists, geneticists, otolaryngologists, oral surgeons, orthodontists, and pediatricians.

Cleft lip is typically repaired within the first few months of life, and the palate is most often surgically closed before speech development.

Extensive dental work is normally deferred until some of the permanent teeth have erupted. Middle-ear disease is usually treated aggressively through surgery in order to prevent long-term hearing loss. In general, the outlook for children with these problems is very favorable, and in many cases the problems associated with clefts are completely remediable. Genetic counseling is extremely important. *See* CONGENITAL ANOMALIES. Robert Shprintzen

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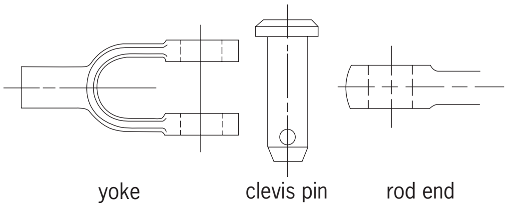
Clevis pin

A fastener with a head at one end and a hole at the other used to join a clevis to a rod. A clevis is a yoke with a hole formed or attached at one end of a rod (see **illus**.). When an eye or hole of a second rod is aligned with the hole in the yoke, a clevis pin can be inserted to join the two. A cotter pin can then be inserted in the hole of the clevis pin to hold it in, yet the fastening is readily detachable. This joint is used for rods in tension where some flexibility is required. Paul H. Black



Clevis pin which joins yoke to rod end.

Click chemistry

A simplified chemical reaction method recognized in 2001 by a group led by Nobel Laureate Prof. K. Barry Sharpless at the Scripps Research Institute. "Click" is meant to signify that joining molecular pieces is as easy as clicking together the two pieces of a buckle. The buckle works no matter what is attached to it, as long as its two pieces can reach each other and the components of the buckle can make a connection only with each other. Click reactions are easy to perform, give rise to their intended products in very high yields with little or no by-products, work well under many conditions (usually especially well in water), and are unaffected by the nature of the groups being connected to each other.

The central question posed by Sharpless and colleagues is whether desired functions can be obtained from molecules made using only click chemical reactions. In this deliberate eschewing of more sophisticated synthetic techniques is an implicit challenge to organic chemists that make complex structures by complex methods (can complex structures be made by simple methods?), and an explicit tip of the hat to the synthesis of functional polymers, which cannot occur without the use of reactions that meet the click chemistry standard. *See* ORGANIC SYNTHESIS.

Reactions. Click reactions share the following attributes. (1) Many click components are derived from alkenes and alkynes, and thus ultimately from the cracking of petroleum. Carbon-carbon multiple bonds provide both energy and mechanistic pathways to be made into reactive structures for click connections. (2) Most click reactions involve the formation of carbon-heteroatom (mostly N, O, and S) bonds. This stands in contrast to much of synthetic organic chemistry of recent years, which has emphasized the formation of carbon-carbon bonds. (3) Click reactions are strongly exothermic by virtue of highly energetic reactants or strongly stabilized products. (4) Click reactions are usually fusion processes (leaving no by-products) or condensation processes (producing water as a by-product). (5) Many click reactions are highly tolerant of and often accelerated by the presence of water. *See* ALKENE; ALKYNE.

These features are illustrated by the case of epoxide ring opening by a wide range of nucleophiles (**Fig. 1**). Since the epoxide is a strained three-membered ring, its ring opening is a strongly favored process. Yet that ring opening is required to occur in a particular way; that is, the nucleophile can attack the epoxide carbon atom only along the C-O bond axis, so by-products are avoided and yields are high. In addition, epoxides are relatively unreactive with water, while the hydrogen bonding ability and polar nature of water both serve to support the epoxide ring-opening reaction by other nucleophiles. *See* ELECTROPHILIC AND NUCLEOPHILIC REAGENTS; EPOXIDE; HYDROGEN BOND.

Most click reactions were discovered many years ago and have been widely appreciated, but have not been tapped for their full potential. They include the following classes of reactions, some of which are shown in **Fig. 2**.

Nucleophilic opening of spring-loaded electrophiles. The opening of the three-membered epoxide, aziridine, aziridinium, and episulfonium rings are all simple and versatile reactions. Included in this category are Michael addition reactions to α,β-unsaturated carbonyl compounds, which are also strongly favored processes.

Mild condensation reactions of carbonyl compounds. The formation of 1,3-dioxolane rings from aldehydes or ketones and of 1,3-diols, hydrazones, and oximes from aldehydes and hydrazines or hydroxylamine ethers, and of heterocycles from α- and β-carbonyl aldehydes, ketones, and esters are highly reliable and widely used reactions. *See* ALDEHYDE; CARBONYL; HETEROCYCLIC COMPOUNDS; KETONE; OXIME.

Cycloaddition reactions. Distinguished by the relatively nonpolar nature of their reactive groups, these fusion reactions comprise a wide range of processes, including the Diels-Alder reaction. Most useful are 1,3-dipolar cycloaddition reactions, with the cream of the crop being the reaction of organic azides with alkynes. *See* AZIDE; DIELS-ALDER REACTION.

Azide-alkyne cycloaddition. The goals and philosophy of click chemistry have been most extensively explored with the uncatalyzed (**Fig. 3***a*) and copper-catalyzed (Fig. 3*b*) versions of the cycloaddition reaction between azides and alkynes to form triazines. The former was first reported by A. Michael in 1893 and was later studied and popularized by the German chemist Rolf Huisgen in 1960s through the 1980s. The latter reaction was discovered independently in 2002 by the research groups of M. Meldal in Holland and K. B. Sharpless in the United States, and requires the use of a terminal alkyne. The abbreviation AAC (azide-alkyne cycloaddition) is used for the uncatalyzed process and CuAAC for the copper-mediated version.

These processes are uniquely useful because of the properties of the reactive substituents. Both azides and alkynes are high in chemical potential energy, and their fusion to make triazoles is exothermic by more than 45 kcal/mol. However, the rate of this reaction is quite slow, normally requiring prolonged heating for unactivated (not strongly electron-deficient or strained) alkynes. The azide and alkyne groups are stable in the presence of the nucleophiles, electrophiles, and solvents common to standard reaction conditions, with the azide being the only 1,3-dipolar reagent to have this quality. Most importantly, azides and alkynes are almost completely unreactive toward biological molecules. They are small and incapable of significant hydrogen bonding, and thus are unlikely to significantly change the properties of structures to which they are attached. Both can be easily introduced into organic compounds.

Click chemistry in situ. Because of their special reactivity—inert toward everything else and only sluggishly reactive with each other—azides and alkynes have been used to assemble molecules that bind very tightly to enzymes by using the enzyme itself as the reaction vessel (**Fig. 4**). The technique, known as click chemistry in situ, involves the tagging of molecules that bind to adjacent locations on an enzyme with azide and alkyne groups. If the derivatized molecules can interact simultaneously with the target in the proper orientation to hold the azide and alkyne units in proximity, a triazole may form to link the enzyme-binding components to each other. Since attachments to any target by two arms is better than either arm alone, the result is invariably a molecule of much higher binding affinity. Prior knowledge of the structure of the target is not required, nor is an assay for enzyme activity necessary. Since no reaction occurs between azides and alkynes at the concentrations used in these experiments without templating by the target enzyme, the formation of a new product is easy to detect by mass spectrometry

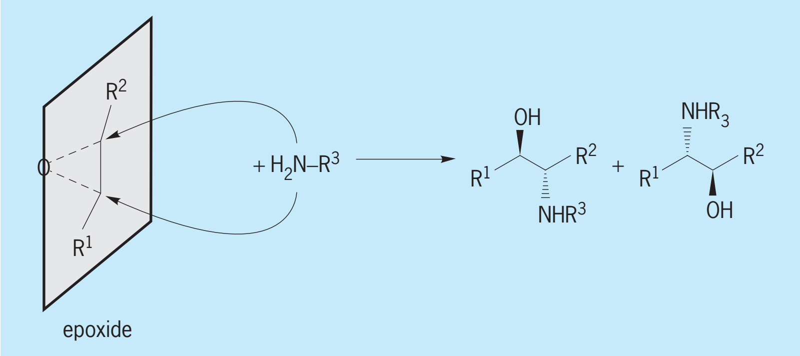


Fig. 1. Ring opening of epoxides with amines, a prototypical click reaction.

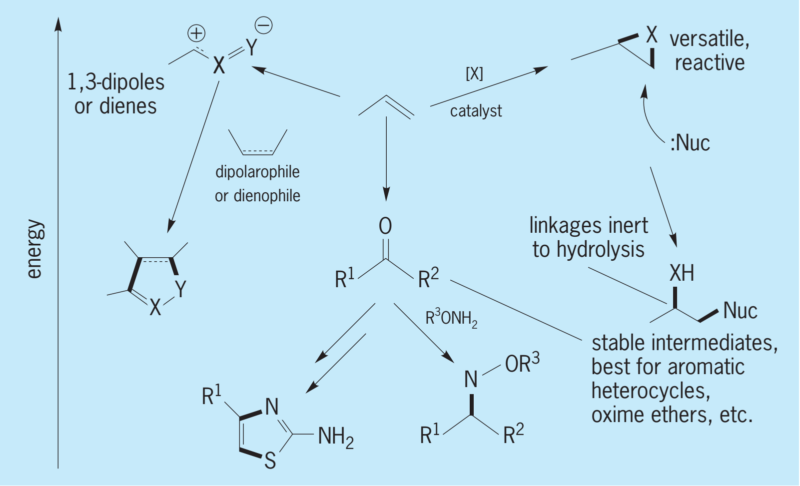


Fig. 2. Click chemistry employs highly energetic but selectively reactive groups.

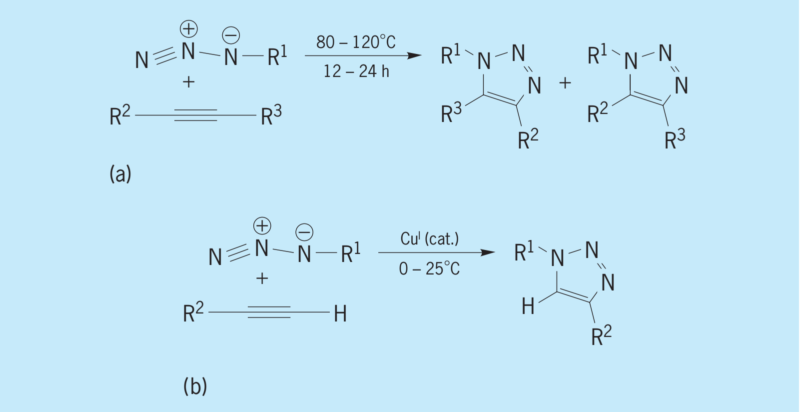


Fig. 3. Azide-alkyne cycloaddition (AAC) reaction to form triazoles: (*a*) Uncatalyzed and (*b*) copper-catalyzed version.

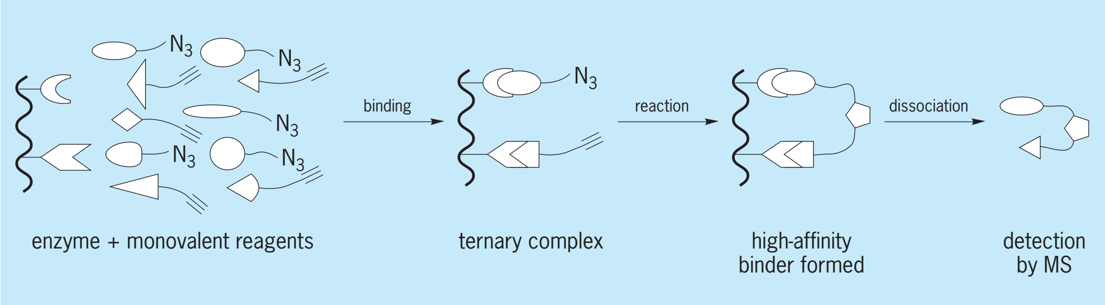


Fig. 4. Click chemistry in-situ technique.

and is proof of the creation of an excellent enzyme inhibitor. *See* ENZYME.

Click chemistry in situ has been used to create novel high-affinity binders to the important neurotransmitter enzyme acetylcholinesterase, the metabolic enzyme carbonic anhydrase, and HIV protease. It has become apparent in these and other studies that the triazole linkage has advantageous properties for drug discovery. Having a strong dipole moment, the capacity for significant hydrogen bonding, and the ability to engage in π-stacking interactions, triazoles can engage in productive interactions with proteins. The creation of this unit from two "invisible" pieces in a pocket of an enzyme is an event that influences the selectivity of bond formation during in-situ drug discovery efforts. The click chemistry in-situ technique is used in many laboratories and pharmaceutical companies around the world as a complement to traditional methods of synthesis and screening. *See* DIPOLE MOMENT.

While not yet used directly in living cells because of the cytotoxicity and attendant bioregulation of copper, the copper-catalyzed reaction has achieved extraordinarily wide use in organic chemistry and materials science. Applications include the synthesis of biologically active compounds, the preparation of conjugates to proteins and polynucleotides, the synthesis of dyes, the elaboration of known polymers and the synthesis of new ones, the creation of responsive materials, and the covalent attachment of desired structures to surfaces.

Conclusion. Click chemistry expands the scope of structures that can be made by expert chemists and nonchemists alike. The rationale is simply that the more tolerant is the connection reaction between chemical pieces, the more diverse the pieces that can be brought to bear on any problem. Chemists possess neither the ability to control reactions as well as living cells do, nor the ability to manufacture large structures such as proteins for every purpose. Therefore, while nature can inspire us, making such complex molecules comes at a fearful cost of time and expense. If indeed it is chemical function that is the goal, keeping it simple is a useful rule.

M. G. Finn

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Client-server system

A computing system that is composed of two logical parts: a server, which provides services, and a client, which requests them. The two parts can run on separate machines on a network, allowing users to access powerful server resources from their personal computers (**Fig. 1**). *See* LOCAL-AREA NETWORKS; WIDE-AREA NETWORKS.

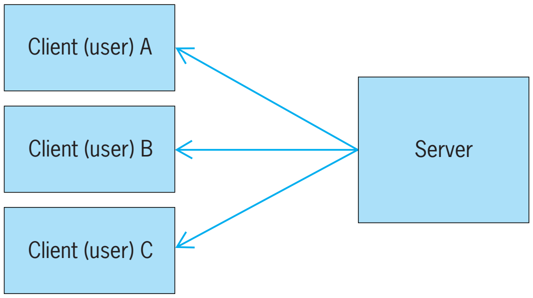

Fig. 1. Client-server system. Clients request services of the server independently but use the same interface.

Client-server systems are not limited to traditional computers. An example is an automated teller machine (ATM) network. Customers typically use ATMs as clients to interface to a server that manages all of the accounts for a bank. This server may in turn work with servers of other banks (such as when withdrawing money at a bank at which the user does not have an account). The ATMs provide a user interface and the servers provide services, such as checking on account balances and transferring money between accounts.

To provide access to servers not running on the same machine as the client, middleware is usually used. Middleware serves as the networking between the components of a client-server system; it must be run on both the client and the server. It provides everything required to get a request from a client to a server and to get the server's response back to the client. Middleware often facilitates communication between different types of computer systems. This communication provides cross-platform client-server computing and allows many types of clients to access the same data.

The server portion almost always holds the data, and the client is nearly always responsible for the user interface. The application logic, which determines how the data should be acted on, can be distributed between the client and the server (**Fig. 2**). The part of a system with a disproportionately large amount of application logic is termed "fat"; a "thin" portion of a system is a part with less responsibility delegated to it. Fat server systems, such as groupware systems and web servers, delegate more responsibility for the application logic to the server, whereas fat client systems, such as most database systems, place more responsibility on the client. *See* HUMAN-COMPUTER INTERACTION.

Multitiered systems. The canonical client-server model assumes two participants in the system. This is called a two-tiered system; the application logic must be in the client or the server, or shared between the two. It is also possible to have the application logic reside in a third layer separate from the user interface and the data, turning the system into a three-tier system. Complete separation is rare in actual systems; usually the bulk of the application logic is in the middle tier, but select portions of it are the responsibility of the client or the server.

The three-tier model is more flexible than the two-tier model because the separation of the application logic from the client and the server gives application logic processes a new level of autonomy. The processes become more robust since they can operate independently of the clients and servers. Furthermore, decoupling the application logic from the data allows data from multiple sources to be used in a single transaction without a breakdown in the client-server model. This advancement in client-server architecture is largely responsible for the notion of distributed data. *See* DISTRIBUTED SYSTEMS (COMPUTERS).

Standard web applications are the most common examples of three-tier systems. The first tier is the user interface, provided via interpretation of Hyper Text Markup Language (HTML) by a web browser. The embedded components being displayed by the browser reside in the middle tier, and provide the application logic pertinent to the system. The final tier is the data from a web server. Quite often this is a database-style system, but it could be a data-warehousing or groupware system. *See* WORLD WIDE WEB.

Software components. The desire to distribute servers across a network and have clients find them on demand has led to the development of component technologies. Components are the smallest self-managing, independent, and useful parts of a system that can work with other components to provide useful services. Each component provides an interface, which is a contract to do certain things asked of it. Therefore, systems can be quickly assembled by reusing existing components. For example, a program that needs to sort a list may ask a sorting component to do this so the programmer writing the new application need not write the sorting code. Components that provide the same interfaces can be interchanged for one another; for example, a user could purchase and install a faster sorting component, and programs using the old sorting component would automatically use the improved version.

Middleware packages. The use of components requires additions to the traditional middleware package that can coordinate components and help components locate one another. The two primary middleware packages providing these services are the Common Object Request Broker Architecture (CORBA) and the Distributed Component Object Model (DCOM).

CORBA. An industry-wide consortium created and advocates the standard known as CORBA. CORBA

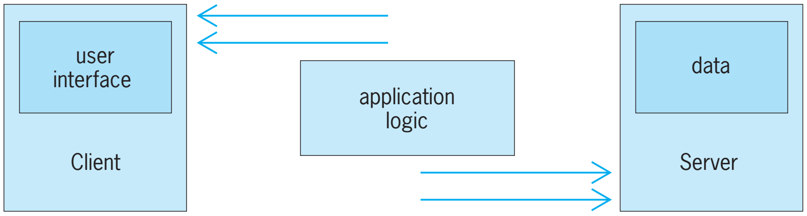

Fig. 2. Distribution of elements of a client-server system. Since the distribution of the user interface and data is fixed, the distribution of the application logic distinguishes fat client systems from fat server systems.

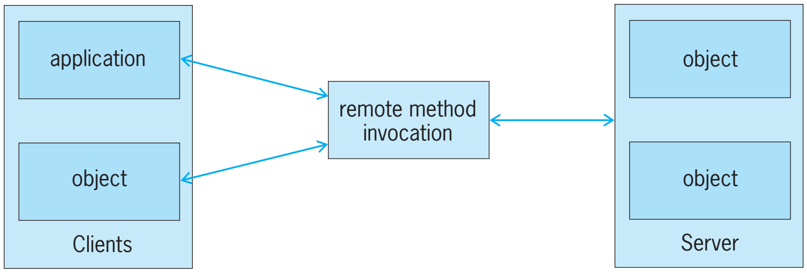

Fig. 3. Client-server computing using distributed objects. Communication between components (denoted by arrows) is facilitated by object request brokers (ORBs), which have been omitted for clarity. The remote method invocation system allows an object on one host to cause a method of an object that resides on another host to be executed on that remote host.

objects can exist anywhere on a network; their location is completely transparent (**Fig. 3**). Details such as an object's language or its operating system are also hidden from clients. Thus, the implementation of an object is of no concern to an invoking object; the interface is the only entity that a client needs to consider when selecting a serving object (Fig. 2).

The most important part of a CORBA system is the object request broker (ORB). CORBA uses the object request broker to establish a client-server relationship between components. The object request broker intercepts service requests from the client objects and routes them to an appropriate server. CORBA uses an interface file written in an interface definition language (IDL) to specify the services that an object can provide, but programmers write code in their language of choice.

When clients request services, the requests are routed to the remote server using a local "stub" object and the object request broker. The stub relieves the application programmer from the burden of routing the message.

CORBA specifies two means by which an object can locate another object in a system. The first is the Naming Service. This service is analogous to the white pages in a phone book: An object looks up another object by the name under which the object registered itself with the object request broker when it was initialized. The second service is the Trading Service, which is like the yellow pages: Objects can ask the Trading Service which objects have registered with certain service characteristics. The trading repository then returns references to salient objects and gives the client information regarding the properties of the services. *See* OBJECT-ORIENTED PROGRAMMING.

DCOM. Like CORBA, DCOM separates interface from functionalty by using an interface definition language. The client-server contract is fulfilled by using object interfaces that make the implementation language and the location of objects transparent. When a DCOM client needs a server, it issues a request for an object supporting the required interface instantiated so that the interface becomes available.

Using interface pointers to mask stublike objects, DCOM supports transparent communication between clients and remote server objects. DCOM uses a model quite similar to the mechanism employed by CORBA to provide location-independent access to objects. Since DCOM provides access to interfaces only (and not objects), there is no means by which to locate specific objects.

Java. Java is a programming language that allows programs to run on a variety of computing platforms without being modified; such a system is referred to as a mobile code system. Mobile code is distinguished from traditional application code in that it is dynamically executed by an application that provides the run-time environment. For code to be considered mobile, it must be portable, meaning the code can be run on a variety of platforms. Java uses bytecodes to provide portability and security. The bytecode system calls for programs to be "compiled" to the point where they can be run on a Java virtual machine, which translates the bytecodes into actual machine instructions in real time. Java virtual machines must adhere to a standard; this ensures that a Java program executes in the same manner on any machine. To provide security, the Java Verifier checks all code scheduled to be executed for malicious code.

Java's promise of "write once, run anywhere" makes it an appealing language in which to author pieces of a client-server system. Java also provides core classes that are a part of standard Java implementations. These core classes provide basic services that many programs require, and can decrease application development times by reducing the amount of code a programmer needs to write and debug.

When coupled with distributed object technology, Java forms a strong basis for the development of a robust system that supports client-server computing. A platform for universal network computing can be created by using Java as a programming language and mobile code system and CORBA or DCOM as an integration technology. Using DCOM or CORBA allows Java components to be split into client- and server-side components in many cases, providing the system with enhanced flexibility in distributing web-based applications. *See* DIGITAL COMPUTER; PROGRAMMING LANGUAGES. Scott M. Lewandowski

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Climate history

The long-term records of precipitation, temperature, wind, and all other aspects of the Earth's climate. The climate, like the Earth itself, has a history extending over several billion years. Climatic changes have occurred at time scales ranging from hundreds of millions of years to centuries and decades. Processes in the atmosphere, oceans, cryosphere (snow cover, sea ice, continental ice sheets), biosphere, and lithosphere (such as plate tectonics and volcanic activity) and certain extraterrestrial factors (such as the Sun) have caused these changes of climate.

The present climate can be described as an ice age climate, since large land surfaces are covered with ice sheets (for example, Antarctica and Greenland). The origins of the present ice age may be traced, at least in part, to the movement of the continental plates. With the gradual movement of Antarctica toward its present isolated polar position, ice sheets began to develop there about 30 million years ago. For the past several million years, the Antarctic ice sheet reached approximately its present size, and ice sheets appeared on the lands bordering the northern Atlantic Ocean. During the past million years of the current ice age, about 10 glacial-interglacial cycles have been documented. Changes in the Earth's orbital parameters, eccentricity, obliquity, and longitude of perihelion are thought to have initiated, or paced, these cycles through the associated small changes in the seasonal and latitudinal distribution of solar radiation. The most recent glacial period ended between about 15,000 and 6000 years ago with the rapid melting of the North American and European ice sheets and an associated rise in sea level, and the atmospheric concentration of carbon dioxide.

The present interglacial climate reached its maximum warmth about 6000 years ago when, compared to the present, the high northern latitudes were slightly warmer, the northern continental interiors were drier, and the monsoon lands of Africa and southern Asia were wetter. These differences appear also to have been caused, at least in part, by differences in Earth's orbital parameters, compared to the present.

Changes of climate spanning centuries to decades occur within the more gradual changes just described. For example, the climate of northern Europe was slightly warmer about 1000 years ago than at present, but colder than at present 100 to 300 hundred years ago, when mountain glaciers advanced beyond present-day limits in Scandinavia and the Alps. The causes of these shorter-term changes of climate are not well understood, although volcanic activity, solar variability, and the internal dynamics of the atmosphere and ocean may all be involved. There is concern that human activities, such as massive deforestation and the burning of fossil fuels, may become causes of climatic change.

The climates of the distant geologic past were strongly influenced by the size and location of continents and by large changes in the composition of the atmosphere. For example, around 250 million years ago the continents were assembled into one supercontinent, Pangaea, producing significantly different climatic patterns than are seen today with widely distributed continents. In addition, based upon models of stellar evolution, it is hypothesized that the Sun's radiation has gradually increased by 10–20% over the past several billion years and, if so, this has contributed to a significant warming of the Earth. *See* CONTINENTS, EVOLUTION OF; GLACIAL EPOCH; PALEOCLIMATOLOGY.

Evidence. Instrumental records of climatic variables such as temperature and precipitation exist for the past 100 years in many locations and for as long as 200 years in a few locations. These records provide evidence of year-to-year and decade-to-decade variability, but they are completely inadequate for the study of century-to-century and longer-term variability. Even for the study of short-term climatic fluctuations, instrumental records are incomplete, because most observations are made from the continents (covering only 29% of the Earth's surface area). Aerological observations, which permit the study of atmospheric mass, momentum and energy budgets, and the statistical structure of the large-scale circulation, are available only since about the mid-1960s. Again there is a bias toward observations over the continents. It is only with the advent of satellites that global monitoring of the components of the Earth's radiation budget (clouds; planetary albedo, from which the net incoming solar radiation can be estimated; and the outgoing terrestrial radiation) became possible. *See* METEOROLOGICAL SATELLITES.

There remain important gaps in the ability of climatologists to describe the present state of the climate. For example, precipitation estimates, especially over the oceans, are poor. Oceanic circulation, heat transport, and heat storage are only crudely estimated. Thus, although climatic changes are discernible from instrumental records, the task of defining the scope of these changes and diagnosing potential causes is difficult.

In spite of the inadequacy of the instrumental records for assessing global climate, considerable evidence of regional climatic variations exists. For example, there is evidence of climatic warming in the polar regions of the Northern Hemisphere during the twentieth century. *See* GREENHOUSE EFFECT.

Evidence of climatic changes prior to instrumental records comes from a wide variety of sources. Tree rings, banded corals, and pollen and trace minerals retrieved from laminated lake sediments and ice sheets yield environmental records for past centuries and millennia. Advanced drilling techniques have made it possible to obtain long cores from ocean sediments that provide geologic records of climatic conditions going back hundreds of millions of years. *See* DENDROCHRONOLOGY; PALYNOLOGY.

Causes. Many extraterrestrial and terrestrial processes have been hypothesized to be possible causes of climatic fluctuations. These include solar irradiance, variations in orbital parameters, motions of the lithosphere, volcanic activity, internal variations of the climate system, and human activities. It is likely that all of the natural processes have played a role in past climatic changes. Also, the climatic response to some particular causal process may depend on the initial climatic state, which in turn depends upon previous climatic states because of the long time constants of lithosphere, oceans, and cryosphere. True equilibrium climates may not exist, and the climate system may be in a continual state of adjustment.

Solar irradiance. Variations in solar irradiance would almost certainly have an influence on climate. In addition to the possible long-term evolution of the Sun, the changing appearance of the Sun, the so-called sunspots, hint at shorter-term variability on the scale of years to centuries. Satellite observations have detected decadal-scale fluctuations in solar radiation on the order of 0.1%. Radiance variability in limited portions of the solar spectrum has also been observed but has not been linked clearly to climate variability. *See* SOLAR RADIATION.

Orbital parameters. Variations of the Earth's orbital parameters (eccentricity of orbit about the Sun, longitude of perihelion, and inclination or tilt of the rotational axis) lead to small but significant variations in incoming solar radiation with regard to seasonal partitioning and latitudinal distribution. These variations occur at times scales of 20,000 to 100,000 years and have been linked to glacial-interglacial cycles and sedimentation cycles in geologic records. *See* EARTH ROTATION AND ORBITAL MOTION.

Lithosphere motions. Sea-floor spreading and continental drift, continental uplift, and mountain building operate over long time scales and are almost certainly important factors in long-term climate. *See* CONTINENTAL DRIFT; MARINE GEOLOGY; OROGENY; PLATE TECTONICS.

Volcanic activity. Volcanic activity produces gaseous and particulate emissions that lead to the formation of persistent stratospheric aerosol layers. It may be a factor in climatic variations at all time scales. *See* VOLCANO.

Internal variability of climate system. Components of the climate system (atmosphere, ocean, cryosphere, biosphere, land surface) are interrelated through a variety of feedback processes operating over a wide range of time scales. These processes could, in principle, produce fluctuations of sufficient magnitude and variability to explain any observed climatic change. For example, atmosphere-ocean interactions may operate over time scales up to centuries, the basic period of overturning of the ocean thermohaline circulation; and atmosphere-ocean-cryosphere interactions may operate over time scales up to tens of millennia, the time required to build a major ice sheet. Several hypotheses have been proposed to explain glacial-interglacial fluctuations as complex internal feedbacks among atmosphere, ocean, and cryosphere. (Periodic buildup and surges of the Antarctic ice sheet and periodic fluctuation in sea ice extent and deep-ocean circulation provide examples.) Atmosphere-ocean interaction is being studied intensively as a possible cause of short-term climatic variations. It has been observed that anomalous ocean temperature patterns (both equatorial and midlatitude) are often associated with anomalous atmospheric circulation patterns. Although atmospheric circulation plays a dominant role in establishing a particular ocean temperature pattern (by means of changes in wind-driven currents, upwelling, radiation exchange, evaporation, and so on), the anomalous ocean temperature distribution may then persist for months, seasons, or longer intervals of time because of the large heat capacity of the oceans. These anomalous oceanic heat sources and sinks may, in turn, produce anomalous atmospheric motions. The Earth's biosphere may also be actively involved in climatic changes. For example, the atmospheric concentration of carbon dioxide is linked to the carbon reservoirs of the continents and oceans via photosynthesis-respiration cycles, and gas exchange at the air-ocean interface. *See* ATMOSPHERIC GENERAL CIRCULATION; BIOSPHERE; OCEAN CIRCULATION.

Human activities. Forest clearing and other large-scale changes in land use, changes in aerosol loading, and the changing concentration of carbon dioxide in the atmosphere are examples of possible mechanisms through which human activities may influence the large-scale climate. Because of the large observational uncertainties in defining the state of the climate, it has not been possible to establish the relative importance of human activities (as compared to natural processes) in recent climatic fluctuations. There is, however, considerable concern that future human activities may lead to large climatic variations (for example, continued increases in atmospheric carbon dioxide concentration due to burning of fossil fuels) by the early twenty-first century. *See* AIR POLLUTION; CLIMATE MODIFICATION.

Modeling. Because of the complexity of the real climate system, simplified numerical models of climate are being used to study particular processes and interactions. Some models treat only the global-average conditions, whereas others, particularly the dynamical atmosphere and ocean models, simulate detailed patterns of climate. These models will undoubtedly be of great importance in attempts to understand climatic processes and to assess the possible effects of human activities on climate. *See* CLIMATE MODELING; CLIMATIC PREDICTION; CLIMATOLOGY.

John E. Kutzbach

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Climate modeling

Construction of a mathematical model of the climate system of the Earth capable of simulating its behavior under present and altered conditions. The Earth's climate is continually changing over time scales ranging from hundreds of years to a few years. Since the climate is determined by the laws of classical physics, it should be possible in principle to construct such a model. The advent of a worldwide weather-observing system capable of gathering data for validation and the development and widespread routine use of digital computers have made this undertaking possible, starting in the mid-1970s.

The first attempts at modeling the planetary climate showed that the Earth's average temperature is determined mainly by the balance of radiant energy absorbed from sunlight and that emitted by the Earth system. About 30% of the incoming radiation is reflected directly to space, and 72% of the remainder is absorbed at the surface (**Fig. 1**). The incoming solar radiation is divided among reflection, absorption by the atmospheric constituents, and absorption by the surface of the planet. The outgoing infrared radiation comes from the surface, atmospheric gases, and clouds. In addition, the atmosphere radiates down to the surface, and the surface gives energy to the atmosphere in the forms of latent and sensible heat. The radiation is absorbed unevenly over the Earth, which sets up thermal contrasts that in turn induce convective circulations in the atmosphere and oceans. Climate models attempt to calculate from mathematical algorithms the effects of these contrasts and the resulting motions in order to understand better and perhaps predict future climates in some probabilistic sense. *See* SOLAR RADIATION; TERRESTRIAL RADIATION.

Climate models differ in complexity, depending upon the application. The simplest models are intended for describing only the surface thermal field at a fairly coarse resolution. These mainly thermodynamical formulations are successful at describing the seasonal cycle of the present climate, and have been used in some simulations of past climates, for example, for different continental arrangements that occurred millions of years ago. At the other end of the spectrum are the most complex climate models, which are extensions of the models used in weather forecasts. These models aim at simulating seasonal and even monthly averages just shortly into the future, based upon conditions such as the temperatures of the tropical-sea surfaces. Intermediate to these extremes are models that attempt to model climate on a decadal basis, and these are used mainly in studies of the impact of hypothesized anthropogenically induced climate change. *See* CLIMATE MODIFICATION.

Climate models are used in a large variety of applications that aid in the understanding of Earth history. Many simple climate model simulations have been used to sort out the mechanisms responsible for climate change in the past. For example, although not yet fully understood, the astronomical theory of the ice ages states that the waxing and waning of the great continental ice sheets has been forced by the periodic changes in the Earth's ellipitical orbit parameters in the past. Similarly, the onset of glaciation in Antarctica and Greenland has been studied by such means. *See* CLIMATE HISTORY.

A problem that has received considerable attention is the greenhouse effect. Models are studied to achieve better understanding of how the increase of atmospheric carbon dioxide and other trace gases from anthropogenic sources is likely to change the climate in the coming decades. The models are compared to past climates ranging from the ice ages to the records of the last hundred years, for which an instrumental record exists. *See* GREENHOUSE EFFECT.

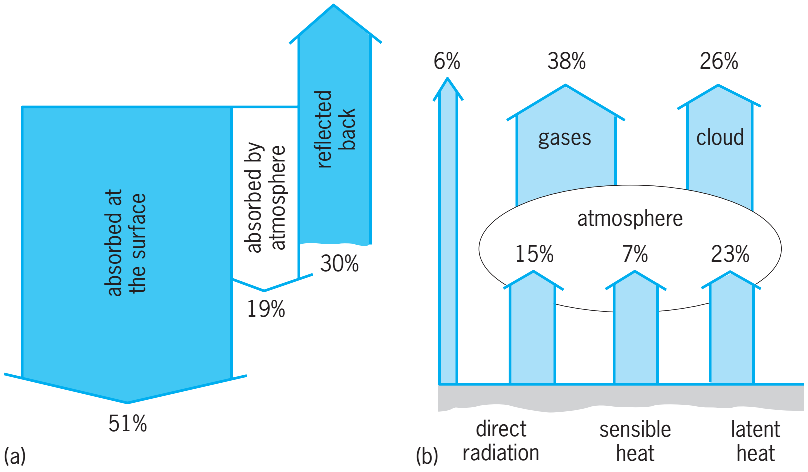

Fig. 1. Schematic diagram of the budget of incoming and outgoing radiation affecting the Earth's climate. (*a*) Solar radiation. (*b*) Terrestrial radiation.

Anatomy of models. Since the main interest of climate modelers is in computing the thermal field over the Earth, a primary objective is to represent the conservation of energy at each location in the system. One requirement is accurate formulations of the absorption and reflection of solar radiation as it passes through the atmosphere and strikes surfaces. Another is the radiation emitted from each mass element in the Earth–atmosphere system. Conversions of heat from latent to sensible must be taken into account as water changes its phase in the system. Clouds must be included since they participate in the radiation transfer and in the changes of water phase. Similarly, snow and ice cover enter both energy disposal accounts. The thermodynamic expression of the conservation of energy is not complete until allowance is made for the flow of matter of a different temperature into a given region. To include this effect, a model of the circulation must be considered, and this in turn is governed by the same thermal contrasts given by the thermodynamic equation.

The circulation of atmospheric and oceanic material is governed by Newton's second law: local acceleration of a fluid element is proportional to total forces on it. In fluid mechanics this is known as the Navier-Stokes equation. It is a nonlinear partial differential equation that is exceedingly complex. Climate models that include a detailed attempt to solve the fluid dynamics equations must be approached by computer simulation. Even here the solutions are known to differ in detail from nature after only a few weeks at most. However, it is thought that statistics, for example, long-term means for the climate of the numerical model and those of nature, should agree; and this has been borne out in numerous tests. *See* NAVIER-STOKES EQUATIONS.

In order to simulate the climate system, the problem must be cast onto a three-dimensional grid in the global ocean–atmosphere volume. The intermediate-sized models typically being used for decadal simulations have a horizontal resolution of about 300 to 600 mi (500 to 1000 km) and vertical resolutions of about 0.6 to 1.8 mi (1 to 3 km). This implies about 25,000 grid points, at each of which the model is keeping track of about six meteorological variables. The system is solved by numerically advancing in time at each grid point, updating at each time step (typically about intervals of 1 h of so-called model time). Simulation of 15 years of model time, which is typical of models that include only simple formulations of the oceanic interaction, may take tens of hours on the fastest computers. About a half dozen models of this type are being investigated around the world. The models as a group simulate the present seasonal cycle of different geographical regions with remarkable fidelity, considering the short time that has passed since the inception of this field. The models are best at simulating the thermal surface field and weakest in modeling such secondary features as precipitation. *See* SIMULATION.

Simulation models which include ocean circulation are important in understanding the adjustment processes in going from one climate state to another. Inclusion of the ocean dynamics adds significantly to the computational burden, since a finer grid is required owing to the importance of small-scale motions. The irregularity of the bottom topography also complicates the problem. Gerald R. North

Feedback mechanisms and sensitivity. Attempts at modeling climate have demonstrated the extreme complexity and subtlety of the problem. This is due largely to the many feedbacks in the system. One of the simplest and yet most important feedbacks is that due to water vapor. If the Earth is perturbed by an increase in the solar radiation, for example, the first-order response of the system is to increase its temperature. But an increase in air temperature leads to more water vapor evaporating into the air; this in turn leads to increased absorption of space-bound long-wave radiation from the ground (greenhouse effect), which leads to an increased equilibrium temperature. This effect, known as a positive-feedback mechanism, is illustrated in **Fig. 2**. Water vapor feedback is not the only amplifier in the system. Another important one is snowcover: a cooler planet leads to more snow and hence more solar radiation reflected to space, since snow is more reflecting of sunlight than soil or vegetation. Other, more subtle mechanisms that are not yet well understood include those involving clouds, oceans, and the biosphere.

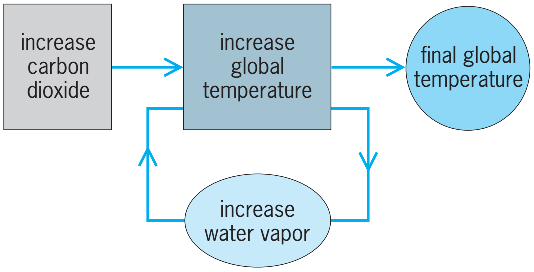

Fig. 2. Water vapor feedback in amplifying the sensitivity of the Earth's climate to increases in atmospheric carbon dioxide concentration. Increases in the Earth's temperature cause an increase in water vapor, causing a warming of the surface because of the greenhouse effect. The net effect is to amplify the response to increases of carbon dioxide.

While water vapor and snowcover feedback are fairly straightforward to model, the less understood feedbacks differ in their implementations from one climate model to another. These differences as well as the details of their different numerical formulations have led to slight differences in the sensitivity of the various models to such standard experimental perturbations as doubling carbon dioxide in the atmosphere. All models agree that the planetary average temperature should increase if carbon dioxide concentrations are doubled. However, the predicted response in planetary temperatures ranges 4.5–9°F (2.5–5.0°C). Regional predictions of temperature or precipitation are not reliable enough for detailed response policy formulation. Many of the discrepancies are expected to decrease as model resolution increases (more grid points), since it is easier to include such complicated phenomena as clouds in finer-scale formulations and coupling with dynamic models of the ocean. Similarly, it is anticipated that some observational data (such as rainfall over the oceans) that are needed for validation of the models will soon be available from satellite sensors. *See* METEOROLOGICAL SATELLITES.

Atmosphere–ocean–land models. Simulating the naturally varying present-day climate and its future evolution can be accomplished only with coupled atmosphere–ocean–land models.

Atmosphere models. Numerical models of the atmosphere are used to reveal its underlying dynamics and to predict the weather. The climatic application of models requires a knowledge of the change in lower-boundary conditions as the model evolves in time: over the oceans, sea surface temperature; and over land, more complex descriptors of the land surface.

Both the ocean and land interact with the atmosphere on multiple time scales. Ocean interactions depend on the thermal capacities of water columns that undergo rapid vertical exchanges, usually about 165–3300 ft (50–1000 m) of water. An unchanging field of sea surface temperature may be used as a model boundary to predict weather a few days in advance (at most) because the huge thermal capacities of the oceans cause hardly any change in the bottom boundary. Dry land, however, interacts with the atmosphere with effective heat capacities of a fraction of a meter of water, so that large thermal variations in interaction with the atmospheric boundary occur over time scales as short as the diurnal cycle. Longer time scales occur for moist soils: for example, soil moisture stores may require several weeks to be depleted. Also, the atmosphere above the boundary layer may require several weeks to be influenced by the underlying boundaries. For simulations or predictions beyond a week, the correct time evolution of the bottom boundary conditions for sea surface temperature and land soil moisture must be calculated.

Coupled models. To consistently simulate both atmospheric and boundary quantities, it is necessary to couple the media and allow them to mutually and consistently evolve. Even to predict evolution of the atmosphere alone, climate models must be coupled atmosphere–ocean–land models.

Numerical models of the ocean are used to understand its underlying dynamics and to predict the sea surface temperature. For these purposes, the fluxes of heat and momentum from the atmosphere must be specified. On sufficiently long time scales, the atmosphere requires sea surface temperatures from the ocean, and the ocean requires momentum and heat fluxes from the atmosphere. Numerical models of the land are used to study basic hydrological processes and to predict temperature, stored moisture, and runoff. Fluxes of heat and water from the atmosphere must be specified because the atmosphere requires land properties and the land requires atmospheric fluxes. Many atmospheric processes must be adequately simulated in order to correctly supply the fluxes of heat, momentum, and moisture to the ocean and to the land surfaces, for example, those processes involving rainfall, cloud optical properties, surface winds, radiation, and atmospheric temperature. These variables, in turn, are affected by the properties of the underlying surface.

Sensitivity studies. Significant properties of the ocean and land components of coupled climate models can be tested and demonstrated by the use of sensitivity studies. These studies assume simple changes in model parameters and assess the significance of the responses. They have demonstrated that changes in surface boundary conditions can have a profound influence on regional rainfall patterns and intensities and can also determine the specifics of how the surface conditions influence atmospheric precipitation.

Surface–precipitation interactions are affected by the heat and moisture supplied by the lower boundary to the planetary boundary layer. Moist convection occurs when an atmospheric column is unstable with respect to a parcel of boundary layer air. Wetter and warmer surfaces promote this instability, as does colder air in the overlying atmosphere. Convection occurring in one location acts to warm and stabilize the atmosphere elsewhere. Therefore, convective rainfall in one location can suppress convection elsewhere. Over land, the diurnal cycle of solar heating promotes the greatest convective instability in the afternoon. Over oceans, warmest sea surface temperatures usually, but not always, produce the greatest convective instabilities. Climate model simulations can test their treatment of surface coupling through comparisons of the simulated and observed diurnal variations of rainfall. These diurnal variations are especially pronounced over land, but they are also notable over the tropical oceans. For example, a model with initially dry soil predicts substantially lower summer convective rainfall in subsequent days, or even weeks, than does a model with initially wet soil. *See* CONVECTIVE INSTABILITY.

Uses of coupled models. Coupled atmosphere–ocean–land models are used to simulate climate over time scales of longer than a few weeks. These models are used to predict future natural variations (that is, variations that occur without human-induced changes of the gas and aerosol composition of the atmosphere) or to project responses to human-induced changes such as the addition of greenhouse gases.

One natural variation is El Niño, the complex of phenomena connected with warm sea surface temperature in the eastern and central tropical Pacific that seems to occur on an irregular 4-year time scale. The simulation of such warm and cold sea surface temperature variations is difficult for the present generation of global coupled climate models. The resolution required for such simulation is approximately 20 km (12 mi), in the tropical Pacific, in order to resolve the thin strip of equatorial upwelling of cold water from below, a crucial process in changing sea surface temperature. Questions such as the dependence of the El Niño cycle on global warming cannot be answered until global coupled models successfully incorporate the full range of processes known to be important for this cycle. By limiting the active extent of the coupled models to the tropical Pacific, such high resolution can easily be attained and predictions of El Niño using such models become possible. Data in the tropical Pacific are used to initialize the forecast, that is, to specify the initial internal state of the upper ocean. The coupled model is then allowed to run freely, and the future evolution of the entire system is predicted. Used in this way, coupled models have provided correct predictions up to a year in advance that have been useful in making economic decisions in nations bordering the tropical Pacific. Extending this approach to the United States is a far more difficult problem for coupled models, but remains a future possibility. *See* EL NIÑO; TROPICAL METEOROLOGY.

In terms of human-induced changes, coupled atmosphere–ocean–land models are used to project a climatic response to the increase of greenhouse gases. Difficulty arises because models are limited in their resolution (that is, in the fineness with which it is possible to subdivide the atmosphere and ocean) and in the parametrization of those processes that cannot be resolved by the present resolution (for example, clouds and turbulence in the atmosphere, small eddies in the ocean).

To project what the climatic response would be to an increase of greenhouse gases, the present climate must first be simulated. Next, an assumption must be made that the composition of the atmosphere will change in a specified way; for example, it may be assumed that carbon dioxide will increase by 1% per year. Current atmosphere–ocean–land models of long-term response to the anthropogenic addition of atmospheric gases have indicated that carbonaceous and sulfate aerosols have a major cooling affect (by direct blocking of the Sun's rays) on regions of the Earth's surface local to the emissions of such constituents. They may also have an indirect cooling effect by acting as cloud condensation nuclei to increase the amount of cloud cover. Future projections of the climatic response to additions of greenhouse

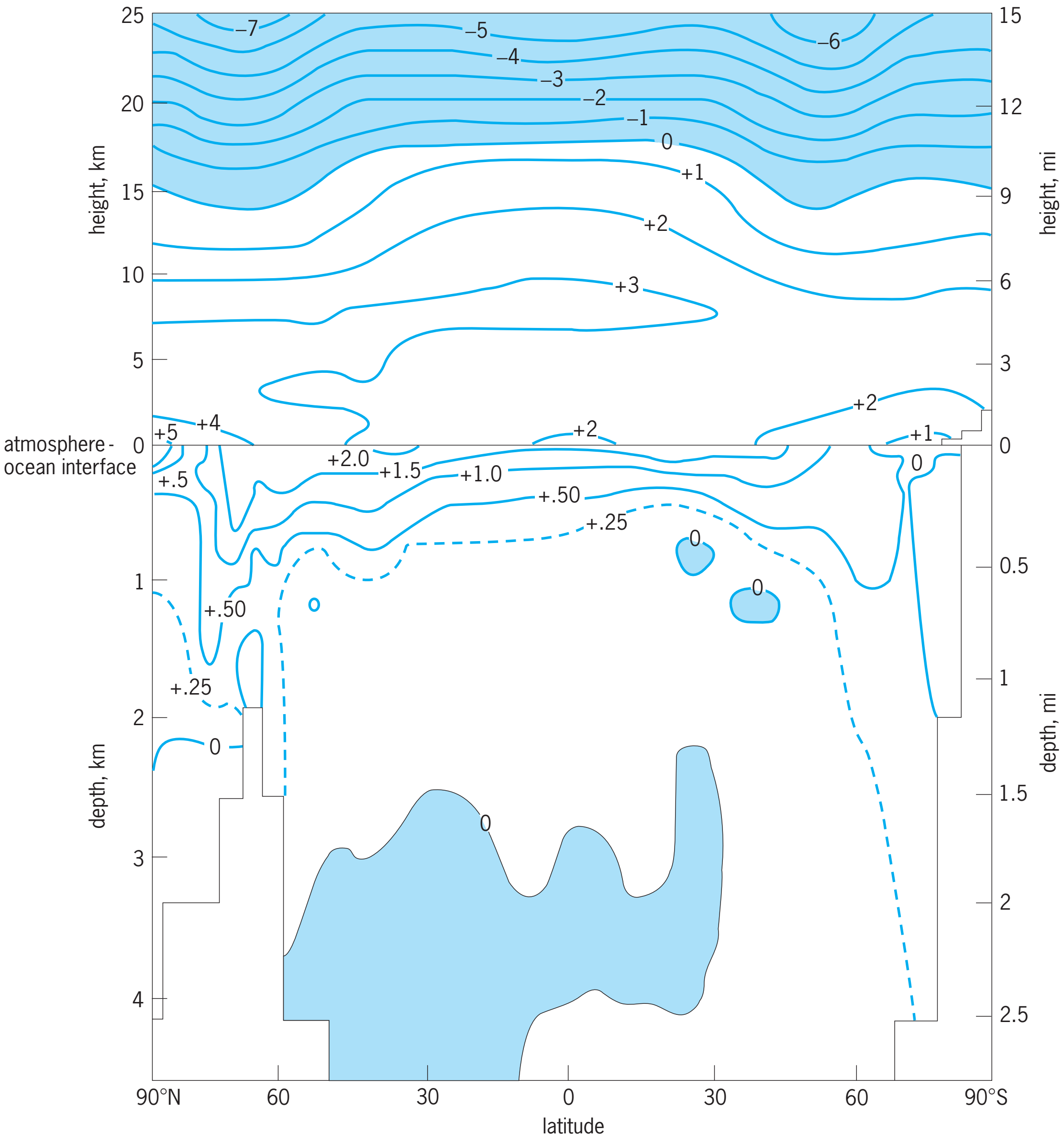

Fig. 3. Model showing the change of temperature (°C) in the atmosphere and ocean averaged over the 60th to 80th year of integration in response to an increase of 1% per year in the concentration of carbon dioxide. The temperature changes are averaged around circles of longitudes. The shaded areas are regions where cooling occurred. 1°C = 1.8°F. (*After S. Manabe, M. J. Spelman, and K. Bryan, Transient response of a coupled atmosphere–ocean model to gradual changes of atmospheric CO$_2$, pt. I: Annual mean response, J. Climate, 4:785–818, 1991*)

gases must include both the direct and poorly understood indirect effects of aerosols. With this information, a 70-year projection of a climate response, using a state-of-the-art coupled model (**Fig. 3**), shows that the higher latitudes warm more than the tropics, the ocean surface temperatures increase less than the surface atmosphere temperatures, the ocean warms very little below 0.6 mi (1 km) in depth, and the stratosphere cools. The model also shows a substantial summer drying of soils in midlatitudes of the summer hemisphere. This drying could have serious consequences if it were to occur. *See* CLIMATIC PREDICTION; CLIMATOLOGY; WEATHER FORECASTING AND PREDICTION. Robert E. Dickinson; E. S. Sarachik

Uncertainties in climate models. Because the Earth's climate is far too complex to reproduce in a laboratory, scientists have developed numerical climate models, based on the conservation of energy, momentum, and mass, which can be used to simulate past, present, and future climate conditions. These models incorporate the key physical parameters and processes that govern the climate behavior. Climate models that simulate the entire global atmosphere are called general circulation models (GCMs). Those models applied to a limited domain are called regional climate models (RCMs). The horizontal resolution of most general circulation models is 100 km (60 mi) or larger. Regional climate models have a horizontal resolution of a few tens of kilometers, but the initial and lateral boundary conditions of the RCMs depend upon the GCM output or reanalysis, which is a combination of the GCMs' output and observations. Consequently, RCMs may have more detailed physics and finer resolution, but the uncertainties of the GCM may pass to the RCMs through initial and/or boundary conditions when the RCM is used to predict the future climate.

Climate models (referring to atmospheric models coupled with ocean and land-soil models, hereafter) can be used to simulate changes in temperature, rainfall, snow cover, winds, soil moisture, sea ice, and ocean circulations for periods from seasons to decades. However, the mathematical models used are obviously simplified versions of the real Earth and cannot capture its full complexity. The nonlinear partial differential equations of the climate systems (that is, Navier-Stokes equations) cannot be solved analytically. In climate models, these equations are converted into the discrete difference equations in both time and space and solved numerically. Many numerical schemes and grid structures have been developed and applied in climate models to obtain the approximate numerical solutions. Theoretically, the numerical solutions should converge to the analytical (or true) solutions, but the accuracy can quickly deteriorate as the number of integrations increases in a model using coarse resolution, inappropriate numerical schemes, or improper grid structure. The discrete mode of the solutions also imposes a constraint that the smallest element that can be resolved by the model is twice the resolution (2Δ). The nonlinear terms of the Navier-Stokes equations can generate waves shorter than 2Δ. Those short waves can be misrepresented as the resolvable waves (that is, aliasing), causing nonlinear instability. Artificial filters or smoothing (which can also be generated by truncation errors of the numerical schemes) have been applied to control these instabilities.

Because of the resolution, climate models cannot resolve individual clouds, small-scale turbulence, detailed features of complex terrain, soil properties, or land distributions. They are called the subgrid-scale properties. The effect of the subgrid-scale properties should be formulated by parametrizations. For example, the effect of the subgrid-scale clouds is assumed as a function of the moisture convergence and other fields, which can be resolved by the models. Meteorologists have proposed various cumulus parametrizations to represent the effect of the subgrid-scale clouds; however, it is very difficult to formulate the cumulus parametrizations or other subgrid-scale features based on rigorous mathematics and physics. Models with a fine resolution can resolve the majority of the flow explicitly and reduce the spurious contributions from the subgrid-scale features. But the subgrid-scale parametrizations are still important, even in J. W. Deardorff's large-eddy simulation of a convective boundary layer with a model resolution of 50 m (160 ft). Subgrid-scale features and short-wave disturbances may affect the large-scale weather/climate pattern through the nonlinear terms of the equations.

Uncertainties also exist in formulating cloud physics, radiation, ocean current, and the effects of aerosol, as well as snow–land-surface, air–sea, sea-ice interactions. For example, using the same observed data as the initial conditions, a comparison of the snow–land-surface models shows considerable variation among the results, and most were unable to reproduce the observations due to deficiencies in numerical schemes, physics, or model resolution. For this reason, land models need to be refined before they can appropriately represent the effect of the soil and snow in a climate system. Better parametrizations in cloud physics, turbulence, radiation, aerosols, sea-ice and air-sea interactions, as well as finer model resolution are required in most models. *See* CLOUD PHYSICS.

The accuracy of the initial conditions is very important for numerical weather forecasting. The initial conditions for a GCM come from the reanalysis, which combines observations and model results, both of which may contain errors. The errors of observations may come from instruments or interpretation errors in both time and space. The sources of errors from modeling may be due to numerical schemes, physics, resolution, as well as initial and boundary conditions used in the model. These errors may be amplified or suppressed during the climate model integration. The result of the numerical simulations can become quite different from the observation after just 1 or 2 weeks.

Since uncertainty always exists in a numerical weather prediction model, scientists have applied ensemble-forecasting techniques. The ensemble method may include running the same model with different initial and boundary conditions (for example, to disturb the initial conditions or to start to integrate the model at different times), running several different models with the same initial/boundary conditions, or running different models with different initial/boundary conditions to estimate the probability of the model forecasting. If the results diverge, the confidence of the results is low; otherwise, the confidence is high. There is no guarantee that the real climates are completely covered by the model results. For example, if all of the models are deficient in describing specific physical process, the ensemble average of these models will also be deficient. The model also may not be able to predict extreme cases, which are needed most.

If a model can reasonably simulate the current weather and produce good short-term forecast (7–14 days), it has a better chance to predict future climate change or simulate the past climate because the climate is an accumulation of daily weather processes. A model with more detailed physics, finer resolutions, and more accurate numerical schemes and initial/boundary conditions usually performs better. Although an RCM can simulate the observations reasonably well even after a few years integration when reanalysis is used as the initial/lateral boundary conditions, it cannot be used alone to predict the climate in the future without coupling with a GCM. On the other hand, it is unlikely that GCM-simulated weather systems will compare favorably with observations after a few weeks of integration. Climate studies usually emphasize statistics instead of describing any single weather event. The climate simulations also depend more on the boundary conditions, which include solar radiation and properties of the soil and ocean, than the initial conditions. Currently, many climate models are being used to simulate the climate in the future or the past. For example, the climate models show that the mean atmosphere becomes warmer under the doubled atmospheric carbon dioxide (CO_2) scenario, with quite different regional responses. When climate models are applied to forecast the future climate, they also encounter uncertainties in volcanic activity, forest fires, the change of trace gases/aerosols and emission, and the change of vegetation and land surface due to human activities. Wen-Yih Sun

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Climate modification

Alteration of the Earth's climate by human activities; humans have the capacity to modify the Earth's climate in several important ways.

Local and regional scale. Conventional agriculture alters the microclimate in the lowest few meters of air, causing changes in the evapotranspiration and local heating characteristics of the air-surface interface. These changes lead to different degrees of air turbulence over the plants and to different moisture and temperature distributions in the local air.

Another example of human influence on climate at a larger scale is that the innermost parts of cities are several degrees warmer than the surrounding countryside, and they have slightly more rainfall as well. These changes are brought about by the differing surface features of urban land versus natural countryside and the unique ways that cities dispose of water (for example, storm sewers). The altered urban environment prevents evaporation cooling of surfaces in the city. The modified surface texture of cities (that is, horizontal and vertical planes of buildings and streets versus gently rolling surfaces over natural forest or grassland) leads to a more efficient trapping of solar heating of the near-surface air. The characteristic scales of buildings and other structures also lead to a different pattern of atmospheric boundary-layer turbulence modifying the stirring efficiency of the atmosphere. *See* MICROMETEOROLOGY; URBAN CLIMATOLOGY.

At the next larger scale, human alteration of regional climates is caused by changes in the Earth's average reflectivity to sunlight. For example, the activities of building roads and highways and deforestation change the reflectivity characteristics of the Earth's surface and alter the amount of sunshine that is reflected to space, as opposed to its being absorbed by the surface and thereby heating the air through contact. Such contact heating leads to temperature increases and evaporation of liquid water at the surface. Vapor wakes from jet airplanes are known to block direct solar radiation near busy airports by up to 20%.

Human activities also inject dust, smoke, and other aerosols into the air, causing sunlight to be scattered back to space. Dust particles screen out sunlight before it can enter the lower atmosphere and warm the near-surface air. An extreme case is popularly referred to as the nuclear winter scenario, where a massive injection of smoke particles into the upper atmosphere occurs during a hypothetical exchange of nuclear blasts. The resulting smoke veil theoretically remains in the atmosphere for up to 6 months and leads to a shading of the world and a resulting cooling of continental interiors by as much as 90°F (50°C) for several months. Ocean and coastal regions would experience less than about 18°F (10°C) of cooling. *See* AIR POLLUTION; NUCLEAR EXPLOSION; SMOG.

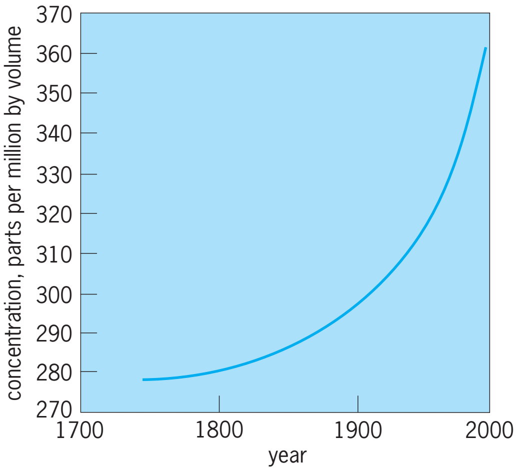
Global scale. Humans are inadvertently altering the atmospheric chemical composition on a global scale, and this is likely to lead to an unprecedented warming of the global atmosphere during the next generation. It comes about by anthropogenic injection into the atmosphere of relatively inert trace gases that perturb the radiation balance of the globe as a whole. Most of this gaseous waste comes from burning fuels that contain carbon and nitrogen. Other sources include inert gases used in aerosol spray cans and cooling devices. *See* ATMOSPHERIC CHEMISTRY.

Since alteration of the atmospheric composition by human activities has taken place for more than 150 years, it is important to ask whether the climate system has started to respond to the forcing. While no definitive answer exists, globally averaged temperature data suggest that on the whole the Earth has been warming over the last 100 years. *See* ATMOSPHERE; CLIMATIC PREDICTION; WEATHER MODIFICATION. Gerald R. North

Global warming. One of the most important and best understood features of the atmosphere is the process that keeps the Earth's surface much warmer than it would be with no atmosphere. This process involves several gases in the air that trap infrared radiation, or heat, emitted by the surface and reradiate it in all directions, including back to the surface. This recycling of heat maintains the surface and lower atmosphere of the Earth at a temperature higher than it would otherwise be.

Heat-trapping gases. The heat-trapping gases include water vapor, CO_2, CH_4, and N_2O. These gases constitute only a small fraction of the atmosphere, but their heat-trapping properties raise the surface temperature of the Earth by a large amount, estimated to be more than 55°F (30°C).

Human activities, however, are increasing the concentrations of CO_2, CH_4, and N_2O in the atmosphere, and in addition industrially synthesized chemicals—chlorofluorocarbons (CFCs) and related compounds—are being released to the air, where they add to the trapping of infrared radiation. Carbon dioxide is released to the air mainly from fossil fuel use, which also contributes to the emissions of CH_4 and N_2O. Agricultural and industrial processes add to the emissions of these gases. These concentration increases add to the already powerful heat-trapping capability of the atmosphere, raising the possibility that the surface will warm above its past temperatures, which have remained roughly constant, within about 3°F (1.7°C) for the past 10,000 years. The atmospheric concentration of CO_2 has increased to about 363 parts per million by volume (ppmv) from its preindustrial value of about 280 ppmv (see **illus.**); CH_4 has increased at a greater rate, from 0.75 ppmv to more than 1.7 ppmv. Nitrous oxide is growing slowly, at about 0.2% per year, and has a present concentration of 0.32 ppbv. The CFCs and related halocarbons have had the fastest rates of growth, up to 15% per year, but their concentrations are very small—300 parts per trillion by volume (pptv) for CFC-11, 535 pptv for CFC-12, and 3 pptv for halon-1301—the fastest growing species. Treaties are in existence that control internationally the production and use of many of the CFCs and related compounds, so their rate of growth has slowed, and for some a small decrease in atmospheric concentration has been observed. Large emissions of sulfur dioxide in industrial regions are thought to result in airborne sulfate particles that reflect sunlight and decrease the amount of heating in the Northern Hemisphere. *See* GREENHOUSE EFFECT.



History of atmospheric CO_2 concentration as inferred from an analysis of bubbles taken from ice cores in the Antarctic. (*After E. M. Neftel, H. Oeschger, and B. Stauffer, Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries, Nature, 315:45–47, 1985; and for measurements since 1970, data from Carbon Dioxide Information Analysis Center home page*)

Climate warming impacts. Estimates indicate that if human-induced emissions of heat-trapping gases continue according to the current pattern the globally averaged surface temperature could increase at a rate of about 0.4°F (0.22°C) per decade in the twenty-first century. This rate of global temperature change is much faster than any sustained global average temperature change documented in the last 10,000 years. Lifeforms have evolved with and are adapted to current climate conditions, including temperature. For this reason it is anticipated that should the warming occur as estimated, there will be serious damage to ecological systems.

Even slow, small climate changes can have large regional effects. There is evidence that about 6000 years ago parts of the Sahara Desert had sufficient rainfall to support vegetation and large mammals, while prairies advanced eastward and replaced forests, in what is now the United States, because of lack of rain. These changes were part of a global change characterized by an average temperature increase of only 2–4°F (1–2°C).

Rapid regional changes in climate occurring more than 10,000 years ago have been deduced from evidence in ice cores and from pollen found in layers in bogs and ponds; these changes were accompanied by major ecological changes in the region of the climate change. For example, about 11,000 years ago in what is now Europe trees were suddenly replaced by shrubs at the time of a large cooling in areas around the North Atlantic. Such events add to the evidence that a rapid climate change can damage ecosystems. Besides ecological damage, higher temperatures will melt glaciers and expand seawater, thereby raising sea level. Some regions will have climate changes considerably larger or smaller than the global average.

Even though the process is called global warming, the focus on temperature is partly for convenience; all climate features are expected to change by varying amounts as part of an overall climate change. For example, the temperature of the stratosphere is expected to decrease, and total precipitation is expected to increase while its annual distribution shifts in time and place. The role of CFCs in climate warming will be to increase the amount of heat trapped in the lower part of the atmosphere but, by destroying ozone in the stratosphere, to increase the ability of heat to leave the atmosphere. The net heating by CFCs will therefore be small; they will produce instead a change in the vertical temperature distribution of the atmosphere.

Climate change theory. There are many difficulties in producing a completely convincing calculation of the rate of average climate warming to be expected, and a specification of the detailed change in each climate parameter that will be experienced in each major region. These difficulties stem from the fact that the climate system consists of many components—atmosphere, oceans and ocean biota, ice caps and sea ice, land surface and ecosystems, and the human societies that are forcing rapid changes in the composition of the air—making the calculation very complex. In addition, small changes in the amount of sunlight reaching the Earth and large volcanic eruptions that place sulfur dioxide in the stratosphere complicate studies of human-induced climate change.

Attempts to simulate the interactions of all of these climate components, though using the largest computers available, require great simplification in the description both of the components and of the interactions among them. These simplifications lead to sizable uncertainties, especially when they involve processes that tend to amplify or diminish the degree of warming. Increased evaporation of water from the oceans as the surface warms and an increased water-holding capacity of the warmer air will lead to a higher water vapor concentration in the atmosphere. Water vapor is a heat-trapping gas; an increase in its average concentration in the air will add its heat-trapping effect to that of the human-emitted gases and amplify the warming. The size of the warming will be decreased by the fact that a warmer Earth will emit more infrared radiation to space, increasing the Earth's heat loss.

Some of the most complicated processes that are important in the calculation describe the role of clouds and the changes that clouds would undergo on a warmer Earth. Clouds both reflect sunlight away from the Earth and trap infrared radiation in the lower atmosphere, so changes not only in the amount of cloud but also in their optical characteristics must be correctly estimated. However, recent progress in climate calculations has contributed to improved agreement between observed climate heating since 1870 and model results, suggesting that the simple treatment of clouds in models is not seriously deficient. The comparison has also been aided by the rapid surface heating since 1975 that provides a larger heating signal compared to random temperature fluctuations. *See* CLOUD PHYSICS.

In addition to the known model deficiencies, there is reason to believe that models in general do not adequately represent sudden changes in complex systems. Thus a gradual change in surface temperature might lead to a sudden reversal of a major ocean current, or a gradual change in rainfall might lead to a collapse of a tropical ecosystem, without either event being foreseen in the model calculations.

All of these difficulties combine to produce a wide range of estimates for the rate of future climate warming. The Intergovernmental Panel on Climate Change (IPCC) of the United Nations estimates that if the current pattern of emissions of heat-trapping gases continues the average surface temperature should increase 0.31–0.43°F (0.17–0.24°C) per decade. But the IPCC asserts that there are enough uncertainties that a faster or slower change cannot be completely ruled out, and the threat of surprises must also be kept in mind. *See* CLIMATE HISTORY; CLIMATE MODELING; HEAT BALANCE, TERRESTRIAL ATMOSPHERIC.

Response to climate warming. The presence of numerical uncertainties and the possibility of surprises increase the difficulty for those who must develop national and international responses to the threat implicit in the human-induced climate change. Their task of selecting a response is made simpler, however, by the fact that the principal driving force for such a climate change—the use of fossil fuels—is also the driving force for a number of other atmospheric problems. Urban air pollution, regional pollution by low-altitude ozone, visibility problems over scenic vistas, and acid precipitation all involve fossil fuel emissions, so that an uncertainty in specific aspects of any one problem does not shift the focus away from reduced fossil fuel use as the core strategy for slowing harmful human impacts on the atmosphere. *See* ACID RAIN. John Firor

Climate Change Impacts

Substantial uncertainties exist as to the severity, timing, and rate of human-induced global climate change. Nevertheless, there are particular attributes of Earth's physical processes, natural ecosystems, and human socioeconomic activities that would be affected by a changing climate.

Climatic change is often broadly discussed in global terms, but the impacts of a warmer Earth would be experienced at the local and regional levels. Many potential impacts may be considered undesirable from an environmental or socioeconomic perspective, whereas others may be seen as beneficial. Although it is difficult to predict with certainty what the impacts of a possible global climate change may be in particular regions, a range of possible consequences can be described.

Physical processes. Global warming is projected to be greater in the higher latitudes and polar regions than in the tropics, causing a decrease in the difference in temperatures between the poles and the tropics as well as altering global atmospheric circulation patterns. This in turn would change the timing, distribution and amount of regional precipitation, affect the occurrence and location of extreme weather events such as hurricanes and tornadoes, alter the timing of mountain snowmelt and river basin runoff, reduce high-latitude snow and ice cover, and eventually lead to rising sea levels around the world. *See* ATMOSPHERIC GENERAL CIRCULATION; HURRICANE; PRECIPITATION (METEOROLOGY); TORNADO.

Natural ecosystems. The projected climate change may occur at a faster rate than any natural climatic warming has occurred in the past 10,000 years—a period covering the entire history of human civilizations. A rapid warming, or abrupt shifts in regional climate, could harm biological communities that have developed under relatively stable climatic conditions over the past several centuries and exist within relatively narrow ranges of average climatic conditions.

Terrestrial natural ecosystems would be the first to be affected by global warming, followed by marine ecosystems. The terrestrial environment is sensitive not only to average climatic conditions but also to extreme conditions such as extended periods of high or low temperatures, droughts, floods, and other weather hazards. Some species of vegetation can survive and reproduce under a broad range of climate conditions. Other species require not only a stable climate but a narrow range of meteorological extremes such as high and low temperatures, precipitation, and soil moisture. The Intergovernmental Panel on Climate Change, created by the United Nations in 1988, has concluded that over the next 50 years projected changes in regional temperatures and precipitation could cause climatic zones to shift hundreds of kilometers toward the polar regions. Some biotic communities may be capable of adapting to a climatic shift of such magnitude, while others would experience substantial loss that could include some species extinction. *See* EXTINCTION (BIOLOGY).

In the Northern Hemisphere's midlatitude temperate zone spanning North America and the Eurasian landmass, such a large climatic shift would have a tremendous impact on forest ecosystems. Individual tree species might not be able to migrate into climatic zones similar to those that they presently occupy. If climate change were to proceed more rapidly than temperate forests could successfully migrate poleward, large-scale demise of trees could be anticipated. Climate change could cause weather-related stress for individual tree species, exposing them to pest damage. Changes in forestry would also affect associated flora and fauna that are adapted to existing forest ecosystems and climatic conditions. *See* FOREST ECOSYSTEM.

According to the IPCC, the permafrost that presently underlies the 20–25% of the Northern Hemisphere that is perenially frigid may begin to thaw during the next 40–50 years. Degradation of the permafrost cover would damage high-latitude surface ecosystems, destabilize terrain, and cause soil erosion. *See* PERMAFROST.

Rising sea levels would inundate low-lying river estuaries and coastal wetlands (including tropical mangrove forests), which support established biotic communities. Again, the degree of environmental impact would be a function of both the rate and extent of sea-level rise, as rapid change would not permit adaptation by biotic communities. In addition, some low-elevation islands could be partially inundated, with substantial impacts to coastal ecology and freshwater supplies as well as to terrestrial biota.

The biological productivity and diversity of marine ecosystems would be affected by changes in water temperature and, in the long term, changes in ocean currents and ocean circulation. Inundation of estuaries and coastal wetlands would adversely affect the reproductive cycles of valuable fish and shellfish species. *See* BIOMETEOROLOGY; CLIMATOLOGY; ECOSYSTEM; MARINE ECOLOGY.

Steven L. Rhodes

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Climatic prediction

The description of the future state of the climate, that is, the average or expected atmospheric and Earth-surface conditions, for example, temperature, precipitation, humidity, winds, and their range of variability. *See* CLIMATOLOGY.

Seasonal and interannual climate predictions, made many months in advance, provide useful information for planners and policy makers. Various countries are working on operational (systematic and regular) climate prediction products, and by the beginning of the twenty-first century climate prediction will be added to weather prediction as an operational mission requirement of the world's major meteorological services. *See* METEOROLOGY.

Jay S. Fein

Seasonal to Interannual Prediction

It is well known that the Earth revolves around the Sun in a periodic orbit giving rise to a well-defined annual cycle in the Earth's climate, and that the annual cycle in the incident solar radiation is nearly identical from one year to the next. The question as to why the winter climate of one year is so different from the winter climate of another year has long interested climate scientists, because an understanding of the causes of interannual variations of the Earth's climate might provide some clues about the predictability of these variations. *See* SOLAR CONSTANT; SOLAR RADIATION.

The fundamental reason for departures from perfectly periodic variations in the atmosphere and oceans—in spite of the fact that the solar forcing is nearly perfectly periodic—is that the physical laws that determine the motions of air and water in the Earth-atmosphere-ocean system are inherently nonlinear and chaotic. The internal instabilities of this nonlinear dynamical system are capable of producing a nonperiodic behavior even if the external forcing (the Sun) is perfectly periodic. Because of the nonlinear nature of the mathematical equations describing motions in the Earth-atmosphere-ocean system, it is impossible to predict these motions for a long time in the future. One major endeavor of researchers in the field of meteorology and oceanography is to determine the range at which different properties of the nonperiodic components of atmospheric and oceanic motions can be predicted.

Weather prediction. The day-to-day changes of weather cannot be predicted for a long time because even minute errors in observations amplify with time and become quite large within a few days or a few weeks, destroying the value of the forecast. The track of a storm seen on a weather map for a given day, for example, can be predicted for several days; but beyond a week or two the storm intensity, structure, and position are unpredictable. Improvements in weather-observing systems and the use of more complete equations in the weather prediction models will improve the quality of weather forecasts and the time for which they are valid, but the limitations arising from the amplification of imperceptible errors in the initial conditions of the forecast calculation will always restrict detailed weather forecasts to periods of a week or two in the future.

Despite this fundamental limitation in the ability of meteorologists to predict day-to-day changes in weather, it seems possible to predict seasonal averages of weather with sufficient accuracy to be of benefit to society. For example, even if it is not possible to predict the life cycle of individual weather disturbances that provide the monsoon rainfall over Asia, it may be possible to predict the seasonal mean rainfall over the monsoon region. *See* MONSOON METEOROLOGY; WEATHER FORECASTING AND PREDICTION.

Boundary conditions at Earth's surface. The conditions at the Earth's surface lower boundary of the atmosphere (for example, surface temperature, soil moisture and vegetation, or snow and sea ice cover) can have large variations from one year to another. It has been proven by statistical analysis of observations and by experiments using mathematical climate models that interannual changes in these boundary conditions are directly responsible for interannual changes in the seasonal mean climatic conditions in many parts of the globe. Therefore, if changes in these boundary conditions could be predicted, it would be possible to predict changes in seasonal mean climatic conditions in certain regions of the globe. Since changes in the boundary conditions are caused by interactions with the atmosphere, there is no guarantee that they are predictable. However, boundary conditions change rather slowly, and therefore they can be assumed to persist for periods up to a season. Thus it is possible to predict seasonal mean climatic conditions for the coming season (to the extent that they are influenced by the anomalous boundary conditions) by using the current boundary conditions. For longer periods, the boundary conditions cannot be assumed to persist, so that prediction of climatic conditions must necessarily involve coupled models of the land-atmosphere-ocean system, which enable prediction of future boundary conditions. *See* CLIMATE MODELING.

Seasonal predictions. For seasonal climate predictions to be useful, the seasonal climate variability caused by interactions with the atmosphere's lower boundary (for example, sea surface temperature) must be significantly larger than the changes in the atmosphere that can occur in the absence of any boundary forcing (normally referred to as the natural variability). The natural variability of seasonal mean climate is different in different seasons and in different regions. Therefore, the extent to which seasonal mean climate variations can be usefully predicted is also different for different regions. For example, the weather fluctuations over North America are far more vigorous during the winter season than during the summer season. The weather fluctuations over large parts of the tropics are far less energetic (day-to-day changes are generally small) compared to those in the higher latitudes. Therefore, the seasonal mean climate in the tropics is far more predictable than that in the higher latitudes. Likewise, seasonal mean climate in high latitudes is more predictable in summer than in winter.

Tropical droughts. Most of the tropical regions, and especially the regions that experience monsoons, have well-defined rainy seasons. For example, most of the annual rainfall over India and sub-Saharan Africa occurs during the summer monsoon season (June–September), and over northeast Brazil during March–May. Although the individual rainfall episodes occur in association with individual clouds and weather-scale disturbances, it is the large-scale convergence of moisture, generally associated with the intertropical convergence zone, that is responsible for the seasonal mean rainfall. Most of the tropical droughts and floods can be understood as space-time shifts in the annual cycle. For example, severe droughts in northeast Brazil occur whenever the intertropical convergence zone remains farther north of its mean position during the rainy season. Likewise, droughts over India and Australia are often associated with the eastward shift of the mean climatological rainfall maximum, giving rise to large increases in rainfall in the central Pacific. An important discovery was the recognition that these space-time shifts of rainfall maxima in the tropics are due to changes in the boundary conditions of sea surface temperature and land surface conditions. The tropical atmosphere has a unique property, distinct from that of mid and high latitudes, that seasonal and interannual variations are largely determined by changes in the slowly varying boundary conditions at the Earth's surface. Therefore, the prospects for long-range forecasting in the tropics are good. *See* DROUGHT; PRECIPITATION (METEOROLOGY); TROPICAL METEOROLOGY.

Extratropical variations. Seasonal climate variations in the extratropics are not as strongly controlled by the boundary conditions, but are strongly influenced by the internal dynamical processes in the atmosphere. For example, a major blocking event over North America can significantly change the monthly or even seasonal mean climate for that year. Prediction of seasonal and interannual variations during the winter season is particularly difficult because the day-to-day fluctuations are highly energetic and so give rise to large uncertainty in the prediction of the seasonal mean climate. Some evidence, however, indicates that large changes in the boundary conditions in the tropics, causing large changes in tropical rainfall and therefore atmospheric heating, can produce predictable effects even in the extratropics. This result is possible because the tropical influences can propagate away from the Equator and influence the extratropical climate variations. This mechanism of tropical-extratropical interaction has given some hope for seasonal and interannual prediction in the extratropics.

The day-to-day variations in the extratropics in the late spring and summer season bear some similarity to the tropical weather variations because they are not as energetic or intense as during the winter season. This reduction in the uncertainty due to the internal dynamical processes should make it possible to predict the influences of slowly varying boundary conditions in the spring and summer season. Relationships between spring rainfall and summer droughts over North America are good examples of predictability due to the effects of the land surface boundary conditions. *See* ATMOSPHERIC GENERAL CIRCULATION; STORM.

El Niño Southern Oscillation (ENSO). The outstanding example of interannual climate variability is the occurrence of multiyear episodes of warm and cold sea surface temperature in the central and eastern tropical Pacific; these episodes are generally referred to as El Niño. These variations are a consequence of the interactions between the upper layers of the ocean and the overlying atmosphere. Changes in the prevailing southeasterly winds over the equatorial Pacific can produce changes in the wave activity in the upper layers of the ocean and the upwelling of cold water, giving rise to changes in sea surface temperature, which in turn can produce changes in the surface winds. This mutual enforcement of oceanic and atmospheric changes (a form of instability of the coupled ocean-atmosphere system) is responsible for multiyear variations in sea surface temperature in the equatorial Pacific and the associated changes in sea-level pressure. In particular, the simultaneous occurrence of higher-than-average pressure in the Pacific Ocean and lower-than-average pressure in the Indian Ocean, and vice versa, is noteworthy. This recurrent seesaw pattern of pressure changes is referred to as the Southern Oscillation.

Associated with these changes in sea surface temperature, surface pressure, and surface wind are large changes in rainfall along the equatorial belt. During the episodes of colder-than-average sea surface temperature in the central and eastern Pacific and stronger-than-average southeasterly trades, the maximum seasonal rainfall is found at the extreme western position near the warmest surface waters of western Pacific. During these years, monsoon rainfall over India and Australia is generally above average. During the episodes of warmer-than-average sea surface temperature in the central and eastern Pacific and weaker-than-average surface winds, the rainfall maximum shifts eastward, producing severe droughts over India and Australia and heavy floods over the central Pacific and the west coast of South America. Actually, there are global effects of these changes in sea surface temperature, rainfall, and circulation in and over the tropical Pacific Ocean.

The discovery of these interrelationships among sea surface temperature, rainfall, and circulation, and the ability to predict these variations by using coupled models of the ocean-atmosphere system, has established a scientific basis for prediction of seasonal and interannual climate variations by using dynamical models of the climate system.

Forecasts. Several countries, including the United States, routinely issue forecasts for the coming season. These forecasts, generally issued in terms of probabilities of occurrence of above- or below-average temperature and rainfall, are based on empirical methods in which certain properties of atmospheric circulation, rainfall, and surface boundary conditions (generally sea surface temperature and snow cover) in the preceding months are used to forecast the climate for the coming season. It is generally accepted that there is some skill in these forecasts. Efforts have been made to develop and implement dynamical models of varying complexity of the coupled land-atmosphere-ocean system to predict seasonal and interannual variations. J. Shukla

Decadal-to-Century Climate Prediction

While the potential benefits of being able to predict climate on the decadal-to-century time scale are very large, so too are the problems associated with trying to make such predictions. To understand the nature of these problems, it is useful to consider first the decadal-to-century prediction of the change in the surface temperature averaged over the Earth, and then to consider the even more difficult problem of predicting the geographical distributions of surface temperature and the other climatic quantities of importance to humanity, especially precipitation.

Global average temperature. To facilitate thinking about predicting future global average surface temperature, it is necessary to consider the past behavior of this quantity. The observed record of decadal average temperature, T, relative to its value in 1860–1869 (**Fig. 1**) shows that during the first six decades of the

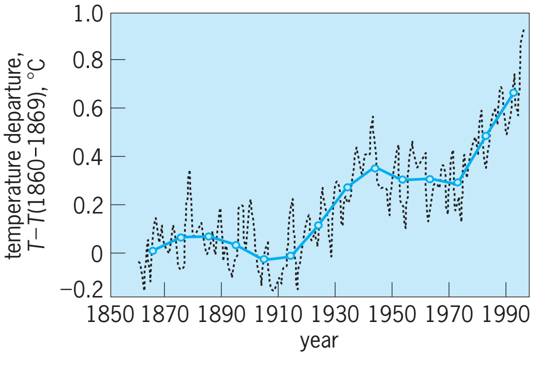

Fig. 1. Observed decadal-average global-average surface temperature (solid line) and observed annual-average global-average surface temperature (broken line). Temperature change in °F equals 1.8 times the temperature change in °C.

record, 1860–1869 to 1910–1919, T varied very little, with no discernible trend. From 1910–1919 to 1940–1949, T increased each decade. This warming trend then ceased. Then T increased from 1970–1979 to 1990–1998 such that it was 0.66°C (1.19°F) warmer in 1990–1998 than in 1860–1869. In order to understand why the decadal average temperature varied in this manner, to determine if predictions of such variations can be made and by what means, it is necessary to consider the transfer of energy across the top of the Earth's atmosphere.

When the amount of infrared thermal radiation emitted by the Earth to space equals the amount of solar radiation absorbed by the Earth from the Sun (240 W m^{-2}), the net input of energy into the atmosphere-Earth system is zero. If somehow the net input energy becomes positive, energy will enter the system, the decadal average temperature will increase, and the infrared radiation emitted to space (which depends on the decadal average temperature) will increase. Conversely, if the net energy input becomes negative, energy will leave the system, the decadal average temperature will decrease, and the infrared radiation emitted to space will decrease. In either case the net input of energy into the atmosphere-Earth system will be restored to zero. Consequently, any factor that causes the net energy input to become nonzero can cause the decadal average temperature to vary. To predict the change in this temperature value, the change in the net energy input from zero (the radiative forcing) must be predicted.

One factor that has changed the net energy input since the mideighteenth century, and will likely change it in the future, is the rising concentrations of atmospheric greenhouse gases: carbon dioxide, methane, nitrous oxide, and chloroflurocarbons (whose emission is now restricted by international convention). Acting alone, the increaseing greenhouse gases would have made the net energy input positive by about 2.6 W m^{-2} in 1998 (**Fig. 2**). Another factor influencing the net energy input is the input of sulfur dioxide gas into the atmosphere near the Earth's surface by the anthropogenic burning of sulfur-containing coal and oil. This gas is chemically converted into sulfate aerosol particles, which enhance the reflection of solar radiation to space in cloudless air. It is thought that these particles also act as nuclei for the formation of cloud droplets, smaller than would be the case in their absence, which therefore enhance the reflection of solar radiation in cloudy air. The enhanced reflection in clear and cloudy air reduces the absorption of solar radiation by the Earth, which, acting alone, would make the net energy input negative. The size of this anthropogenic sulfate aerosol radiative forcing is quite uncertain, particularly that for cloudy air. One estimate gives a value of about -1.1 W m^{-2} in 1998 (Fig. 2). *See* GREENHOUSE EFFECT; TERRESTRIAL RADIATION.

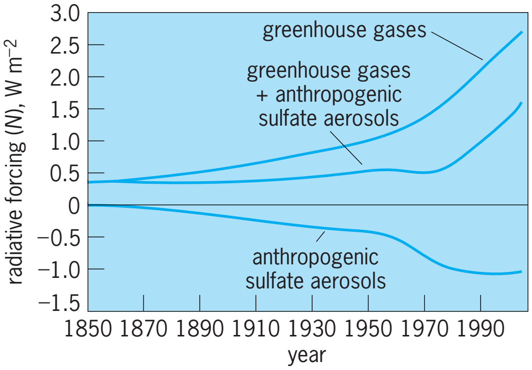

Fig. 2. Radiative forcing of climate by greenhouse gases and anthropogenic sulfate aerosols, together with their sum. The greenhouse gas forcing is taken to be zero in 1765, and the anthropogenic sulfate aerosol forcing is taken to be zero in 1850.

If the future radiative forcing of climate change could be predicted as a function of time, to make a prediction of the resulting climate change a climate model would be needed. A climate model is the mathematical expression of the fundamental laws of nature, for the present example, conservation of energy. The resulting equations express the time rate of change of the decadal average temperature at any time in terms of the value of the decadal average temperature at that time. Starting from the known value of this temperature at some initial time, the time rate of change of the decadal average temperature is calculated from the equations and multiplied by a small time interval; and the result is added to the initial temperature value to give a value at a future time. This procedure is then repeated to predict temperatures at further time increments. The climate model must include the ocean as well as the atmosphere, for the rate of heat removal from the upper ocean by transport into the deeper ocean, together with the net energy input into the atmosphere-Earth system at a given time, determines the rate at which the decadal average temperature changes in time.

In one simple climate model, the ocean is divided vertically into many layers, with the uppermost being the mixed layer wherein temperature is uniform with depth. Also, the ocean in each hemisphere is divided horizontally into a polar region where bottomwater is formed, and a nonpolar region where there is vertical upwelling. In the nonpolar region of each hemisphere, heat is transported upward toward the surface by the water upwelling there, and downward by physical processes whose effects are treated as an equivalent diffusion. Heat is also removed from the mixed layer in the nonpolar region of each hemisphere by transport to the polar region and downwelling toward the bottom. This heat is ultimately transported upward from the ocean floor in the nonpolar region.

Several quantities must be prescribed in this simple climate model. One of the most important is the sensitivity of the climate system, a parameter that represents the change in the global average surface temperature resulting from a radiative forcing equal to that caused by doubling the concentration of carbon dioxide (the net energy input equals 4.4 W m^{-2}) after sufficient time has passed for the net energy input to be restored to zero. The value of the sensitivity is quite uncertain. The most comprehensive climate models that predict this value—the general circulation models—give values that range from about 1.5 to about 4.5°C (2.7 to 8.1°F). The simple climate model can be used to estimate the sensitivity of the climate system, together with the radiative forcing of the anthropometric sulfate aerosol for a specific year, by minimizing the discrepancy between the simulated and observed decadal average temperature, together with the discrepancy between the simulated and observed interhemispheric temperature difference. The resulting decadal average temperature simulated by the model does reproduce the overall increase in the observed decadal average temperature, but not the detailed variations.

One possible reason for the discrepancy between the observed and simulated temperatures is that one or more factors influencing the net energy input may not have been taken into account. For example, some scientists believe that the energy emitted by the Sun has varied over time, thereby causing a variation in the solar radiation entering the top of the Earth's atmosphere—the solar irradiance. Although there are no useful observations of solar irradiance prior to 1978, when satellite observations began, and although these satellite observations show irradiance variations that are too small to influence the decadal average temperature by more than a few hundredths of a degree Celsius, observations of sunspots since the seventeenth century and of solar magnetic activity during the twentieth century, plus astronomical observations of Sun-like stars since 1970, suggest that variations of solar irradiance sufficiently large to influence the decadal average temperature cannot be ruled out. Other scientists believe that variations in the occurrence of large volcanic eruptions may influence the decadal average temperature by varying the amount of solar radiation reflected to space. Although the sulfate aerosols created in the stratosphere by the injection of sulfur dioxide gas there by large volcanic eruptions do tend to reflect more solar radiation to space and decrease the decadal average temperature, the episodic nature of volcanic eruptions limits the temporal influence of a single volcanic eruption to less than a decade. It is argued, nevertheless, that the variation in the number of large volcanic eruptions per decade can significantly influence the decadal average temperature. Yet another factor which can influence the net energy input is the aerosol particles released into the lower atmosphere by biomass burning, such as by tropical deforestation and slash-and-burn agriculture. Furthermore, changes in the fraction of solar radiation reflected by the Earth's surface—the surface albedo—due to anthropogenic modifications of the surface can also change the net energy input. *See* ALBEDO.

A different possible reason for the discrepancy is that, even if there were no changes in the net energy input due to factors such as those described above, the decadal average temperature might vary because of interactions between the atmosphere and ocean, or by variations within the ocean itself. A well-known example of an atmosphere-ocean interaction is the El Niño Southern Oscillation, which occurs irregularly over the tropical Pacific Ocean with a time scale of 3–7 years. One analysis of the discrepancy suggests that it is likely the result of a temperature oscillation within the North Atlantic Ocean, with a time scale of about 65 years.

Distributions of temperature and precipitation. Although the future course of global average surface temperature can, in principle, be predicted with a simple climate model, the prediction of the geographical distributions of temperature and other climatic quantities requires a much more complex climate model, one at the other terminus of the climate model hierarchy.

Only the general circulation model determines the geographical and vertical distributions of an ensemble of climatic quantities, including temperature, wind, water vapor, clouds and precipitation in the atmosphere; soil moisture, soil temperature, and evaporation on the land; and temperature, currents, salinity, and sea ice in the ocean. The mathematical equations in general circulation models that express the fundamental laws of nature are so complex, however, that they can be solved only at discrete geographical and vertical locations, and only over discrete time intervals. A typical general circulation model divides the atmosphere into thousands of three-dimensional volumes, each having dimensions of about 250 km (155 mi) in both the north-south and east-west directions, and 1 km (0.6 mi) in the vertical direction. Reducing these dimensions is severely constrained by the speed of available supercomputers. For example, increasing the horizontal resolution of a general circulation model from 250 km (155 mi) to 25 km (16 mi) would increase the required computer time a thousandfold, from about 2 weeks to compute a greenhouse-gas induced change in equilibrium climate—the climate change when the net energy input is restored to zero—to more than 30 years.

The constraint on horizontal resolution imposed by available supercomputers also has profound significance for the physical processes that can be included in a general circulation model. In particular, the Earth's climate system encompasses physical processes ranging in horizontal size from 40,055 km (24,889 mi) for disturbances that span the entire circumference of the Earth, to about one-millionth of a meter (0.00004 in.) for the condensation of water vapor onto aerosol particles and dust to form clouds. General circulation models using supercomputers explicitly include physical processes having horizontal sizes of about 250 km (155 mi) and larger. Worse yet, the physical processes smaller than 250 km (155 mi) cannot be ignored, because their effects significantly determine climate and climate change. Thus, climate modelers face the dilemma that their models cannot resolve the small-scale physical processes, and they cannot ignore the effects. This is the major difficulty in modeling the Earth's climate.

The approach taken to overcome it is to determine the effects of the unresolved physical processes on the scales resolved by a general circulation model by using information available only on the resolved scales. This approach is called parametrization. The principal differences among general circulation models lie in their different parametrizations, particularly of cloud and precipitation processes. These parametrization differences have a significant influence on the climate simulated by the general circulation models.

The geographical distributions of the change in surface air temperature simulated by general circulation models for a doubling of the carbon dioxide concentration show that although there are similarities in the regional temperature changes simulated by the global circulation models, there are also marked differences. This fact is even more apparent in the changes in precipitation simulated by the general circulation models. This fact is not surprising because many of the physical processes that determine precipitation have horizontal scales smaller than the resolutions of the general circulation models, and it is these unresolved processes that have had to be parametrized in the models. To improve this situation will require that at least mesoscale meteorological processes, with horizontal sizes down to 50 km (31 mi), be explicitly resolved by the models. A fivefold increase in the horizontal resolution of the general circulation models and an attendant 125-fold increase in computer speed will be required. Such high-speed supercomputers, capable of performing several trillion mathematical operations per second, are projected to be available about the year 2000.

However, to be able to predict the regional climate on a decadal-to-century time scale requires the knowledge of the three-dimensional distributions of temperature, salinity, and velocity in the ocean at the beginning of the prediction period. The panoceanic measurement system required to obtain this knowledge does not yet exist. Michael E. Schlesinger

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Climatology

The scientific study of climate. Climate is the expected mean and variability of the weather conditions for a particular location, season, and time of day. The climate is often described in terms of the mean values of meteorological variables such as temperature, precipitation, wind, humidity, and cloud cover. A complete description also includes the variability of these quantities, and their extreme values. The climate of a region often has regular seasonal and diurnal variations, with the climate for January being very different from that for July at most locations. Climate also exhibits significant year-to-year variability and longer-term changes on both a regional and global basis.

Climate has a central influence on many human needs and activities, such as agriculture, housing, human health, water resources, and energy use. The influence of climate on vegetation and soil type is so strong that the earliest climate classification schemes were often based more on these factors than on the meteorological variables. While technology can be used to mitigate the effects of unfavorable climatic conditions, climate fluctuations that result in significant departures from normal cause serious problems even for modern industrialized societies and more so for the less developed ones. The goals of climatology are to provide a comprehensive description of the Earth's climate over the range of geographic scales, to understand its features in terms of fundamental physical principles, and to develop models of the Earth's climate for sensitivity studies and for the prediction of future changes that may result from natural and human causes. *See* CLIMATE MODELING; CLIMATIC PREDICTION.

Physical basis of climate. The global mean climate and its regional variations can be explained in terms of physical processes. For example, the temperature is warmer near the Equator than near the poles (see **table** and **Figs. 1** and **2**). This is because the source of heat for the Earth is the radiant energy coming from the Sun (insolation), and the Sun's rays fall more directly on the Equator than on the poles. The circulations in the atmosphere and in the oceans transport heat poleward and thereby reduce the Equator-to-pole temperature difference that is continually forced by insolation. The energy released by the rising of warm air in the tropics and the sinking of cold air in high latitudes drives the great wind systems of the atmosphere, such as the trade winds in the tropics and the westerlies of middle latitudes. *See* ATMOSPHERIC GENERAL CIRCULATION; OCEAN CIRCULATION; TROPICAL METEOROLOGY; WIND.

The flux of solar energy at the mean distance of the Earth from the Sun is about 1367 $W \cdot m^{-2}$. The supply of energy per unit of the Earth's surface area is controlled by geometric and astronomical factors. Because the axis of rotation of the Earth is inclined at an oblique angle to the plane of the Earth's orbit, the declination angle of the Sun undergoes a seasonal variation as the Earth makes its annual circuit around it. The declination angle is equivalent to the latitude at which the Sun is directly overhead at noon. The declination angle varies between 23.5° N at northern summer solstice (June 21) and 23.5° S at northern winter solstice (December 22), for the current

Temperature (T) and precipitation (P) for selected stations in North America, South America, and Antarctica*

Station	Latitude, degrees	T_{annual}	T_{Jan}	T_{July}	P_{annual}	P_{Jan}	P_{July}
Alert	82.50 N	−18.0	−32.1	3.9	156	8	18
Barrow	71.30 N	−12.5	−26.8	3.9	109	5	20
Fairbanks	64.80 N	−3.4	−23.9	15.4	287	23	47
Baker Lake	64.30 N	−12.3	−33.6	10.7	213	7	36
Anchorage	61.17 N	1.8	−10.9	13.9	373	20	47
Juneau	58.37 N	4.5	−3.8	12.9	1288	102	114
Edmonton	53.57 N	2.8	−14.7	17.5	447	25	83
Seattle	47.45 N	10.8	3.9	18.2	980	153	19
Montreal	45.50 N	7.2	−8.9	21.6	999	80	93
Des Moines	41.53 N	10.5	−5.2	25.2	789	32	77
Salt Lake City	40.78 N	10.7	−2.1	24.7	353	34	15
Washington, D.C.	38.85 N	13.9	2.7	25.7	1087	82	107
San Francisco	37.62 N	13.8	9.2	17.1	475	102	t
Nashville	36.12 N	15.6	4.4	26.8	1146	139	94
Los Angeles	33.93 N	18.0	13.2	22.8	373	78	t
Birmingham	33.57 N	17.8	8.1	27.6	1349	128	131
Phoenix	33.43 N	21.4	10.4	32.9	184	19	20
New Orleans	29.95 N	20.0	12.3	27.3	1369	98	171
Havana	23.17 N	24.6	21.8	27.0	1126	54	108
Acapulco	16.83 N	27.6	26.1	28.7	1401	8	230
Caracas	10.60 N	26.1	24.4	26.4	545	42	72
Guayaquil	02.18 S	25.5	26.5	24.2	811	199	0.3
Manaus	03.13 S	27.5	26.7	27.6	2294	279	65
Brazilia	15.78 S	20.4	21.2	18.0	1643	248	6
Rio de Janeiro	22.90 S	23.7	26.1	20.9	1218	211	52
Antofagasta	23.47 S	16.2	19.8	13.2	1.9	0.0	0.3
Santiago	33.45 S	14.4	21.2	8.1	264	0.1	69
Buenos Aires	34.58 S	16.9	23.7	10.6	1029	104	61
Puerto Aisen	45.50 S	9.2	13.9	3.9	3001	203	331
Comodoro Rivadavia	45.78 S	12.6	18.6	6.9	216	16	21
Punta Arenas	53.00 S	6.0	10.4	1.3	362	40	24
Melchior	64.32 S	−3.6	1.0	−9.3	1116	42	90
Byrd Station	80.02 S	−27.9	−14.6	−35.1	39	7	2.5
Amundsen Scott	90.00 S	−49.4	−28.7	−60.3	1.5	t	t

*Temperature is in degrees Celsius; °F = (°C × 1.8) + 32. Precipitation is in millimeters; 1 mm = 0.04 in. t indicates trace of precipitation.

alignment of the Earth's orbit. The approximate sphericity of the Earth and the annual variation of the declination angle of the Sun cause the incoming solar radiation to be a function of latitude and season (**Fig. 3**). The annual mean insolation is largest at the Equator and decreases toward the poles. The seasonal variation is largest at high latitudes. At the poles 6 months of daylight alternate with 6 months of darkness. The Earth is closer to the Sun during summer in the Southern Hemisphere, so this region receives about 7% more insolation at this time than the Northern Hemisphere. *See* INSOLATION.

About half of the energy from the Sun that is incident at the top of the atmosphere is transmitted through the atmosphere and absorbed at the Earth's surface (**Fig. 4**). About 30% is reflected back directly to space, and another 20% is absorbed in the atmosphere. The fraction of the incoming solar radiation that is reflected to space is called the albedo. The albedo increases where clouds or surface ice and snow are present. It increases toward the poles because the amount of cloud cover and surface ice increases and because the Sun is closer to the horizon. The albedo of desert areas is generally higher than that of heavily vegetated areas or oceans. The solar energy that reaches the surface may be used to raise the surface temperature, or the energy can be used to evaporate water. The energy that is used to evaporate water (latent heat) is later released into the atmosphere when the water vapor condenses to form clouds and returns to the surface in the form of precipitation (**Fig. 5**). *See* ALBEDO; PRECIPITATION (METEOROLOGY).

Greenhouse effect. In order to achieve an energy balance, the solar energy that is absorbed by the Earth must be balanced by an equal amount of energy that is returned to space. The Earth emits radiative energy at frequencies that are substantially different from those of the Sun because of the Earth's lower temperature. The Earth emits primarily thermal infrared radiation [wavelengths from 4 to 200 micrometers], whereas most of the energy from the Sun arrives in the form of visible and near-infrared radiation (0.4–4 μm). The atmosphere is much less transparent to Earth's thermal radiation than to solar radiation, because water vapor, clouds, carbon dioxide, and other gases in the atmosphere absorb thermal radiation. Because the atmosphere prevents thermal radiation emitted from the surface from escaping to space, the surface temperature is warmer than it would be in the absence of the atmosphere. The combination of the relative transparency of the atmosphere to solar radiation and the blanketing effect of the gases in the atmosphere that absorb thermal radiation is often referred to as the greenhouse effect. The greenhouse effect on Earth is quite important. For example, the net emission of 21 units of

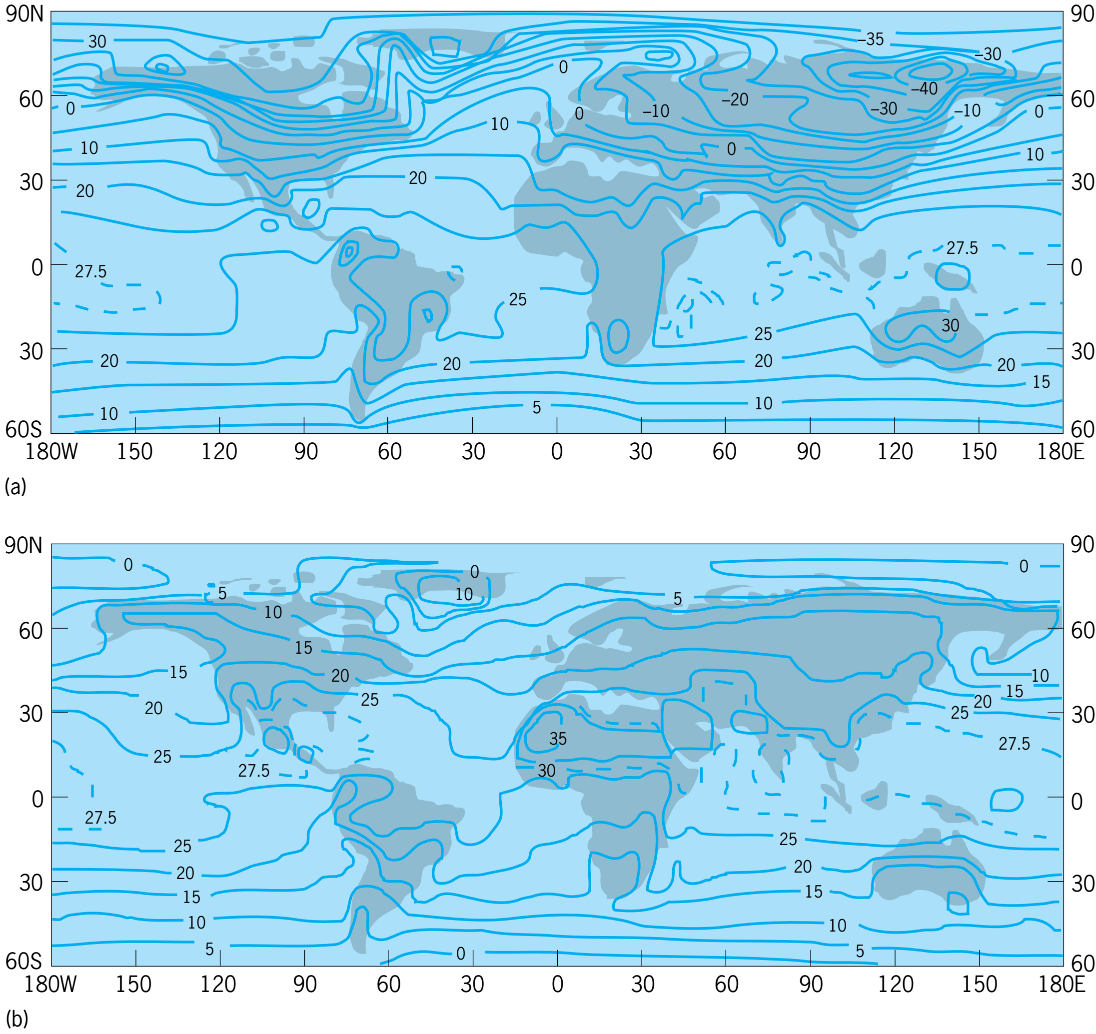

Fig. 1. **Mean surface temperature (°C) for (*a*) January and (*b*) July. Note the cold temperatures in the centers of the large northern landmasses in January. The broken contour line (27.5) is included to give more information concerning the tropics. °F = (°C × 1.8) + 32. (*After D. L. Hartmann, Global Physical Climatology, Academic Press, 1994*)**

infrared thermal radiation from the surface (Fig. 4) is the difference between a downward flux from the atmosphere of 89 units and a surface emission of 110 units. The downward flux of infrared radiation from the atmosphere is nearly double the solar radiation directly absorbed by the surface. *See* ATMOSPHERE; GREENHOUSE EFFECT.

Clouds affect the energy emission of the Earth.

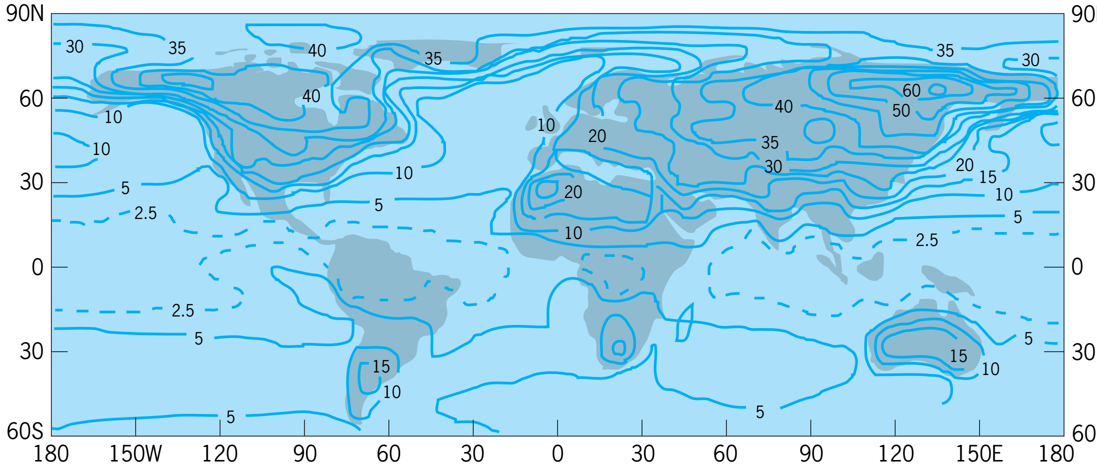

Fig. 2. **Annual range of temperature (°C), the difference between the warmest and the coldest months. The broken contour line (27.5) is included to give more information concerning the tropics. °F = (°C × 1.8) + 32. (*After D. L. Hartmann, Global Physical Climatology, Academic Press, 1994*)**

The thermal emission is low over tropical regions where high, cold clouds are present, such as the major precipitation regions of equatorial Africa, South America, southern Asia, Indonesia, and the band of clouds along the Equator. Because the albedo is higher, less solar energy is absorbed when clouds are present. Since clouds decrease both the solar energy absorbed and the terrestrial energy emitted to space, the net effect of tropical convective clouds on the energy balance of the Earth is less than their individual effects on solar and terrestrial energy. As a result, the distribution of the net radiative energy exchange at the top of the atmosphere does not clearly reflect the influence of the tall cloud so clearly. In general, the net radiation shows a strong influx of energy at those latitudes where the insolation is strongest. *See* TERRESTRIAL RADIATION.

A striking feature of the distribution of net radiation during July is the low values over the Sahara and Arabian deserts compared with the surrounding ocean and moist land areas. This is because desert sand has a relatively high albedo, so that less solar radiation is absorbed there. In addition, few clouds and little water vapor are present in the atmosphere over the deserts to absorb the thermal radiation emitted by the very hot surface. Since the emitted thermal radiation is high and the absorbed solar radiation is low, desert areas often show a net loss of radiative energy. This fact plays a central role in the maintenance of desert dryness. The loss of radiative energy is often balanced by convective transport of heat energy into the desert regions by the atmosphere. This results in downward motion of dry air, which flows outward near the ground and prevents the moist surface air of surrounding regions from reaching the desert interior. *See* DESERT.

Continentality. Annual temperature ranges are much greater near the center of continents in middle and high latitudes than they are over oceans. Land and ocean areas have very different seasonal variations because of their different capacities to store heat. Because the ocean is a fluid, its upper 150–300 ft (50–100 m) is generally in direct thermal communication with the surface. Therefore solar energy incident on the surface can be absorbed in this large heat reservoir without raising the surface temperature very much. In addition, over the oceans it is possible for solar energy to evaporate water and thus never be realized as heat at the surface. In contrast,

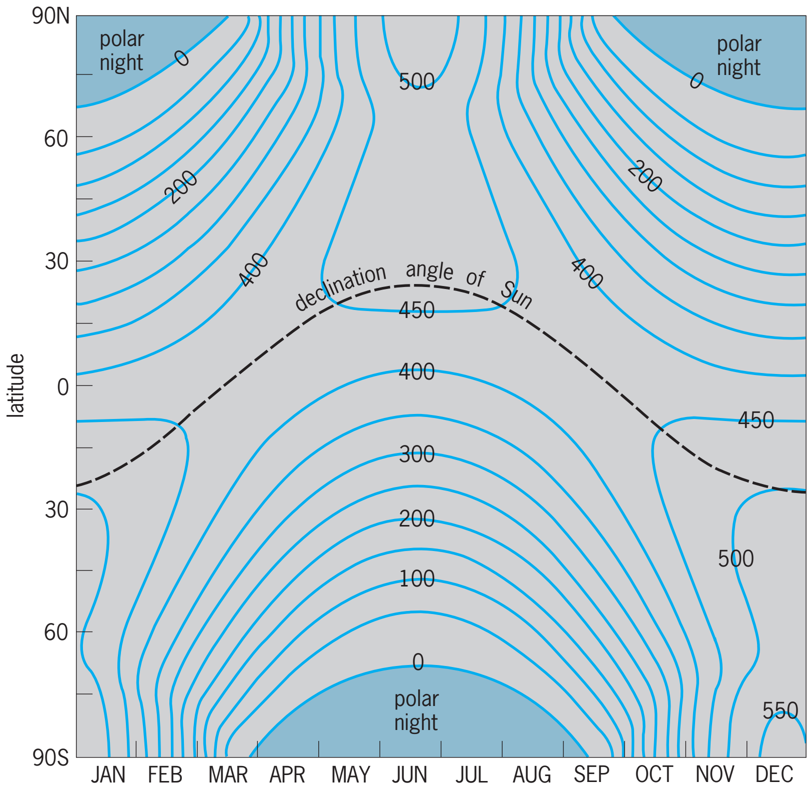

Fig. 3. Daily-average solar energy incident at the top of the atmosphere as a function of latitude and season in watts per square meter of surface area.

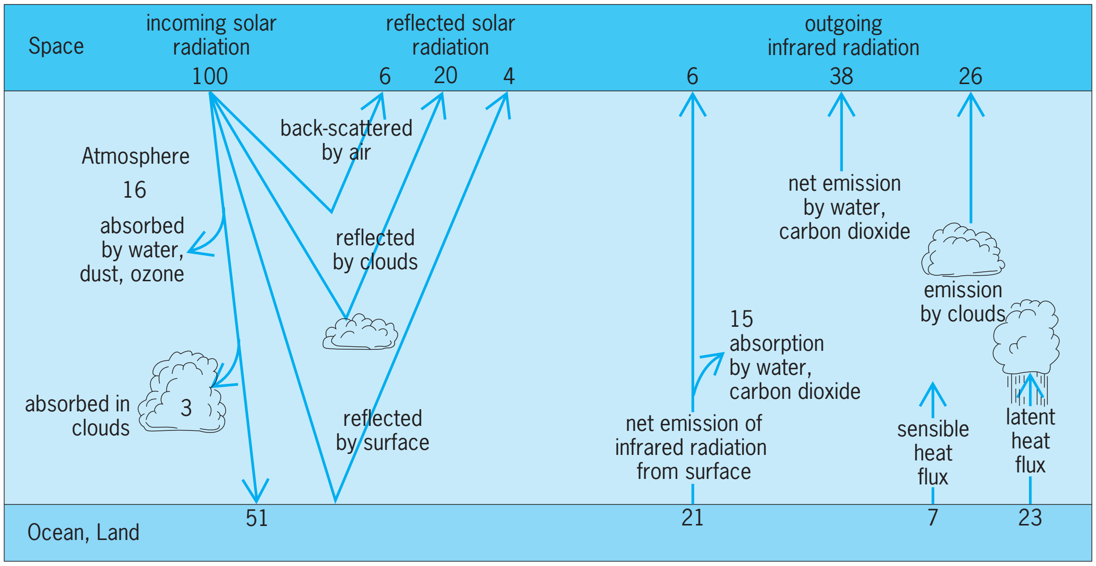

Fig. 4. Annual-mean global energy balance for the Earth–atmosphere system. Numbers given are percentages of the globally averaged solar energy incident upon the top of the atmosphere. (*After J. M. Wallace and P. V. Hobbs, Atmospheric Science: An Introductory Survey, Academic Press, 1977*)

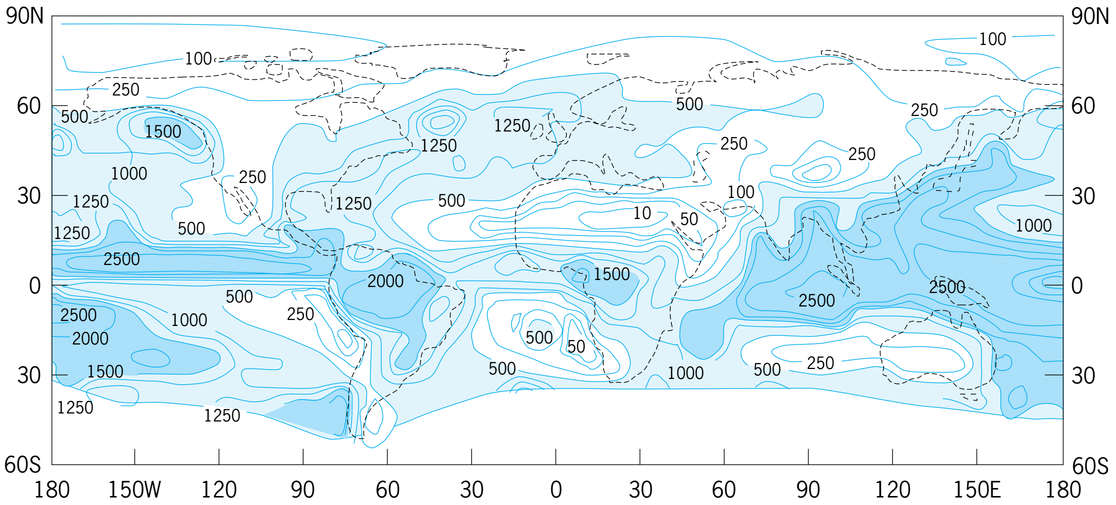

Fig. 5. **Geographic distribution of annual mean precipitation in millimeters. (*After D. L. Hartmann, Global Physical Climatology, Academic Press, 1994*)**

over land only about the first meter of soil is in thermal contact with the surface, and much less water is available for evaporation. During the winter, the ocean can return heat stored during the summer to the surface, keeping the surface relatively warm. The land cools off very quickly in winter, warms up rapidly in summer, and experiences large day-night differences. Continental climates in middle latitudes are characterized by hot summers and cold winters, whereas climates that are over or near the oceans are more equable with milder seasons (Figs. 1 and 2).

The distinction between maritime and continental climates can be seen by comparing the annual variations of temperature and precipitation for Tatoosh Island, Washington, with those for Minneapolis, Minnesota (**Fig. 6**). The temperature at Tatoosh Island

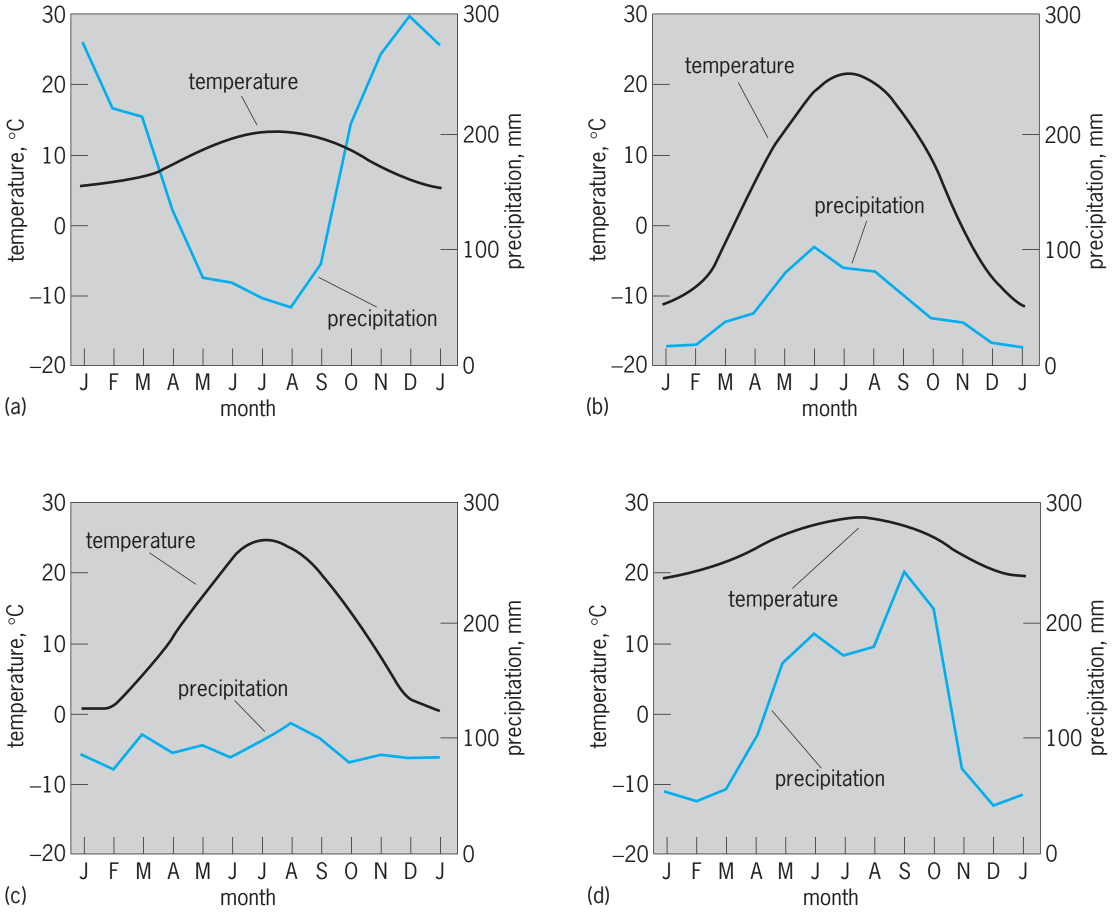

Fig. 6. **Annual variation of monthly mean temperature and precipitation at (*a*) Tatoosh Island, Washington; (*b*) Minneapolis, Minnesota; (c) New York, New York; and (*d*) Miami, Florida. °F = (°C × 1.8) + 32; 1 mm = 0.04 in.**

varies between a mean of 42°F (5.6°C) for January and a mean of 56°F (13.3°C) for August. This narrow temperature range results from the strong influence of the ocean, which is adjacent to and upwind of the Pacific coast, and has a small seasonal variation in temperature because of its large capacity to store and release heat. Although it is at nearly the same latitude, Minneapolis has a much larger annual variation of monthly mean temperatures, with readings of 12°F (−10.9°C) for January and 72°F (22.4°C) for July. Figures 1 and 2 show the large annual variation of temperature near the centers of the continents. *See* MARITIME METEOROLOGY.

The annual variation of precipitation is also very different in the two climate regimes (Fig. 6). At Tatoosh Island the precipitation peaks in the winter season in association with rainfall produced by the cyclones and fronts of wintertime weather. In Minneapolis the precipitation peaks in the summer season. Most of this precipitation is associated with thunderstorms. Adequate precipitation during the warm summer season is an essential ingredient of the agricultural productivity of the American Midwest.

New York City shows an annual variation of temperature and precipitation that is a combination of maritime and continental. It is near the Atlantic Ocean, but because the prevailing winds are out of the west, it also comes under the influence of air that has been over the continent. It has a fairly large annual variation of temperature, but monthly mean precipitation is almost constant through the year (Fig. 6*c*). It receives precipitation both from winter storms and summer thunderstorms. Miami, Florida is in the subtropics at 26°N. The annual variation of insolation is small, so that the seasonal variation of temperature is also modest. The precipitation shows a strong seasonal variation, with maximum precipitation during the summer half-year associated primarily with thunderstorm activity. *See* THUNDERSTORM.

General circulation of atmosphere and climate. Many aspects of the Earth's climate are influenced by the nature of the circulation that results from the radiative heating of the tropics and cooling of the polar regions. In the belt between the Equator and 30° latitude the bulk of the poleward atmospheric energy transport is carried by a large circulation cell, in which air rises in a narrow band near the Equator and sinks at tropical and subtropical latitudes. The upward motion near the Equator is associated with intense rainfall and wet climates, while the downward motion away from the Equator results in the suppression of rainfall and very dry climates (Fig. 5). Most of the world's great deserts, including the Sahara, Australian, Arabian, Kalahari, and Atacama, are in the belts between 10 and 30° latitude.

In middle latitudes the poleward flow of energy is produced by extratropical cyclones rather than by a mean circulation cell. These storms are thousands of miles wide and are characterized by poleward motion of warm, moist air and equatorward motion of cold, dry air. Most of the wintertime precipitation in middle latitudes is associated with weather disturbances of this type.

Surface features are also of importance in determining local climate. Mountain ranges can block the flow of moist air from the oceans, resulting in very low rainfall beyond the mountain ranges. The dryness of the Great Basin of North America and the Gobi Desert of Asia is maintained in this way. On the upwind side of mountain ranges, forced ascent of moist air can result in very moist climates; this occurs, for example, on the west slope of the coastal mountains of western America and the south slope of the Himalayas during the summer monsoon. The downwind sides of such mountains are often very dry, since the moisture precipitates out on the upwind side. Two locations that show the effect of topography on local climates are Puerto Aisén, Chile, and Comodoro Rivadavia, Argentina, which are both located near a latitude of 45°S (see table). Puerto Aisén is on the westward and upwind side of the Andes mountains in a deep valley that is exposed to the midlatitude westerly winds coming off the Pacific Ocean. It receives more than 10 ft (3 m) of precipitated water annually. Only a few hundred miles downwind of the Andes on the Atlantic seaboard, Comodoro Rivadavia receives only about 8 in. (0.2 m) of precipitation each year.

Complete climate system. The climate of the Earth results from complex interactions among externally applied parameters, like the distribution of insolation, and internal interactions among the atmosphere, the oceans, the ice, and the land (**Fig. 7**). The composition of the atmosphere, which plays a key role in determining the surface temperature through the greenhouse effect, has been radically changed by the life-forms that have developed, and continues to be modified and maintained by them. The atmosphere and the oceans exchange heat, momentum, water, and important constituent gases such as oxygen and carbon dioxide. The exchange of constituent gases is strongly influenced by life in the ocean. The hydrologic cycle of evaporation, cloud formation, and precipitation as rain or snow is intimately connected to the climate through the effects of water vapor, clouds, and surface ice on the radiation balance of the planet. Vegetation interacts strongly with the hydrologic cycle over land to determine the soil moisture, surface albedo, evaporation, precipitation, and surface water runoff. *See* HYDROLOGY.

Evolution of Earth's climate. The climate of the Earth is unique among the planets in the solar system. All of them evolved out of material in the rotating cloud from which the solar system was formed. The subsequent evolution of the planets' atmospheres depended critically on the mass of each planet and its distance from the Sun.

The mass of the Earth and its distance from the Sun are such that water can exist in liquid form rather than being frozen or escaping to space. The liquid water formed the oceans and led to the development of photosynthetic life, which reduced the carbon dioxide content and increased the molecular oxygen content of the atmosphere. Planets closer to the Sun receive more solar energy per unit area and are thus much hotter than the Earth. The surface of Venus is sufficiently hot that water vapor cannot

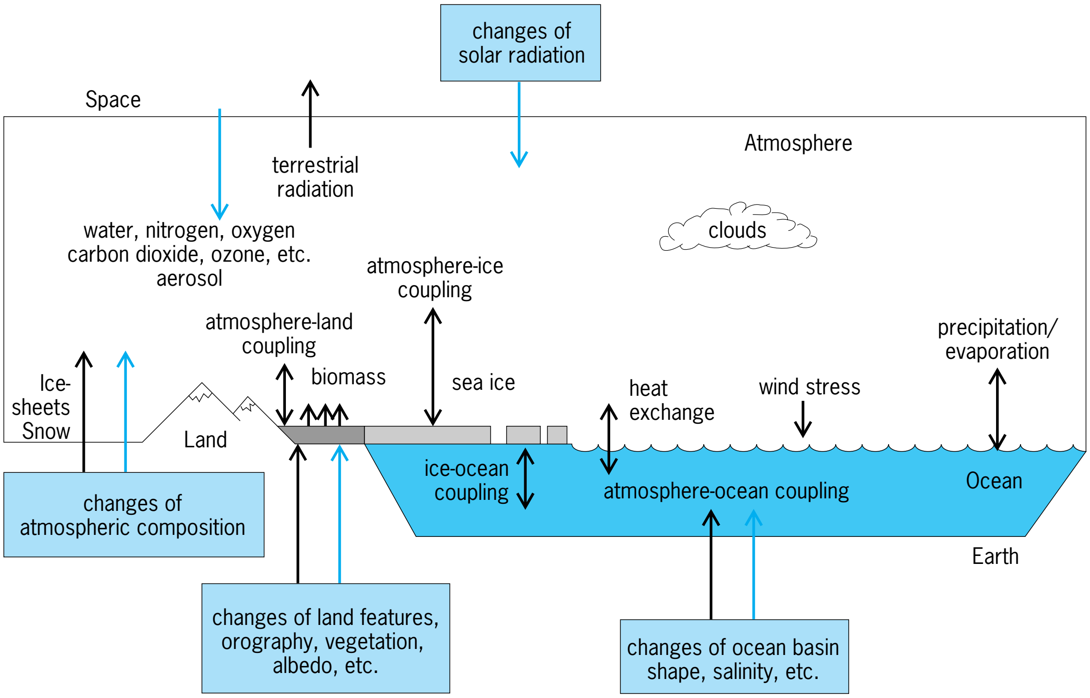

Fig. 7. Schematic illustration of the processes and interactions in the climate system. The colored arrows indicate externally applied conditions, and black arrows show internal processes that act to influence climate change. (*After J. G. Lockwood, Causes of Climate, Halstead Press, 1979*)

condense. Venus has a very thick atmosphere composed mostly of carbon dioxide. On Mars, which is farther from the Sun than the Earth and therefore colder, water freezes, leaving a very thin atmosphere of carbon dioxide. Thus the basic climatic conditions of a relatively circular orbit at a favorable distance for the Sun led to a drastically different evolutionary history for the Earth than for the neighboring planets. *See* ATMOSPHERE, EVOLUTION OF; SOLAR SYSTEM.

History of Earth's climate. Direct measurements allow the estimation of global mean surface temperature of the Earth for only about the last 100 years (**Fig. 8**). Global surface air temperature rose by about 0.9°F (0.5°C) between 1880 and 1940 and then declined slightly in the following three decades. The decade of the 1980s contained some of the warmest years on record.

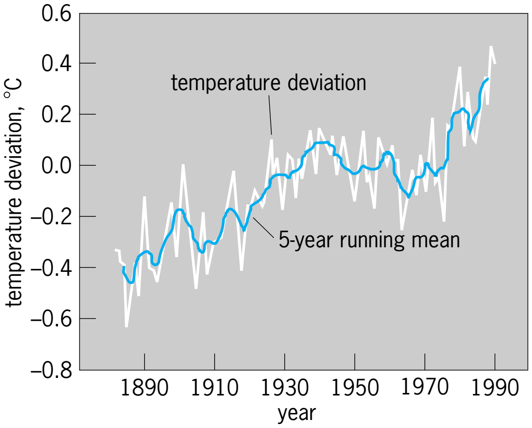

Fig. 8. Global surface air temperature change (°C) over the last century inferred from measurements. Temperature deviation is from 1951–1980 mean. °F = (°C × 1.8) + 32. (*After D. L. Hartmann, Global Physical Climatology, Academic Press, 1994*)

Evidence of climate variations in prehistoric times must be obtained from proxy indicators in dated sediments, such as pollen spores, the shells of small animals, or isotopic abundances, or from geologic features such as terminal moraines of glaciers or dry lake beds. A wealth of geological evidence exists to indicate that the Earth underwent a great glaciation as recently as 20,000 years ago. During this period, ice sheets nearly 2 mi (3 km) thick covered parts of North America and western Europe. Variations in the relative abundance of oxygen isotopes in deep-sea cores indicate that there has been a succession of periods of major glaciations separated by relatively warm, ice-free periods called interglacials during the last million years of Earth history (**Fig. 9**). *See* GLACIAL EPOCH; PALEOCLIMATOLOGY.

Analyses of time series show a relationship between global ice volume and known variations in the Earth's orbit. The parameters of the Earth's orbit include the eccentricity, which measures the departure from a circular orbit to a more elliptical one; the obliquity, which measures the tilt of the axis and therefore the magnitude of the annual variation in the declination angle of the Sun; and the longitude of perihelion, which measures the season at which the Earth makes its closest approach to the Sun. These parameters control the seasonal and latitudinal distribution of insolation. Because ice sheets form primarily on land and much of the land area is in northern latitudes, ice sheets form more readily when the summertime insolation is relatively low, which allows some of the winter snow accumulation to survive the summer season. The global climate responds to the presence of the ice sheets through a process called ice-albedo feedback. Ice sheets are more reflective to solar radiation than other surfaces, so that their presence tends to reduce the amount of solar heat absorbed by the Earth. This in turn leads to a cooling of the planet and a greater tendency for the ice sheets to grow. *See* EARTH ROTATION AND ORBITAL MOTION.

Evidence from air bubbles trapped in glacial ice indicates that there were lower atmospheric concentrations of greenhouse gases such as carbon dioxide and methane during past glacial ages than there is at present. The concentration of carbon dioxide 20,000 years ago during the last glacial age was only about 190 parts per million by volume (ppmv), compared with the preindustrial level of 280 ppmv and the current concentration of 355 ppmv. During past glacial periods, the rather low values of carbon dioxide are thought to have been produced by changes in ocean chemistry and biology. Such low greenhouse gas concentrations contribute significantly to the cooling associated with glacial advances.

Future climate changes. Past relationships between the Earth's orbital parameters and global ice volume indicate that the Earth will undergo another major glacial age within about 25,000 years from now. Currently, however, the composition of the Earth's atmosphere is changing rapidly as a result of human influences. Of climatic interest are industrial gases that are transparent to solar radiation entering the Earth's atmosphere, but are opaque to the thermal radiation emitted by the Earth. Gases with these characteristics are called greenhouse gases. In order to achieve an energy balance in the presence of increased concentration of greenhouse gases, the Earth's surface must warm, so that its thermal emission will increase to offset increasing downward emission of thermal energy from an atmosphere that is becoming more effective at intercepting outgoing thermal radiation, if other factors remain the same. The principal greenhouse gases are carbon dioxide, which is increasing principally because of the burning of coal and oil; methane or natural gas, whose increase is related to agriculture and coal and gas mining; nitrous oxide, which is a product of the decay of fixed nitrogen in plants or artificial fertilizer; and chlorofluorocarbons, which are gases used in industry for refrigeration, foam-blowing, and cleaning, and as aerosol propellants. Carbon dioxide is expected to contribute most of the increase in atmospheric thermal opacity due by the year 2030.

Within the next 100 years, if current trends continue, climate models indicate that human activities will result in a climate that is 4–8°F (2.2–4.4°C) warmer than it is today. The magnitude of this increase is similar to that between the present climate and the last glacial age, and would represent an extremely rapid warming by the standards of natural climate variability and change. Studies also suggest increased probability of drought during the summer growing season in midlatitude agricultural areas and rising sea levels that may be 27 in. (70 cm) higher than present levels by the year 2080. *See* CLIMATE HISTORY; CLIMATE MODIFICATION; DROUGHT; MESOMETEOROLOGY; METEOROLOGY; MICROMETEOROLOGY.

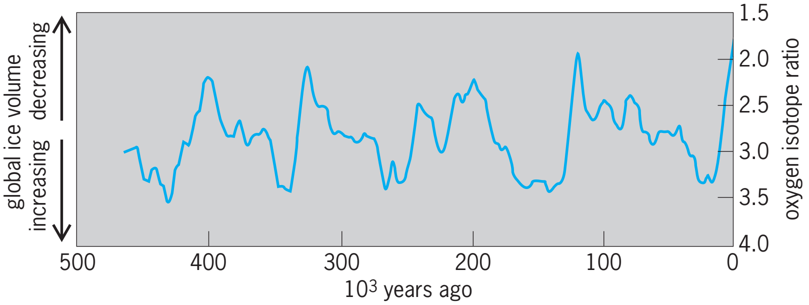

Fig. 9. Climate of the past half-million years. Oxygen isotope ratios are from ocean sediments, which reflect variations in the global volume of ice in glaciers and ice sheets (*After J. Imbrie, Ice Ages: Solving the Mystery, Enslow Publishers, 1979*)

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Clinical immunology

A branch of clinical pathology concerned with the role of the immune defense system in disease. The subject encompasses diseases where a malfunction of the immune system itself is the basic cause, together with diseases where some external agent is the initiating factor but an excessive response by the immune system produces the actual tissue damage. It also extends to the monitoring of the normal immune response in infectious diseases and to the use of immunological techniques in disease diagnosis. *See* CLINICAL PATHOLOGY.

Clinical immunology is a specialization born of the rapid expansion of knowledge in basic immunology together with the recognition that many diseases have an immunological component. Some areas of medicine which might logically be classified as clinical immunology were developed before immunology emerged as a separate discipline, and these have become the province of other medical departments. For example, vaccination against infectious disease is part of the practice of pediatrics, and asthma is treated by respiratory physicians.

Immune defense system. Many features of the immune system make it prone to shift from protecting the body to damaging it. This complex system not only must distinguish between the body's own cells and a foreign invader but must also recognize and eliminate the body's own cells if they are damaged or infected with a virus. The recognition receptors used to make this fine distinction between "self" and "not self" are not encoded in the genes. Rather, they are assembled following random rearrangement of information carried in small gene segments. During their development, immune system cells are subjected to a selective process, those bearing potentially useful receptors being preserved while those bearing dangerous, self-reactive receptors are eliminated. This process is closely balanced, and some potentially self-reactive cells often persist.

The cells that carry these highly discriminating surface receptors are the lymphocytes. They are migratory cells, concentrated in lymph nodes and also found among the white cells of blood. Lymphocytes are of two types: B cells (which are formed in bone marrow) and T cells (which are formed in the thymus). CD8 T cells on activation directly kill the body cells presenting the foreign antigens. CD4 T cells on activation produce short-range factors (cytokines) that recruit and activate macrophages and natural killer cells, which in turn release their own cytokines. These less specific cells are also the first line of defense early in infection. If this complex immune response system is not well controlled, it can cause substantial damage to normal cells besides eliminating abnormal cells and foreign invaders. *See* CELLULAR IMMUNOLOGY; CYTOKINE.

Immunodeficiency diseases. Immune deficiencies may be acquired as a consequence of an external factor such as an infection or may be inherited as a genetic defect. Immunodeficient individuals are subject to recurrent infections by organisms that are not normally a hazard. Some immunodeficiencies affect only one part of the immune system. In Di George's syndrome, T lymphocytes are deficient because of a developmental failure of the thymus. Hypogammaglobulinemia results from a developmental failure of B lymphocytes. Chronic granulomatosis disease results from an enzyme deficiency in phagocytic cells. *See* IMMUNOLOGICAL DEFICIENCY.

AIDS. Acquired immunodeficiency syndrome (AIDS) is a worldwide epidemic. It is caused by infection with the human immunodeficiency virus (HIV), transmitted sexually or through contaminated blood transfusion or by use of contaminated needles for injections. In the late stages of the disease, there is a massive loss of CD4 T cells, resulting in susceptibility to multiple infections. *See* ACQUIRED IMMUNE DEFICIENCY SYNDROME (AIDS).

Autoimmune diseases. Many diseases have an autoimmune component, that is, the central cause of the disease, or much of the pathology, is due to the action of the immune system on the body's own tissues. The factor triggering self-reactivity is usually unknown; it may be a viral infection. In some diseases there is a genetic predisposition according to the human cell surface antigen (HLA) type of the individual.

In some autoimmune diseases one particular organ is targeted, as in thyroiditis, where antibodies react with thyroid hormones; or in juvenile onset diabetes, where the insulin-producing cells of the pancreas are attacked. In others, a widespread but particular cell type is the target. One example is autoimmune hemolytic anemia, where antibodies initiate complement lysis of red cells. Finally, some complex diseases with multiple targets are the result of autoimmune phenomena. For example, systemic lupus erythematosus can affect most organs of the body, especially kidney, skin, and joints, and is associated with antibodies against many intracellular components, including deoxyribonucleic acid (DNA). Rheumatoid arthritis is another multisystem disease, but synovial joints bear the brunt of the inflammatory response, and an antibody against the body's own immunoglobulin (rheumatoid factor) is often present. *See* ANTIBODY; AUTOIMMUNITY; IMMUNOGLOBULIN.

Hypersensitivity or allergic states. These represent an extreme response of particular individuals to environmental antigens that are not intrinsically harmful. Examples are allergies to drugs, food components, pollen, or house-dust mites. The nature of the response varies, but the most common response involves immunoglobulin E antibodies. When complexed with the antigen, these bind to the surface of mast cells, triggering the release of histamine and other pharmacological agents. This is the basis of atopic diseases, including dermatitis, allergic rhinitis (hay fever), bronchial asthma, and even extreme anaphalactic shock. *See* ALLERGY.

Cancer. The body mounts an immune response against at least some forms of cancer. It is not yet clear whether it is possible to generate an effective immune response against all types of cancer cells. Some forms of cancer represent the uncontrolled proliferation of component cells of the immune system itself. These include myelogenous leukemia (phagocytic cells), lymphatic leukemia (B lymphocytes), and multiple myeloma (antibody-producing cells). *See* CANCER (MEDICINE).

Transplantation. The response of the immune system to cells of another individual was first apparent in blood transfusion, where a match for the A, B, O, and other blood groups was needed to avoid a reaction. The transplantation of skin or internal organs presents the more difficult task of matching the complex HLA antigens. These major histocompatibility complex proteins, whose normal function is to present antigenic fragments to T cells, can trigger an especially vigorous T-cell response. The best available matching for HLA type, as well as careful immunosuppression, is needed for graft survival. *See* IMMUNOLOGY; TRANSPLANTATION BIOLOGY.

Therapy. There are several approaches to suppressing excessive immune reactivity. Drugs with a general toxicity for dividing cells have been used, although now more selective and better-tolerated drugs such as cyclosporin may be employed. The most widely used immunosuppressive agents are corticosteroids, which affect many body systems but have a particularly strong action on lymphoid cells. Desensitization, or modifying the nature of the response by injecting small amounts of the foreign antigen, is sometimes used to treat allergic states. *See* IMMUNOSUPPRESSION.

There are few therapies for enhancing immune responses. Bone marrow transplantation is used to restore the immune system in some immunodeficiency diseases. Passive transfer of preformed antibody protects against some infections, and transfusion of immunoglobulin is used to treat immunoglobulin deficiencies. However, vaccination or immunization, the introduction of modified forms of an infectious agent in order to develop specific protection against infectious diseases, is one of the most effective of all medical procedures. *See* IMMUNOLOGICAL DEFICIENCY; VACCINATION.

The clinic. Many large hospitals have separate clinical immunology departments. However, clinical immunology also is part of the practice of other specialists, such as endocrinologists who treat individuals with thyroiditis or diabetes, or hematologists who treat individuals with pernicious anemia. In addition, common immunological diseases such as allergies or rheumatoid arthritis are often handled in specialized clinics. Individuals in a pediatric clinical immunology department are typically children with immunodeficiency diseases or leukemias. Hematologists and oncologists may be involved in their treatment. The adult patients of a clinical immunology department are usually a diverse group, ranging from hospitalized patients requiring continuous care (for severe allergic responses, late-stage AIDS, infection following immunosuppression) to outpatients whose progress needs regular but not continuous monitoring (for immunoglobulin deficiencies being treated by immunoglobulin transfusion, autoimmune diseases being treated with immunosuppressive drugs).

Clinical immunologists take blood samples as a convenient indicator of the status of the immune system. These samples are analyzed in the laboratory. Other immunological tests use the skin as an indicator of the immune response, most often to test for hypersensitive or allergic states. Test materials are placed in contact with the skin or are injected subcutaneously. A local red inflammatory reaction indicates a positive response. A rapid response, that is, within hours, is referred to as immediate hypersensitivity; this indicates the presence of preformed antibody reactive with the test material. A slow response, within days (delayed hypersensitivity), indicates the development of an immune response involving recruitment of lymphocytes. *See* HYPERSENSITIVITY.

Laboratory tests. The specialized clinical immunology laboratory within a hospital is often directed by the same clinician who sees the patients in the clinic, with trained technicians performing most of the actual tests. Most tests utilize blood samples, although other body fluids and tissue samples are occasionally analyzed. Tests on blood may be divided into those that analyze the serum and those that analyze blood cells. The concentration, type, and specificity of antibodies in serum may be measured by using tests that range from simple agglutination assays, through immunoelectrophoresis, to more sophisticated enzyme-linked immunosorbent assays (ELISA). The number of lymphocytes in the blood may simply be counted, or they may be analyzed or separated to test their function in culture. A preliminary separation of lymphocytes from other blood cells may be made by centrifugation procedures. Further separation into subclasses of lymphocytes is usually effected by a combination of immunofluorescence and flow cytometry. The essential reagents are fluorescent-dye conjugated antibodies specific for individual cell surface molecules; that is, after interaction with these reagents, only particular cells acquire a fluorescent label. The cells are then passed across a laser beam, one at a time in a stream, and their fluorescence intensity is measured. In fluorescence-activated cell sorting, the stream of cells is broken into droplets, and droplets containing particular types of cells are deflected and collected. Immunofluorescence may also be used to examine tissue sections under a microscope. The results of these tests are used to help diagnose a disease or to evaluate the effectiveness of a treatment. *See* IMMUNOASSAY; IMMUNOFLUORESCENCE.

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Clinical microbiology

The adaptation of microbiological techniques to the study of the etiological agents of infectious disease. Some of the most significant scientific advances during the latter half of the nineteenth century and the first few decades of the twentieth century were in medical bacteriology. From the work of Louis Pasteur, Robert Koch, Theobald Smith, and others, it was shown that bacteria were responsible for many diseases of humans. During the early part of the twentieth century, the technology for the growth of bacteria was advanced to the extent that pure cultures of bacteria could be studied from defined environments. Not only did bacteria become models for the study of their own biochemical characteristics, but the same technology enabled bacteriologists to isolate and identify bacteria from patients with infectious disease. This spurred the discovery of most of the bacterial diseases that are currently known.

The role of fungi, protozoa, rickettsias, and viruses in human disease was also elucidated during the first half of the twentieth century. The inhibitory power of materials from a fungus called *Penicillium* was discovered in 1928 by Alexander Fleming. His discovery of penicillin and the contributions of many others marked a great era in the treatment of bacterial diseases. The discovery of penicillin was soon followed by that of streptomycin and tetracycline.

For the first time, bacteriologists could detect and identify bacteria and then test in the laboratory the ability of various antibiotics to kill these isolated bacteria. Such was the birth of contemporary clinical microbiology. *See* ANTIBIOTIC.

Clinical microbiologists determine the nature of infectious disease and test the ability of various antibiotics to inhibit or kill the isolated microorganisms. A contemporary clinical microbiologist is also responsible for a wide range of microscopic and cultural studies in mycology, parasitology, and virology. The consultative skill of the clinical microbiologist is sought by many clinicians. The clinical microbiologist is often the most competent person available to determine the nature and extent of hospital-acquired infections, as well as public-health problems that affect both the hospital and the community. The clinical microbiologist is a valuable resource to the hospital and community. As clinical microbiology encompasses all aspects of infectious disease, the various specialties will be discussed individually. *See* EPIDEMIOLOGY; HOSPITAL INFECTIONS.

Bacteriology. Historically, the diagnosis of bacterial disease has been the primary job of clinical microbiology laboratories. Many of the common ailments of humans are bacterial in nature, such as streptococcal sore throat, diphtheria, and pneumococcal pneumonia. Only rarely, however, in recent decades have new bacterial diseases been described. A prime example is the disease legionellosis caused by a hitherto unknown bacterium, *Legionella pneumophila*. *See* LEGIONNAIRES' DISEASE.

The bacteriology laboratory plays a major role in the diagnosis of bacterial diseases. It accepts specimens of body fluids, such as sputum, urine, blood, and respiratory or genital secretions, and inoculates the specimens onto various solid and liquid growth media. Following incubation at body temperature, the microbiologist examines these agar plates and tubes and makes a determination as to the relative numbers of organisms growing from the specimen and their importance in the disease process. The microbiologist then identifies these alleged causes of disease and determines their pattern of antibiotic susceptibility to a few chosen agents.

Clinical microbiologists also microscopically examine these body fluids. They report on the presence of bacteria in body fluids and the cellular response to infection, such as the numbers of white blood cells observed in the specimen. Sometimes the kinds of white blood cells observed can provide hints for the identity of the disease. Such microscopic evaluations can provide a rapid aid in the diagnosis of infectious disease, as well as an assessment of the quality of the specimen. For example, a specimen called "pus" which does not contain white blood cells may not be pus. *See* MEDICAL BACTERIOLOGY.

Mycology. Mycology is the study of fungi. The applications of mycology in the clinical microbiology laboratory include the isolation of fungi which are known to cause disease. In general, diseases caused by fungi are relatively harmless but annoying, such as ringworm and athlete's foot. However, they can be severe, systemic disorders such as blastomycosis, coccidioidomycosis, and histoplasmosis. Fungi can also cause disease in those people whose immunologic processes have been suppressed by drugs or radiation. The diagnosis of fungal infection differs from bacterial infection because of the relatively slower rate of fungal growth. In general, diagnosis of fungal disease is a function of not only isolating and identifying the causative organism and determining which of three or four antifungal antibiotics might be effective, but also determining the patient's antibody response to the disease. *See* MEDICAL MYCOLOGY.

Parasitology. Parasitic diseases are widespread and of worldwide importance to humans. Such diseases include amebic dysentery, malaria, and Chagas' disease. The clinical microbiologist working in parasitology examines specimens of feces and blood for the presence of parasitic agents. These examinations are primarily microscopic, and the agents are identified on the basis of their characteristic structure. Although antiparasitic agents are available for the treatment of such infection, the parasitologist is usually not involved in the determination of the relative effectiveness of these agents on parasites. *See* MEDICAL PARASITOLOGY.

Virology. Virology is a specialized part of clinical microbiology. Because of the nature of viruses and their proclivity for growth only in living cell cultures or in eggs, few clinical microbiology laboratories have facilities for the isolation and identification of viruses. Most of these procedures are best done in large hospitals or in state departments of health. There is a growing trend, however, for smaller hospitals to develop screening virology laboratories in which specimens are brought to the laboratory, placed in tissue culture, and preliminary identification steps taken in order to provide a rapid diagnosis of viral disease. Although only a few drugs exist that can be used to treat virus infections, the early recognition of viral disease may allow the clinician to discontinue the use of powerful antibiotics that are effective only for bacterial diseases. Common virus diseases include influenza, herpes, chicken pox, the common cold, and many nonspecific respiratory infections. Much of the viral diagnosis that is done in the laboratory is by the determination of a specific antibody response to viral disease. The routine clinical microbiology laboratory usually does not become involved in such procedures. A special procedure for the detection of viruses and other organisms that affect infants is called the TORCH screen. It is a procedure for the detection of antibodies to the parasitic disease toxoplasmosis and the viral diseases rubella, cytomegalovirus, and herpes. These diseases may cause devastating health problems in babies. *See* ANIMAL VIRUS; DISEASE; TISSUE CULTURE; VIRUS.

Richard C. Tilton

Technology. While direct microscopy and culture continue to be methodological mainstays in diagnostic microbiology laboratories, the nonculture methods are growing in the variety of applications and the sophistication of the technology.

Antibodies. Polyclonal antibodies raised in animals such as mice, sheep, goats, and rabbits, and monoclonal antibodies produced by hybridization technology are used to detect bacteria, fungi, parasites, or virus-infected cells by using direct or indirect fluorescent techniques. Additional methods include latex agglutination tests to detect particulate antigens and enzyme immunoassays to detect soluble antigens. Some of these technologies can also be used to detect antibodies rather than antigens, usually using the antigen to capture antibody that is in serum. *See* IMMUNOASSAY; MONOCLONAL ANTIBODIES.

Instrumentation. Instrumentation for identification of bacteria and yeastlike fungi and for antimicrobial susceptibility testing includes a variety of technologies. The systems use either microtiter plates or plastic cards containing dried or frozen substrates or antimicrobial agents. A known concentration of the organism to be tested is introduced into the wells, and the plate is incubated until the instrument reader detects sufficient growth. The pattern of growth and reactivity is compared to patterns of known organisms. The likelihood that the test organism is one of them is reported from information maintained in a database. Because urinary tract infections in outpatients are usually caused by a single organism, some of these systems can be directly inoculated with urine. Generally, however, a pure culture must first be obtained by overnight incubation of inoculated agar plates.

Nonamplified hybridization. Probes for deoxyribonucleic acid (DNA) or messenger ribonucleic acid (mRNA) are available for various applications. There are two advantages in testing for mRNA. (1) It is present only if the gene it represents is expressed (contributing to the phenotypic characteristics of the organism). (2) If the gene is expressed, there will be multiple copies of the mRNA, thus increasing the analytical sensitivity of the test. A drawback is that ubiquitous ribonucleases can render a false negative test. Probes are used for direct detection of organisms in clinical material and for culture confirmation.

Amplification. Further increases in analytical sensitivity have been achieved by nucleic acid amplification techniques. Several methods are currently available to clinical laboratories.

In polymerase chain reaction (PCR), double-stranded DNA is denatured; oligonucleotide probes bind to homologous strands of single-stranded DNA, and the enzyme polymerase extends the probes using deoxyribonucleotides in the milieu. Over 30 cycles, the number of copies increases a millionfold. This product is then detected.

In ligase chain reaction (LCR), the enzyme ligase can fill the 3-nucleotide gap between two probes that attach to homologous, target, single-stranded DNA. By cycling in a manner similar to PCR, a million joined copies can be generated in a short period of time, after which they are detected.

In nucleic acid sequence–based amplification (NASBA), reverse transcriptase is used to make double-stranded complementary DNA (cDNA) and the target RNA is digested by ribonuclease H. Another enzyme, T_7 polymerase, is used to make more RNA target from which more cDNA is made.

Molecular typing. Analysis of lipopolysaccharides and proteins by sodium dodecyl sulfate–polyacrylamide gel electrophoresis (SDS-PAGE) and cellular fatty acid analysis by gas-liquid chromatography have given way to nucleic acid–based methods. Restriction enzymes, which cut DNA at a constant position within a specific recognition site usually composed of four to six base pairs, are used to cut chromosomal DNA; the resulting fragments are compared by pulse field gel electrophoresis (PFGE) or ribotyping. Electrophoresis of isolated plasmid DNA is another method for comparing organisms. DNA sequencing can also compare segments of the DNA of organisms from the same genus and species.

Chip arrays. DNA chip or microarray technology is expected to have a greater effect on medicine than either DNA sequencing or PCR. Over 30,000 small cDNA clones of expressed fragments of individual genes (expressed sequence tags, or ESTs) are spotted onto a thumbnail-sized glass chip. Fluorescein-labeled genomic or cDNA from the sample being evaluated is passed over the chip to allow hybridization. A laser measures the fluorescent emissions and a computer analyzes the data. As an example, relevant cDNA fragments from the bacteria, viruses, and protozoa that are known to cause diarrhea or dysentery could be placed on one chip and a stool specimen could be analyzed for all known pathogens at one time. Genes coding for known antimicrobial resistance mechanisms could also be represented so that an appropriate therapeutic agent could be prescribed. *See* CLINICAL PATHOLOGY. Carol A. Spiegel

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Clinical pathology

The discipline in which disease processes are assessed and monitored by the examination of blood, body fluids, secretions, and aspirated specimens. The detection of chemical, morphological, microbiological, and immunological abnormalities in this material is reported as laboratory results. In contrast, anatomical pathology is that branch of pathology dealing with the nature of a disease process through studying the gross and microscopic features of tissues and fluids removed either at postmortem examination (autopsy) or during surgery. However, divisions between anatomical and clinical pathology are somewhat artificial and largely embedded in how pathology evolved in academic practice. Information derived from autopsy examinations, surgical specimens, or clinical laboratory testing provides physicians with the means to confirm a final diagnosis and to evaluate nonsurgical conditions. Such information is used by physicians in diagnosis and in therapy management.

History and Laboratory Administration

Early clinical pathology laboratories were simple, often confined to a single room (**Fig. 1**). A limited number of tests were performed by hand, with visual observation of color changes or turbidity. Microscopes, often monocular, were used primarily to identify abnormal cells in stained smears or blood films, inflammatory cells and atypical crystals in urinary sediment, or foreign particles such as bacteria in direct mounts of clinical specimens. A group of biochemists, working primarily in hospitals in Boston and New York before the outbreak of World War I, soon recognized that quantitative results must be derived from clinical laboratory tests to detect and monitor underlying diseases. Crude instruments such as manometers to measure blood gases, colorimeters to quantify chemical reactions, and fluorometers on which levels of blood electrolytes could be quantified were introduced between the two world wars. During this time, all reagent samples and reagents were dispersed using mouth pipetting, and it was not uncommon to observe lit cigarettes and open caches of food on the workbench, practices that later were strictly forbidden.

Clinical pathology laboratory testing experienced its first transition following WWII. From the late 1950s into the early 1960s, the number of new tests introduced into clinical laboratories multiplied logarithmically, accompanied by ever-increasing sophistication of instrumentation and advances in laboratory organization and administration. A number of new self-operating analytical systems were introduced to replace the laborious and time-consuming hand-operated processes characteristic of early laboratories. Through the advancement of technology, new tests, new procedures, and new reporting systems were made accessible to medical practitioners and their patients. On the other hand, the massive numbers and complexity of tests also placed burdens on those who use this information in patient care. How to determine which tests meet the standards for evidence-based medicine is an ongoing challenge. Testing was made more creditable by instrument testing. The subjective testing by multiple technologists could be standardized to better inform practicing physicians.

In keeping with the continuing increase in the number of laboratory tests and the complexity resulting from the introduction of automation and molecular techniques, nontechnical matters of the organization, administration, and staffing of clinical pathology laboratories has changed dramatically as well. Typically, a laboratory director must oversee the overall operation of the laboratory and relate to physicians and other medical personnel in choosing appropriate diagnostic tests, interpreting laboratory data, and monitoring therapeutic responses. The director also assumes many administrative duties relating to hospital settings and financial affairs. The day-to-day analysis and quality control of test procedures, the review of the accuracy and precision of test results, and the supervision of laboratory personnel are the several activities commonly carried out by clinical scientists and medical technologists with advanced degrees. Materials obtained from patients are commonly assayed by highly trained laboratory scientists and medical technologists. Laboratory assistants and clerical personnel assist in processing specimens and in transcribing, recording, and logging in laboratory test results. Although computer-based

Fig. 1. Clinical pathology laboratory at Christus Santa Rosa Hospital, San Antonio, Texas, 1923.

laboratory information systems are now indispensable, intervention by laboratory personnel is critical to ensure that samples are procured from the correct patient at the correct time and delivered to the correct section in the laboratory.

Role in patient care. Clinical pathology laboratories function as an integral part of the diagnostic cycle beginning as an individual with signs and symptoms suggestive of disease consults a physician.

Specimen collection and processing. After obtaining a clinical history and examining the patient, a physician may order laboratory studies on blood, urine, other body fluids and secretions, or tissue biopsies to establish or confirm a working diagnosis. Specific protocols are followed in the preparation of the patient and in the techniques in collecting a specimen. Specimen collection must be made into a proper container with preservatives or anticoagulants appropriate to the test being requested. Particular attention to proper packaging of the specimen is critical, especially if the delivery time is delayed by transport through long distances.

A visual and/or microscopic examination may be the first evaluation of specimen quality. If unsatisfactory (not meeting a variety of predetermined criteria), particularly misidentifications, the specimen may be rejected with a request for repeat collection. Patient information and test requests are bar-coded into the laboratory information system. The processing and analysis stages follow.

Processing may require centrifugation to separate the cells if the test requested requires an analysis of plasma or serum. Commercially prepared reagent systems and automated or nonautomated electronic instruments have replaced manual testing. Using direct-read instruments and/or special chemical and immunological reagent packages, test results may be obtained within a few minutes. In highly automated laboratories, test results may be transferred directly from the instrument into the hospital computer system, providing clinicians with direct access to results from terminals present on the wards.

Point-of-care testing. On-site or point-of-care laboratory testing has evolved as an alternative testing arrangement to meet the increasing demand for rapid turnaround time of certain test results. Emergency rooms, outpatient clinics, and physician offices, as well as select special-care hospital settings, are particularly served. Rapid-response read-out devices, packaged reaction cassettes that include positive and negative controls, and reagents to perform a variety of "spot" tests are currently available. The license to perform an increasing variety of simple or "waived" tests has been afforded through regulations provided under the Clinical Laboratory Improvement Amendment of 1988 (CLIA-1988).

The menu of waived point-of-care laboratory procedures provides for the immediate assessment of a number of diseases and conditions. Methods for enumerating blood cells, performing a urinalysis, measuring abnormal levels of chemical constituents such as glucose and cholesterol, determining early pregnancy, and detecting several bacterial and viral infections are currently available. Many of these tests can be performed on a small quantity of blood, 25–50 microliters obtained by a simple finger stick precluding the need for a vena puncture. Again, each of these areas of point-of-care testing must be carefully monitored for accuracy and reproducibility of test results under strict administrative supervision and careful quality control. When all such parameters are in place, the availability of test results within 5 min or less provides for the immediate implementation of an appropriate therapeutic regimen.

Quality control. The clinical laboratory generates data that are converted into information that the physician may use to supplement his clinical knowledge of the patient. Laboratory directors and personnel are obligated to have in place systems of quality maintenance for all of its practices in supplying laboratory test information. Established testing standards must be applied to the assay. In practice, a control sample containing a known amount of the substance being tested is treated in exactly the same way as the patient sample.

This known sample interjection concept of quality control was developed from industrial models used in the 1950s. Included within the run of each batch of specimens is a pair of control samples that contain a known concentration of analyte, commonly set at both high- and a low-level readings. The control results must come within a fixed standard deviation before the specimen results can be approved. Thus, observing a drift in the results of the control samples provides a means to detect reagent deterioration, operator errors, or technical problems that may have occurred during analysis. All specimen test results must be checked against the quality control results before a report is issued. Each analytical instrument must be calibrated and paced through test runs, and all storage compartments and heat-controlled devices must be checked daily for temperature maintenance. All quality control data must be posted on daily log charts that are clearly visible and in usable formats.

Laboratory inspection and accreditation. The College of American Pathologists (CAP) in 1961 launched a laboratory inspection program focused initially on hospital laboratories. Standards were developed for technical performance. Meeting these standards, directed toward continuous improvement of laboratory testing in health care, is rewarded by accreditation. The thrust of the quality-improvement efforts remains educational, and the inspections currently are carried out by volunteer pathologists, Ph.D. scientists, and medical technologists. Through collaborative efforts of the CAP with regulatory agencies, such as the state public heath departments, the FDA, the American Association of Blood Banks, the American Association of Clinical Chemists, and the Joint Commission on Hospital Accreditation, among others, a highly sophisticated and integrated system of ongoing laboratory surveillance and regulation has evolved, leading to high-quality performance.

Proficiency standards are monitored by requiring participating laboratories to analyze, in 3- or 4-month cycles, a set of proficiency test samples that are indistinguishable from those obtained from a patient. The analytical results derived from these proficiency samples are then surveyed by independent observers. When aberrations are spotted, corrective actions must be immediately put in place.

Evidence-based medicine. Resource constraints combined with demands by physicians and the public to have the best evidence about medical testing have led to new approaches to medicine in the clinical laboratory. Clinical epidemiology, also known as evidence-based medicine, has grown in importance as an approach to medical treatment as well as testing and diagnosis. Evidence-based medicine focuses on objective measurements of diagnostic and prognostic accuracy and therapeutic effectiveness, and the implementation of best practices based upon those measurements.

Clinical Laboratory Subsections

Evolution of laboratory testing and its complexities has directed the laboratory's functioning into separate sections and disciplines. Although this division varies from laboratory to laboratory, the following sections and subsections are common:

- Chemical pathology
  - General chemistry
  - Spirometry (measurement of lung breathing capacity and blood gases)
  - Toxicology, in particular the monitoring of drugs of abuse
  - Radiometry (measuring minute amounts of radiant energy) and enzyme immunoassay (determination of binding between antigens and antibodies)
  - Medical microscopy/urinalysis
  - Electrophoresis
- Hematology
  - Morphologic hematology, involving glass-slide preparation and microscopy
  - Chemical hematology for the detection of hemoglobinopathies
  - Blood clotting and dissolution (fibrinolysis)
  - Flow cytometry (fluorescence microscopics) for the determination of cell markers
- Immunohematology
  - Transfusion medicine (blood bank)
  - Donor recruitment and service
  - Transfusion preparations (cross matching)
  - Component separation (red cells, white cells, platelets, plasma)
  - Plasmapheresis (separating out directly from the patient certain blood components)
- Microbiology
  - General aerobic bacteriology
  - Anaerobic bacteriology: bacteria that grow only in the absence of oxygen
  - Mycobacteriology: the agents of tuberculosis
  - Mycology: the agents of fungal infections
  - Parasitology: the animal parasites causing disease in humans
  - Virology: minute microorganisms having only a core of nucleic acid and a protein envelope
  - Immunology and serology: the diagnosis of disease by detection of antigens and antibodies
  - Antimicrobial susceptibility testing: determination of the best drug to use in the treatment of infections

Chemical pathology. Chemical pathology, also known as clinical chemistry or clinical biochemistry, encompasses determination of the presence or quantity of chemicals present in blood, serum, plasma, urine, cerebrospinal fluid, or other body fluids.

The age of automation, which has become so much a part of the modern chemical pathology laboratory, began in the late 1950s with the Technicon Autoanalyzer, possessing the following features:

1. A pipetting robot that procured small volumes of sample from tiny cups placed in a rotating carousel.
2. Streams of liquid passed through a series of plastic tubes connected to reagent baths.
3. A peristaltic proportioning pump under which the reagent tubes passed, propelling a measured amount of sample and reagents in air-segmented aliquots, coming together in a mixing coil housed in a constant-temperature water bath.
4. A photometric flow-through cell through which a light beam passed, producing proportional electrical currents from a photovoltaic cell that activated a recording needle that traced quantitative peak-and-valley line grafts on a roll of moving paper.

Upon this foundation has evolved ever-increasing innovations in robotic, electronic, and computer-based technology. Automated instruments now find service in several subsections of the chemical laboratory: blood gas analysis, toxicology and therapeutic drug monitoring, core chemistry, immunoassay, electrophoresis, and urinalysis. The ultimate extension of this technology is the sequential "streaming" of instruments currently utilized in larger reference laboratories, where the specimen is advanced along an automatic hands-off treadmill assembly, passing through a series of stations including centrifugation, sampling, analysis, and computer-based reporting (**Fig. 2**).

Core chemistry. In the core chemistry section of the laboratory are evaluated many different chemicals in blood samples, including electrolytes such as sodium, potassium, calcium, and chloride ions. Quick measurement of these ions often permits doctors to avoid delays in making accurate diagnostic decisions. Other important molecules are also quantified in this laboratory section; for example, creatinine and urea nitrogen are widely employed to evaluate kidney function.

Blood gas analysis. The blood gas analysis section is found in almost all chemical pathology laboratories. Included among the chemicals analyzed are gases that are dissolved or bound to other molecules, ions,

Fig. 2. Overview of a 2005 automated chemical analysis system. Specimen racks are placed on a movable track that moves sequentially through sampling, read-out, and reporting stations in the course of multitest analyses.

small metabolic molecules, and proteins. Establishing the blood pH as well as the quantity of oxygen and carbon dioxide permits physicians to determine rapidly the acid–base status of patients. From these test results a quick diagnosis may be made on patients with drug poisoning, kidney malfunction, and diabetic ketoacidosis—an acute illness in some diabetics.

Toxicology. In the toxicology and therapeutic drug monitoring sections of the laboratory, suspected patient overdose and poisoning are investigated through the analysis of blood, urine, or other samples for the presence of drugs or drug metabolites. Early identification of the cause of patient overdose permits physicians to begin therapy quickly and often makes the difference in patient outcome. Medication drug levels are also evaluated in this section of the laboratory. Physicians are thus able to tailor the medication and dosage to provide the best therapy for patients. *See* TOXICOLOGY.

Immunochemistry. Larger molecules such as proteins are often measured using immunoassays in the immunochemistry section. Immunoassays use antibodies to detect and quantify the specific antibody target. For example, ferritin, a molecule used to evaluate iron deficiency, is typically measured using antiferritin antibodies. Patient antibodies directed against viruses or bacteria such as hepatitis C, human immunodeficiency virus (HIV), cytomegalovirus, and *Helicobacter pylori* are measured in this section of the laboratory. *See* IMMUNOCHEMISTRY.

Electrophoresis. Electrophoresis is the process through which large molecules are separated by exposing them to an electric field through a solid porous medium, such as agarose or polyacrylamide. Such separation can be visualized with certain dyes and evaluated either visually or by instrument densitometry. Serum protein electrophoresis (SPEP) allows pathologists to identify patterns to detect or monitor patients with multiple myeloma. Electrophoresis is also commonly used to assay urine (urine protein electrophoresis, UPEP) and cerebrospinal fluid. The diagnosis of multiple sclerosis is supported by certain findings seen after the electrophoresis of cerebrospinal fluid. *See* ELECTROPHORESIS.

Urinalysis. The urinalysis section of the laboratory is dedicated to measuring chemicals present in urine as well as the microscopic analysis of solid-formed elements in the urine. Such formed elements include red blood cells, white blood cells, crystals, casts, and bacteria. For example, abnormalities detected in the urinalysis laboratory are often some of the earliest signs of kidney failure. *See* URINALYSIS.

Hematology. Blood is an easily accessible source of human material for analysis. Several blood cell types circulate in the serum and become available for study after blood is drawn (phlebotomy) from a patient's vein or artery.

Microscopy. Blood cells may be scrutinized directly by smearing a drop of blood on a glass slide, applying a stain, and examining the cells under the

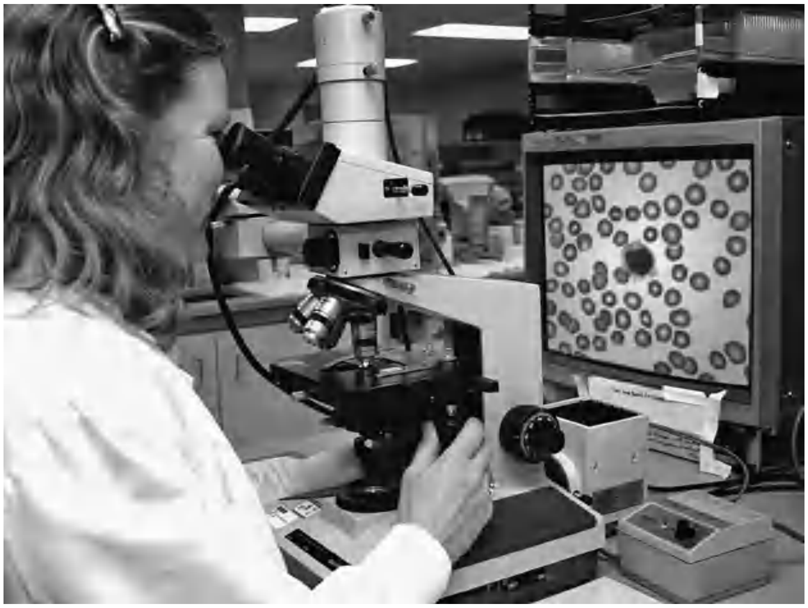

Fig. 3. Microscopic examination of a stained peripheral blood smear. The field of view used for cell identification observed by the microscopist is projected on the monitor screen located behind the microscope.

microscope. Valuable information is there before the eyes of the microscopist, and key observations may point immediately to a diagnosis or direct the physician to additional testing (**Fig. 3**). *See* MICROSCOPE.

Automatic counting. Examinations of the blood are facilitated by the use of automated counting instruments. Among these is the Coulter Counter, introduced in the 1960s. The major features of its operation include:

1. The aspiration of a small sample of blood by negative vacuum pressure into a fine-bore tube that channels the test specimen into the reading chamber of the instrument.
2. The tube is of such small diameter that the individual blood cells are partitioned out in single file.
3. Each cell in turn passes through a reading device, by which its diameter, color, nuclear density, and light transmission properties are measured.
4. This information is electronically captured to produce a multidot graph called a histogram by which the several cell types can be separated and enumerated.
5. Either red cell or differential white cell counts can be automatically generated depending on how the sample was processed before aspiration into the instrument.

Thus, cellular components are separated into red cells (blood), white cells (granulocytes, lymphocytes, and monocytes), and platelets. These different cell types are categorized and sorted electronically, resulting in computer-generated reports. Problems in relationship of cells or cells out of the range of size, shape, and content are flagged for review by the technologist or hematologist. An extension of this technology is the three-part and five-part automated differential counters by which the percentage of these white cells is displayed and printed out on a multicolored histogram, eliminating manual cell counting.

Molecular targeting. As with most testing procedures in the clinical laboratory, technology in hematology has advanced far beyond the counting and visual categorization of cells. Rapid developments in genomics and proteomics, as applied to hematologic disorders, have supplanted the simple hands-on, glass-slide examination of blood cells and test-tube shaking for the observation of clotting, practices that now have limited usefulness in defining a clinical problem. Basic knowledge in molecular and cellular biology, molecular immunology, and genetics have been translated into specific diagnostic and therapeutic testing methods. In further similar developments, clinicians look forward to these same reactions of specific molecular targeting for therapy of hematologic and coagulation disorders. *See* BLOOD; HEMATOLOGIC DISORDERS.

Flow cytometry. In a sense, flow cytometers are specialized fluorescence microscopes attached to a computer that translates signals to data. Specific bands of fluorescence are measured through a series of optic beam splitters and filters, as a flow of single cells passes through a light source. Through this method cells, such as blood cells, are analyzed and sorted. Physical characteristics of cells such as size, shape, and internal complexity can be measured. Any component or fraction that can be detectable by fluorescence is opened for examination. Fluorescence technology with high speeds (1000 cells per second or more) combined with the capability of correlating quantitative dots from simultaneous measurements on each cell has led to widespread use in the biological and medical fields.

In medicine, flow cytometry is used to identify lymphocyte subsets in conditions of immunodeficiency, and in immunophenotyping for leukemia and lymphoma. One common use is immunophenotyping of peripheral blood, lymph node, and bone marrow samples to establish the presence of clonality or leukemia. A wide range of cell surface antigens are present on hematopoetic cells. Flow cytometry is geared to their identification and allows the sorting of these cells into normal or abnormal expression patterns. *See* LEUKEMIA.

Microbiology. The implementation of automation in the clinical microbiology laboratory progressed more slowly than in other sections of the clinical laboratory. The tried and true conventional culture recovery methods of Robert Koch and making bacterial identifications by visually observing color reactions in reaction tubes are still used to varying degrees. As a prelude to automation, several laboratory supply companies introduced packaged kits in the 1960s, in which a series of dehydrated biochemical substrates were contained within miniaturized cupules embedded in a plastic strip. First was the Roche Enterotube, a pencil-shaped plastic tube containing 12 chambers with slants of differential culture media. Then followed the API 20E strip, containing 20 cupules containing dehydrated substrates, which is still used today. The color reactions within the reagent chambers of each of these systems is read visually, from which a biocode number linked to a bacterial identification is derived. *See* MEDICAL BACTERIOLOGY.

Automated bacterial identification. The impetus for the automation of bacterial identifications came in the mid-1970s as part of the NASA space program. The challenge was to design a small instrument that would be capable of identifying bacterial species encountered in space flights, particularly from environmental samples collected from the Moon. The outcome was the AMS bacterial identification system, since marketed under the name VITEK® (bioMerieux, Inc). The key feature of this system is a multiwell reagent card that, after inoculation of a bacterial suspension, is inserted into the incubation chamber of the instrument. The results of 30 biochemical reactions are provided by the instrument, available as soon as 4 h for biochemically active bacterial species. Competitive systems are also available for use in microbiology laboratories. Each of these widely used systems also has cards for the determination of antimicrobial susceptibility test results, replacing in many laboratories the time-honored method of measuring the zones of inhibition surrounding antibiotic-impregnated filter paper disks (**Fig. 4**).

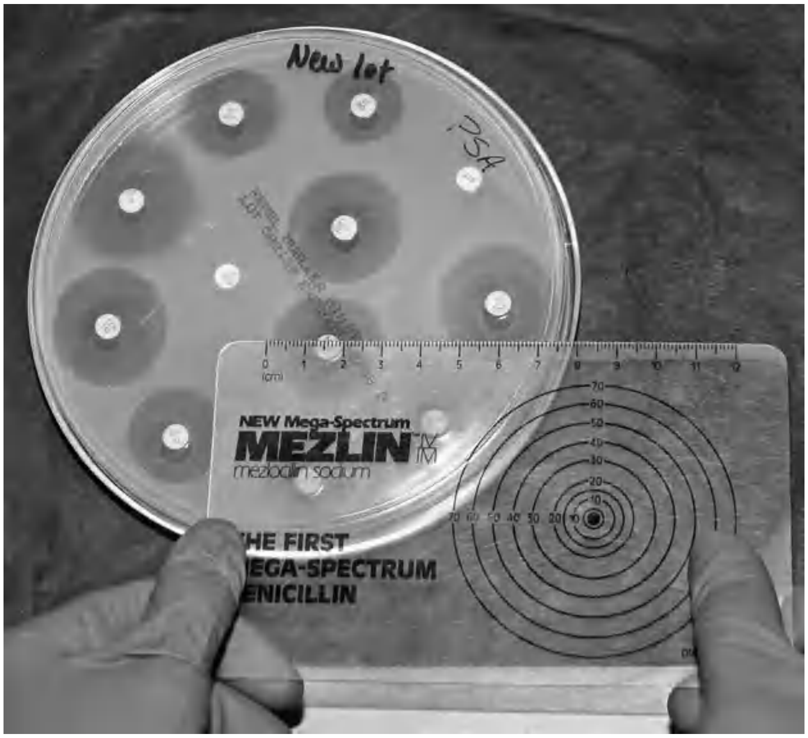

Fig. 4. Disk diffusion antimicrobial susceptibility plate illustrating assessment of antibiotic action by measuring zones of inhibition surrounding antibiotic-impregnated filter paper disks.

Continuous-read blood culture systems. The recent introduction of automated continuous-read blood culture systems has been a major breakthrough in providing the more timely detection of bloodborne infections. Previously, blood cultures were prepared by injecting a given volume of venous blood into bottles containing an enriched culture medium. The inoculated bottles were placed into a 35°C incubator. After 24–48 h of incubation, each bottle was visually observed against a strong transmitted light source for the detection of turbidity as a signal for bacterial growth. Subcultures were made of any turbid bottle to identify the organism.

In continuous-read systems, culture bottles are placed in a holding chamber within the instrument. Located in the bottom of each bottle is a pH-sensitive plastic disk that undergoes a color change when acid is produced by growing bacteria in the culture broth. As a threshold color change is achieved, the system automatically produces both a visual and an audio “alert.” The distinct advantage of this system, in addition to being more labor-saving, is the detection of positive blood cultures in as short a time as 4 h after collection.

Immunoassay. The introduction of immunoassays in the late 1960s has impacted in microbiology as well. Using a technology developed by the 1975 Nobel Prize winners George Köhler and César Milstein, monoclonal antibodies are now produced by hybridizing “immortal” antibody-secreting cancer cells (myeloma cells) from mice with a genetically equivalent cell producing a specific antibody. These specific antibodies can be used to detect the complementary antigens on bacterial cell walls, by which species identifications can often be directly made without the need for culture. Immunoassay can also be used to detect cell-surface antigens using monoclonal antibodies labeled with fluorescent dyes. Using this technology, more than 140 different antigens and adhesion molecules have been demonstrated on the surfaces of bacteria, white blood cells, platelets, and lymphocytes. *See* IMMUNOASSAY.

Blood banking and transfusion medicine. The blood bank and the transfusion service are sections of the laboratory dedicated to preparing, storing, and dispensing blood products as well as testing those who donate blood and those who will receive blood products. One hundred years ago, transfusions posed a significant risk to both the donor and recipient. Advances in laboratory testing for blood antigens and infectious disease has made the blood supply and the transfusion process relatively safe. Blood products are critical for treating trauma patients in the emergency department, surgical patients in the operating room, and patients with bleeding or clotting disorders.

Processing of blood for transfusion begins with the blood donor. Most blood donors are individuals who voluntarily give about $^1/_2$ liter of blood in a procurement procedure lasting about 20–30 min. Other donors selectively donate platelets, plasma, or red blood cells, using apheresis technology, a process that typically requires between 45 and 90 min. Patient donors are screened for many infectious diseases to maximize the safety of the blood supply. After a donation, patient blood is processed into components such as platelet concentrate, fresh frozen plasma, red blood cell concentrate, or cryoprecipitate. These components are then stored at the appropriate temperature until used.

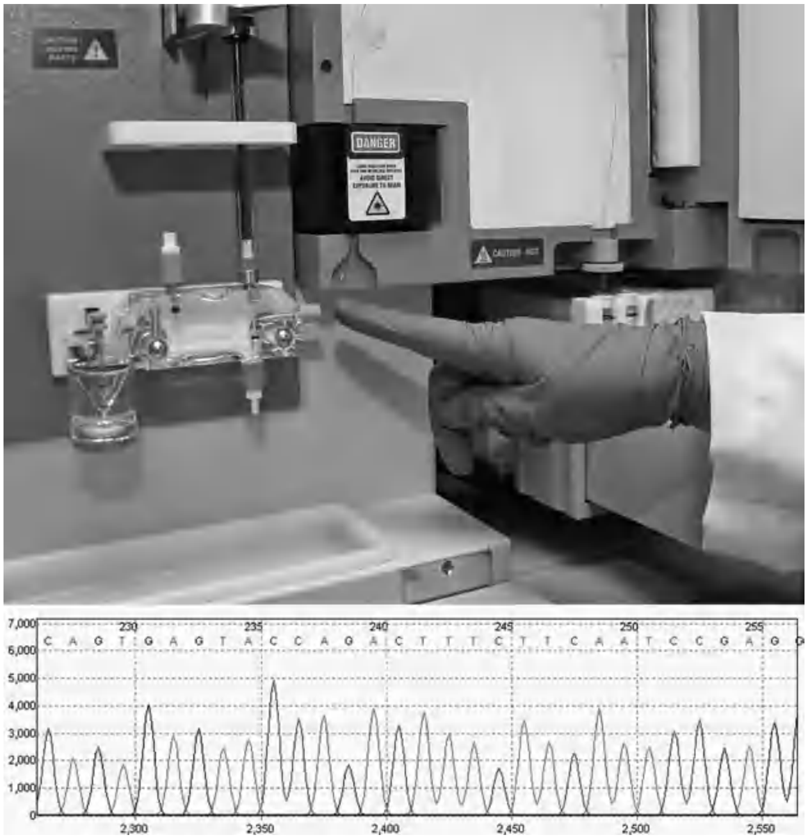

Fig. 5. Capillary electrophoresis is used for DNA sequencing. Data are processed by a computer which then converts the findings into a graphic display. This information is converted to identification of mutations, deletions, and insertions relating to human disease.

Prospective blood recipients are tested to determine their blood type and to detect the presence of antibodies and blood antigens. Using blood type and antibody screening information, blood products are selected that minimize the probability of any adverse transfusion reaction between donor and recipient blood. Many uses for blood products have evolved. For example, red blood cell concentrates are used to treat severe bleeding and anemia. Platelet concentrates are used to treat patients who are bleeding or at risk of bleeding due to lack of platelets. Fresh frozen plasma is used to replenish clotting factors in those with deficiencies or to avert severe bleeding.

The clinical pathologist is trained in blood banking and transfusion medicine and provides advice to other physicians about the best products to use in treating individual patients. In addition, the clinical pathologist oversees the collection of donor blood and the testing of recipients. The clinical pathologist also uses apheresis technology to treat patients. For example, apheresis is often employed to remove harmful antibodies or cells from patients with a wide variety of diseases such as Guillain-Barre syndrome or thrombotic thrombocytopenic purpura. *See* TRANSFUSION.

Recent Advances

A transition in the clinical pathology laboratory began in the early 1990s and is still progressing—the introduction of molecular biology and genetics.

Molecular and genetic biology. This technology, based on the direct amplification and analysis of DNA from a variety of biological cells, facilitates the diagnosis of diseases associated with defects and alterations in genes, including many hereditary diseases and cancers known to have a genetic association. These techniques have also allowed the direct and rapid identification of a variety of microorganisms that cause infectious diseases. For example, the detection of certain DNA sequences in *Mycobacterium tuberculosis*, the cause of tuberculosis, extracted directly either from infected body secretions or from bacterial cells recovered in culture, can lead to a diagnosis within hours, in contrast to the 2 to 3 weeks previously required. As part of forensic examinations, human beings, both alive and postmortem, can be identified based on direct molecular analysis of shed cells, aspirated body fluids, and/or autopsy specimens. The working parts of a nucleic acid sequencing instrument with the resultant printout of the graph depicting the peaks of the individual nucleotides are illustrated in **Fig. 5**. An analysis of the individual presence and sequence of these nucleotides provides information about gene defects and hereditary diseases. *See* DEOXYRIBONUCLEIC ACID (DNA); GENE.

Molecular pathology-laboratory. The molecular pathology laboratory is one of the newest additions to clinical laboratories. Its creation follows advances in molecular biology over the past 30 years such as the polymerase chain reaction, nucleic acid hybridization, and DNA sequencing. The term "molecular pathology" may be a bit misleading since all other laboratory areas also measure molecules in some form. The term, however, is reserved at present for the measurement of molecules using the most advanced technologies. Molecular pathology laboratories include tests for the detection of DNA fragments related to infectious disease, certain types of cancer, and genetic disease (**Fig. 6**).

Most cases of chlamydia and gonorrhea are diagnosed using nucleic acid testing for the organism responsible for each disease. Other organisms such as

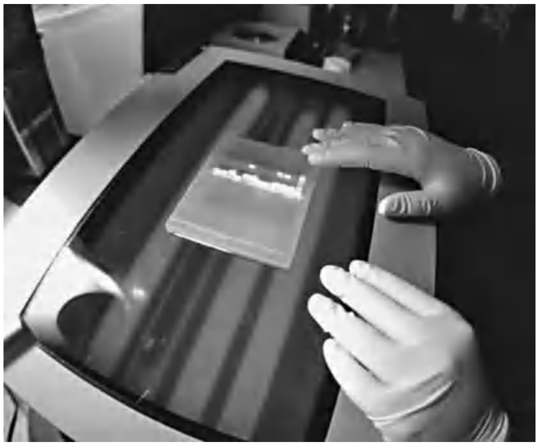

Fig. 6. Examination of an agarose gel with an ultraviolet light source to identify diagnostic fragments of DNA (orange-yellow fluorescent bands in the gel).

human papilloma virus (HPV) are also detected using DNA probes or polymerase chain reaction technology. In addition to detection of infectious diseases, treatment for patients with hepatitis C is monitored increasingly with viral load testing, in which the RNA from the virus is measured as treatment progresses. Patients with HIV infections are monitored the same way. In the workup of hematologic malignancies, the type of malignant cells can be detected by molecular analysis.

Molecular pathology techniques such as immunoglobulin and T-cell receptor gene rearrangements are often employed to help in the diagnosis of a specific type of leukemia or lymphoma. In addition, several types of cancer have characteristic chromosomal translocations. These translocations are usually detected using cytogenetics; however, in some cases DNA-based techniques are used to detect translocations of chromosomal material.

In addition to diagnosis and monitoring the therapy of infectious diseases and cancer, molecular pathology is often the only method by which genetic diseases may be detected prior to the development of symptoms. It is also the most powerful method for identifying patients who are carriers of genetic mutations. Several tests for genetic mutation analysis are commonly used for identifying Huntington's disease, factor V Leiden mutation, muscular dystrophy, and many other conditions. *See* HUMAN GENETICS; MUTATION.

The molecular pathology laboratory is likely to see expansion in both scale and scope. For example, methods to quickly measure large numbers of genes, messenger RNAs, proteins, and small metabolic molecules simultaneously have been developed. These advancements have led to the formation of several new disciplines: genomics, transcriptomics, proteomics, and metabolomics. The clinical pathologist as a laboratory physician becomes responsible for developing these sophisticated testing methods and interpreting results for other physicians.

Elmer W. Koneman; C. William Reiquam; Bradley B. Brimhall

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Clock (mechanical)

A mechanical device for indicating the passage of time. Most clocks contain a means for producing a regularly recurring action, such as the swing of a pendulum, the oscillation of a spiral spring and balance wheel, the vibration of a tuning fork, the oscillation of a piezoelectric crystal, or the comparison of a high-frequency signal with the radiation from the hyperfine structure of the ground state of atoms. This article describes the refinements of mechanical clocks. *See* ATOMIC CLOCK; QUARTZ CLOCK; WATCH.

Basic movement. The recurring action of a mechanical clock depends on the swing of a pendulum, or the oscillation of a balance wheel and balance spring or hairspring, or the vibration of a tuning fork, mechanisms capable of repeating their cyclic movements with great regularity. A counting mechanism, consisting of a gear train with calibrated dial and indicating hands, sometimes with a striking mechanism, marks the number of oscillations that have occurred, although the graduations are in seconds, minutes, and hours. A weight or spring ordinarily supplies power to operate the oscillating and the counting mechanisms. However, temperature changes, accelerations, automatic windings, or electricity may provide the power. (The conventional electric clock is not an independent timepiece but is a repeater whose accuracy depends on a remote primary clock.) Usually an escapement transmits power from the counting mechanism to the oscillating mechanism. The accuracy of a clock depends primarily on the escapement.

Escapements. Figure 1 depicts an anchor or recoil escapement. Anchor A is connected loosely to the pendulum and swings about C. At some time after midswing, a tooth of the wheel escapes from pallet P_1 or P_2, giving the pallet a push to maintain oscillation. The other pallet then checks another tooth, the curve of the pallet forcing the wheel slightly backward. The reaction helps to reverse the pendulum swing and to correct for circular error.

Figure 2 shows a deadbeat escapement. Faces F are circles about C so that the wheel is stationary

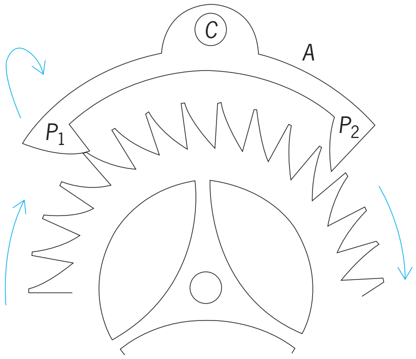

Fig. 1. Anchor escapement. Common in domestic pendulum clocks, this escapement tends to compensate for changes in amplitude of the swing because of irregularly cut gears and varying lubrication.

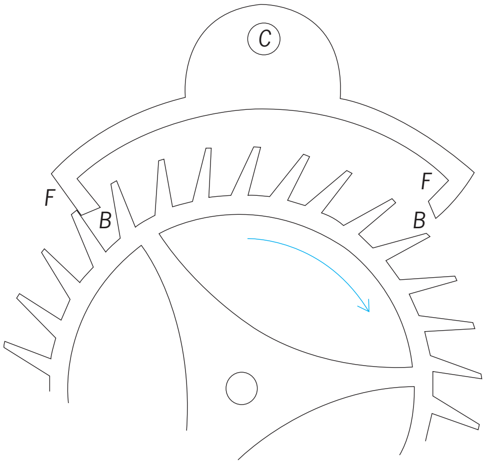

Fig. 2. Deadbeat escapement. Although lacking the corrective feature of the recoil type, this escapement gives better performance if well made.

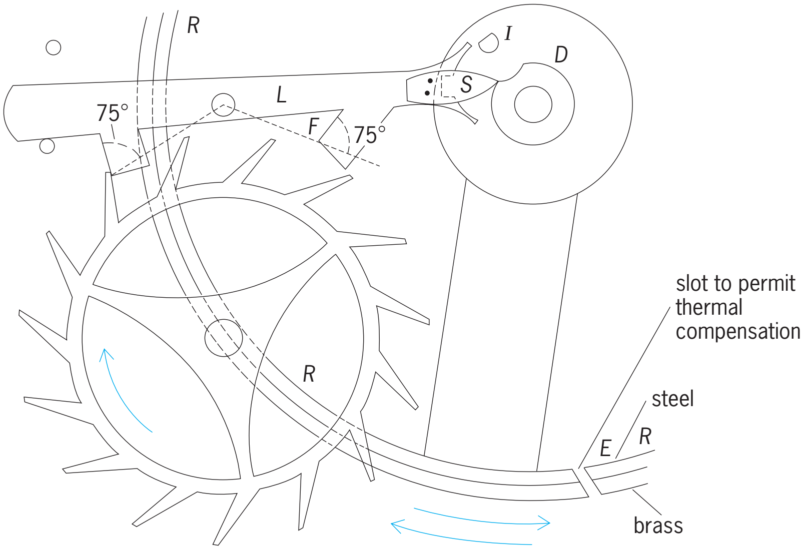

Fig. 3. Lever escapement. Used in good spring clocks and watches, it is detached from the balance wheel during most of a cycle, thus promoting accurate timekeeping.

except near midswing when a thrust on *B* allows a tooth to escape. **Figure 3** shows a lever escapement in which a balance wheel swings through a much larger angle than does a pendulum. Balance wheel and escapement are connected only while impulse pallet *I* is in a notch of lever *L*. As *I* enters a notch, it pushes the lever and then receives an impulse from it. Disk *D* and safety pallet *S* prevent the lever from moving accidentally before *I* returns; thus the mechanism tolerates appreciable vibration. The escapement pallets are similar to those of Fig. 2, but faces *F* are drawn or inclined so that the escape wheel moves slightly forward after each tooth locks; this motion pulls *S* clear of *D*, leaving the balance wheel completely detached. *See* ESCAPEMENT.

In the escapement of **Fig. 4**, the balance wheel is completely detached except for three brief action periods: (1) when pallet *P* presses detent *D* to unlock catch *L*, (2) when an impulse is being given to pallet *I*, and (3) when *P* lifts gold spring *G* on its return half swing. *See* CHRONOMETER.

Power supply. A weight gives uniform power, but a spring develops less force as it runs down. A fuzee by which a cord or chain is unwrapped from an increasing spiral on the first gear provides uniform force from a spring. Alternatively, there may be a remontoir with a small secondary spring driving the clock and being rewound frequently by the mainspring or by an electric motor.

Wind and snow apply large force to the hands of outdoor turret clocks. A gravity escapement isolates the pendulum from such forces. In this design, first used on the Great Westminster Clock (Big Ben), which has run since the mid-1800s with nearly chronometric accuracy, the escape wheel alternately lifts two weighted arms away from the pendulum as it swings out and releases them alternately against the pendulum as it swings back. The maintaining pushes come from the weighted arms rather than directly from the driving power.

Temperature compensation. The rate of a pendulum or balance wheel decreases if it expands with rising temperature. Expansion is counteracted by using two metals of different expansion coefficients. In a compensated balance wheel, rim *R* is of brass and steel fused together and cut (Fig. 3). Small screw weights added near free end *E* increase the effect; near the spoke they counteract it. Alternatively, the hairspring can be of an alloy that changes in stiffness with temperature.

Shortt clock. For still greater accuracy, in the Shortt or free-pendulum clock, a master pendulum is enclosed in an airtight and nearly evacuated case in a constant-temperature cellar. This pendulum swings freely for about 30 s until wheel *W* is released by electromagnet *E* and rolls along arm *A* attached to the pendulum rod (**Fig. 5**). Near the end of the swing, wheel *W* rides down slope *B*, giving the pendulum the slight impulse needed to maintain oscillation for another 30 s. In falling off, wheel *W* triggers the circuit and is reset by electromagnet *F*. The trigger

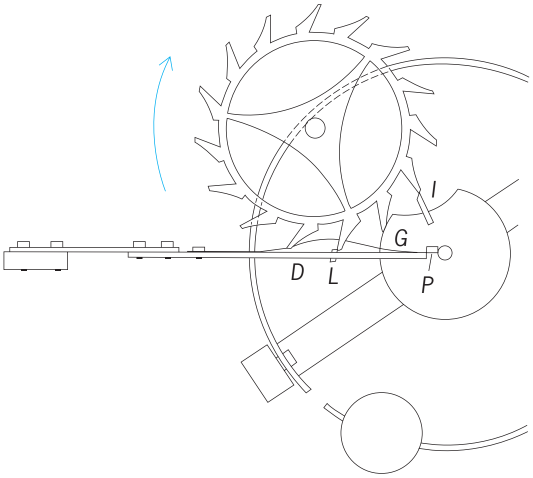

Fig. 4. Escapement used in ships' chronometers. It is sensitive to sudden movements but otherwise can keep within 1 s/day; pallets need no oil.

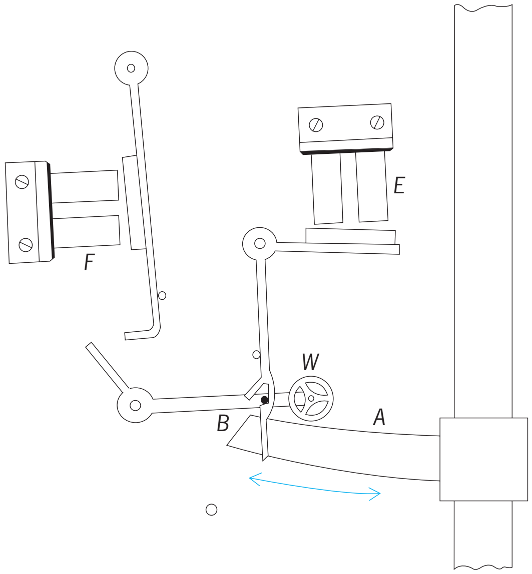

Fig. 5. Shortt free-pendulum clock. The master has only a pendulum and impulse giver; escapement and counting gears are in a separate slave clock (not shown).

pulse also serves as a synchronizing signal to a slave clock which is a complete clock with pendulum and indicating mechanism. If the slave is slow, the pulse accelerates one swing of its pendulum. *See* HOROLOGY; TIME.

Robert D'E. Atkinson

Tuning-fork mechanism. In the Accutron design the balance wheel and hairspring are replaced by a precision tuning fork which is driven with energy from a tiny battery. A permanent magnet and a surrounding magnetic cup are mounted on each tine of the tuning fork, which vibrates 360 times per second. Fixed coils of wire extend into the area between each magnet and cup, lying inside the magnetic field but not in contact with the moving parts of the tuning fork. Passing a current through one of these coils causes it to become an electromagnet which, depending on the polarities involved, will either repel or attract the corresponding magnet and cup assembly. Conversely, motion of the magnet and cup assembly within its electromagnetic coil causes a voltage to be induced, the polarity being determined by the direction of motion. This electromagnetic system serves three purposes: (1) It drives the tuning fork by converting electrical energy into mechanical impulses, (2) allows a determination of the tuning-fork amplitude by measuring the induced voltage, and (3) permits the accurate determination of the point within each tuning-fork cycle when the driving impulse should be applied. Conversion of the vibrational motion of the tuning fork to rotary motion is achieved by a simple ratchet and pawl mechanism.

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Clock paradox

The phenomenon occurring in the special theory of relativity wherein two observers who start together with identical clocks and then undergo different motions can have different total elapsed time on their clocks when they rejoin later. This effect is a well-defined, mathematically consistent prediction of special relativity which has been verified by experiment but, historically, it has been referred to as a paradox because of erroneous reasoning in the manner in which the effect is commonly analyzed. The clock-paradox phenomenon arises because there is no notion of absolute simultaneity in the theory of special relativity.

The clock-paradox effect is illustrated by the following hypothetical example. (In the context of the example the effect usually is referred to as the twin paradox.) Two identical twins are separated as young adults. One of the twins remains on Earth and, for the purposes of the discussion, is assumed to undergo inertial motion. (In fact, in the context of general relativity, the twin on Earth would be viewed as accelerating—only freely falling observers would be viewed as inertial—but in this example the corrections made to the effect by performing a proper, general-relativistic analysis would be negligible.) The other twin is placed in a rocket ship which accelerates very rapidly away from Earth until it is receding from Earth at nearly the speed of light. After coasting for a while at this speed, the rocket ship turns around and accelerates very rapidly back toward Earth, so that it soon is traveling at nearly the speed of light. The rocket ship then lands on Earth and the twins rejoin. The twin on Earth is old (and everything else on Earth has aged considerably), but the twin in the rocket ship (and everything else therein) has barely aged at all.

Comparison of path lengths. To explain the nature of this prediction of special relativity and why it has been thought to be paradoxical, it is useful to consider the following elementary phenomenon in ordinary euclidean plane geometry, which is mathematically very closely related to the clock paradox. In particular, two points A and B (**Fig. 1***a*) and the straight line segment AB connecting these points are considered, as well as a third point C and the path ACB comprising the straight line segments AC and CB. Then, although both paths AB and ACB start at A and end at B, they have different total lengths. Indeed, in the simple case where C is equidistant from A and B, by the pythagorean theorem, the lengths of the two paths are related by Eq. (1), where L' denotes

$$L' = L\sqrt{1 + \left(\frac{2d}{L}\right)^2} \qquad (1)$$

the length of the path ACB, L denotes the length of AB, and d denotes the perpendicular distance of C from AB.

It is possible to use the following method to calculate the increased length of the path ACB given by Eq. (1). A series of closely spaced lines is drawn

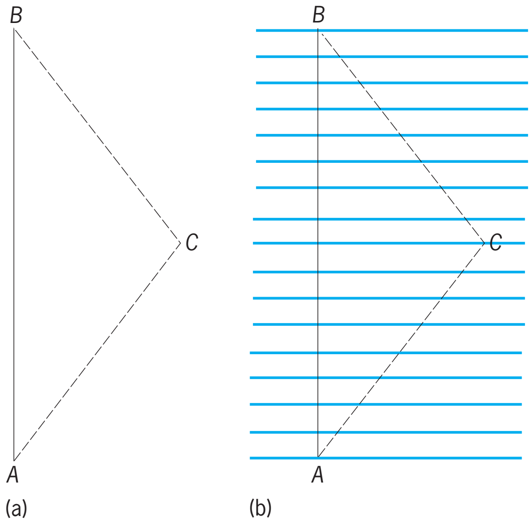

Fig. 1. Comparison of path lengths and elapsed times. (*a*) Straight line *AB* and broken straight line *ACB* connecting points *A* and *B* in euclidean plane geometry. This figure can also represent the world lines of an inertial observer and a "twin." (*b*) Method for comparing the lengths of *AB* and *ACB* in euclidean plane geometry. It can also be used to compare the elapsed time on clocks carried by an inertial observer and a "twin."

perpendicular to AB (Fig. 1*b*). An adjacent pair of such lines is considered, both of which intersect AC. Then it can be seen that the length of the portion of AC lying between these two lines is greater than the corresponding portion of AB by the factor $\sqrt{1+(2d/L)^2}$. The same result holds if two adjacent lines are considered which intersect CB rather than AC. However, the total length of AB can be obtained by summing the lengths of all of the portions of AB lying between adjacent perpendicular lines. By doing the sum, it is possible to correctly rederive the result that ACB is longer than AB by the factor $\sqrt{1+(2d/L)^2}$.

However, an apparent distance paradox arises from an attempt to redo this calculation as follows. A series of lines is drawn perpendicular to AC (**Fig. 2***a*).

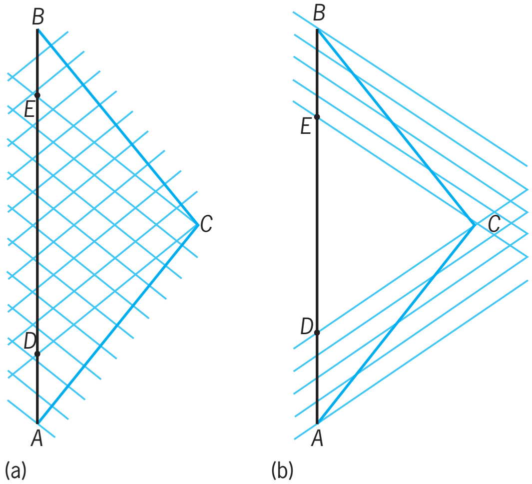

Fig. 2. Alternate methods for comparing (*a*) the lengths of *AB* and *ACB* in euclidean plane geometry, and (*b*) the elapsed times on the clocks carried by an inertial observer (world line *AB*) and a "twin" (world line *ACB*).

The portion of AC lying between adjacent lines now will be shorter than the corresponding portion of AB by the factor $\sqrt{1+(2d/L)^2}$. The same will be true for a similar calculation for the segment CB. Therefore, it might also seem possible to derive the manifestly false conclusion that the path ACB is shorter than the straight line AB by the factor $\sqrt{1+(2d/L)^2}$.

It is not difficult to spot the fallacy in this latter argument. When the series of lines is drawn perpendicular to CB, they will intersect the lines perpendicular to AC (Fig. 2*a*). As a consequence, this argument implicitly double counts a portion, DE, of AB. When a correction is made for this double counting, the correct conclusion that ACB is longer than AB by the factor $\sqrt{1+(2d/L)^2}$ is restored.

Comparison of elapsed times. The original diagram (Fig. 1*a*) may also be used to represent the twin-paradox phenomenon if it is now viewed as a space-time diagram with the vertical axis corresponding to time t and the horizontal axis corresponding to the spatial dimension x, so that "forward in time" corresponds to "upward" in the diagram. At event A, the twins separate, and the first twin undergoes inertial motion in space-time represented by the straight line AB. The segment AC represents the portion of the world line of the second twin while rapidly receding from the first twin, whereas CB represents the portion of the second twin's world line during the return. The comparison of the elapsed time T along the world line AB with the elapsed time T' along the world line ACB differs from the previous distance calculation only in that lorentzean geometry rather than euclidean geometry must be used in the analysis. Taking account of the sign change occurring in the lorentzean analog of the pythagorean theorem, the elapsed times are related by Eq. (2), where

$$T' = T\sqrt{1-\left(\frac{2d}{cT}\right)^2} = T\sqrt{1-\left(\frac{v}{c}\right)^2} \qquad (2)$$

$v = 2d/T$ is the magnitude of the relative velocity of the twins, and c is the velocity of light. In special relativity, the "straight line" (that is, inertial motion) AB has longer elapsed time than the motion represented by the world line ACB or, indeed, any other noninertial motion between A and B. *See* LORENTZ TRANSFORMATIONS.

The ratio of T' to T also can be calculated by the analog of the method of drawing lines perpendicular to AB (Fig. 1*b*), and this method correctly reproduces Eq. (2). There is also a calculation analogous to that of drawing lines perpendicular to AC and CB (Fig. 2*a*), where the lines are perpendicular to AC and CB in the lorentzean geometry of space-time (Fig. 2*b*). A careless use of this method yields the conclusion that T' is longer than T, resulting in the clock paradox. This paradox is easily resolved by noting that this method fails to count the portion DE of AB.

Experimental verification. The clock-paradox phenomenon has been observed directly in an experiment performed in 1971 by J. C. Hafele and R. E. Keating, who observed differences in elapsed times of atomically stabilized clocks flown in airplanes as compared with ones on the ground. In this experiment the special relativistic effect is so small, since the velocities achieved by airplanes are much smaller than *c*, that the tiny corrections due to general relativity cannot be neglected, so the experiment actually must be viewed as verifying the analogous clock effect in general relativity rather than purely the clock effect of special relativity described here. *See* RELATIVITY; SPACE-TIME.

Robert M. Wald

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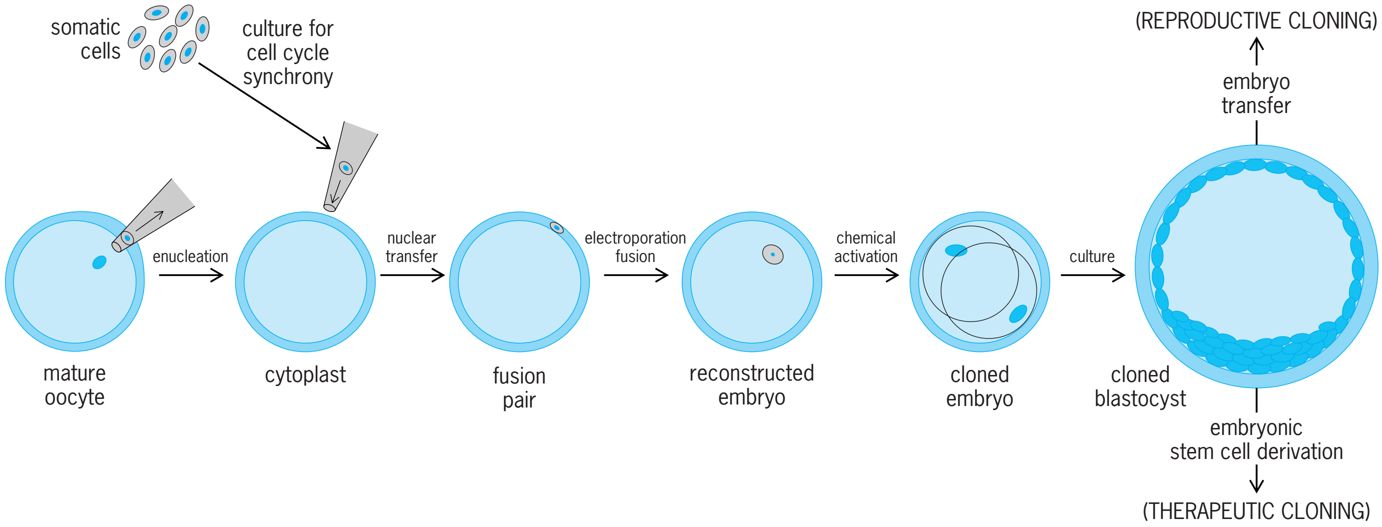
Cloning

The asexual creation of a genetic copy, a capability possessed by plants but not by most animals. Thus, plants generate genetic copies spontaneously, and rooting "cuttings" is widely used by horticulturists to propagate millions of clones annually. In animals, only some lower invertebrates can be cloned by "cutting"; for example, earthworms when bisected will regenerate the missing half, resulting in two whole, genetically identical individuals. However, asexual reproduction and cloning do not normally occur in vertebrates except for the special case of identical twinning. This is despite the fact that individual cells, called blastomeres, within the very early embryo are totipotent; that is, each is capable, if evaluated on its own, of developing into a viable term pregnancy and infant.

A major scientific interest in cloning revolves around the question of whether the hereditary material in the nucleus of each cell remains intact throughout development, regardless of the cell's fate. On a more practical level, the production of genetic copies of mammals could support the rapid improvement of livestock herds by propagation of valuable founder animals, the creation and production of disease models or transgenic animals for biomedical research, and the preservation of the genetic contribution of a particularly valuable animal, even after death. Therapeutic cloning, a variation that involves the isolation of embryonic stem cells, may provide new cell-based medical approaches to the treatment of human diseases or degenerative conditions.

Reproductive cloning. Scientific inquiry into reproductive cloning in animals began with a "fantastical experiment" suggested by Hans Spemann in 1938 that involved the insertion of a nucleus into an ovum bereft of its own genetic material. This experiment was eventually conducted in 1952 by Robert Briggs and Thomas King in an amphibian, the northern leopard frog, and the technology was quickly extended to a number of other lower vertebrates and invertebrates, and eventually to mammals. The first step in mammalian reproductive cloning is removal of the genetic material from an egg by micromanipulation to create an enucleated egg called a cytoplast. Then genetic material from a donor cell is added, in the form of an intact cell or an isolated nucleus, to produce a diploid, reconstructed embryo. The cell cycle of the nuclear donor cell may be temporarily slowed or stopped in advance of nuclear transfer. Development of the nuclear transfer embryo is triggered chemically, and the cloned embryo is subsequently transferred into a host mother in order to establish a pregnancy (see **illustration**).



Mammalian somatic cell cloning. The starting requirements include a cohort of mature fertile eggs and a nuclear donor source. Reproductive cloning in mammals involves the transfer of a nucleus or an entire donor cell into an enucleated egg or cytoplast, followed by the subsequent reprogramming of that nucleus by the egg, to the degree that the events of development are recapitulated in the cloned embryo. Therapeutic cloning is accomplished by conducting nuclear transfer with a nuclear donor cell derived from the patient, a skin fibroblast perhaps, transferred into a cytoplast. The resulting nuclear transfer embryo, after culture to the blastocyst stage, would then provide a source of inner-cell-mass cells from which an embryonic stem cell line could be derived.

When the nuclear donor cell originates from an embryo, the process is called embryonic cloning, first reported in cattle and sheep in 1986 and in primates in 1997. When the donor nucleus is derived from a fetus or a juvenile or adult animal and is not a germ cell, the process is called somatic cell cloning. This form of cloning was thought to be impossible in mammals even as recently as 1995, when scientists in Scotland cloned sheep from differentiating embryonic cells. In 1996, the birth of Dolly, a cloned sheep, was the first successful generation of a viable mammal derived from the transfer of an adult cell (a mammary gland cell).

Successful somatic cell cloning in other species (including the cow, mouse, goat, pig, rabbit, cat, horse, mule, and rat) quickly followed. A wide variety of somatic cells—even those that are unequivocally, terminally differentiated—have been used as nuclear donors. It now appears logical that cloning will be possible in all mammals, given an adequate opportunity to define the unique conditions required by each species.

While dramatic progress has been realized in somatic cell cloning, virtually nothing is known about how the process works, and significant limitations continue to undermine efforts to produce viable offspring. Thus, somatic cell cloning is characterized by high fetal and neonatal wastage, along with age-onset health problems (including obesity, hepatic and immune impairment, and premature death) in surviving clones. It is in fact amazing that somatic cell cloning works at all, given that over the course of normal development as a cell specializes, some genes are silenced temporarily or in some cases permanently. In order for the events of development to be accurately recapitulated following nuclear transfer of a differentiated cell, the donor nucleus must be reprogrammed so that it ceases to express genes of importance to a differentiated or somatic cell in favor of those important to a young embryonic cell; reprogramming is a responsibility of the cytoplast that must occur in a timely manner following nuclear transfer, perhaps along with dramatic remodeling of chromosomal architecture. In addition, nuclear reprogramming must ensure retention of the pattern of expression of imprinted genes, that is, those genes that are differentially expressed depending on their maternal or paternal origin. The inappropriate or abnormal expression of imprinted genes, as regulated by epigenetic changes (factors that alter the expression of genes rather than the genes themselves) such as DNA methylation, can impact placental development and fetal wastage.

Other possible explanations for the losses associated with somatic cell cloning are that clones age prematurely because the nuclear donor cells have shortened telomeres (chromosome tips) and because of heteroplasmy, the presence of more than one type of mitochondrial DNA in a cell. Since mitochondrial DNA is contributed by both the cytoplast and by the injection of a donor cell or nucleus preparation, clones are not exact genetic copies; indeed, they can be phenotypically quite different from one another. Fetal exposure to unique environments is another factor that results in phenotypic differences. *See* CELL DIFFERENTIATION; CELL DIVISION; GENE; SOMATIC CELL GENETICS.

Therapeutic cloning. In therapeutic cloning, embryos are produced by nuclear transfer, as in reproductive cloning, but with the intent of isolating embryonic stem cells rather than transferring cloned embryos into a host to produce a pregnancy. Embryonic stem cells are undifferentiated cells present in the embryo that are pluripotent; that is, they are capable of giving rise to all of the major cell lineages in the adult body but unable to generate a functioning organism. Adult stem cells exist and can be recovered in limited numbers from a host of different tissues or organs. They can, in theory, be used in cell-based therapies to treat human disease, but their low numbers and limited developmental potential are drawbacks. It is now clear that the pre-implantation-stage embryo contains a cohort of stem cells confined to the inner cell mass at the blastocyst stage, and these embryonic stem cells can be harvested, propagated, and established as permanent cell lines. These embryonic stem cells could be stored frozen until needed and then thawed and used directly for transplantation into the patient, or after their fate was directed into the desirable cell type in vitro by exposure to the appropriate chemical signals (see illustration).

Embryonic stem cells are the most primitive, most mitotically capable stem cells, and they hold virtually unlimited promise in the treatment of diseases attributable to the loss or dysfunction of known cell types. This cell-based therapy, as envisioned, would involve the transplantation of embryonic stem-cell-derived progeny that had been induced to differentiate into the missing or dysfunctional cells. Transplantation of allogeneic stem cells (stem cells from another individual of the same species) or their progeny, however, is complicated by the likelihood of host-graft rejection. As an alternative to overcome this problem, the patient could generate his or her own embryonic stem cells by contributing the donor nucleus or cell in somatic cell cloning, thereby creating self-cells transparent to the immune system such that their transplantation would not elicit an immune response. Proof-of-principle experimentation with adult cells in therapeutic cloning has now been reported in both mice and humans. *See* STEM CELLS.

Future research. An immediate focus of cloning research is to overcome the low success rates with somatic cell cloning in order to extend this technology to other nonhuman species. Undoubtedly, improvements will be realized with additional experience and increased surveillance at birth, with cloned pregnancies treated as high risk. This is already happening with cattle as substantial financial incentive exists in the cattle industry to produce cloned animals, and with mice due to their amenability to laboratory experimentation. Scientists are asking what kinds of cells make the best donors, what environments are most conducive to early development of the cloned embryo, what cell cycle stages are optimal for reprogramming, and how reprogramming can be initiated in the test tube. It seems reckless to extend reproductive cloning to humans at present because of the unacceptable risks imposed on the embryo, fetus, and neonate. Additional ethical considerations have been addressed extensively, for instance, in a United States National Bioethics Advisory Commission report issued in 1997. Therapeutic cloning in humans is less controversial, since it is not associated with efforts to produce cloned children and may represent a viable approach to treat human disease. Clearly, though, ethical concerns do persist with therapeutic cloning, based on the requirement to recruit egg donors in order to create a cloned embryo and then the need to destroy the embryo in the process of deriving embryonic stem cell lines. An alternative to creating individual embryonic stem cell lines by therapeutic cloning may ultimately be the development of stem cell banks that can be used to match the needs of all patients.

While many challenges lie ahead for somatic cell cloning, the mere demonstration that this process is possible in mammals is a highly significant beginning. Ongoing research efforts will lead to a better understanding of the molecular correlates to reprogramming, information that in turn will allow the development of in vitro conditions for reprogramming (for instance, the use of readily available cytoplasm as might be harvested from amphibian eggs). Ultimately, reprogramming will be accomplished with chemically defined reagents and, in the process, we will have developed profound new insights into the events underlying development in mammals, humans included. *See* GENETIC ENGINEERING.

Don P. Wolf

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Closed-caption television

A service, primarily for deaf people, that allows individual viewers to display the dialog of a television program in a readable form on the television screen. In the United Kingdom the service is called subtitling. Closed-caption television was introduced in the United States in 1980.

Caption preparation. Captions for television programs can be prepared in three ways. (1) Off-line captioning is used when the television program has been prerecorded. This is the preferred method for creating captions in that they can be caused to appear on different parts of the home television screen, for example, under the individual speaking, and they can be displayed in close synchronism with the dialog. Also, the caption display can be edited if necessary to a comfortable reading rate of about 125 words per minute. (2) Live television broadcasts that are scripted in advance, such as presidential State of the Union speeches, employ a live display captioning method. Here the script is stored in a computer in advance of the broadcast. During the broadcast the script appears as roll-up captions at the bottom of the screen. (3) In live broadcasts, where a script is not available, real-time captions have to be generated during the broadcast. This is by far the most difficult way to caption a television program. Highly skilled court reporters using a stenograph keyboard and an associated computer create the captions, often at instantaneous rates of 200–250 words per minute. In this method, inevitably, typographical errors are often generated.

Caption transmission. Prior to being broadcast, the captions are digitally encoded and inserted into the vertical blanking interval (VBI) of the television picture. In the United States and Canada, a single VBI line is allocated exclusively for the captioning service. In other countries such as the United Kingdom and Australia, the captions are integrated with other text material on a series of VBI lines that are used to deliver Teletext service to a more general audience. As the Teletext transmission data rate is about ten times the caption-only service data rate, it cannot be used in videocassette recorder (VCR) applications. This led to the caption-only system being introduced in home-television movies in the United Kingdom in the early 1990s.

Digital television. The world's terrestrial television systems are in the process of converting from analog to digital broadcasting. In the United States, the Federal Communication Commission (FCC) has adopted the Advanced Television Standards Committee (ATSC) system. Europe has adopted the Digital Video Broadcasting–Terrestrial (DVB-T) system. Elsewhere in the world, those countries that previously adopted the United States or European analog television standards are typically adopting the respective digital television standards. However, the International Telecommunications Union (ITU) recommendation on a digital video, audio, and ancillary data multiplex model has been adopted worldwide. Captions have been classified as an ancillary service and will be multiplexed with other ancillary services such as text services.

Captioned program service growth. Legislative and regulatory actions are spurring the worldwide introduction and growth of captioned television service. In many countries, specific goals have been set as to the percentage of television programs that must be captioned by the broadcasters. In the United States, it is illegal to sell a television set with a screen size 12 in. (30 cm) or larger that does not contain caption decoder circuitry built in by the manufacturer. *See* TELEVISION. John E. D. Ball

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Closed-circuit television

Television transmitted to a particular audience at specific locations via coaxial cables, telephone wires, fiber-optic strands, microwave radio systems, or communications satellites, as compared to open-circuit (broadcast) television intended for the general public. *See* COAXIAL CABLE; COMMUNICATIONS CABLE; COMMUNICATIONS SATELLITE; MICROWAVE; OPTICAL COMMUNICATIONS; TELEPHONE SERVICE.

The usual closed-circuit television picture display device is a television receiver. Most receivers use a cathode-ray tube to produce the visible image, although other devices such as flat-panel displays have become common. *See* CATHODE-RAY TUBE; ELECTRONIC DISPLAY; FLAT-PANEL DISPLAY DEVICE; LIQUID CRYSTALS; TELEVISION RECEIVER.

Applications. Closed-circuit television applications include information display, remote monitoring, instruction, cable television programming, and teleconferences and special events.

Information display. Flight times in airports are displayed by closed-circuit television, typically on large cathode-ray-tube video screens. A video screen may be used to display an image of the sales floor to a cashier at the front of a store; this setup is frequently installed for security reasons. In both examples, closed-circuit television provides information, but different methods are used for generating the video. The airport display usually shows text produced by a computer. The store screen shows the image of the sales floor produced by a video camera. These applications exemplify simple forms of closed-circuit television used to connect a source of information to a restricted group of viewing locations.

Remote monitoring. Many types of closed-circuit television systems produce pictures intended for distant viewing. These images may include those taken from a space probe passing close to a distant planet, or pictures of blast furnaces or other industrial operations that could be hazardous to human observers. At the opposite extreme, the low cost of modern video equipment makes practical the use of small cameras to observe sleeping children at home and to enjoy video images of people far away while chatting with them on the Internet.

Parking lots at shopping centers, store cashier locations, bank and hotel lobbies, and other public places are often equipped with closed-circuit television surveillance cameras and displays. These systems may be designed to function in nearly total darkness to detect suspicious activities or in brilliant surroundings to watch for hot spots in factory processes. Medical and scientific equipment and industrial robots often incorporate specialized closed-circuit television systems. Modern closed-circuit television cameras used for remote monitoring are sensitive, rugged, relatively inexpensive, and durable, with long service lives. Most modern solid-state designs use charge-coupled imaging devices. Video signals are often recorded on magnetic tape for future use. *See* CHARGE-COUPLED DEVICES.

Instruction. Closed-circuit television has been available for many years for educational uses. Many universities and school systems employ television for teaching. Classrooms may be equipped with closed-circuit television cameras, recorders, and receivers. Lesson material is often presented via video tape recordings, CD-ROMs, or DVD recordings. In other cases, classroom receivers are supplied with signals from specially reserved broadcast channels (called ITFS channels, for Instructional Television Fixed Service), cable television channels, or satellite channels. Audio circuits installed at viewing locations sometimes allow two-way conversations between lecturer and students. *See* COMPACT DISK; MAGNETIC RECORDING.

Cable television. Cable television was originally developed to improve broadcast reception in difficult receiving situations—for example, to bring distant signals from broadcast television stations to residents of mountain valleys or to serve viewers in cities where large buildings prevent satisfactory reception of broadcast signals. Contemporary cable systems continue to distribute signals from local and distant television stations, but they now offer additional television services not available from broadcast stations, such as satellite-distributed news, music, movies, weather information, and locally originated community-based programming. Cable systems offer services to an estimated 65 million households in the United States (75% of the total) using either coaxial cables or fiber-optic strands for signal delivery. *See* CABLE TELEVISION SYSTEM.

Wider availability has reduced the cost of using fiber-optic strands for high-speed signal transmission. High-speed interconnections enable closed-circuit television systems to utilize important new kinds of digitally based services. For example, many telephone and cable television companies provide fiber-optic connections to schools and classrooms. These permit relatively inexpensive two-way video and audio connections between schools and among school systems, enabling great flexibility in system design and utilization.

Teleconferences and special events. Closed-circuit television is used to conduct conferences among geographically separated groups of people. Signals from television-equipped meeting rooms or studios are distributed by fiber-optic circuits, communications satellites, or the Internet to convention centers, school or university classrooms, motels, hotels, or corporate locations. Two-way audio is typically provided, and conferences may involve many hundreds or thousands of people. Sports or musical events may also be televised and distributed in this fashion for viewing in suitably equipped theaters or auditoriums. *See* TELECONFERENCING.

Technology. Closed-circuit television systems frequently utilize equipment that produces signals based on broadcasting industry specifications. However, in contrast to the many possible designs for closed-circuit television systems, broadcast television is always limited to the use of standardized signals for its transmissions. The standardized television broadcast system used at present in the United States, Canada, Mexico, Japan, and some other countries was devised in the 1950s by the National Television Systems Committee (NTSC). NTSC systems display 30 complete television pictures (frames) per second, and each frame is composed of 525 horizontal scanning lines arranged from top to bottom. *See* TELEVISION STANDARDS.

Video cameras, television receivers, videocassette recorders, and accessories are produced in large quantities for NTSC broadcast applications. The NTSC system is well suited for home entertainment, but its signal structure is technically limited by the requirement for simple, inexpensive home receivers and video tape recorders. Inauguration of improved kinds of advanced television systems, most of them digital, is under way in many countries. Such technologies will eventually permit higher picture quality and the mass production of affordable receivers with new features. These features will eventually also become available for closed-circuit applications.

Special requirements. Closed-circuit television systems are not required to use NTSC signals, but many do, mainly for economic reasons. In many applications, normal NTSC-based closed-circuit television equipment is satisfactory. If the transmission path to the viewer is of low quality, however, special steps must be taken. In such cases, the signal can be modified to meet more closely the characteristics of the transmission system. For example, channel bandwidth can be reduced without loss of image resolution if the user accepts reduced quality in the representation of image motion. In that case, a rate lower than the normal 30 frames per second can be chosen. This is called slow-scan closed-circuit television.

Still-frame video images sometimes suffice. A high-quality still frame can be transmitted with picture elements being stored for seconds or even minutes in a memory system and then assembled for display after receipt of all data. This allows use of transmission channels having limited bandwidth. Most video pictures from space are transmitted at low frame rates over narrow-bandwidth communications channels, and complete reception requires several seconds. Narrow-band channels are also found on the Internet, where both slow-scan and still images are often used. *See* INTERNET; REMOTE SENSING.

NTSC broadcast signal characteristics may also be poorly suited to other kinds of specialized closed-circuit television applications. Some applications require high image resolution, great sensitivity to light, the ability to respond to infrared or ultraviolet light, or very rugged system components. Closed-circuit television requirements for high-resolution display can be satisfied by increasing the number of image scanning lines and the overall video channel bandwidth. Industrial standards exist for high-resolution closed-circuit systems. Cameras and monitors are available to meet other specialized requirements.

Advanced developments. The digital revolution has affected the design of all kinds of television equipment. Video signals can be converted into digital form and processed by specialized computers, called digital signal processors. Visual special effects are often seen on entertainment television, including slow motion, still frames, rotations, inversions, and picture shape changes. They are accomplished by use of digital signal processing systems. In closed-circuit television applications, digital processing can make transmission via the Internet practical and can also provide image enhancement. The excellent pictures from weather and surveillance satellite imaging systems are obtained with digital signal processing and enhancement. High-performance solid-state camera sensors and the digital processing of video signals, taken together, have extended the applications of closed-circuit television systems. The advanced television systems now entering service make use of the advantages of digital signal processing to provide high-quality images to the home, to the class-room, and to industrial locations. *See* DATA COMPRESSION; IMAGE PROCESSING; TELEVISION. Frederick M. Remley

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Clostridium

A genus of bacteria comprising large anaerobic spore-forming rods that usually stain gram-positive. Most species are anaerobes, but a few will grow minimally in air at atmospheric pressure.

The clostridia are widely distributed in nature, and are present in the soil and in the intestinal tracts of humans and animals. They usually live a saprophytic existence, and play a major role in the degradation of organic material in the soil and other natural environments. A number of clostridia release potent exotoxins and are pathogenic for humans and animals. Among the human pathogens are the causative agents of botulism (*Clostridium botulinum*), tetanus (*C. tetani*), gas gangrene (*C. perfringens*), and an antibiotic-associated enterocolitis (*C. difficile*). *See* ANAEROBIC INFECTION; TOXIN.

Characteristics. Clostridial cells are straight or slightly curved rods, 0.3–1.6 micrometers wide and 1–14 μm long. They may occur singly, in pairs, in short or long chains, or in helical coils. The length of the cells of the individual species varies according to the stage of growth and growth conditions. Young cultures of most species of *Clostridium* are gram-positive and stain readily with the usual aniline dyes, but in older cultures and clinical specimens the organisms frequently stain gram-negative. Most clostridia are motile with a uniform arrangement of flagella. *See* CILIA AND FLAGELLA.

The endospores produced by clostridia are dormant structures capable of surviving for prolonged periods of time, and have the ability to reestablish vegetative growth when appropriate environmental conditions are provided. The spores of most clostridia are resistant to heat, chemical agents, and radiation and thus provide the organism with a selective advantage in its native habitat, enabling it to survive under the most adverse environmental conditions. The spores of clostridia are oval or spherical and are wider than the vegetative bacterial cell. Among the distinctive forms are spindle-shaped organisms, club-shaped forms, and tennis racket–shaped structures.

Clostridia are obligate anaerobes: they are unable to use molecular oxygen as a final electron acceptor and generate their energy solely by fermentation. Clostridia exhibit varying degrees of intolerance to oxygen. Some species are sensitive to oxygen concentrations as low as 0.5%, but most species can tolerate concentrations of 3–5%. The sensitivity of clostridia to oxygen restricts their habitat to anaerobic environments; habitats that contain large amounts of organic matter provide optimal conditions for their growth and survival.

A primary property of all species of *Clostridium* is their inability to carry out a dissimilatory reduction of sulfate. Most species are chemoorganotrophic. The substrate spectrum for the genus as a whole is very broad and includes a wide range of naturally occurring compounds. Extracellular enzymes are secreted by many species, enabling the organism to utilize a wide variety of complex natural substrates in the environment. Four nutritional groups are recognized: saccharolytic species (species that break down sugars), proteolytic species (species that hydrolyze proteins and peptides), species that are both saccharolytic and proteolytic, and species that are neither but are specialized on one or a few substrates. A number of saccharolytic species ferment carbohydrates, with the production of such compounds as butyric acid, butanol, isopropanol, and acetone. Proteolytic species metabolize proteins, often with the production of foul-smelling amines.

Pathogens. Species of *Clostridium* associated with human disease are divided into four major groups on the basis of the types of diseases: histotoxic clostridia cause a wide variety of tissue infections; enterotoxigenic clostridia produce gastrointestinal disorders; *C. tetani* is the etiologic agent of tetanus; and *C. botulinum* is the etiologic agent of botulism. In all clostridial diseases, pathogenesis is attributable to potent exotoxins released by the organism.

Histotoxic forms. *Clostridium perfringens* is the most important of the histotoxic clostridia that cause tissue infections in humans, especially of the muscle tissue (clostridial myonecrosis, or gas gangrene). This short, plump, nonmotile rod (2–4 μm wide) is more aerotolerant than most other anaerobes. Its strains produce at least 12 different toxins and enzymes, many of which have lethal, cell-destroying, and hemolytic (red blood cell–destroying) properties. A number of nonlethal enzymes are also produced, and apparently contribute to the invasiveness of the organism. These include collagenase, deoxyribonuclease, and hyaluronidase. *See* GANGRENE.

Other histotoxic clostridia include *C. novyi* and *C. septicum*. More than 30 additional species have been isolated from human clinical specimens, but most of these are considered to be nonpathogenic opportunistic organisms.

In individuals with malignancies of the cecum or with leukemia, invasion of the bloodstream by *C. septicum* or *C. perfringens* may lead to a life-threatening fulminating septicemia. *Clostridium perfringens* can also cause food poisoning if large numbers of an enterotoxin-producing strain are ingested. A more severe form of food poisoning, called enteritis necroticans, is caused by type C strains of *C. perfringens*. It is seen most often in malnourished children in the less developed countries. *See* FOOD POISONING.

Enterotoxigenic forms. *Clostridium difficile* causes pseudomembranous colitis, a severe disease associated with the administration of antibiotics. The antibiotics most often involved include clindamycin, ampicillin, and the cephalosporins. *Clostridium difficile* is widespread in the environment and is part of the normal intestinal flora of about 3% of healthy adults. When antibiotic-sensitive organisms are eliminated from the intestine, there is an overgrowth of *C. difficile*, severe intestinal mucosa damage, and resultant clinical disease.

Clostridium tetani. This species is the causative agent of tetanus. It is a long, thin rod that forms a round terminal spore that gives the sporulating organism a characteristic drumstick appearance. The organisms are widely distributed in the soil and in the gastrointestinal tracts of humans and other animals. The spores remain viable in the soil for many years and provide the primary source of infection. Often after a simple puncture wound from a nail or splinter contaminated with soil containing the organisms, they multiply locally at the site and elaborate a potent neurotoxin (tetanospasmin) which is responsible for all of the symptoms of tetanus. *See* TETANUS.

Clostridium botulinum. The most common form of botulism is an intoxication that usually follows the ingestion of a preformed toxin produced by *C. botulinum*. There are seven types (A to G) of *C. botulinum* based on the immunologically distinct type of toxin produced. The production of a specific type of botulinum toxin is determined by the specific bacteriophage carried by the organism. Types A, B, and E are responsible for most cases of human botulism. The toxins are neurotoxins and are among the most toxic compounds known. They act on neuromuscular junctions by inhibiting the release of acetylcholine. *See* ACETYLCHOLINE.

The spores of *C. botulinum* are widely distributed in soils, lake sediments, and decaying vegetation in many parts of the world. They are very resistant to heat and can withstand 212°F (100°C) for 3–5 h; moist heat at 250°F (121°C) will kill them in 15 min. In the canning of food (especially vegetables), if the spores on contaminated food are not killed, they will germinate and release toxins when conditions become sufficiently anaerobic. *See* BOTULISM; FOOD PRESERVATION.

Disease in animals. A number of diseases in mammals and birds are caused by the ingestion of toxins elaborated by toxinogenic species of *Clostridium. Clostridium botulinum* causes grass or fodder sickness of horses, silage disease in cattle, limberneck in chickens, lamziekte in cattle, and dust sickness in wild birds. Type C botulinum toxin causes large epidemics of botulism in aquatic birds. In the western United States, the disease is the major natural cause of death of wild ducks. Other species of clostridia associated with major diseases in animals are *C. chauvoei*, *C. haemolyticum*, *C. novyi* type B, *C. septicum*, and *C. tetani*. *See* MEDICAL BACTERIOLOGY.

Hilda P. Willett

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Cloud

A suspension of minute droplets or ice crystals produced by the condensation of water vapor. This article presents an outline of cloud formation upon which to base an understanding of cloud classifications. For a more technical consideration of the physical character of atmospheric clouds, including the condensation and precipitation of water vapor, *see* CLOUD PHYSICS; FOG.

Rudiments of cloud formation. A grasp of a few physical and meteorological relationships aids in an understanding of clouds. First, if water vapor is cooled sufficiently, it becomes saturated and is in equilibrium with a plane surface of liquid water (or ice) at the same temperature. Further cooling in the presence of such a surface causes condensation upon it; in the absence of any surfaces, no condensation occurs until a substantial further cooling provokes condensation upon ions or random large aggregates of water molecules. In the atmosphere, even in the apparent absence of any surfaces, nuclei always exist upon which condensation proceeds at barely appreciable cooling beyond the state of saturation. Consequently, when atmospheric water vapor is cooled sufficiently, condensation nuclei swell into minute water droplets and form a visible cloud. The total concentration of liquid in the cloud is controlled by its temperature and the degree of cooling beyond the state in which saturation occurred, and in most clouds approximates to 1 g/m^3 (0.001 oz/ft^3) of air. The concentration of droplets is controlled by the concentrations and properties of the nuclei and the speed of the cooling at the beginning of the condensation. In the atmosphere these are such that there are usually about 100,000,000 droplets/m^3 (2,800,000 droplets/ft^3). Because the cloud water is at first fairly evenly shared among them, these droplets are necessarily of microscopic size, and an important part of the study of clouds concerns the ways in which they become aggregated into drops large enough to fall as rain.

The cooling which produces clouds is almost always associated with the upward movements of air which carry heat from the Earth's surface and restore to the atmosphere that heat lost by radiation into space. These movements are most pronounced in storms, which are accompanied by thick, dense clouds, but also take place on a smaller scale in fair weather, producing scattered clouds or dappled skies. *See* STORM.

Rising air cools by as much as 10°C for each kilometer of ascent, so that even over equatorial regions temperatures below 0°C (32°F) are encountered a few kilometers above the ground, and clouds of frozen particles prevail at higher levels. Of the abundant nuclei which facilitate droplet condensation, very few cause direct condensation into ice crystals or stimulate the freezing of droplets, and especially at temperatures near 0°C (32°F) their numbers may be vanishingly small. Consequently, at these temperatures, clouds of unfrozen droplets are not infrequently encountered (supercooled clouds). In general, however, ice crystals occur in very much smaller concentrations than the droplets of liquid clouds, and may by condensation alone become large enough to fall from their parent cloud. Such ice nuclei are particles of clay, or sometimes bacteria,

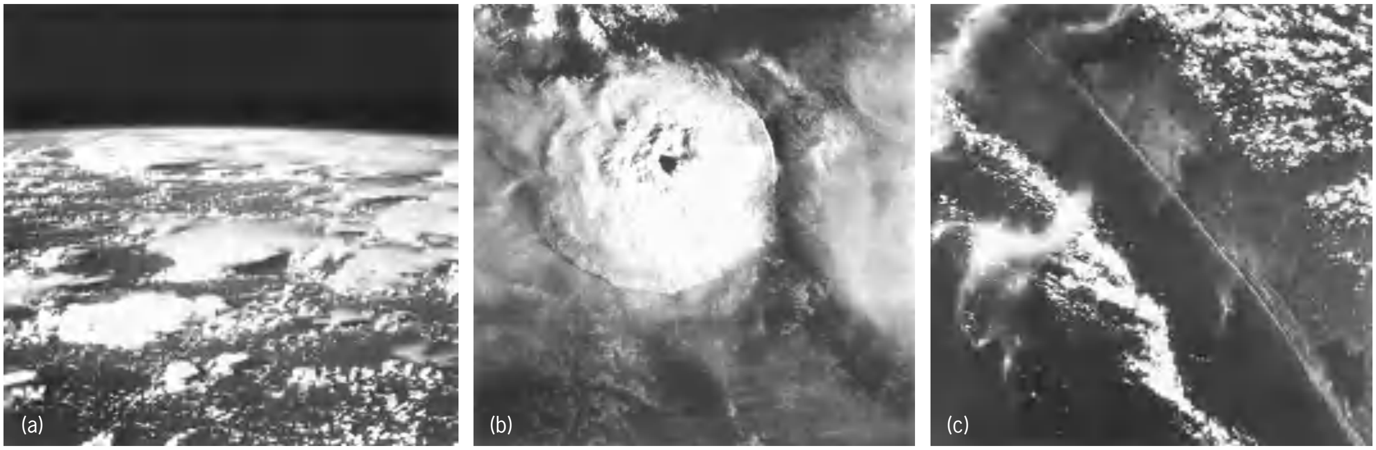

Fig. 1. Clouds as photographed by meteorological satellites. (*a*) A garden of thunderstorms, showing the anvils, forming at the tropopause inversion. (*b*) A hurricane, showing the eye. (*c*) Convective cloud over land and sea-breeze clouds.

mixed upward from the Earth's surface. All cloud droplets freeze by self-nucleation (ice crystal formation by random motion of the water molecules) at temperatures below −35 to −40°C (−31 to −40°F). Even small high clouds may produce or become trails of snow crystals, whereas droplet clouds are characteristically compact in appearance with well-defined edges, and produce rain only when well developed vertically (2 km or 1.5 mi, or more, thick).

Clouds play a major role in the heat balance of the Earth by scattering back sunlight to space. The heat balance is also affected by clouds' absorbing and scattering thermal radiation from regions partly above the cloud. Changes in cloud particle size and concentration by anthropogenic effects—air pollution from various sources—may influence the heat balance, thus offsetting the effects of carbon dioxide warming. *See* CLIMATE MODIFICATION.

Nacreous and noctilucent clouds. Clouds sometimes occur at much higher levels in the atmosphere, particularly when the temperature falls below −90 to −95°C (−130 to −139°F). Nacreous clouds (or polar stratospheric clouds) occur at heights near 25 km (17 mi) in the Arctic and Antarctic winter or early spring. They are visible when their level is illuminated by the Sun from some 20° below the horizon, so that the observer is on the surface in darkness. Such low temperatures occur preferentially in wave disturbances propagating upward and downstream of surface mountain ranges. Particles are composed of sulfuric acid (possibly injected by extreme volcanic events) and nitric acid, water ice, and combinations thereof as hydrates, usually some 1–5 micrometers in diameter. Such clouds are sometimes colored (particularly when particles are unfrozen supercooled or saturated droplets), a phenomenon

Fig. 3. Small cumulus. (*U.S. Weather Bureau*)

Fig. 2. Cirrus, with trails of slowly falling ice crystals at a high level. (*F. Ellerman*, *U.S. Weather Bureau*)

Fig. 4. Overcast of stratus, with some fragments below the hilltops. (*U.S. Weather Bureau*)

Fig. 5. View from Mount Wilson, California. High above is a veil of cirrostratus, and below is the top of a low-level layer cloud. (*F. Ellerman*, *U.S. Weather Bureau*)

Fig. 6. Cirrocumulus, high clouds with a delicate pattern. (*A. A. Lothman*, *U.S. Weather Bureau*)

which also occurs in lower-level clouds because of sunlight diffraction from regions containing particles of near-uniform size; hence the alternative name, mother of pearl clouds. At higher levels, near 80 km (50 mi), at the temperature minimum near −80°C (−112°F), noctilucent clouds form and can be viewed under similar circumstances, with viewing time extended for an even lower Sun because of the additional height. The particles tend to be smaller (by about one-tenth); however, these clouds show a much more fibrous structure than nacreous clouds and are not colored. Observation of these clouds is associated with north-south-oriented mountains which give rise to gravity waves in easterly circumpolar flow, being more frequent in Scandinavia, Alaska, and northern Canada. Particles making up these clouds may form the substrate for chemical reactions leading to destruction of ozone.

Classification of clouds. The contrast in cloud forms mentioned above was recognized in the first widely accepted classification, as well as in several succeeding classifications. The first was that of L. Howard in 1803, recognizing three fundamental types: the stratiform (layer), cumuliform (heap), and cirriform (fibrous). The first two are indeed fundamental, representing clouds formed respectively in stable and in convectively unstable atmospheres, whereas the clouds of the third type are the ice clouds which are in general higher and more tenuous and less clearly reveal the kind of air motion which led to their formation. Succeeding classifications continued to be based upon the visual appearance or form of the clouds, differentiating relatively minor features, but later in the nineteenth century increasing importance was attached to cloud height, because direct measurements of winds above the ground were then very difficult, and it was hoped to obtain wind data on a great scale by combining observations of apparent cloud motion with reasonably accurate estimates of cloud height, based solely on their form. With the advent of satellite and rocket observations in the 1970s, a broader perspective became available for examination of clouds on a global basis. Such pictures readily show the distribution of clouds from systems as a midlatitude cyclone, hurricane, or the intertropical convergence zone; they show the influence of land and ocean in initiating convective motion; examples are given in **Fig. 1**. *See* METEOROLOGICAL ROCKET; METEOROLOGICAL SATELLITES; SATELLITE METEOROLOGY.

WMO cloud classification. The World Meteorological Organization (WMO) uses a classification which, with minor modifications, dates from 1894 and represents a choice made at that time from a number of competing classifications. It divides clouds into low-level (base below about 2 km or 1.5 mi), middle-level (about 2 to 7 km or approximately 1 to 4.5 mi), and high-level (between roughly 7 and 14 km or approximately 4 to 8.5 mi) forms within

Fig. 7. Altocumulus, which occurs at intermediate levels. (*G. A. Lott*, *U.S. Weather Bureau*)

Fig. 8. Altostratus, a middle-level layer cloud. Thick layers of such clouds, with bases extending down to low levels, produce prolonged rain or snow, and are then called nimbostratus. (*C. F. Brooks*, *U.S. Weather Bureau*)

Fig. 9. Cumulonimbus clouds photographed over the upland adjoining the upper Colorado River valley. (*Lt. B. H. Wyatt, U.S.N., U.S. Weather Bureau*)

the middle latitudes. The names of the three basic forms of clouds are used in combination to define 10 main characteristic forms, or genera.

1. Cirrus are high white clouds with a silken or fibrous appearance (**Fig. 2**).
2. Cumulus are detached dense clouds which rise in domes or towers from a level low base (**Fig. 3**).
3. Stratus are extensive layers or flat patches of low clouds without detail (**Fig. 4**).
4. Cirrostratus forms from an abundance of cirrus as a layer, well above and distinct from the lower layer cloud (**Fig. 5**).
5. Cirrocumulus is formed of high clouds broken into a delicate wavy or dappled pattern (**Fig. 6**).
6. Stratocumulus is a low-level layer cloud having a dappled, lumpy, or wavy structure. See the foreground of Fig. 5.
7. Altocumulus is similar to stratocumulus but lies at intermediate levels (**Fig. 7**).
8. Altostratus is a thick, extensive, layer cloud at intermediate levels (**Fig. 8**).
9. Nimbostratus is a dark, widespread cloud with a low base from which prolonged rain or snow falls.
10. Cumulonimbus is a large cumulus which produces a rain or snow shower (Fig. 1*a*; **Fig. 9**).

Classification by air motion. Modern studies of clouds have been stimulated by the need to know their composition from the viewpoint of aircraft and rocket penetration, which gives rise to icing, turbulence, and lightning hazards, and by the discovery that seeding of supercooled clouds could, on occasion, give rise to enhanced precipitation. *See* WEATHER MODIFICATION.

These studies show that the external form of clouds gives only indirect and incomplete clues to the physical properties which determine their evolution. Throughout this evolution the most important properties appear to be the air motion and the size-distribution spectrum of all the cloud particles, including the condensation and ice-forming nuclei. These properties vary significantly with time and position within the cloud, so that cloud studies demand the intensive examination of individual clouds with aircraft, radar, and satellites. Nevertheless, the overall cloud shape does give information on the formation process. Lenticular clouds with smooth tops may form from smooth air flow with little environmental mixing (**Fig. 10**); clouds with irregular tops (Figs. 3

Cloud classification based on air motion and associated physical characteristics

Kind of motion	Typical vertical speeds, cm/s*	Kind of cloud	Name	Characteristic dimensions, km†		Characteristic precipitation
				Horizontal	Vertical	
Widespread slow ascent, associated with cyclones (stable atmosphere)	1–10	Thick layers	Cirrus, later becoming: cirrostratus altostratus altocumulus	10^3	1–2	Snow trails
			nimbostratus	10^3	10	Prolonged moderate rain or snow
Convection, due to passage over warm surface (unstable atmosphere)	10^2	Small heap cloud	Cumulus	1	1	None
	10^3	Shower- and thundercloud	Cumulonimbus	10	10	Intense showers of rain or hail
Irregular stirring causing cooling during passage over cold surface (stable atmosphere)	$10–10^2$	Shallow low layer clouds, fogs	Stratus Stratocumulus	$<10^2$ $<10^3$	<1	None, or slight drizzle or snow

*1 cm = 0.4 in. †1 km = 0.62 mi.

Fig. 10. A cloud formed by moist air flowing over a mountain. Note the smooth upper profile, indicating low-turbulence flow. (*Courtesy of John Hallet*)

and 9) show that mixing is strong. The former has nonturbulent, laminar air motions and give a smooth flight; the mixing clouds give modest to strong turbulence and a bumpy flight. An observer of clouds can readily see motions of convective clouds; motions in other systems can be viewed by time-lapse photography at 5–50-s intervals, or sequential satellite pictures at intervals of several hours. From a general meteorological point of view, a classification can be based upon the kind of air motion associated with the cloud, as shown in the **table**.

Frank H. Ludlam; John Hallett

Cloud physics

The study of the physical and dynamical processes governing the structure and development of clouds and the release from them of snow, rain, and hail (collectively known as precipitation). *See* PRECIPITATION (METEOROLOGY).

The factors of prime importance are the motion of the air, its water-vapor content, and the number and properties of the particles in the air which act as centers of condensation and freezing. Because of the complexity of atmospheric motions and the enormous variability in vapor and particle content of the air, it seems impossible to construct a detailed, general theory of the manner in which clouds and precipitation develop. However, calculations based on the present conception of laws governing the growth and aggregation of cloud particles and on simple models of air motion provide reasonable explanations for the observed formation of precipitation in different kinds of clouds.

Cloud formation. Clouds are formed by the lifting of damp air which cools by expansion under continuously falling pressure. The relative humidity increases until the air approaches saturation. Then condensation occurs (**Fig. 1**) on some of the wide variety of aerosol particles present; these exist in concentrations ranging from less than 2000 particles/in.^{3} (100/cm^3) in clean, maritime air to perhaps 10^7/in.^{3} (10^6/cm^3) in the highly polluted air of an industrial city. A portion of these particles are hygroscopic and promote condensation at relative humidities below 100%; but for continued condensation leading to the formation of cloud droplets, the air must be slightly supersaturated. Among the highly efficient condensation nuclei are the salt particles produced by the evaporation of sea spray, but it appears that particles produced by human-made fires and by natural combustion (for example, forest fires) also make a major contribution. Condensation onto the nuclei continues as rapidly as the water vapor is made available by cooling of the air and gives rise to droplets of the order of 0.0004 in. (0.01 mm) in diameter. These droplets, usually present in concentrations of several thousand per cubic inch, constitute a nonprecipitating water cloud.

Mechanisms of precipitation release. Growing clouds are sustained by upward air currents, which may vary in strength from about an inch per second to several yards per second. Considerable growth of the cloud droplets (with falling speeds of only about 0.4 in./s or 1 cm/s) is therefore necessary if they are to fall through the cloud, survive evaporation in the unsaturated air beneath, and reach the ground as drizzle or rain. Drizzle drops have radii exceeding 0.004 in. (0.1 mm), while the largest raindrops are about 0.24 in. (6 mm) across and fall at nearly 30 ft/s (10 m/s). The production of a relatively few large particles from a large population of much smaller ones may be achieved in one of two ways.

Coalescence process. Cloud droplets are seldom of uniform size for several reasons. Droplets arise on nuclei of various sizes and grow under slightly different conditions of temperature and supersaturation in different parts of the cloud. Some small drops may remain inside the cloud for longer than others before being carried into the drier air outside.

A droplet appreciably larger than average will fall faster than the smaller ones, and so will collide and fuse (coalesce) with some of those which it overtakes (**Fig. 2**). Calculations show that, in a deep cloud containing strong upward air currents and

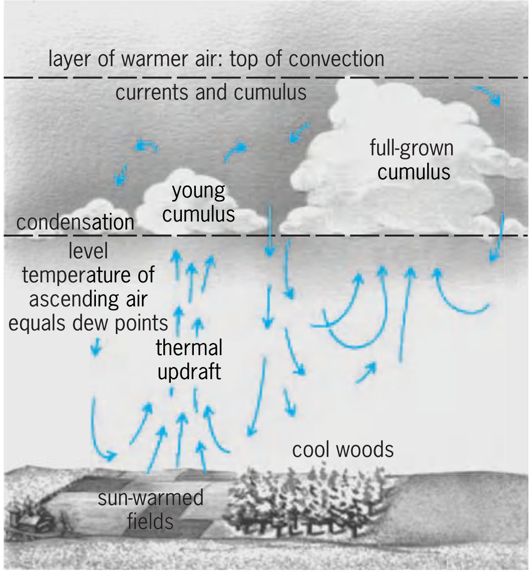

Fig. 1. Conditions leading to birth of a cumulus cloud.

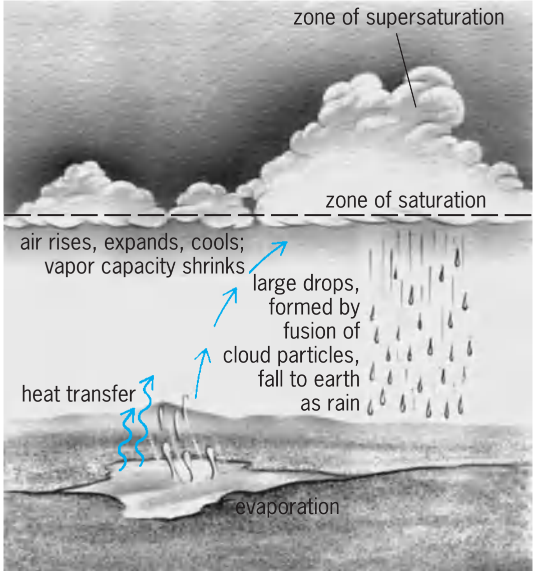

Fig. 2. Diagram of the steps in the formation of rain.

high concentrations of liquid water, such a droplet will have a sufficiently long journey among its smaller neighbors to grow to raindrop size. This coalescence mechanism is responsible for the showers that fall in tropical and subtropical regions from clouds whose tops do not reach the 32°F (0°C) level and therefore cannot contain ice crystals which are responsible for most precipitation. Radar evidence also suggests that showers in temperate latitudes may sometimes be initiated by the coalescence of waterdrops, although the clouds may later reach to heights at which ice crystals may form in their upper parts.

Initiation of the coalescence mechanism requires the presence of some droplets exceeding 20 micrometers in diameter. Over the oceans and in adjacent land areas they may well be supplied as droplets of sea spray, but in the interiors of continents, where so-called giant salt particles of marine origin are probably scarce, it may be harder for the coalescence mechanism to begin.

Ice crystal process. The second method of releasing precipitation can operate only if the cloud top reaches elevations where temperatures are below 32°F (0°C) and the droplets in the upper cloud regions become supercooled. At temperatures below −40°F (−40°C) the droplets freeze automatically or spontaneously; at higher temperatures they can freeze only if they are infected with special, minute particles called ice nuclei. As the temperature falls below 32°F (0°C), more and more ice nuclei become active, and ice crystals appear in increasing numbers among the supercooled droplets. But such a mixture of supercooled droplets and ice crystals is unstable. The cloudy air, being usually only slightly supersaturated with water vapor as far as the droplets are concerned, is strongly oversaturated for the ice crystals, which therefore grow more rapidly than the droplets. After several minutes the growing crystals will acquire definite falling speeds, and several of them may become joined together to form a snowflake. In falling into the warmer regions of the cloud, however, the snowflake may melt and reach the ground as a raindrop.

Precipitation from layer-cloud systems. The deep, extensive, multilayer-cloud systems, from which precipitation of a usually widespread, persistent character falls, are generally formed in cyclonic depressions (lows) and near fronts. Such cloud systems are associated with feeble upcurrents of only a few centimeters per second, which last for at least several hours. Although the structure of these great raincloud systems, which are being explored by aircraft and radar, is not yet well understood, it appears that they rarely produce rain as distinct from drizzle, unless their tops are colder than about 10°F (−12°C). This suggests that ice crystals may be responsible. Such a view is supported by the fact that the radar signals from these clouds usually take a characteristic form which has been clearly identified with the melting of snowflakes.

Production of showers. Precipitation from shower clouds and thunderstorms, whether in the form of raindrops, pellets of soft hail, or true hailstones, is generally of greater intensity and shorter duration than that from layer clouds and is usually composed of larger particles. The clouds themselves are characterized by their large vertical depth, strong vertical air currents, and high concentrations of liquid water, all these factors favoring the rapid growth of precipitation elements by accretion.

In a cloud composed wholly of liquid water, raindrops may grow by coalescence with small droplets. For example, a droplet being carried up from the cloud base would grow as it ascends by sweeping up smaller droplets. When it becomes too heavy to be supported by the vertical upcurrents, the droplet will then fall, continuing to grow by the same process on its downward journey. Finally, if the cloud is sufficiently deep, the droplet will emerge from its base as a raindrop.

In a dense, vigorous cloud several kilometers deep, the drop may attain its limiting stable diameter (about 0.2 in. or 5 mm) before reaching the cloud base and thus will break up into several large fragments. Each of these may continue to grow and attain breakup size. The number of raindrops may increase so rapidly in this manner that after a few minutes the accumulated mass of water can no longer be supported by the upcurrents and falls out as a heavy shower. The conditions which favor this rapid multiplication of raindrops occur more readily in tropical regions.

The ice crystals grow initially by sublimation of vapor in much the same way as in layer clouds, but when their diameters exceed about 0.004 in. (0.1 mm), growth by collision with supercooled droplets will usually predominate. At low temperatures the impacting droplets tend to freeze individually and quickly to produce pellets of soft hail. The air spaces between the frozen droplets give the ice a relatively low density; the frozen droplets contain large numbers of tiny air bubbles, which give the pellets an opaque, white appearance. However, when the growing pellet traverses a region of relatively high air temperature or high concentration of liquid water or both, the transfer of latent heat of fusion from the hailstone to the air cannot occur sufficiently rapidly to allow all the deposited water to freeze immediately. There then forms a wet coating of slushy ice, which may later freeze to form a layer of compact, relatively transparent ice. Alternate layers of opaque and clear ice are characteristic of large hailstones, but their formation and detailed structure are determined by many factors such as the number concentration, size and impact velocity of the supercooled cloud droplets, the temperature of the air and hailstone surface, and the size, shape, and aerodynamic behavior of the hailstone. Giant hailstones, up to 4 in. (10 cm) in diameter, which cause enormous damage to crops, buildings, and livestock, most frequently fall not from the large tropical thunderstorms, but from storms in the continental interiors of temperate latitudes. An example is the Nebraska-Wyoming area of the United States, where the organization of larger-scale wind patterns is particularly favorable for the growth of severe storms. *See* HAIL.

The development of precipitation in convective clouds is accompanied by electrical effects culminating in lightning. The mechanism by which the electric charge dissipated in lightning flashes is generated and separated within the thunderstorm has been debated for more than 200 years, but there is still no universally accepted theory. However, the majority opinion holds that lightning is closely associated with the appearance of the ice phase, and the most promising theory suggests that the charge is produced by the rebound of a small fraction of the supercooled cloud droplets that collide with the falling hail pellets. *See* LIGHTNING.

Basic aspects of cloud physics. The various stages of the precipitation mechanisms raise a number of interesting and fundamental problems in classical physics. Worthy of mention are the supercooling and freezing of water; the nature, origin, and mode of action of the ice nuclei; and the mechanism of ice-crystal growth which produces the various snow crystal forms.

It has been established how the maximum degree to which a sample of water may be supercooled depends on its purity, volume, and rate of cooling. The freezing temperatures of waterdrops containing foreign particles vary linearly as the logarithm of the droplet volumes for a constant rate of cooling. This relationship, which has been established for drops varying between 0.0004 and 0.4 in. (10 μm and 1 cm) in diameter, characterizes the heterogeneous nucleation of waterdrops and is probably a consequence of the fact that the ice-nucleating ability of atmospheric aerosol increases logarithmically with decreasing temperature.

When extreme precautions are taken to purify the water and to exclude all solid particles, small droplets, about 0.00004 in. (1 μm) in diameter, may be supercooled to −40°F (−40°C) and drops of 0.04 in. (1 mm) diameter to −31°F (−35°C). Under these conditions freezing occurs spontaneously without the aid of foreign nuclei.

The nature and origin of the ice nuclei, which are necessary to induce freezing of cloud droplets at temperatures about −40°F (−40°C), are still not clear. Measurements made with large cloud chambers on aircraft indicate that the most efficient nuclei, active at temperatures above 14°F (−10°C), are present in concentrations of only about 30/ft^3 (10/m^3) of air, but as the temperature is lowered, the number of ice crystals increases logarithmically to reach concentrations of about 25/ft^3 (1/liter) at −4°F (−20°C) and 2500/ft^3 (100/liter) at −22°F (−30°C). Since these measured concentrations of nuclei are less than one-hundredth of the number that apparently is consumed in the production of snow, it seems that there must exist processes by which the original number of ice crystals are rapidly multiplied. Laboratory experiments suggest the fragmentation of the delicate snow crystals and the ejection of ice splinters from freezing droplets as probable mechanisms.

The most likely source of atmospheric ice nuclei is provided by the soil and mineral-dust particles carried aloft by the wind. Laboratory tests have shown that, although most common minerals are relatively inactive, a number of silicate minerals of the clay family produce ice crystals in a supercooled cloud at temperatures above −0.4°F (−18°C). A major constituent of some clays, kaolinite, which is active below 16°F (−9°C), is probably the main source of highly efficient nuclei.

The fact that there may often be a deficiency of efficient ice nuclei in the atmosphere has led to a search for artificial nuclei which might be introduced into supercooled clouds in large numbers. Silver iodide is a most effective substance, being active at 25°F (−4°C), while lead iodide and cupric sulfide have threshold temperatures of 21°F (−6°C) for freezing nuclei.

In general, the most effective ice-nucleating substances, both natural and artificial, are hexagonal crystals in which spacings between adjacent rows of atoms differ from those of ice by less than 16%. The detailed surface structure of the nucleus, which is determined only in part by the crystal geometry, is of even greater importance. This is strongly indicated by the discovery that several complex organic substances, notably steroid compounds, which have apparently little structural resemblance to ice, may act as nucleators for ice at temperatures as high as 30°F (−1°C).

The collection of snow crystals from clouds at different temperatures has revealed their great variety of shape and form. By growing the ice crystals on a fine fiber in a cloud chamber, it has been possible to reproduce all the naturally occurring forms and to show how these are correlated with the temperature and supersaturation of the environment. With the air temperature along the length of a fiber ranging from 32 to −13°F (0 to −25°C), the following clear-cut changes of crystal habit are observed (**Fig. 3**): hexagonal plates–needles–hollow prisms–plates–stellar dendrites–plates–prisms. This multiple change of habit over such a small

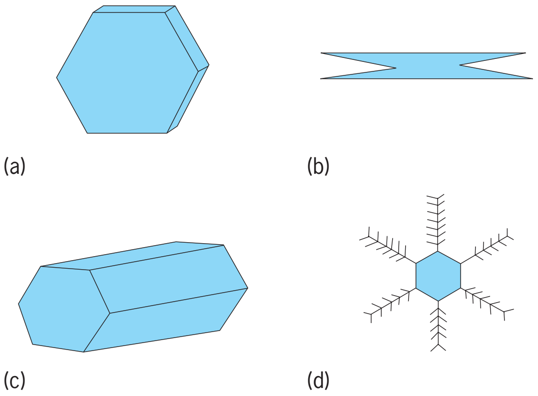

Fig. 3. Ice crystal types formed in various temperature ranges: (*a*) Thin hexagonal plate at 32 to 27°F (0 to −3°C), 18 to 10°F (−8 to −12°C), 3 to −13°F (−16 to −25°C). (*b*) Needles at 27 to 23°F (−3 to −5°C). (*c*) Hexagonal prismatic column at 23 to 18°F (−5 to −8°C), below −13°F (−25°C). (*d*) Dendritic star-shaped crystal at 10 to 3°F (−12 to −16°C).

temperature range is remarkable and is thought to be associated with the fact that water molecules apparently migrate between neighboring faces on an ice crystal in a manner which is very sensitive to the temperature. Certainly the temperature rather than the supersaturation of the environment is primarily responsible for determining the basic shape of the crystal, though the supersaturation governs the growth rates of the crystals, the ratio of their linear dimensions, and the development of dendritic forms. *See* SNOW.

Artificial stimulation of rain. The presence of either ice crystals or some comparatively large waterdroplets (to initiate the coalescence mechanism) appears essential to the natural release of precipitation. Rainmaking experiments are conducted on the assumption that some clouds precipitate inefficiently, or not at all, because they are deficient in natural nuclei; and that this deficiency can be remedied by seeding the clouds artificially with dry ice or silver iodide to produce ice crystals, or by introducing waterdroplets or large hygroscopic nuclei. In the dry-ice method, pellets of about 0.4-in. (1-cm) diameter are dropped from an aircraft into the top of a supercooled cloud. Each pellet chills a thin sheath of air near its surface to well below −40°F (−40°C) and produces perhaps 10^{12} minute ice crystals, which subsequently spread through the cloud, grow, and aggregate into snowflakes. Only a few pounds of dry ice are required to seed a large cumulus cloud. Some hundreds of experiments, carried out mainly in Australia, Canada, South Africa, and the United States, have shown that cumulus clouds in a suitable state of development may be induced to rain by seeding them with dry ice on occasions when neighboring clouds, untreated, do not precipitate. However, the amounts of rain produced have usually been rather small.

For large-scale trials designed to modify the rainfall from widespread cloud systems over large areas, the cost of aircraft is usually prohibitive. The technique in this case is to release a silver iodide smoke from the ground and rely on the air currents to carry it up into the supercooled regions of the cloud. In this method, with no control over the subsequent transport of the smoke, it is not possible to make a reliable estimate of the concentrations of ice nuclei reaching cloud level, nor is it known for how long silver iodide retains its nucleating ability in the atmosphere. It is usually these unknown factors which, together with the impossibility of estimating accurately what would have been the natural rainfall in the absence of seeding activities, make the design and evaluation of a large-scale operation so difficult.

Little convincing evidence can be found that large increases in rainfall have been produced consistently over large areas. Indeed, in temperate latitudes most rain falls from deep layer-cloud systems whose tops usually reach to levels at which there are abundant natural ice nuclei and in which the natural precipitation processes have plenty of time to operate. It is therefore not obvious that seeding of these clouds would produce a significant increase in rainfall, although it is possible that by forestalling natural processes some redistribution might be effected.

Perhaps more promising as additional sources of rain or snow are the persistent supercooled clouds produced by the ascent of damp air over large mountain barriers. The continuous generation of an appropriate concentration of ice crystals near the windward edge might well produce a persistent light snowfall to the leeward, since water vapor is continually being made available for crystal growth by lifting of the air. The condensed water, once converted into snow crystals, has a much greater opportunity of reaching the mountain surface without evaporating, and might accumulate in appreciable amounts if seeding were maintained for many hours.

Trials carried out in favorable locations in the United States and Australia suggest that in some cases seeding has been followed by seasonal precipitation increases of about 10%, but rarely have the effects been reproduced from one season to the next, and overall the evidence for consistent and statistically significant increases of rainfall is not impressive. Indeed, as the experiments have been subjected to stricter statistical design and evaluation, the claims have steadily became more modest, and the difficulty of improving on natural processes has become increasingly apparent.

During the 1960s and 1970s, remaining trials were carried out in some 75 countries, and at one time about 25% of the land area of the United States was being seeded. However, by the late 1980s the activity was much reduced and had virtually ceased in Australia and many other countries. Nevertheless, China and Israel persevered. The Israeli experiments were unique in that they appeared to have produced rainfall increases on the order of 15% year after year for about 15 years. No convincing explanation for this has yet emerged. *See* CLOUD; WEATHER MODIFICATION.

Basil J. Mason

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Clove

The unopened flower bud (see **illus.**) of a small, conical, symmetrical, evergreen tree, *Eugenia caryophyllata*, of the myrtle family (Myrtaceae). The cloves are picked by hand and dried in the sun or by artificial means. The crop is uncertain and difficult to grow. Cloves, one of the most important and useful spices, are strongly aromatic and have a pungent flavor. They are used as a culinary spice for flavoring pickles, ketchup, and sauces, in medicine, and for perfuming the breath and the air in rooms. The essential oil distilled from cloves by water or steam has even more uses. The chief clove-producing countries are Tanzania with 90% of the total output, Indonesia, Mauritius, and the West Indies. *See* MYRTALES; SPICE AND FLAVORING.

Perry D. Strausbaugh; Earl L. Core

Closed (cloves) and open flower buds on a branch of the evergreen tree *Eugenia caryophyllata*.

Clover

A common name used loosely to designate the true clovers, sweet clovers, and other members of the plant family Leguminosa. This article discusses true clovers, sweet clover, and clover diseases.

True Clovers

The true clovers are plants of the genus *Trifolium*, order Rosales. There are approximately 250 species in the world. Collectively they represent the most important genus of forage legumes in agriculture. Different species constitute one or more crops on every continent. As indicated by the number of species and their ecotypes (subspecies) that have been collected and described, the center of origin appears to be southeastern Europe and southwestern Asia Minor. Many species are found in countries that border the Mediterranean Sea. About 80 species are native to the United States, most of them occurring in the general regions of the Rocky and Cascade mountains and the Sierra Nevada. Although these native clovers are not used as crop plants, they contribute to the range for grazing and wild hay and also supply nitrogen to associated grasses. Of those that are now named, it is possible that many are variants of other species. Only a few are native to the humid Eastern states. Most clovers are highly palatable and nutritious to livestock. The name clover is often applied to members of legume genera other than *Trifolium*. *See* ROSALES.

Characteristics. The true clovers are herbaceous annual or perennial plants. However, many perennial species behave as biennials or annuals under attacks of disease or insects, unfavorable climatic or soil conditions, or improper management. In general, clovers thrive under cool, moist conditions although one native species, desert clover (*T. gymnocarpum*), tolerates semiarid conditions. Annual species usually behave as winter annuals where winter conditions are not severe, and as summer annuals at northern latitudes and high altitudes.

Clovers grow best in areas where adequate supplies of calcium, phosphorus, and potassium are naturally present in the soil or where these elements are applied in limestone and fertilizers. They grow from a few inches to several feet tall, depending on the species and the environmental conditions. The leaves have three to five roundish to spearlike leaflets. The florets, ranging from 5 to 200 in number, are borne in heads. Colors include white, pink, red, purple, and yellow, and various mixtures. The basic haploid chromosome numbers of the species are 6, 7, and 8. Somatic chromosomes range from 12 to about 130, forming diploids, tetraploids, and polyploids. The flowers of some species are self-sterile and must be cross-pollinated before seed will form; the flowers of other species may be self-fertile and capable of self-pollination; others are self-fertile but do not set seed unless the flowers are tripped and the pollen scattered onto the stigma. Cross-pollination and tripping of flowers are effected principally by bees that visit the flowers for nectar and pollen. Seed color ranges from yellow to deep purple, some being bicolored. There are approximately 60,000–700,000 seeds per pound.

Uses. Clovers are used for hay, pasture, silage, and soil improvement. Certain kinds may be used for all purposes whereas others, because of their low growth, are best suited for grazing. All kinds, when well grown in thick stands, are good for soil improvement. Thoroughly inoculated plants add 50–200 lb of nitrogen per acre (56–222 kg per hectare) when plowed under for soil improvement, the amount added depending on growth, thickness of stand, and length of growing season. Clovers may be grown alone, in combination with grasses and other legumes, or with small grains. In the humid states, or where irrigated, clovers are sown most

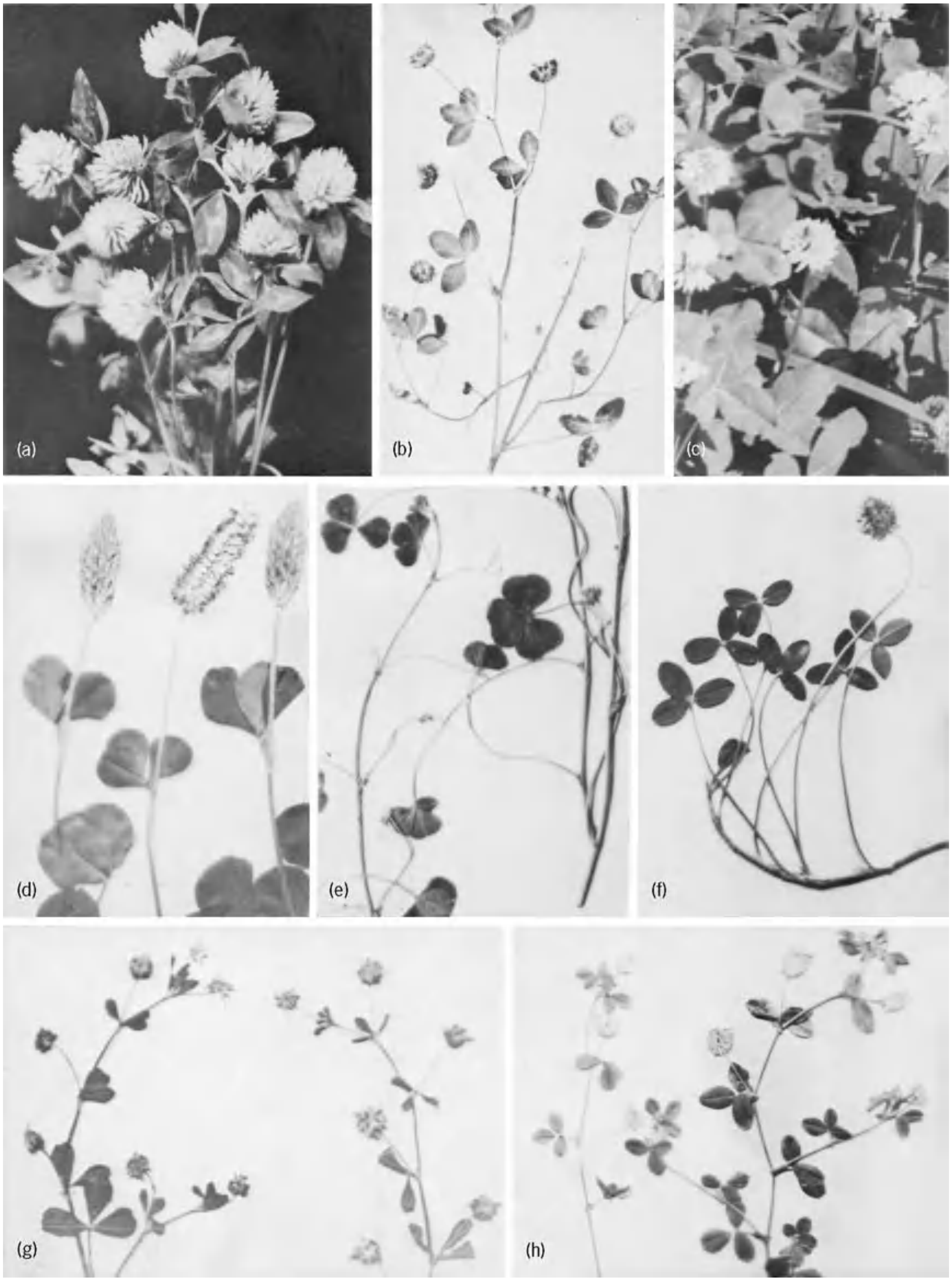

Fig. 1. Important clovers. (*a*) Red clover (*Trifolium pratense*). (*b*) Alsike clover (*T. hybridum*). (*c*) White clover (*T. repens*). (*d*) Crimson clover (*T. incarnatum*). (*e*) Subclover (*T. subterraneum*). (*f*) Strawberry clover (*T. fragiferum*). (*g*) Persian clover (*T. resupinatum*). (*h*) Large hop clover (*T. campestre* or *procumbens*). (*USDA*)

frequently with small-grain companion crops. In the Corn Belt they are generally spring-seeded, whereas in the Southern states and in the West Coast region they should be seeded in the fall for best results.

Important species. All the clover species of agricultural importance in the United States are introduced (exotic) plants. **Figure 1** shows some of the species most widely used: red clover (*T. pratense*), alsike clover (*T. hybridum*), white clover (*T. repens*), crimson clover (*T. incarnatum*), subclover (*T. subterraneum*), strawberry clover (*T. fragiferum*), persian clover (*T. resupinatum*), and large hop clover (*T. campestre*, or *procumbens*). Other clovers of regional importance, mostly adapted to specific environmental conditions, are rose clover (*T. hirtum*), berseem clover (*T. alexandrinum*), ball clover (*T. nigrescens*), lappa clover (*T. lappaceum*), big-flower clover (*T. michelianum*), and arrowleaf clover (*T. vesiculosum*).

Species characteristics. The following sections discuss the characteristics of the most important species.

Red clover. Red clover is composed of two forms, medium and mammoth, producing two and one hay cuts, respectively. The large purplish-red flower heads are round. An upright-growing perennial, red clover generally persists for 2 years in the northern United States, but behaves as a winter annual in the South. When planted alone or with small grain, seeding rates are 10–15 lb/acre (11–17 kg/hectare). When seeded with grass and other mixtures, 4–8 lb/acre (4.9–9.0 kg/ha) is sufficient. Under favorable growth conditions, seed yields average 70 lb/acre (79 kg/ha); in the West under irrigation they may reach 600–800 lb/acre (675–900 kg/ha). There are several varieties and strains of red clover such as Kenland, Pennscott, Lakeland, Dollard, and Chesapeake. These produce higher yields of forage and are more persistent than common red clover.

Alsike clover. Alsike clover is an upright-growing species that behaves like a biennial. The growth pattern, seeding methods, mixtures, and uses are similar to those of red clover. The flower heads are much like those of white clover in shape and size, but are slightly more pinkish. Alsike clover is more tolerant of wet, poorly drained soils than red clover and occurs widely in mountain meadows of the West.

White clover. White clover, an inhabitant of lawns and closely grazed pastures, is the most important pasture legume in the humid states. The flowers are generally white, but sometimes they are tinged with pink. The stems grow on the soil surface and root at the joints (nodes) as the plant spreads. There are three main types, large, intermediate, and small, with all gradations between. Ladino is the best-known and most widely seeded variety of the large type, and Louisiana Sl represents the intermediate type. The small type is found principally in pastures that are continuously and closely grazed. All types are nutritious and are relished by all classes of livestock and poultry. The protein content ranges from 15 to 30%, depending on plant age and the succulence of growth. Ladino white clover is sometimes used for silage and hay. White clover is mainly grown with low-growing grasses, not being tolerant of the tall-growing kinds. Seeding rates vary from $^1/_2$ to 2 lb/acre (0.6 to 2.3 kg/ha) depending on the seed mixture. For successful growth, it is important to use the variety or strain best adapted to the particular climatic and soil conditions. Limestone and fertilizer must usually be used to get a thick stand and good growth. Spring seeding is recommended for the Northern states and fall seeding for regions having mild winters. For best growth of the clover, grass-clover mixtures should be grazed or cut frequently.

Crimson clover. Crimson clover is used principally as a winter annual for pasture and as a soil-improving crop from the latitude of the Ohio River southward, and along the West Coast. The yellow seed, approximately 120,000 per pound (260,000 per kilogram), are planted at the rate of 15–20 lb/acre (17–22 kg/ha) during the late summer and fall months in a prepared seedbed or on grass which is closely grazed or cut. The seedlings make a rosette of leafy growth during the winter months. With the advent of spring, growth is rapid; the plant reaches $1^1/_2$–3 ft (0.4–0.9 m) in height and the flower stems elongate, terminating with pointed crimson flower heads in late spring or early summer. The plant dies when the seed matures. Seed yields average about 250 lb/acre (280 kg/ha) even though large quantities are lost by shattering. Crimson clover is seeded alone, with small grains and grasses, or on grass turf. During the winter it may be grazed when growth reaches 4 in. (10 cm), although if it is too heavily grazed, regrowth is slow. The greatest return for soil improvement is obtained when the largest growth is plowed under. There are several varieties of crimson clover, including Dixie, Auburn, Autauga, Chief, Talladega, and many local strains. When conditions are favorable, all of these will reseed, forming volunteer stands in the fall from seed shattered the previous spring. Common crimson clover does not reseed. When used with Bermuda or other perennial summer-growing grasses, the tall growth of the grass must be closely grazed or clipped.

Subclover. Subclover, a winter annual extensively used for grazing in the coastal sections of the Western states, is the basic pasture crop of the sheep and cattle industry of Australia. The seed are blue-black and the largest of any clover species (about 60,000 per pound or 132,000 per kilogram). The flower heads on decumbent stems are inconspicuous. As the seed develop, fishhook-shaped appendages are produced which, by their twisting action, pull them into the soil, and hence the name subclover. Seed production is large, but the seed are difficult to harvest. When once established, fall stands develop from seed produced the preceding months. The Australian varieties Mount Barker, Tallarook, and Nangeela have proved to be best adapted to most conditions in the United States. Subclover appears to have considerable promise as a pasture legume under many conditions in the southern United States, but better adapted varieties are needed. Eugene A. Hollowell

Berseem clover. Berseem, or Egyptian clover (*T. alexandrinum*), is used as a cool-season annual forage crop in the states of Washington, Oregon, California, and Arizona and in the southeastern United States, and as a summer annual in northern areas. It is an upright-growing legume with oblong leaflets and hollow stems. It produces yellowish-white florets in heads and has short tap roots. In southern Florida, plants may obtain a height of 18–24 in. (45–60 cm) during a growing season from October to May and heights of 34–42 in.

(19–105 cm) in Arizona. Berseem clover's greatest potential is probably as green-chopped forage or pasture. It provides high-quality forage with a crude protein concentration of 20–24% on a dry-weight basis. Berseem clover produces an abundance of seed with yields exceeding 990 lb/acre (1100 kg/ha). Berseem flowers are essentially self-sterile, with cross pollination being accomplished by honeybees.

Cultivars of berseem clover are classified according to their branching behavior; branching influences the number of cuttings that can be made. The cultivars Miscawi and Kahdrawi, which exhibit basal branching, can yield four cuttings per growing season, whereas the Saidi produces both basal and apical branching and can be cut twice. The Fahl cultivar exhibits apical branching and can be cut only once; Nile and Hustler cultivars were developed in the United States and are equal to or superior to Miscawi. A somewhat hardier cultivar Multicut, which tolerates temperatures down to 23°F (−5°C), was released in 1988 for use in parts of California and Mexico; it produces five or six cuttings under irrigation. The release in 1984 of the winter-hardy, reseeding cultivar Bigbee, extended the range of adaptation of berseem clover to Tennessee and Oklahoma and enabled producers to obtain reseeding stands. Prior to the release of Bigbee, berseem clover was considered to be a nonwinter-hardy, nonreseeding annual forage legume. W. E. Knight

Other clovers. Strawberry clover, a perennial, is a nutritious pasture plant similar in growth habit to white clover, for which it is frequently mistaken. The pinkish flower head looks like a strawberry, and hence the common name. It is highly tolerant of the wet, salty soil common to the Western states.

Persian clover is a winter annual used mostly for pasture and soil improvement but is also an excellent silage plant. It is particularly adapted to the wet, heavy soils of the lower southern part of the United States. The flowers are light purple, and the mature seed are enclosed in balloonlike capsules that shatter easily, float on water, and are readily blown about by the wind. Persian clover is relished by all classes of livestock.

Large hop clover and small hop clover, widely distributed as winter annuals in the Southern states, are used in pastures. They are more tolerant of low soil fertility than the other species and less productive, but are highly palatable to livestock. The flower heads are bright yellow and, when mature, look like the flowers of the hop plant. The two species are similar.

Rose clover is a relatively new winter annual and appears to be best adapted to the foothill rangelands of California.

Other species are ball clover, lappa clover, bigflower clover, and arrowleaf clover, all winter annuals. Lappa clover grows best in the heavy dark marl soils of the South, whereas ball, big-flower, and arrowleaf clovers appear to be more widely adapted. All are used for pasture, although bigflower and arrowleaf clovers may also be used for hay.

Seaside clover (*T. willdenovii*), white-tipped clover (*T. variegatum*), and long-stalked clover (*T. longipes*) are the most widely distributed of the native western species. All produce thick stands and good growth under varying conditions. *See* GENETICS; LEGUME FORAGES; REPRODUCTION (PLANT).

Sweet Clover

Sweet clover is the common name applied to all but one species of legumes of the genus *Melilotus*, order Rosales. The exception is sour clover (*M. indica*).

Origin and distribution. There are approximately 20 species of sweet clover. Some of the biennial species have an annual form. The roots of the biennials develop crown buds from which the second-year growth arises; the roots of annuals do not develop crown buds. Sweet clovers are native to the Mediterranean region and adjacent countries, but several are widely scattered throughout the world, generally by chance introduction. None is indigenous to the United States. White sweet clover (*M. alba*) and yellow sweet clover (*M. officinalis*) are important forage and soil-improvement plants in the United States and Canada and are found growing along roadsides and in waste places in every state (**Fig. 2**). Sour clover, a yellow-flowered winter annual, is of some value for soil improvement only along the Gulf Coast and in southern New Mexico, Arizona, and California. Improved varieties of white and yellow sweet clovers are available for farm use.

Uses. Sweet clover is used as a field crop in regions of the United States and Canada where the rainfall is 17 in. (42 cm) or more during the growing season, where the soil is neutral, or where

Fig. 2. White sweet clover (*Melilotus alba*). (*USDA*)

limestone and other needed minerals are applied. It is most extensively grown in the Great Plains and Corn Belt, either alone or in rotations with small grains and corn, and is used for grazing, soil improvement, and hay.

Except for those of certain improved varieties, the plants are somewhat bitter because of the presence of coumarin. External and internal bleeding of animals may result from feeding spoiled sweetclover hay or improperly preserved silage containing sweet clover, a decomposition product of coumarin (4-hydroxycoumarin, commonly called dicumarol), which develops during spoilage, being the toxic principle. Research has led to its use in medicine and for making warfarin, a rodenticide.

Eugene A. Hollowell

Diseases

Diseases of clovers are caused by bacteria, fungi, nematodes, viruses, a mycoplasma, and air pollutants. These diseases reduce forage yield, quality, and stand. Frequently, perennial clovers are productive for only 1 or 2 years because of diseases. Crop losses are best minimized by growing adapted cultivars that are tolerant of or resistant to one or more of the major diseases. Fungi and viruses are the most important pathogens.

Fig. 3. Red clover roots cut longitudinally to show type of injury caused by crown and root rot organisms.

Fig. 4. Typical petiole and stem lesions of northern anthracnose disease of red clover, caused by the fungus *Kabatiella caulivora*.

Fungal diseases. Fungi, including *Pythium, Fusarium*, and *Sclerotinia*, cause root and crown rots that reduce stand establishment and persistence (**Fig. 3**). These pathogens can attack clover plants at any developmental stage. Plants not killed are weakened, and are thus predisposed to further injury from physical and biological stress.

Fungi, including *Stemphylium, Colletotrichum*, and *Kabatiella*, cause leaf and stem diseases, which usually do not kill the plants but reduce their productive and competitive capabilities (**Fig. 4**).

Viral diseases. Most clovers are susceptible to destructive viruses that cause leaf mottling and distortion and reduced plant vigor. Viruses may be seed-borne or spread by insects and mowing. *See* PLANT PATHOLOGY; PLANT VIRUSES AND VIROIDS.

Kenneth T. Leath

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Clupeiformes

The single order of the teleost fishes in the subdivision Clupeomorpha. Clupeiforms, including anchovies, herrings, sardines, shads, and allies, are classified in two suborders, five families, 83 genera, and about 357 species. A unique feature of clupeiforms is the ear–swim bladder connection (otophysic connection) composed of a pair of anterior extensions of the swim bladder that enter the skull to connect with the utriculus of the inner ear. They are further distinguished by a series of median scutes (keel-like scales) along the abdomen before and behind the pelvic fin (some species have predorsal scutes as well as ventral scutes), and a single scute is present at the insertion of the pelvic fins. The body is compressed in most species; fin spines are lacking, as are an adipose fin and gular plate; the jaws are not protractile; the pelvic fins are abdominal in position and free from the shoulder girdle; the pectoral fin is placed low on the side; and a mesocoracoid arch is present; the upper jaw is bordered by premaxillae and maxillae, but the detention is usually feeble; the cycloid scales are usually thin and loosely attached, especially in anchovies; the air bladder is connected to the gut (physostomous); and there is no leptocephalus larva.

Clupeiforms are mostly silvery and typically occur in large schools, feeding on plankton that is strained from the water by numerous long gill rakers. A notable exception is the wolf herring (*Chirocentrus*) of the Indo-Pacific, which is a predator with strong teeth.

Some of the great fisheries of the world are based on the conversion of plankton by clupeiform fishes. These include the tremendous anchovy fishery off western South America, the California fisheries for anchovy and (until depleted) Pacific sardine, the menhaden fisheries of the western Atlantic, and the herring and sardine fisheries of northern seas. The catch is processed variously into oil, fertilizer, or fish meal or is prepared directly for human consumption. Indirectly, clupeiforms are of tremendous importance in the food cycles of piscivorous fishes and of some sea birds which depend on them as dietary staples.

Clupeiform fishes have left a rich fossil record, especially from the Upper Cretaceous to the early Tertiary, but appeared first in the Upper Jurassic.

Denticipitidae. This family, in the suborder Denticipitoidei, comprises one fossil species, probably from the Miocene, and one extant species, *Denticeps clupeoides* (denticle herring), known from the coastal rivers of Nigeria and Cameroon. It differs from other clupeiforms in having a complete lateral line, denticles variously placed on the skull and branchiostegal rays, and 16 principal caudal fin rays.

Commerson's anchovy (*Stolephorus commersonnii*). Maximum size approximately 10 cm (4 in.). (*Photo © by John E. Randall*)

Clupeoidei. This suborder comprises the remainder of the clupeiforms and is distinguished by the lateral line not extending onto the body, but essentially limited to a cephalic canal system extending onto the operculum; and 19 principal caudal fin rays.

Engraulidae. Anchovies, which make up this family, are for the most part small, delicate fishes that have a conical snout overhanging a large mouth (see **illustration**). The maxilla is extremely long, reaching beyond the large eye and often to the margin of the operculum. Gill rakers are long and numerous; teeth are absent in jaws of most species—however, the large piscivorous species have large jaw teeth. Scales are thin and cycloid and usually deciduous, even when carefully handled. There are 16 genera and 139 species, with about 17 species occurring in freshwater and the rest in the Atlantic, Indian, and Pacific oceans. Thirty species occur in North American waters, 23 of which are in the genus *Anchoa*. Most of the freshwater species are from South America.

Pristigasteridae. In this family the mouth is superior in most species, otherwise it is terminal; jaw teeth are small (one genus has canine teeth); abdominal scutes are present; and the anal fin is long, with 30 to 92 rays. This family comprises nine genera and 34 species. Four species are freshwater and the rest occur in tropical and subtropical Atlantic, Indian, and Pacific oceans. Five species occur on the Pacific coast of Mexico.

Chirocentridae (wolf herring). This family consists of only one genus and two species that are characterized by an elongate, highly compressed body and fanglike jaw teeth. It has a spiral valve in the intestine, an uncommon feature for a teleost fish. The pelvic fin is small, the scales are small; the pelvic scute is reduced; and abdominal scutes are absent. These fishes occur in the western Pacific and the western Indian oceans to South Africa and the Red Sea.

Clupeidae. This family includes herrings, shads, sardines, sprats, pilchards, and menhadens. Two long, rodlike postcleithra distinguish most members of this family from other clupeiforms. In addition, the mouth is terminal and abdominal scutes are present, except in the subfamily Dussumieriinae (round herrings). The family is composed of five subfamilies, 50 genera, and 181 species, 50 of which occur in freshwater, some of which are anadromous. The rest are marine species that occur worldwide, mostly in tropical waters. Eleven genera and 33 species occur in North American waters.

Distribution and ecology. Some herrings and a few anchovies live in lowland rivers and lakes, and others such as the shad and alewife enter rivers to reproduce; but the majority of clupeiforms occur in bays or shore waters of tropical, temperate, or even northern seas, where they commonly make up enormous schools. None inhabits deep water. Most clupeiforms feed on plankton or other minute organisms, thus they are efficient converters from the base of the food chain to fish flesh.

Reeve M. Bailey; Herbert Boschung

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Clutch

A coupling device which permits the engagement and disengagement of coupled shafts during rotation. There are four major types: positive, friction, hydraulic, and electromagnetic.

Positive clutch. This type of clutch is designed to transmit torque without slip. It is the simplest of all shaft connectors, sliding on a keyed shaft section or a splined portion and operating with a shift lever on a collar element. The jaw clutch is the most common type of positive clutch. This is made with square jaws (**Fig. 1***a*) for driving in both directions, or spiral jaws (Fig. 1*b*) for unidirectional drive. Engagement speed should be limited to 10 revolutions per minute (rpm) for a square-jaw clutch and 150 rpm for a spiral-jaw clutch. If desengagement under load is required, the jaws should be finish-machined and lubricated. *See* MACHINE KEY; SPLINES.

Friction clutch. This type of clutch is designed to reduce coupling shock by slipping during the engagement period. It also serves as a safety device by slipping when the torque exceeds its maximum rating. The three common designs for friction clutches are cone, disk, and rim, according to the direction of contact pressure. *See* FRICTION; TORQUE.

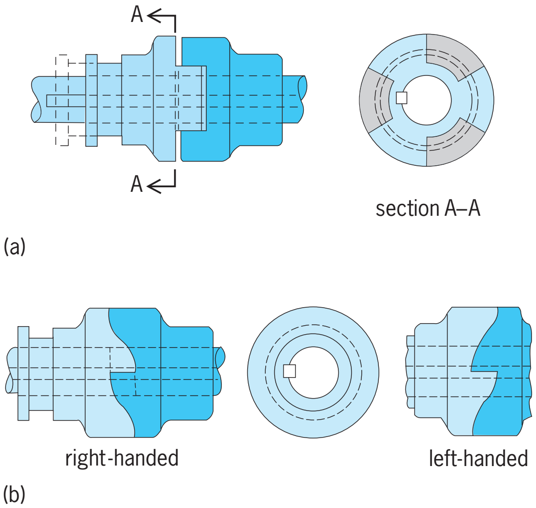

Fig. 1. Positive clutches. (*a*) Square-jaw clutch. (*b*) Spiral-jaw clutch. (*After E. A. Avallone and T. Baumeister III, eds., Marks' Standard Handbook for Mechanical Engineers*, 9th ed., McGraw-Hill, *1987*)

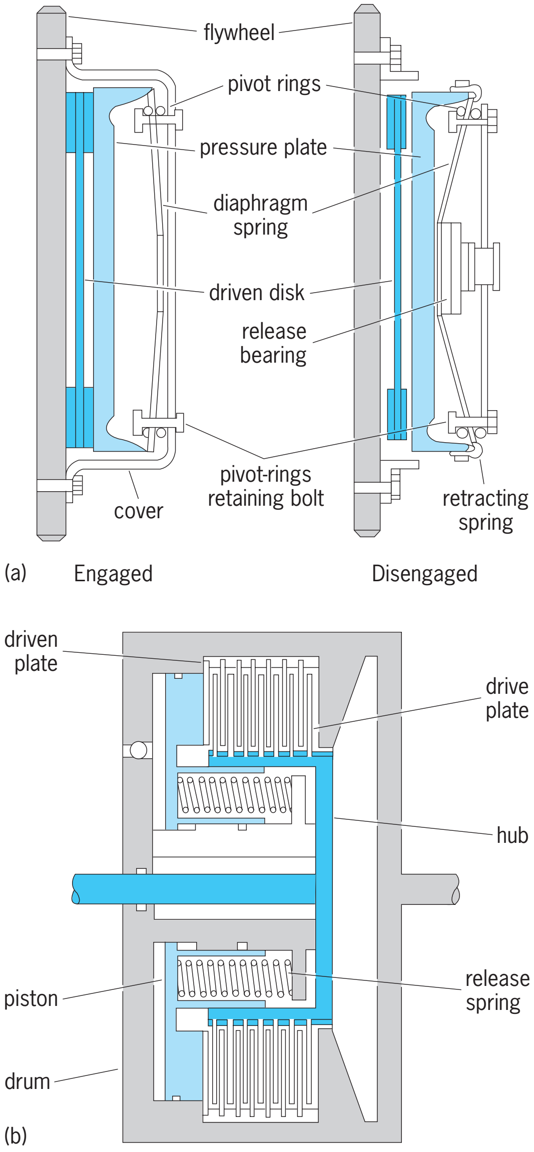

Fig. 2. Friction clutches. (*a*) Plate clutch. (*b*) Multidisk clutch. (*After E. A. Avallone and T. Baumeister III, eds., Marks' Standard Handbook for Mechanical Engineers*, 9th ed., McGraw-Hill, *1987*)

Cone clutch. This is an axial type clutch. The surfaces of the cone clutch are sections of a pair of cones. This shape uses the wedging action of the mating surfaces under relatively small axial forces to transmit the friction torque. These forces may be established by the compression of axial springs or by the outward displacement of bell-crank levers to apply axial thrust to the conical surfaces.

Disk clutch. This is also an axial-type clutch. The disk clutch may consist of a single plate or multiple disks (**Fig. 2**). With the development of improved friction material, disk clutches have become more common than cone clutches, with wide applications in the industrial and automotive fields. Disk clutches are not subjected to centrifugal effects, present a large

Friction materials for clutches and design data*

Material	Friction coefficient		Maximum temperature		Maximum pressure	
	Wet	Dry	°F	°C	lb/in.^{2}	kPa
Cast iron on cast iron	0.05	0.15–0.20	600	320	150–250	1000–1750
Powdered metal† on cast iron	0.05–0.1	0.1–0.4	1000	540	150	1000
Powdered metal† on hard steel	0.05–0.1	0.1–0.3	1000	540	300	2100
Wood on steel or cast iron	0.16	0.2–0.35	300	150	60–90	400–620
Leather on steel or cast iron	0.12	0.3–0.5	200	100	10–40	70–280
Cork on steel or cast iron	0.15–0.25	0.3–0.5	200	100	8–14	50–100
Felt on steel or cast iron	0.18	0.22	280	140	5–10	35–70
Woven asbestos† on steel or cast iron	0.1–0.2	0.3–0.6	350–500	175–260	50–100	350–700
Molded asbestos† on steel or cast iron	0.08–0.12	0.2–0.5	500	260	50–150	350–1000
Impregnated asbestos† on steel or cast iron	0.12	0.32	500–750	260–400	150	1000
Carbon graphite on steel	0.05–0.1	0.25	700–1000	370–540	300	2100

*From J. E. Shigley and L. D. Mitchell, *Mechanical Engineering Design,* p. 742, McGraw-Hill, 1983.
†The friction coefficient can be maintained within ± 5% for specific materials in this group.

friction area in a small space, establish uniform pressure distribution for effective torque transmission, and are capable of effectively dissipating the generated heat to the external housing. The disk clutch may be operated dry, as in most automobile drives, or wet by flooding it with a liquid, as in heavier automotive power equipment and in industrial engines. The advantage of wet operation is the ability to remove heat by circulating the liquid enclosed in the clutch housing. Typical friction materials for clutches and design data are shown in the **table**.

Rim clutch. This is another form of frictional contact clutch that has surface elements applying pressure to the rim either externally or internally. Rim clutches may be subdivided into two groups: those employing either a frictional band or block (**Fig. 3**) to make contact with the rim; and the overrunning clutch (**Fig. 4**), employing the wedging action of a roller or ball. The clutches of the former type may have hinged shoes connected by an expanding or contracting kinematic mechanism on a hub fixed to one shaft and riding of a drum or rim attached to a hub on a second shaft. They have expansion rings or external bands that, when displaced, are capable of transmitting torque to the clutch rim. The rim may be grooved to increase the surface area; the clutch may have a double grip, internal and external; or pneumatically expanding flexible tubes may set the friction surfaces against the rim (**Fig. 5**). Because the clutch rotates with the shaft when it is engaged, its balancing must be considered.

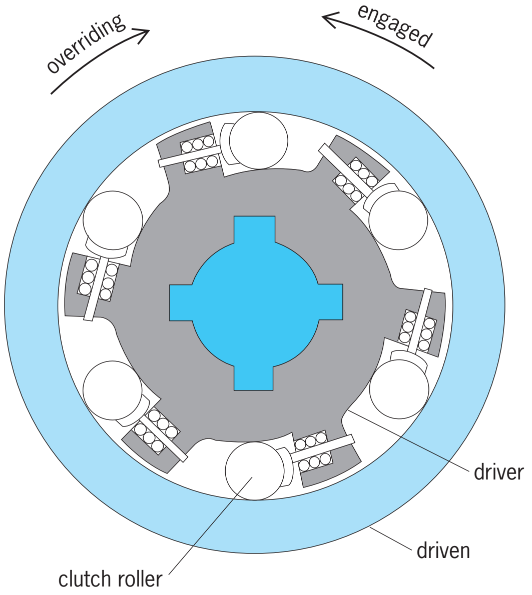

Fig. 4. Overrunning clutch. (*After E. A. Avallone and T. Baumeister III*, *eds.*, *Marks' Standard Handbook for Mechanical Engineers*, *9th ed.*, *McGraw-Hill*, *1987*)

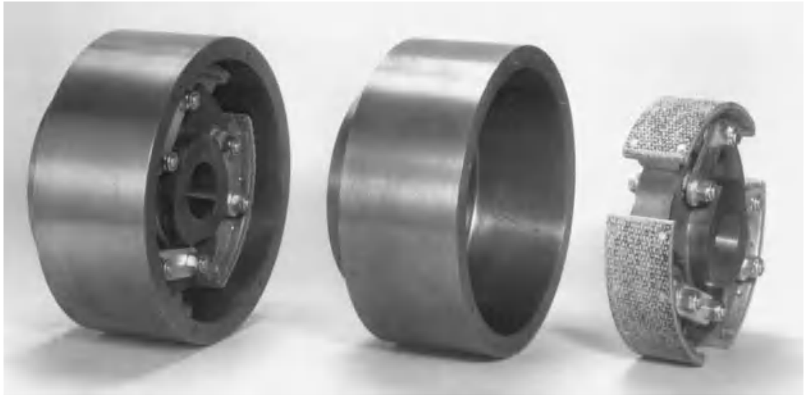

Fig. 3. Internal-expanding centrifugal-acting rim clutch. (*Hilliard Corp.*)

For overrunning clutches, the driven shaft can run faster than the driving shaft. This action permits freewheeling as the driving shaft slows down or another source of power is applied. Effectively this is a friction pawl-and-ratchet drive, wherein balls or rollers become wedged between the sleeve and recessed pockets machined in the hub. The clutch does not slip when the second shaft is driven, and is released automatically when the second shaft runs faster than the driver. Specially shaped struts or sprags may replace the balls; springs may be used to hold the pawl elements in position. Mechanisms have been devised to reverse the direction of operation. *See* PAWL; RATCHET.

Hydraulic clutch. Clutch action is also produced by hydraulic couplings, with a smoothness not possible

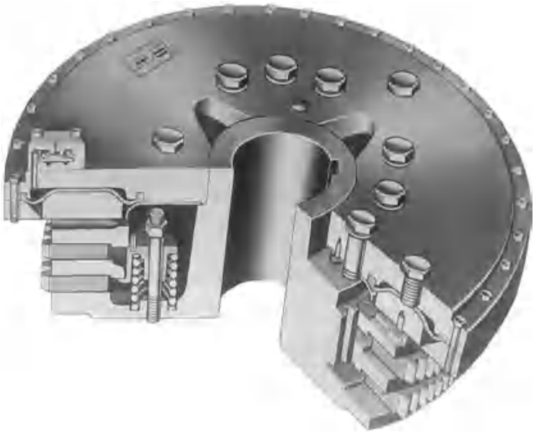

Fig. 5. External-contracting clutch that is engaged by expanding the flexible tube with compressed air. (*Twin Disc, Inc.*)

when using a mechanical clutch. Automatic transmissions in automobiles represent a fundamental use of hydraulic clutches. *See* AUTOMOTIVE TRANSMISSION; FLUID COUPLING; HYDRAULICS.

Electromagnetic clutch. Magnetic coupling between conductors provides a basis for several types of clutches. The magnetic attraction between a current-carrying coil and a ferromagnetic clutch plate serves to actuate a disk-type clutch. Slippage in such a clutch produces heat that must be dissipated, and wear that reduces the life of the clutch plate. Thus the electromagnetically controlled disk clutch is used to engage a load to its driving source. A typical unit 24 in. (61 cm) in diameter and weighing about 600 lb (270 kg) develops 2400 ft-lb (3300 joules) of torque when excited at 2 amperes and 115 dc volts; at a maximum safe speed of 1200 rpm it transmits 540 hp (400 kW). Multiple interleaved disks alternately splined to the driving and driven shafts provide a compact structure (**Fig. 6**). There are three basic types of electromagnetic clutches: magnetic fluid and powder, eddy-current, and hysteresis. *See* ELECTROMAGNET.

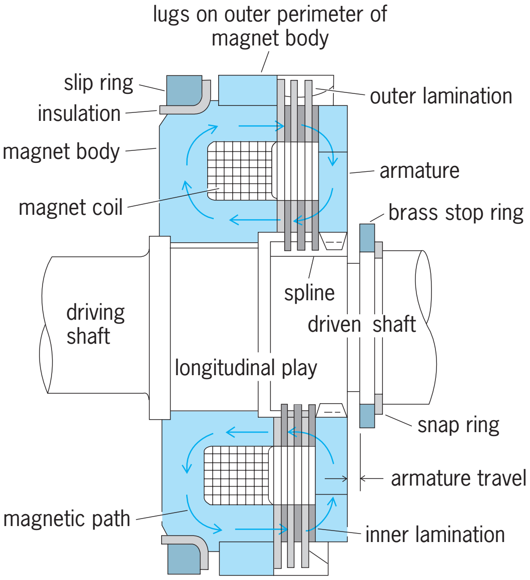

Fig. 6. Electromagnetically activated multiple-disk clutch.

Magnetic fluid and powder clutch. These may use finely divided magnetic particles in an oil carrier or be of the dry can type. Upon the application of a magnetic field, the particles tend to coalesce, thereby creating viscous or friction forces between the clutch members. The wet type provides the smoother operation; the dry type is freer from loss of particles. Torque at a fixed moderate excitation is independent of slip.

Eddy-current clutch. The current that is induced by a magnetic field can serve as the torque-transmitting means. In the eddy-current clutch, a coil-carrying direct current in one rotating member establishes poles that generate currents in the adjacent smooth conductive ring of the mating member. The coupling acts as an untuned damper and therefore does not transmit torsional vibration. An eddy-current clutch consists of a separately excited motor and generator that are combined into a single machine. Clutch action can be obtained by electrically connecting a generator on the driving shaft to a motor on the driver. *See* DYNAMOMETER; EDDY CURRENT; ELECTRIC ROTATING MACHINERY.

Hysteresis clutch. For low-power applications where continuous control with slip is needed, as in instrument servos, a hysteresis clutch may be used. Direct-current excitation of a coil in one part generates a steady flux field that magnetizes an iron ring on the other part, the ring having high magnetic retentivity. The action induces poles in the iron ring. Attraction between the induced poles in the ring and the control field produces a torque that opposes rotation between the two parts of the clutch. Within its load limit the hysteresis clutch transmits rotation without slip. As with the eddy-current clutch, there is no contact surface to wear so that the characteristics are stable and the life is long. *See* HYSTERESIS; SHAFTING; TORQUE CONVERTER.

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Bibliography. E. A. Avallone and T. Baumeister III (eds.), *Marks' Standard Handbook for Mechanical Engineers,* 10th ed., 1996; J. E. Shigley and L. D. Mitchell, *Mechanical Engineering Design,* 4th ed., 1993.

Cnidaria

A diverse phylum of aquatic animals that are characterized by the possession of (1) intrinsic nematocysts, (2) a single body space that opens to the external medium, (3) radial or biradial symmetry, (4) tissue level of organization, and (5) diploblastic structure. With few exceptions, a cnidarian also has tentacles surrounding the mouth (the opening of the body cavity to the exterior). Most definitions of the phylum include the feature metagenesis; however, although the life cycle of many cnidarians involves this alternation between an asexually reproducing polyp and a sexually reproducing medusa, this is not true of two entire classes (Anthozoa and Staurozoa) and of some members of class Hydrozoa. The name Coelenterata, which has been used for this phylum, is being supplanted because, as sometimes used, it included the sponges (Porifera) and comb jellies (Ctenophora), as well as the animals now called cnidarians. *See* CTENOPHORA; PORIFERA.

Taxonomy

Cnidarians include jellyfish, corals, sea anemones, the Portuguese man-of-war, hydroids, and the freshwater hydras. For many years, the phylum was divided into three classes, but four are now accepted and a fifth has been proposed: (1) Anthozoa (sea anemones, corals, sea fans, sea pens, and sea pansies), (2) Hydrozoa (hydroids, hydras, and hydromedusae), (3) Scyphozoa ("true" jellyfish), (4) Cubozoa (box jellies; formerly included in Scyphozoa), (5) Staurozoa (the Stauromedusae; formerly included in Scyphozoa) [see **table**]. All except a few hydrozoans are marine (**Fig. 1**). The Hydrozoa, Scyphozoa, Cubozoa, and Staurozoa are collectively referred to as

A classification of the phylum Cnidaria

Subdivision	Characteristics	Representative genera
Class Anthozoa	All marine	
Subclass Octocorallia	Almost exclusively colonial, each polyp with eight tentacles and mesenteries; also called Alcyonaria	
Order: Alcyonacea	Soft corals, sea fans, precious coral; sclerites in most species; thin or thick coenenchyme or stolonic network connects polyps; some with axial skeleton	*Alcyonium, Anthomastus, Clavularia, Corallium, Muricea, Tubipora*
Helioporacea	Blue coral; calcareous skeleton of aragonite; also called Coenothecalia	*Heliopora*
Pennatulacea	Sea pens and pansies; colony retractile, with bilateral symmetry	*Pennatula, Renilla, Virgularia*
Subclass Hexacorallia	Tentacles and mesenteries more or less hexamerously arranged; also called Zoantharia	
Order: Actiniaria	Sea anemones; solitary (may be clonal); live at all depths in all seas	*Actinia, Dactylanthus, Edwardsia, Metridium*
Antipatharia	Thorny or black corals; axial skeleton	*Antipathes, Dendrobranchia*
Ceriantharia	Tube anemones; solitary; lack pedal disc	*Cerianthus*
Corallimorpharia	Resemble corals; lack skeleton; tentacles radially arranged	*Corallimorphus, Corynactis*
Rugosa	Solitary or compound corals; calcareous skeleton; all fossil	*Lambeophyllum, Petraia, Syringaxon*
Scleractinia	True or stony corals; solitary and colonial; half of species reef formers	*Astrangia, Fungia, Porites*
Tabulata	"Honeycomb corals"; colonial, calcareous, tabulate corallites; all fossil	*Favosites*
Zoanthidea	Mat anemones; no skeleton; solitary or colonial, many commensal	*Palythoa, Parazoanthus, Zoanthus*
Class Cubozoa	Velarium present; largely tropical, subtropical	*Carybdea, Tripedalia*
Class Hydrozoa	Most marine; few species fresh-water	
Order: Actinulida	Hydroid generation represented by actinula-like form	*Halamohydra, Otohydra*
Anthoathecata	Athecate hydroids, hydrocorals, chondrophores	*Clava, Hydra, Millepora, Pennaria, Tubularia, Velella*
Limnomedusae	Some species commensal; hydroids naked	*Craspedacusta, Gonionemus*
Leptothecata	Hydroids with a hydrotheca	*Obelia, Plumularia, Sertularia*
Trachymedusae	Polypoid generation absent	*Aglantha, Liriope*
Narcomedusae	Holopelagic; most without polypoid generation; some parasitic	*Aegina, Cunina, Tetraplatia*
Siphonophora	Polymorphic colonies; planktonic	*Abyla, Forskalia, Physalia*
Class Scyphozoa	All marine	
Subclass Scyphomedusae	Tetramerous medusae that are produced through strobilation and grow through ephyra stage	
Order: Coronatae	Coronal furrow; lack ocelli	*Atolla, Linuche, Nausitho, Periphylla*
Semaeostomeae	Pedalia and coronal furrow lacking	*Aurelia, Cyanea, Pelagia*
Rhizostomeae	Numerous small mouths; no marginal tentacles	*Cassiopeia, Cephea, Rhizostoma*
Subclass Conulata	Tetramerous cone-shaped to elongate pyramidal; unattached; tentacles on oral margin; all fossil	
Order Conularida	Characters of subclass	*Conularia, Conulariella, Paraconularia*
Class Staurozoa	Sessile medusae; largely temperate	*Haliclystus, Lucernaria*

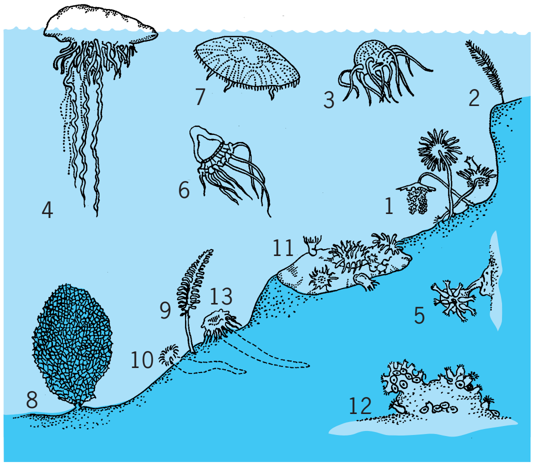

Fig. 1. Marine cnidarians in typical habitats (not to scale): 1, *Tubularia* (solitary hydroid); 2, *Plumularia* (colonial hydroid); 3, *Gonionemus* (hydromedusa); 4, *Physalia* (Portuguese man-of-war); 5, *Haliclystus* (stauromedusa); 6, *Periphylla* (scyphomedusa); 7, *Aurelia* (scyphomedusa); 8, *Gorgonia* (sea fan); 9, *Pennatula* (sea pen); 10, *Edwardsia* (sea anemone); 11, *Epiactis* (sea anemone); 12, *Astrangia* (stony coral); and 13, *Cerianthus* (tube anemone). 1–4 are members of Hydrozoa, 5 is a member of Staurozoa, 6 and 7 are members of Scyphozoa, and 8–13 are members of Anthozoa. (*After T. I. Storer and R. L. Usinger, General Zoology, 3d ed., McGraw-Hill, 1957*)

the Medusozoa because at least some species in each class have a medusa in the life cycle, whereas no anthozoans do. *See* ANTHOZOA; CUBOZOA; HYDROZOA; SCYPHOZOA; STAUROMEDUSAE.

General Morphology

The two basic body forms of cnidarians—the polyp and the medusa—typically live in different habitats (the former benthic, the latter pelagic), and although they appear superficially rather different, they share many features (**Fig. 2**). Of the two epithelial tissue layers, the endoderm (also termed the gastrodermis) lines the single body space, the coelenteron (also termed the gastrovascular cavity), and the ectoderm (also termed the epidermis) forms the external surface. [The name Coelenterata is derived from the term coelenteron (meaning "hollow gut")] Between ectoderm and endoderm is the mesoglea, which varies from a thin, acellular cementing layer to the thick, cellular and fibrous gelatinous layer that is the "jelly" of jellyfishes.

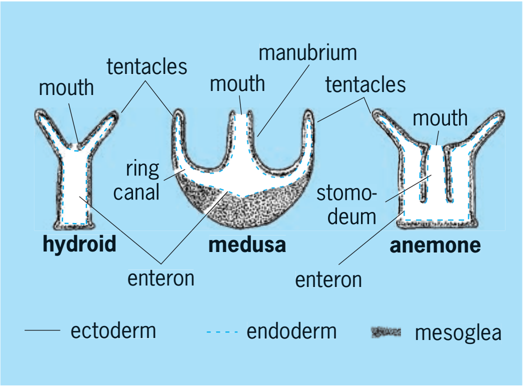

Fig. 2. Comparison of hydrozoan polyp, medusa (inverted), and anthozoan polyp. (*After T. I. Storer and R. L. Usinger, General Zoology, 3d ed., McGraw-Hill, 1957*)

The ectoderm is, in general, a single layer of cells, varying in form from flat and squamous to tall and columnar. It may be ciliated; in its food-gathering mode, the ciliary beat can move material toward the mouth from the surface of the animal and its tentacles, but in its cleaning mode, the direction is reversed. The endoderm may also be ciliated: cilia circulate water through the coelenteron and move food around within it.

Being at the "tissue grade" of construction, cnidarians lack organs and, therefore, organ systems. Their diploblastic structure means that they essentially consist of folded sheets of epithelia—and so have been termed "origami animals." Types of cells in the epithelia (both ectoderm and endoderm) include gland cells (that produce mucus and digestive enzymes), sensory cells, undifferentiated interstitial cells, ciliated cells, and cnidocytes (cells that produce cnidae, including nematocysts). Epitheliomuscular cells, in which the elongated cell base contains contractile fibrils, may constitute the entire musculature of simple polyps, such as most hydroids, but sea anemones and medusae have distinct muscle cells (contrary to many textbooks).

Polyp. A polyp is typically benthic (lives associated with the bottom of an ocean, lake, or stream), sessile, cylindrical, and elongated along the oral-aboral axis. The mouth, at the polyp's free (distal) end, is almost invariably surrounded by few to many hollow or solid tentacles (depending on the taxonomic group) arrayed in whorls or radially (or both). The aboral (proximal) end of a polyp (commonly referred to as the base or pedal disk may be adapted for attachment to a solid substratum or for burrowing into a soft substratum; but in colonial species, it arises from another polyp or the common tissue mass. With strong bilaterality in some taxa, especially Class Anthozoa, the polyp's symmetry is typically tetraradial, hexameral, octameral, or decameral, but it may be otherwise. An anthozoan polyp has sheets of tissue extending radially from the column wall into the coelenteron; some or all of these mesenteries connect with the actinopharynx (or stomodeum), a tube of tissue extending partway into the coelenteron from the mouth (Fig. 2, right). The mesoglea of a polyp may be little more than an adhesive, holding the two cell layers together (as in many hydroids), or it may be thick, spongy, and with many cells (as in some sea anemones). Polyps range in length from 1 mm to 2 m.

Medusa. A medusa is typically pelagic (lives free in the water), with thick mesoglea; its "body" is termed a bell due to its form. The outer (aboral) surface of the bell is termed the exumbrella and the underside (oral part), the subumbrella. The mouth commonly opens at the end of a tube of tissue (the manubrium) that extends from the underside of the bell (Fig. 2, center); there may be some tentaclelike structures immediately around the mouth, but typically the tentacles are located at the margin of the bell. Conventionally portrayed with the tentacles hanging downward and the exumbrella pointing toward the surface of the sea, most medusae spend much of their time in postures other than this. The mouth, commonly via the manubrium, leads to the central coelenteron. Radial canals may run between the cavity and the margin on the subumbrellar side, and they commonly communicate with a ring canal that is continuous around the margin; canals may also run from the ring canal along the tentacles. The mesoglea serves as a type of internal skeleton, against which muscles act, and its elasticity returns the bell to its original shape after each contractile pulse.

Cnidae

The name of phylum Cnidaria is derived from "cnidae," microscopic structures that are the phylum's most distinctive feature, and the most complex secretory product made by any animal. Each is formed within a cell (a cnidocyte) and consists of a capsule and a tubule that is coiled or folded within the capsule. When discharge occurs, the tubule emerges from one end of the capsule; typically, the tubule is many times longer than the capsule. There are three types of cnidae: nematocysts are formed by all cnidarians (and only cnidarians); spirocysts are restricted to the Subclass Hexacorallia of Class Anthozoa; and ptychocysts are restricted to Order Ceriantharia of Subclass Hexacorallia.

Nematocysts. When a nematocyst (a "stinging capsule," not a "stinging cell" as it is sometimes called) is appropriately stimulated, its tubule rapidly everts (turns inside out, like a coat sleeve). Some types are used offensively (they are the means by which the exclusively carnivorous cnidarians capture their food) and some types are used defensively. Some types of hydrozoan nematocysts have a cnidocil (a trigger) that must be stimulated for discharge to occur, but in other cnidarians, it appears that the sensation triggering discharge is received at some distance from the nematocyst, and nerves transfer the impulse that stimulates discharge. Thus, a cnidarian has some control over the use of its nematocysts, although previously nematocysts were thought to discharge upon appropriate stimulation, without any control by the animal. Such control is reasonable; each nematocyst can be used only once, so producing them represents a large portion of the energy budget of a cnidarian.

Approximately 30 morphological types of nematocysts have been identified, differing in capsule shape, tubule length, diameter, and spination. However, all seem to fall into one of three functional categories (**Fig. 3**): a volvent has an unarmed tubule that wraps around and entangles prey; a penetrant has a tubule armed with barbs that penetrates prey and may deliver a toxin; and a glutinant has a sticky tubule that hangs on to prey so that it can be carried to the mouth, or helps to anchor the cnidarian to an object

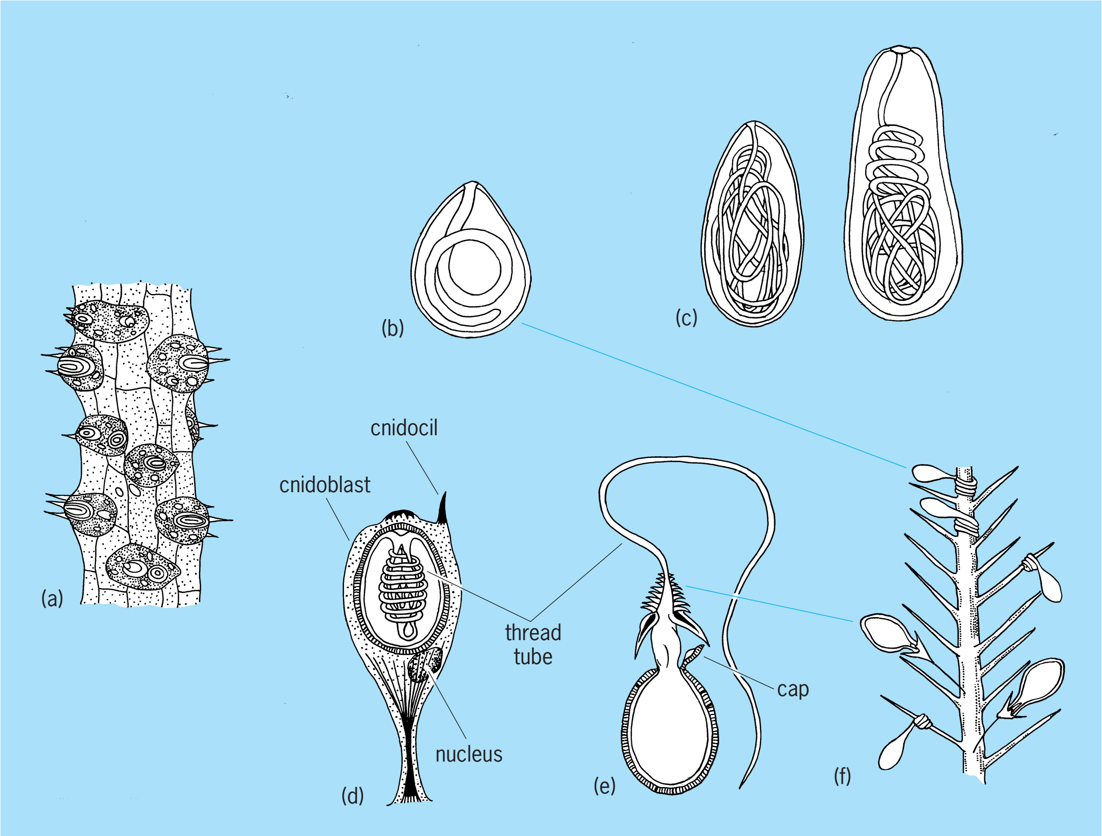

Fig. 3. Nematocysts of Hydra. (*a*) Tentacle with nematocyst batteries. (*b*) Volvent. (*c*) Glutinant. (*d*) Penetrant before discharge. (e) Penetrant discharged. (*f*) Discharged nematocysts on bristle of a crustacean. (*After T. I. Storer and R. L. Usinger, General Zoology, 3d ed., McGraw-Hill, 1957*)

(for example, glutinants appear to be important in attaching its tentacles to the substratum when *Hydra* somersaults).

The double-walled nematocyst capsule is made of collagenous proteins. Nematocysts are typically densest in the tentacles, where types important in prey capture are particularly abundant. Nematocysts are limited to the ectoderm of hydrozoans, whereas in Scyphozoa and Anthozoa, they occur in both ectoderm and endoderm. In sea anemones, certain types are restricted to the filaments on the mesenteries, and they seem to contain digestive enzymes. Some types of nematocysts can be painful to humans, and cubozoan stings may cause vasomotor dysfunction and even death. *See* TOXIN.

Although formed only by cnidarians, nematocysts may occur in other kinds of animals. Some flatworms, comb jellies, and nudibranchs that feed on cnidarians can store the capsules in their own bodies without causing them to discharge. Oriented so the eversible end of the capsule is at the surface of the animal's body, these "kleptocnidae" can be used to defend the cnidarian predator.

Spirocysts and ptychocysts. Spirocysts are especially common in tentacles, where they seem to function in entangling prey. The single-walled spirocyst capsule is thin, and the tubule is long, unarmed, spirally coiled, and of uniform diameter. Spirocysts stain with acid dyes, whereas nematocysts stain with bases. Ptychocysts are larger than either nematocysts or spirocysts (although they, too, are intracellular and therefore microscopic), and the tubule of each is folded within the capsule. Ptychocysts occur largely on the exterior surface of the body of a ceriantheid, where their discharged tubules entangle, forming a feltwork that incorporates mud and organic matter to create the tube that is typical of these "tube anemones."

Functional Morphology

Cnidarians lack organs and therefore organ systems. Because the endoderm and ectoderm are each a single cell thick, all their cells are in contact with either the external medium or the fluid in the coelenteron, allowing gas exchange and excretion to be carried out by individual cells. Other physiological functions are described below.

Nerves and sensory structures. The nerves form a meshwork, with no centralized ganglia. However, the individual nerve cells and the synapses are polarized, like those of other metazoans (previously the system was considered unpolarized). Nerves are situated at the base of the ectoderm and endoderm, with a variable number of connections across the mesoglea, in some animals particularly around the mouth and in the tissue connecting members of a colony. Some medusae have sensory structures such as eyespots or statocysts (which function in balance) along the ring canal, on the tentacle bases, or on marginal structures. Cubozoan eyes are the most highly developed of these sensory structures: they can form images. In other cnidarians that lack discrete sensory structures, there is evidence that at least some nerves are sensitive to particular stimuli. For example, scleractinian corals typically expand at night and contract by day; thus they appear to be able to detect light despite lacking any structure that is recognizably light sensitive.

Functionally, in at least some species, there appear to be nervous pathways specialized for rapid conduction and others for slower, more general spread of impulses. Colonies of some species are functionally integrated by means of nerves, whereas in other species, the members of the colony function more independently. In the former case, stimulation of a single polyp may provoke contraction of many other members of the colony, whereas in the latter case, it will cause contraction only in the area of stimulation. Potentiation is demonstrable in some cnidarians, with a single stimulus causing only a local contraction, and succeeding stimuli at the same location causing a more widespread response. Many cnidarians show simple reflexes, such as righting movements and swallowing.

Swimming contractions of medusae are coordinated by nerves. In species that have them, marginal sensory structures generally regulate these actions. When the structures are removed, swimming movements stop unless the medusa is artificially stimulated; when some of the structures are removed, movement of the medusa is uncoordinated and erratic. In the laboratory, if a preparation constituting a ring from the margin of a medusa is stimulated, a wave of contraction is initiated. *See* NERVOUS SYSTEM (INVERTEBRATE).

Muscles. The column and tentacles of a polyp have an ectodermal longitudinal muscle layer, and an endodermal, circular muscle layer; the contractile elements are located subepithelially. Most small organisms have epitheliomuscular cells (**Fig. 4***c*), but

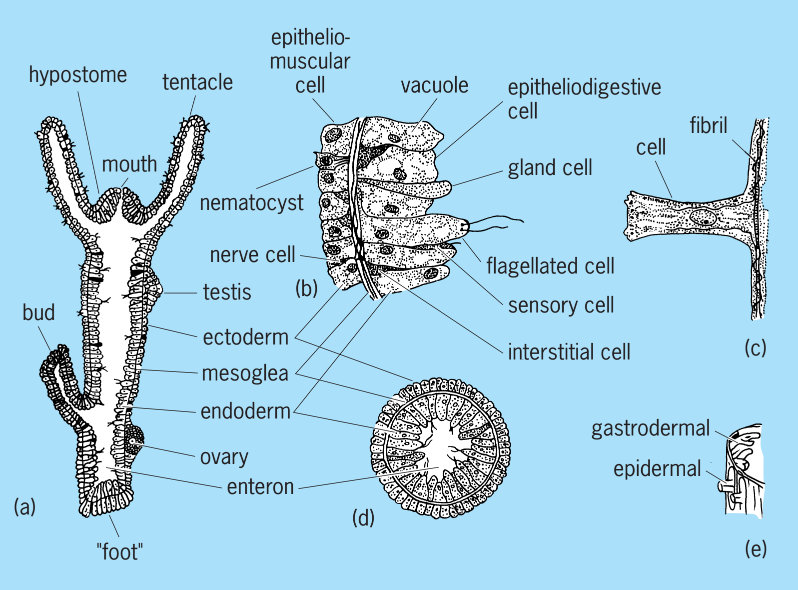

Fig. 4. Histological sections of Hydra. (*a*) Longitudinal section. (*b*) Enlarged cross section through column. (*c*) Epitheliomuscular cell. (*d*) Cross section of tentacle. (*e*) Fibril arrangement of the epitheliomuscular cells. (*After T. I. Storer and R. L. Usinger, General Zoology, 3d ed., McGraw-Hill, 1957*)

many larger ones have discrete muscle cells, which in some medusae are striated. The primary swimming muscles of medusae are large subumbrellar bands, oriented both circularly and radially. In many anthozoans, hypertrophy of the circular muscle at the margin of the oral disk forms a sphincter muscle that allows the animal to close up like a drawstring purse; in some taxa, this muscle is embedded in the mesoglea. In addition to column and tentacle musculature, anthozoan polyps have longitudinal and radial muscles in the mesenteries; the former are the major means by which anthozoan polyps shorten. The muscles work against the hydrostatic skeleton or the mesoglea, depending on the taxon and the part of the body.

Skeleton. The body form of most polyps and some medusae is maintained at least in part by a hydrostatic skeleton, which constitutes water in the coelenteron (and tentacles in the groups with hollow tentacles) maintained under a slight positive pressure through the action of muscles surrounding the cavity and closure of the mouth. By contracting its circular muscles, the polyp or medusa can narrow and extend in length, and by contracting its longitudinal muscles, it can broaden and shorten. When contraction is excessive, some water is expelled through the mouth and, in polyps and some species, through pores at the tentacle tips or in the body wall; expansion can occur again only by pumping water in to reinflate the animal. The mesoglea imparts rigidity and elasticity to the system. Hydrostatic pressure can also be important in supporting colonies (such as those of sea pens), although mechanical support by skeletons made of calcium carbonate and organic materials such as chitin is widespread in the phylum.

The ectoderm of most hydrozoan polyps, some scyphozoan polyps, and all scleractinian corals secretes an exoskeleton, which supports and protects the organism. The hydrozoan skeleton is tubular, surrounding the living tissue. Although typically made of chitin or sclerified protein, and therefore rather flexible, in some taxa it is calcified and rigid. Some hydrozoan skeletons are elaborate, with an ornamented cup into which each polyp may withdraw; others are simple, covering only the column of the polyp. In some colonial pelagic hydrozoans, such as the by-the-wind sailor *Velella*, part of the skeleton may be specialized for flotation. All scleractinians form calcareous exoskeletons, which vary from delicate, branched structures to massive encrusting formations. The living animal tissue overlies the skeletal material, with the polyps occurring in cups or depressions in the skeleton; in colonies, the polyps abut one another or are connected by sheets of living tissue.

Members of several anthozoan groups have an axial skeleton, which is also secreted by ectodermal cells and hidden in life by the polyps and common colony tissue, so it can be seen only after the death of the animals that made it. Composed of sclerified proteins, this tough skeleton is flexible; it is calcified to a greater or lesser extent in some taxa, and flexibility diminishes with calcification. An axial skeleton is characteristic of the hexacoral antipatharians (black corals) and octocoral gorgonians (sea fans and sea whips) and pennatulaceans (sea pens).

Cells of some hydrozoans and anthozoans secrete calcareous sclerites (also known as spicules). Varying in size from microscopic to several millimeters in length, many sclerites are needlelike in form, but others are more globular. In most octocorals, they function to support and strengthen the living tissue in which they are scattered. Some sclerites in some species surround individual polyps or groups of polyps, clearly functioning to protect them. In two groups of octocorals, the sclerites are fused to form solid skeletons. Their morphology is akin to that of hydrozoan corals, with the polyps living in tubes surrounded by protective and supportive skeleton, but, as in scleractinians, the skeleton is covered by tissue in life.

Locomotion. Solitary polyps of many species can creep slowly along the substratum; some can lose contact and be carried by currents. Whether this has functional significance is unclear. A *Hydra* polyp can move in a somersault fashion by alternately attaching the base and tentacles to the substrate. The polyps of a few species of anemones can "swim": some do so by paddling their tentacles—whereas others do so by flexing the column. A few others routinely roll along the sea floor; some of them have suctorial structures on the column that allow them to remain stationary as well. Polyps of *Hydra* and small sea anemones may hang from the surface film of water bodies. One species of sea anemone secretes from its base a chitinous mass that traps air, forming a float from which the anemone hangs as it drifts across the open ocean.

Colonies of polyps can also move about. A sea pansy peduncle anchors the colony in soft substrata and can be released so that the colony can be passively moved by water motion; the peduncle may also function to pull the colony along. The most common examples of motile colonies are the siphonophores and chondrophores, pelagic hydrozoan "superorganisms" (consisting of polyps and/or medusae) such as the Portuguese man-of-war (*Physalia*) and the by-the-wind sailors (*Velella*) that are mistakenly thought by some people to be jellyfish.

A medusa swims by contracting muscles that encircle the edge of the bell, thereby reducing the volume of the subumbrellar space. The water that is forced outward jets the medusa in an aboral direction. In medusae of Class Hydrozoa, a thin sheet of tissue (the velum) extends inward from the margin of the bell, reducing the effective diameter of the subumbrellar aperture, and helping the animal to steer. Cubomedusae have an analogous structure, known as the velarium. Once the circular muscles relax, the resilient and elastic mesoglea returns the umbrella to its original form.

Feeding, digestion, and nutrition. All cnidarians are exclusively carnivorous. (Although there have been claims of phytophagous behavior in some cnidarians such as soft corals, there is no evidence that these animals possess enzymes capable of digesting plant material.) Larger prey items are secured by the tentacles: the tubules of some nematocysts hold onto the prey while the tubules of other types of cnidae deliver toxins to kill it. The tentacles then pass the prey to the mouth, where it is swallowed into the coelenteron. Tiny prey items may be trapped in mucus on the tentacles and oral disk, and carried by ciliary action to the mouth and into the coelenteron.

Gland cells that produce digestive enzymes are abundant in the endoderm. It is likely that in cnidarians that have endodermal nematocysts, the nematocysts also deliver digestive enzymes to prey items. Although some enzymes may be released into the coelenteron, most or all digestion takes place when the prey comes into contact with the endoderm so that the enzymes can be brought directly to the prey. In scyphozoans, gland cells tend to be most abundant on the gastric tentacles, and in anthozoans they are most abundant in the filaments along the free edges of the mesenteries: these structures wrap around the prey, making close contact between it and the gland-rich endoderm. Once the prey is broken into small particles, the particles are engulfed by endodermal cells and digestion is completed in food vacuoles. Thus, digestion in cnidarians is intracellular, although extracellular proteases effect the first stages of food processing.

Distribution of the compounds, in the absence of a circulatory system, depends at least in part on diffusion from the endodermal cells in which digestion occurs. Wandering ameboid cells may also play a role in distributing these materials, particularly to ectodermal cells in animals with a thick mesoglea, because they are more efficient than diffusion at crossing the mesoglea.

Some cnidarians appear to feed seldom or never. Two alternatives to feeding are uptake of dissolved organic matter and acquisition of small organic molecules from photosymbionts. At least some cnidarians can acquire dissolved organic matter directly from seawater, but not all their ectodermal cells have this capability, so this seems to be a specialized type of nutrition. Many cnidarians, particularly polyps, that live in the photic zone contain intracellular photosymbionts, but this is far from universal. In the marine environment, most photosymbionts are dinoflagellates known as zooxanthellae; the photosymbionts of all freshwater and some marine species are green algae known as zoochlorellae. Photosymbionts are generally contained in endodermal cells, but in a small number of species they are ectodermal; a single animal cell may contain several photosynthetic cells. A large proportion of the carbon fixed by the zooxanthellae (and a smaller proportion of that fixed by zoochlorellae) is released to the animal host; reciprocally, the photosymbiont obtains from its animal host carbon dioxide and nitrogenous wastes. Nearly all reef-forming corals contain zooxanthellae; some of these corals can acquire 100% of their required energy from zooxanthellae, but it appears these animals must ingest animal prey to obtain other compounds such as amino acids and vitamins. *See* FEEDING MECHANISMS (INVERTEBRATE).

Reproduction and Development

Cnidarians of all species reproduce sexually, although not all individuals may be capable of sexual reproduction. Cnidarians of many, but not all, species can reproduce asexually through a variety of mechanisms. The capacity to regenerate is widespread, but seems especially characteristic of animals that can propagate asexually. Thus, pieces cut from most medusae or many sea anemones will not survive, and the part that is excised may not be replaced. *See* REGENERATION (BIOLOGY).

Metagenesis. Metagenesis, the alteration between medusa and polyp generations, is commonly considered a characteristic feature of the phylum as a whole (**Fig. 5**). In metagenesis, a medusa is produced asexually by a polyp (which may also asexually produce polyps), and a medusa produces gametes that, through the processes of fertilization and development, result in polyps. Clearly, anthozoans, which are exclusively polypoid, do not undergo metagenesis; this is also true of the groups of hydrozoans that exist only as polyps or medusae. Staurozoa, too, has only one generation (a sedentary medusa or medusa-like polyp).

Many hydrozoans produce free-swimming medusae that have relatively long lives and are carried some distance from their hydroid before forming and releasing gametes. However, in some taxa the medusa is reduced so that it essentially constitutes a package of gametes that lives only long enough to spawn shortly after release from the hydroid; in others, it is not released at all, spawning while still attached to the hydroid. The ultimate reduction involves the disappearance of a morphologically distinct medusa, with gametes formed in structures on the polyps that are remnants of the medusa and essentially constitute a gonad of the hydroid.

Sexual reproduction. Since cnidarians lack organs, they do not have true gonads; rather, gametes are formed in localized areas, which are often referred

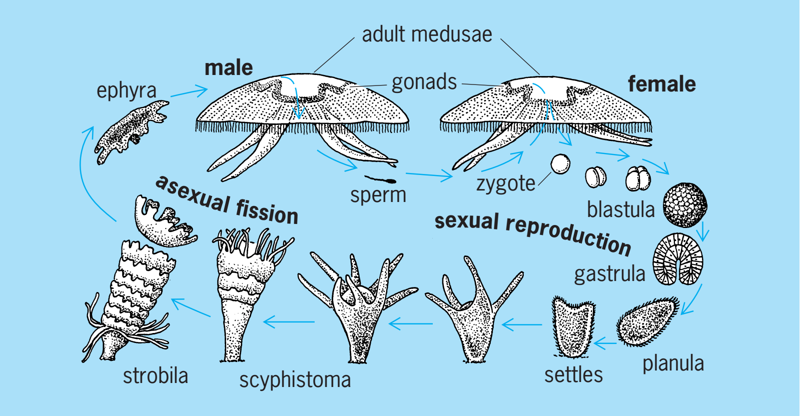

Fig. 5. Life cycle of jellyfish *Aurelia aurita*, class Scyphozoa. (*After T. I. Storer and R. L. Usinger, General Zoology, 3d ed., McGraw-Hill, 1957*)

to as gonads. Thus, there are no accessory sexual structures or ducts to permit the passage of gametes. Gametogenic tissues typically produce gametes only during certain times of the year; at other times, there is no evidence of their existence. Cnidarians lack a germinal cell line, so it is unclear if gametes develop from undifferentiated cells (such as interstitial cells) or if they can develop from cells of any type. In hydrozoans, gametes are produced in the ectoderm, on the manubrium or beneath the radial canals of medusae, and almost anywhere on a hydroid polyp (although in any group or species, gametogenic tissue forms in a characteristic position). Gametes in groups other than Hydrozoa are formed from endodermal cells: in scyphomedusae they develop on the floor of the coelenteron, and in anthozoans they develop in the mesenteries between the filaments and the retractor muscles.

Most cubozoans, hydrozoans, scyphozoans, and staurozoans are gonochoric (have separate sexes); hermaphroditism is widespread in Anthozoa, although most anthozoans are gonochoric. Hermaphroditic species may be self-fertile, but most cross-fertilize. Typically, a cnidarian sheds its gametes into the water surrounding the animal, where fertilization occurs and the embryo develops. However, in some cnidarians, the eggs are fertilized within the body; the developing embryo may be retained in the body or on its surface for its entire duration or for only a part of it.

The first stage of embryogenesis results in the formation of a ciliated blastula (Fig. 5). Gastrulation produces a gastrula that elongates into the typical larva of the phylum, the planula, which is free-swimming, ciliated, mouthless, and pear-shaped (the anterior is the broad end) and has an elongate anterior tuft of sensory cilia. At metamorphosis, if the planula is destined to become a polyp, it attaches by its anterior end, developing a mouth and tentacles at its posterior end. If the the planula is to become a medusa, the anterior end becomes the exumbrellar surface of the bell, and the mouth develops from the posterior end. In some hydrozoans, the planula develops a mouth and tentacles while still swimming; the animal at this stage is termed an actinula. The actinula of some species may attach and develop into a polyp, whereas in others it metamorphoses into a medusa. *See* INVERTEBRATE EMBRYOLOGY; REPRODUCTION (ANIMAL).

Asexual reproduction. If the individuals produced by asexual means separate, they are collectively termed a clone. If the individuals remain attached to one other, they collectively constitute a colony (although it is true that the elements, being genetically identical, are clonal).

One mode of asexual reproduction is budding (a term that is incorrectly applied to any mode of vegetative propagation). Budding involves the creation of a new individual from an outgrowth of an existing organism or the living tissue between individuals (as in Fig. 4*a*). This is the typical mode of formation of hydroid and many scleractinian colonies. Budding is also the means by which hydromedusae are produced by a hydroid colony. Budding is very rare in sea anemones.

Some scleractinian colonies are created by longitudinal fission of existing polyps. In the few medusae that normally propagate asexually, most (or all) do so by binary fission. Some individual sea anemones propagate asexually through longitudinal fission, and others through transverse fission. Transverse fission is the means by which a scyphozoan polyp (at the stage known as a scyphistoma) forms medusae: the distal end develops into an incipient medusa (the ephyra). In some species, these form one at a time, whereas in others, several form simultaneously like a stack of dinner plates of diminishing maturity proximally. When mature, the ephyra pops off the top of the polyp and swims away (Fig. 5).

Small pieces of hydroids may detach and wander about as undifferentiated, elongated entities called frustules, each of which can attach and develop into a new polyp and, ultimately, a colony. Basal bits of sea anemones can also detach and move off and are each capable of developing into a whole anemone. A few species of anemones can even regenerate a whole individual from a cast-off tentacle.

Asexual progeny are genetically identical, at least initially, but may differ morphologically. The most dramatic example of this is a polyp giving rise to a medusa. Even among polyps, in a hydrozoan or octocoral colony, individuals can be very different morphologically. Polymorphic colonies may contain individuals specialized to feed; others specialized to reproduce; and others to protect, propel, or support the colony. In hydrozoan Class Siphonophora, which constitutes the acme of polymorphism, the colony is also highly integrated neurologically and behaviorally. Polymorphism does not occur in scleractinian coral colonies.

Somatic mutation will cause members of a clone or colony to diverge genetically. In colonies that live decades or centuries (like those of some scleractinians), considerable genetic diversity can accumulate.

Ecology

Hydra, the animal used as an exemplar of the phylum, could hardly be less typical—a solitary hydrozoan that lacks a medusa, makes no skeleton, and lives in freshwater. Only a few hydrozoans besides it occur in freshwater. The other 10,000 or so species of cnidarians occur in all oceans and from the highest intertidal to the greatest hadal depths. Medusae are important predators in the pelagic realm, as sea anemones can be in some benthic environments; scleractinians are the primary constructors of one of the most important ecosystems in shallow tropical waters—coral reefs. Calcifying cnidarians do not occur below about 5 km (3 mi) depth, and those at high latitudes do not form large colonies. Both limitations seem due to the saturation state of calcium carbonate in the sea, which is greatest in shallow tropical waters and declines with latitude and depth. Moreover, for reasons that are not entirely understood, the robust skeletons that are important in reef formation are deposited only by corals that possess zooxanthellae (mostly scleractinians, but also a few species of hydrozoans and octocorals).

Only about half the approximately 1500 species of scleractinians participate in forming coral reefs; the others live at high latitudes and below the photic zone. The so-called deep-sea coral reefs are species-rich areas physically structured by skeletons of scleractinian corals, like their shallow counterparts. The diversity of corals, however, is low, and their skeletons are relatively delicate—they would be easily broken in many of the habitats where tropical shallow reefs thrive. *See* ECOLOGY; OCTOCORALLIA (ALCYONARIA); REEF; SCLERACTINIA. Daphne G. Fautin

Fossils and Phylogeny

Cnidaria has a long and impressive fossil record stretching back to the Precambrian, about 700 million years ago. Thus, the known duration of this phylum equals or exceeds that of other animal phyla. Forms with skeletons (primarily the Conulata, Tabulata, Rugosa, and Scleractinia) have left fairly complete fossil records, whereas primarily soft-bodied forms, such as most hydrozoans, scyphozoans, alcyonarians, and anemone-like animals, are represented by few fossils.

Fossils of the earliest-known cnidarians have been found in Late Precambrian rocks on several continents; the Ediacaran is an especially well-preserved fauna known from southern Australia. These early soft-bodied cnidarians were both pelagic medusoid forms and benthic polypoid forms, and seem to represent all the major classes, indicating that cnidarian origins are truly ancient. Appearing in the succeeding Cambrian strata is the extinct group Conulata (**Fig. 6***a*), which possibly belongs in Scyphozoa. These forms are represented in the fossil record by a thin, steep-sided, pyramidal, chitino-phosphatic external skeleton.

Fossils of two of the three major orders of anthozoans with calcium carbonate skeletons, the Rugosa (tetracorals) and the Tabulata (Figs. 6*b*, *c*, and *d*), appear in rocks of the succeeding Ordovician system. Both groups quickly diversified, and include colonial forms that helped form carbonate banks and reefs. In addition, the rugosans are represented by many solitary forms known as horn corals. Rugose corals, especially, were numerous and widespread in the Early Permian, but in the later part of that period their diversity dwindled, the more complex, bank-forming groups disappearing first. Both tabulate and rugose corals disappeared during the great wave of Late Permian extinctions, along with many other marine invertebrates. *See* PERMIAN; RUGOSA; TABULATA.

There are no corals in the Early Triassic, although the last Conulata have been reported from beds of this age. Scleractinians first appear in Middle Triassic strata (Figs. 6*e*, *f*). Scleractinians cannot have evolved from rugosans because they differ in fundamental morphology and there are no transitional forms in the Early Triassic. Thus, it is inferred that all the coral

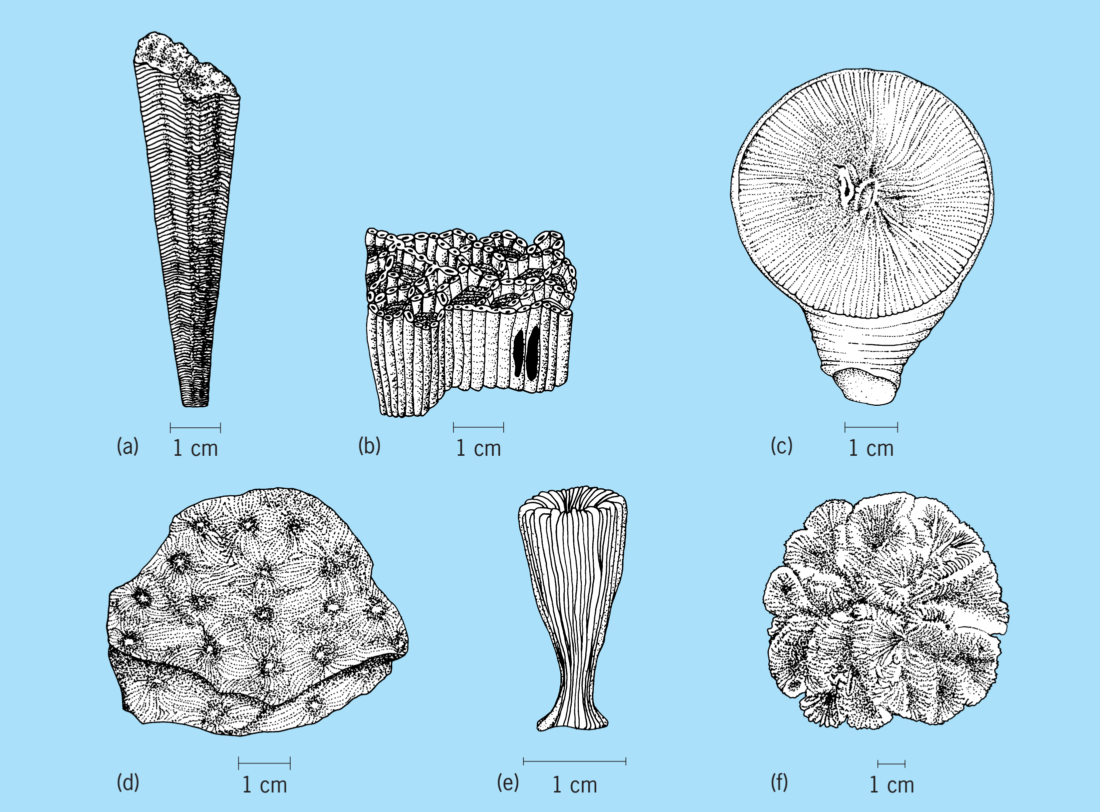

Fig. 6. Cnidarian fossils. (*a*) *Paraconularia*, Middle Paleozoic Conulata. (*b*) *Halysites*, Middle Paleozoic tabulate coral. (*c*) *Bethanyphyllum*, Devonian solitary rugose coral. (*d*) *Billingsastraea*, Devonian colonial rugose coral. (*e*) *Parasmilia*, Late Mesozoic and Cenozoic solitary scleractinian coral. (*f*) *Isophyllia*, Recent colonial scleractinian coral. (*After R. C. Moore, ed., Treatise on Invertebrate Paleontology, pt. F, Geological Society of America and University of Kansas Press, 1956*)

groups arose independently from soft-bodied anthozoans. These coral ancestors are often referred to as "anemones," and sometimes even as Actiniaria, but there is no evidence that those animals had the features characterizing modern sea anemones—or any other currently extant group of naked polyps. The origin of scleractinians is more mysterious because the first fossils of them are remarkably diverse, with many of the modern taxa represented. By the Jurassic, scleractinians had begun to form coral reefs similar to modern reefs of the tropics; it has been hypothesized that the acquisition of zooxanthellae is what allowed this development. However, many died out in the great Cretaceous-Tertiary (K-T) extinction, so that early Tertiary reefs were formed by bivalve mollusks, not corals. It was not until the Oligocene that scleractinians once again became dominant reef formers. *See* CRETACEOUS; TERTIARY.

Molecular evidence is likely to play a large part in understanding cnidarian evolution, since few members of the phylum leave phylogenetically informative fossils (because they are soft-bodied). A longstanding conundrum was whether Anthozoa is the basal group and development of the medusa generation followed or whether Anthozoa is derived from some ancestral cnidarian by loss of the medusa generation. Data that could be used to resolve this debate were problematic until the advent of gene analysis. Molecular analysis revealed that the mitochondrial chromosome in members of the Medusozoa (Cubozoa, Hydrozoa, Scyphozoa, and Staurozoa) is linear, whereas that of Anthozoa is circular, as in all other animals. This is clear evidence that Medusozoa is derived ("advanced"), relative to Anthozoa.

The phylogenetic relationships within each group are beginning to be understood, but many questions remain. *See* ANIMAL EVOLUTION; PHYLOGENY.

Daphne G. Fautin; Calvin H. Stevens

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Cnidospora

A subphylum of spore-producing Protozoa containing the two classes Myxosporidea and Microsporidea. Myxosporidea contains the three orders Myxosporida, Actinomyxida, and Helicosporida. Microsporida is the only order in the class Microsporidea. Cnidospora are parasites of cells and tissues of invertebrates, fishes, a few amphibians, and turtles. *See* MICROSPORIDEA; MYXOSPORIDEA.

A distinctive structure of this subphylum is the spore, which contains one or more protoplasmic masses called sporoplasms. The spore also contains one or more filaments which lie coiled within the spore proper or within one or more polar capsules. The spore membrane may consist of a single chitinous piece or two or more parts called valves.

When the spore is ingested by a new host, the filaments are extruded and at the same time the sporoplasm is released. The sporoplasm, now called an amebula, reaches the specific site of infection directly through the intestinal wall or by way of the bloodstream. The amebula becomes a trophozoite, a stage in the life cycle, which feeds and grows at the expense of the host. Asexual reproduction by repeated binary fission, multiple fission, internal and external budding, or plasmotomy results in cells which develop into sporonts and eventually into sporoblasts, producing one or more spores. *See* SPOROZOA.

Because of similarity in multinucleated trophozoites, some protozoologists suggest that the Cnidospora have evolved from "slime mold–like" (Mycetozoia) ancestors. *See* PROTOZOA.

Ross F. Nigrelli

Coal

A brown to black combustible rock that originated by accumulation and subsequent physical and chemical alteration of plant material over long periods of time, and that on a moisture-free basis contains no more than 50% mineral matter. The plant debris accumulated in various wet environments, commonly called peat swamps, where dead plants were largely protected from decay by a high water table and oxygen-deficient water. The accumulating spongy, water-saturated, plant-derived organic material known as peat is the precursor of coal. Over time, many changes of the original vegetable matter are brought about by bacteria, fungi, and chemical agents. The process progressively transforms peat into lignite or brown coal, subbituminous coal, bituminous coal, and anthracite. This progression is known as the coalification series. Increasingly deeper burial under hundreds to thousands of feet of younger sediments is required to advance coalification to the bituminous coal and anthracite stages. The pressure exerted by the weight of the overlying sediment and the heat that increases with depth, as well as the length of exposure to them, determine the degree of coalification reached.

The types of plants contributing to peat accumulations vary greatly, depending on when in geologic time the peat was formed, that is, how far plants had evolved at the time, and on the regional and local environments of deposition (for example, water depth and its fluctuations, climate, and flooding by nearby streams or the sea). *See* FOSSIL FUEL; KEROGEN; LIGNITE; PEAT.

Formation

Economic coal deposits originate from accumulations of plant material (peat) in wetlands commonly referred to as moor, swamp, mire, bog, fen, muskeg, or peatland. Most peat-forming plant material accumulates at or close to the place of growth (autochthonous origin), but some organic material may be transported before deposition, for instance, along beaches or in lakes (allochthonous origin). Autochthonous peats often form in various kinds of regionally coexisting depositional environments; low-lying swamps with forested, marshy, and open water environments (low moors) and raised peat bogs (high moors) are common peat-forming environments. Allochthonous plant material may contribute significantly to otherwise autochthonous peat deposits as open water areas develop and disappear in the evolutionary course of a peat swamp. Coal beds commonly are underlain by seat earths, remnants of ancient soils in which the initial swamp plants were rooted (hence the common occurrence of stigmaria in seat earths). *See* BOG; MUSKEG; SWAMP, MARSH, AND BOG.

Peat. Examples of present-day peat accumulation abound both in humid temperate climates and in subtropical to tropical climates. In North America, peat-forming environments are found in the Everglades of Florida, the Okefenokee Swamp of Georgia and Florida, the Dismal Swamp of Virginia, and in numerous depressions with poor drainage that were created during the ice ages in the plains between the Rocky and Appalachian mountains. In the tropics, thick peat deposits are known in the coastal areas of Sumatra and Borneo, for instance. Ultimate preservation of deposits of peat depends on long-term subsidence of the area and on burial under younger sediments. *See* DEPOSITIONAL SYSTEMS AND ENVIRONMENTS; SEDIMENTOLOGY.

The nature of a peat deposit depends on the kind of plants composing the accumulation: sedges, reeds, and other herbaceous vegetation; forest trees and bushes; mosses; and so forth. Such differences create different coal facies that can still be identified in highly coalified coal seams. *See* COAL PALEOBOTANY.

Freshly deposited plant material is attacked by microorganisms, fungi, and chemical agents in air and water, enzymes and oxygen in particular. This commonly leads to degradation of the plant material to the point where the original plant structure is no longer recognizable, and new organic compounds are formed. Cellulose, a major constituent of cell walls, and proteins are much less resistant to decomposition than other chemical plant constituents such as lignin, tannins, fats, waxes, and resins. Humic acids and other humic substances are important decomposition products resulting from the peatification process. Fungi and aerobic bacteria depend on the presence of oxygen to degrade the organic material. During burial, as oxygen is consumed, anaerobic bacteria take over degradation. Woody material passes through a plastic, gelatinous stage before it solidifies to huminite and eventually vitrinite. As burial depth increases, overburden pressure causes increasing compaction that reduces the porosity of the mass and expels moisture, while increasing temperature with greater burial promotes chemical changes in the organic components of the coal. Peat is transformed into coal through the process of coalification. Important by-products of the coalification process are water, carbon dioxide, and, especially in the more advanced stages, methane. *See* CELLULOSE; DIAGENESIS; HUMUS; LIGNIN.

Coal seams. Minable coal seams occur in many different shapes and compositions. Some coal seams can be traced over tens, even hundreds, of miles in relatively uniform thickness and structure. The extensively mined Herrin coal bed of the Illinois Basin and the Pittsburgh coal bed of the northern Appalachian Basin are examples. They are 6–8 ft (2–2.5 m) thick over thousands of square miles. These coals originated in peat swamps that developed on vast coastal plains during the Pennsylvanian Period. The German brown coal deposits near Cologne are characterized by very thick coal deposits (300 ft or 100 m). However, their lateral extent is much more limited than are the two examples from the United States. These peat deposits formed in a gradually subsiding structural graben bounded by major faults. Land lay to the south and the sea to the north. Only a relatively small portion of the subsiding graben block provided optimal conditions for peat accumulation over a long period of time. Thus each coal bed has its own depositional history that determined many of its characteristics. *See* CARBONIFEROUS; CRETACEOUS; GRABEN; PENNSYLVANIAN; TERTIARY.

Coal seams are commonly composed of a number of benches of alternating coal and more or less carbonaceous shale. The shale represents periods when the peat accumulation was interrupted by flooding from a river or the sea, or, more rarely, interrupted by volcanic ash deposition (tonsteins). The individual benches of a coal bed vary laterally in thickness and composition, sometimes quite rapidly. The degree of variability is related to the stability of conditions during accumulation. Fluvial and lacustrine depositional environments produce greater lateral variability than deltaic or coastal plain environments. *See* SHALE.

Analyses

Many kinds of chemical, physical, petrological, and technological analyses are commonly performed on coal samples to ascertain characteristics and origin. The selection of analyses depends on the information needed. Many of these analyses have been standardized at both national and international levels [for example, American Society for Testing and Materials (ASTM) and International Standardization Organization (ISO)].

Megascopic coal description. Megascopic descriptions, often with the help of a hand lens, are routinely performed in the field, in mines, and on diamond drill cores. The detail of description varies between merely distinguishing coal from impure coal, carbonaceous shale, and other rocks, and quite detailed descriptions in terms of coal types or lithotypes.

Megascopic descriptions are used primarily during geologic investigations to characterize lateral variations in thickness and structure. Their value in predicting specific coal properties such as ash content or coal rank is limited, and they are generally considered to be only the first step in the characterization of a coal deposit. However, megascopic descriptions are the principal basis for coal resource and reserve determinations.

Proximate analysis. This is probably the most commonly performed type of chemical analysis on coal samples. It involves determination of the ash, moisture, volatile matter, and fixed-carbon contents, which total 100%.

High-temperature ash. Combustion of the organic material at 1290–1380°F (700–750°C) leaves behind the high-temperature ash. At these high temperatures, certain minerals disintegrate, leading to both loss of volatile products and reaction with oxygen from the air to form oxides. Some volatile decomposition products react with the ash before they can escape. Therefore, the weight of the high-temperature ash may differ significantly from the weight of the coal's original mineral matter. High-temperature ash is composed primarily of unaltered, altered, and newly formed oxides and silicates (in particular, unaltered quartz and feldspars, altered clay minerals, and newly formed mullite, hematite, and magnetite).

Moisture content. This term has different meanings depending on when, how, and on what sample type it is determined, for example, as received, surface, air-dried, bed, inherent, and equilibrium moistures. The determination may be made on raw or cleaned coal, on selected grain sizes, and so forth. The moisture content in the fully saturated stage, but without presence of surface moisture, is used for determining coal rank. Bed, inherent, and equilibrium moistures are representative of this type of moisture content.

Volatile matter and fixed carbon. These are derived from a small-scale retorting test which is performed under rigidly controlled conditions at a temperature of 1740 ± 36°F (950 ± 20°C). The process results in the disintegration of coal into volatile matter, a complex mixture of gases (exclusive of water), and a cokelike residue rich in carbon (fixed carbon).

Mineral matter. This term refers to both inorganic constituents that occur as discrete mineral grains and so-called inorganic elements that are more or less homogeneously distributed through coal. Minerals that were present before combustion can be approximated from a chemical analysis of the ash (through a normative analysis). A more accurate way to analyze for mineral matter in coal is by oxidation of the organic matter in a low-temperature asher in which an oxygen plasma, activated by a radio-frequency field, is passed over the coal sample. Because the oxidation occurs at the relatively low temperature of 250–300°F (120–150°C), most minerals remain essentially unaltered and the resulting ash can be subjected to a wide range of analyses (in particular, x-ray diffraction) to determine the minerals present. The Parr formula provides a simple method to estimate the original total amount (but not the composition) of the mineral matter in a given coal; its main purpose is to adjust the ash weight by correcting for the disintegration of iron sulfides and other reactions during combustion (that is, loss of sulfur dioxide, and reaction of iron with oxygen in air). *See* MINERAL; X-RAY DIFFRACTION.

Ultimate (elemental) analysis. The elements carbon, hydrogen, oxygen, sulfur, and nitrogen make up essentially all the organic substance of coal and are determined, along with moisture and ash, by the ultimate analysis. The first four of these so-called organic elements are also present in common inorganic components of coal such as the moisture, and the carbonate, sulfide, sulfate, and oxide minerals, making attribution to either the organic or the inorganic constituents of coal potentially difficult. Ultimate analyses are significantly more involved than proximate analyses. Both analyses are now commonly done on sophisticated computer-controlled instruments.

Calorific or heating value. This parameter is determined by observing temperature changes that result from combustion of a known quantity of coal in an adiabatic bomb calorimeter. In the United States, the calorific value is reported in British thermal units given off per pound of coal burned (Btu/lb); the equivalent SI unit is megajoules per kilogram (MJ/kg) or, until relatively recently, cal/g or kcal/kg (1000 Btu/lb = 2.326 MJ/kg = 560 kcal/kg). The calorific value of a coal is influenced not only by the nature of the organic material of which it is made but also by the proportion of noncombustible material present, primarily mineral matter and moisture. *See* CALORIMETRY; THERMOCHEMISTRY.

Major, minor, and trace elements. Coal contains most elements in the periodic table, at least in trace amounts. Elements not yet identified may be present below detection limits. The total concentrations of the ash-forming elements in whole coals ranges from more than 0.5% for major inorganic elements such as aluminum, calcium, iron, and silicon; to 0.02–0.5% for minor elements such as potassium, magnesium, sodium, titanium, chlorine, and others; to less than 0.02% (200 parts per million) for trace elements such as arsenic, beryllium, cadmium, and mercury. Knowledge of the concentration of these elements is required when evaluating coals for combustion and conversion (for example, relative to corrosion, boiler fouling, and poisoning of catalysts) and to assess potential negative environmental and health impacts resulting from coal use. *See* PERIODIC TABLE.

In the United States, 16 minor and trace elements in coal are included in the list of hazardous air pollutants (HAPs) of the 1990 Amendments to the Clean Air Act (**Table 1**).

Analytical methods that are frequently used to determine minor and trace elements in coal include flame and graphite furnace atomic absorption spectrometry, x-ray fluorescence (XRF) spectrometry, optical emission photographic spectrometry, and neutron activation analysis. Inductively-coupled-plasma (ICP) atomic emission spectrometry and ICP mass spectrometry have been used because of their higher sensitivity for certain elements. To study spatial distribution of trace elements, techniques such as laser ablation ICP mass spectrometry, secondary-ion

TABLE 1. Minor- and trace-element content of cleaned coal shipped by mines in Illinois, in parts per million

Element	Arithmetic mean	Standard deviation
Antimony	0.9	0.7
Arsenic	7.5	8.1
Beryllium	1.2	0.7
Cadmium	0.5	0.9
Chlorine	1671.0	1189.0
Chromium	14.0	6.1
Cobalt	3.5	1.3
Fluorine	93.0	36.0
Lead	24.0	21.0
Manganese	38.0	32.0
Mercury	0.09	0.06
Nickel	14.0	5.0
Phosphorus	87.0	83.0
Selenium	1.9	0.9
Thorium	1.5	0.4
Uranium	2.2	1.9

mass spectrometry, and synchrotron-radiation XRF microprobe have been developed. *See* ACTIVATION ANALYSIS; ATOMIC SPECTROMETRY; MASS SPECTROMETRY; X-RAY FLUORESCENCE ANALYSIS.

Macerals. Macerals are the microscopically recognizable constituents of coal. Microscopic analyses are normally performed on representative crushed coal samples embedded in epoxy and polished for observation under incident light, generally with oil immersion objectives, at a magnification of 400–750×. A sufficiently large number (500–1000) of points evenly distributed over the sample are selected for maceral analysis to determine the percent of macerals in the sample by volume. The measuring spots are only a few micrometers in diameter.

The reflected-light method permits identification of a few nonclay minerals during maceral analysis. However, much more accurate determinations of the amount and composition of mineral matter are accomplished through other analyses, in particular, low-temperature ashing followed by x-ray diffraction analysis of the ash.

Reflectance of vitrinite. The percentage of normally incident light that is reflected from the polished surface of vitrinite under oil immersion has become a commonly used measure of coal rank. A reflected-light microscope equipped with a photomultiplier is used. The small size of the measuring spot, about 5 micrometers in diameter, and the large magnification used (500–1000×) permit selection of highly comparable material for this analysis, in contrast to chemical analyses that test bulk coal with variable mixtures of macerals and minerals. Vitrinite is the preferred material on which to measure reflectance, because of its common occurrence in most coals, its homogeneous appearance, its easy recognition under the microscope, and the considerable range in reflectance exhibited by the maceral, depending on a coal's rank.

Density, porosity, and internal surface area. Because of the large proportion of very small pores (a few angstroms to a few tens of angstroms in diameter) in coal, true values for these parameters are difficult to obtain with standard methods. Only very small molecules or atoms (for example, helium) are able to penetrate these micropores. Determinations with gases or liquids whose molecules are of the same order of magnitude as or larger than the micropores and their entrances yield only apparent values. For example, in one experiment the internal surface area of a sample of bituminous coal was measured separately with nitrogen and then carbon dioxide; the values obtained were 9 and 205 m^2/g, respectively. Another method to estimate the internal surface area is by measuring the heat of wetting with various liquids; but with this method, too, the molecules of the liquids do not necessarily penetrate all pores and thus do not measure the entire internal surface area.

Washability. A large proportion of mined bituminous and higher-rank coal is cleaned before it is used. Washability tests are performed in the laboratory on drill core and test pit samples to predict the cleanability of a given coal when mined. Coal samples are crushed to sizes comparable to those anticipated to be produced by the mine and are subjected to float-sink tests in heavy liquids. The amounts floating and sinking in each gravity fraction are measured, and their ash and sulfur contents as well as other parameters (for example, heating value) are determined. The data are tabulated and plotted to produce washability curves that characterize the coal's cleanability.

The fine fraction of mined coal [<0.3–0.5-mm (0.01–0.02-in.) grain size] is difficult or impossible to clean by the float-sink method. Instead of utilizing the differences in specific gravity of particles of the crushed raw coal, differences in the surface properties of coal and minerals (hydrophobic versus hydrophilic) are employed in the flotation method used to clean coal fines. However, since this method is relatively expensive, fine coal has commonly been discarded (in slurry ponds) without cleaning.

Plastic and coking properties. A significant use of coal is in making coke, which involves heating finely crushed coal in coke ovens in the absence of air. Bituminous coals generally become plastic or fluid during heating as they disintegrate into gases, liquids, and solids (char, coke); certain bituminous coals, commonly blends of several coals of different rank, can form a coke that is strong enough for use in blast furnaces. Several empirical tests have been used widely for many years to characterize the behavior of coal during heating and to predict its coke-forming ability.

Free Swelling Index (FSI). This is probably the most widely used test. It requires rapid heating of 1 g (0.35 oz) of finely ground coal to a temperature of 1508 ± 9°F (820 ± 5°C) in a lid-covered crucible. A coke button is formed, and its shape is compared to standard shapes 1–9 and reported in half-step increments. The FSI test provides a rapid and inexpensive first assessment of the coke-forming behavior of a coal.

Plastometer test. In a Gieseler plastometer, 5 g of finely crushed coal is heated in a retort; a small stirrer submerged in the sample applies constant torque while the temperature is raised at a rate of 5.4°F/min

(3°C/min). As the coal becomes plastic and fluid during heating, the stirrer's rate of rotation is recorded. The temperatures of initial softening, maximum fluidity, and resolidification, as well as the maximum dial movement in dial divisions per minute (ddpm), are recorded. These data differ characteristically for coals of different rank and composition and provide good indicators of a coal's coking properties.

Dilatometer test. This test is widely used outside the United States to characterize the behavior of coal during heating in the range 570–1020°F (300–550°C). A finely ground sample of coal is heated inside a crucible with a piston resting on the sample. The displacement of the piston is recorded as a percentage of the original sample volume. While the sample is heated at a rate of 5.4°F/min (3°C/min), the coal becomes plastic and fluid and releases gas, expands, then solidifies to coke. Volume change is plotted against temperature; the resulting curve reveals much about the coking characteristics of a given coal.

Other tests. The Gray-King and ROGA tests, commonly performed in several European countries, are essentially standardized laboratory-scale coking tests which produce useful index numbers. *See* COKE.

Strength and hardness. Strength and hardness are important coal properties in mine stability, coal winning, and comminution for preparation and utilization. A number of tests are commonly performed in the laboratory to obtain information on a coal's compressive and shearing strengths and hardness; an example is the Hardgrove grindability test. The values thus obtained are only index numbers because of the small size of sample used. They must be translated with caution when full-scale industrial operations are involved.

Ash fusion. During combustion of coal in boilers, the noncombustible portion, such as minerals and inorganic elements, either is volatilized or becomes ash, which forms deposits within the boiler or is removed as fly ash or bottom ash. The ash-fusion test identifies the temperatures at which the ash undergoes major phase changes. In general, for combustion uses of coal, ash that fuses at high temperatures (above 2400°F or 1538°C) is preferred to ash that fuses at low temperatures (below 2000°F or 1093°C). The range of ash-fusion temperatures is about 1600–2800°F (871–1538°C). The properties and relative abundances of minerals present may be critical in the formation of ash deposits in a boiler, as well as in the corrosion of boiler tubes. High alkali and alkali chloride contents are known to cause such problems in boilers. Boilers are designed for certain ash fusion properties.

Classification Schemes

The parameters obtained from coal analyses are used to classify coal for general as well as specific purposes. Both national and international standardization organizations have adopted classification schemes that are used in the coal trade, for statistical purposes, and to compile coal resources and reserves by classification category. One of the most widely used classification systems is the American Society for Testing and Materials (ASTM) Standard Classification of Coals by Rank (**Table 2**).

The European Commission for Europe—UN (UN/ECE) Working Party on Coal developed a new

TABLE 2. American Society for Testing and Materials classification of coals by rank (in box, ASTM standard D 388) and other related coal properties

ASTM class	ASTM group	1000 Btu/ lb[1]	Agglomer-ating[2]	Volatile matter,[3] %	MJ/kg[1]	Maximum reflectance,[4] %	Moisture,[1] %	C,[3] %	O,[3] %	H,[3] %
	Peat	1.0–6.0	No	72–62	2.3–14.0	0.2–0.4	95–50	50–65	42–30	7–5
Lignite	Lignite B	>6.3[5]	No	65–40	<14.7[5]	0.2–0.4	60–40[5]	55–73	35–23	7–5
	Lignite A	6.3–8.3[5]	No	65–40	14.7–19.3[5]	0.2–0.4	50–31[5]	55–73	35–23	7–5
Subbituminous	Subbituminous C	8.3–9.5[5]	No	55–35	19.3–22.1[5]	0.3–0.6	38–25[5]	60–80[6]	28–15[6]	6.0–4.5
	Subbituminous B	9.5–10.5[5]	No	55–35	22.1–24.4[5]	0.3–0.6	30–20[5]	60–80[6]	28–15[6]	6.0–4.5
	Subbituminous A	10.5–11.5[5]	No	55–35	24.4–26.7[5]	0.3–0.7	25–18[5]	60–80[6]	28–15[6]	6.0–4.5
Bituminous	High volatile C	10.5–13.0[5]	Yes	55–35	24.4–30.2[5]	0.4–0.7	25–10[5]	76–83[6]	18–8[6]	6.0–4.5
	High volatile B	13.0–14.0[5]	Yes	50–35	30.2–32.6[5]	0.5–0.8[6]	12–5[6]	77–84[6]	12–7[6]	6.0–4.5
	High volatile A	≥14.0	Yes	45–31	≥32.6	0.6–1.2[6]	7–1[5]	78–88[6]	10–6[6]	6.0–4.5
	Medium volatile	>14.0	Yes	31–22[5]	>32.6	1.0–1.7[5]	<1.5	84–91	9–4	6.0–4.5
	Low volatile	>14.0	Yes	22–14[5]	>32.6	1.4–2.2[5]	<1.5	87–92	5–3	6.0–4.5
Anthracite	Semianthracite	>14.0	No	14–8[5]	>32.6	2.0–3.0[5]	<1.5	89–93[6]	5–3[6]	5–3[5]
	Anthracite	>14.0	No	8–2[5]	>32.6	2.6–6.0[5]	0.5–2	90–97[6]	4–2[6]	4–2[5]
	Meta-anthracite	>14.0	No	≤2	>32.6	>5.5[5]	1–3	>94[6]	2–1[6]	2–1[5]

[1] Moist, mineral-matter-free.

[2] Agglomerating coals form a button of cokelike residue in the standard volatile-matter determination that shows swelling or cell structure or supports a 500-g weight without pulverizing. The residue of nonagglomerating coal lacks these characteristics.

[3] Dry, mineral-matter-free.

[4] Reflectance of vitrinite under oil immersion.

[5] Well suited for rank discrimination in range indicated.

[6] Moderately well suited for rank discrimination.

SOURCE: Modified from H. H. Damberger et al., in B. R. Cooper and W. A. Ellingson (eds.), *The Science and Technology of Coal and Coal Utilization*, 1984.

standard that attempts to incorporate both coal rank and coal facies parameters; this standard is intended for the characterization of coal resources in the ground. Another group of experts of ECE developed a codification system for coals traded. This standard replaces the UN/ECE's 1956 classification scheme for hard coal, which combines rank (class), caking (group), and coking (subgroup) parameters into a three-digit code system; this scheme has not been widely used.

For the purpose of classification, coal analyses must be standardized, through computation, to a common basis, such as ash-free (af), moisture-free (mf) or dry (d), moisture-and-ash-free (maf) or dry ash-free (daf), mineral-matter-free (mmf), dry mineral-matter-free (dmmf), and so forth. Generally, chemical laboratories determine values on an air-dried basis; from these all other bases can be easily computed.

Coal Facies

The coal facies reflects the environments of deposition during accumulation of plant material. The types of plants growing, their preservation, and the kinds and amounts of mineral matter introduced vary with the depositional environments. Coal facies can be recognized both megascopically and microscopically through all or most ranks.

Nonbanded coal. Nonbanded coals are homogeneously fine-granular and devoid of distinct megascopic layers. They have a greasy luster and conchoidal fracture. They formed from subaqueous deposition of finely comminuted plant detritus, commonly with significant amounts of spore or pollen grains, algal remains, wax and resin granules, and various other small plant fragments. Well-known nonbanded coals are cannel coal (composition dominated by spores) and boghead coal (predominance of algae). Transitions exist to oil shales. Their proper identification requires microscopic analysis. *See* OIL SHALE; SAPROPEL; TORBANITE.

Nonbanded coals are relatively rare. They may form entire coal seams or layers within banded coal.

Banded coal. This is the most common coal type. In bituminous coal, recognizable bands are composed of lithotypes such as vitrain, attrital coal, and fusain, and of impure coal. The banding is less pronounced in lower rank (subbituminous, lignitic) coals and may be difficult to discern in anthracites. Most bands are between a fraction of a centimeter to several centimeters thick.

Vitrain. This lithotype, also referred to as bright coal, is highly lustrous in bituminous coals and enhances their banded appearance. Vitrain represents the coalified remains of relatively large fragments of wood and the bark of stems, branches, and roots of trees and bushes. In bituminous coal, it forms bands and lenses of very bright coal, generally a few millimeters to 10 mm thick. In lignite the remains of woody material lack the shiny luster.

Attrital coal. This lithotype represents the fine-grained ground mass of banded coal in which layers of vitrain and fusain are embedded. Attrital coal is highly variable in appearance and composition. It exhibits a finely striated, granulose, or rough texture, much like nonbanded coal. Relatively lustrous attrital coal is often referred to as clarain, dull attrital coal as durain. Dull attrital coal commonly contains relatively high amounts of finely dispersed mineral matter, clays and quartz in particular.

Fusain. In most banded coals fusain represents only a subordinate proportion of the total volume, and it generally occurs in lens-shaped laminae and thin bands that rarely exceed a few centimeters in thickness. Fusain resembles charcoal; it is fibrous, very friable, and has a silky luster. It tends to be concentrated on selected bedding surfaces, forming planes of weakness in coal beds. Its many pores are often filled with secondary mineral matter that strengthens it and reduces its friability.

Impure coal. This type of coal is defined as containing 25–50% of ash by weight on the dry basis. The mineral impurities were introduced either during deposition, mostly as clay or as fine-grained detrital mineral matter (bone coal), or later as secondary mineralization (mineralized coal). Bone coal has a dull appearance; it is commonly finely striated. When scratched with a knife or nail, it forms a brown powder; the scratch mark appears shiny. Pyritized coal is the most common mineralized coal.

Maceral groups. Macerals are the microscopically recognizable organic constituents of coal, equivalent to minerals of other rocks. However, unlike minerals, their chemical and physical properties are not fixed but vary over a wide range depending upon coal rank and facies. Submicroscopic inorganic impurities are considered part of macerals.

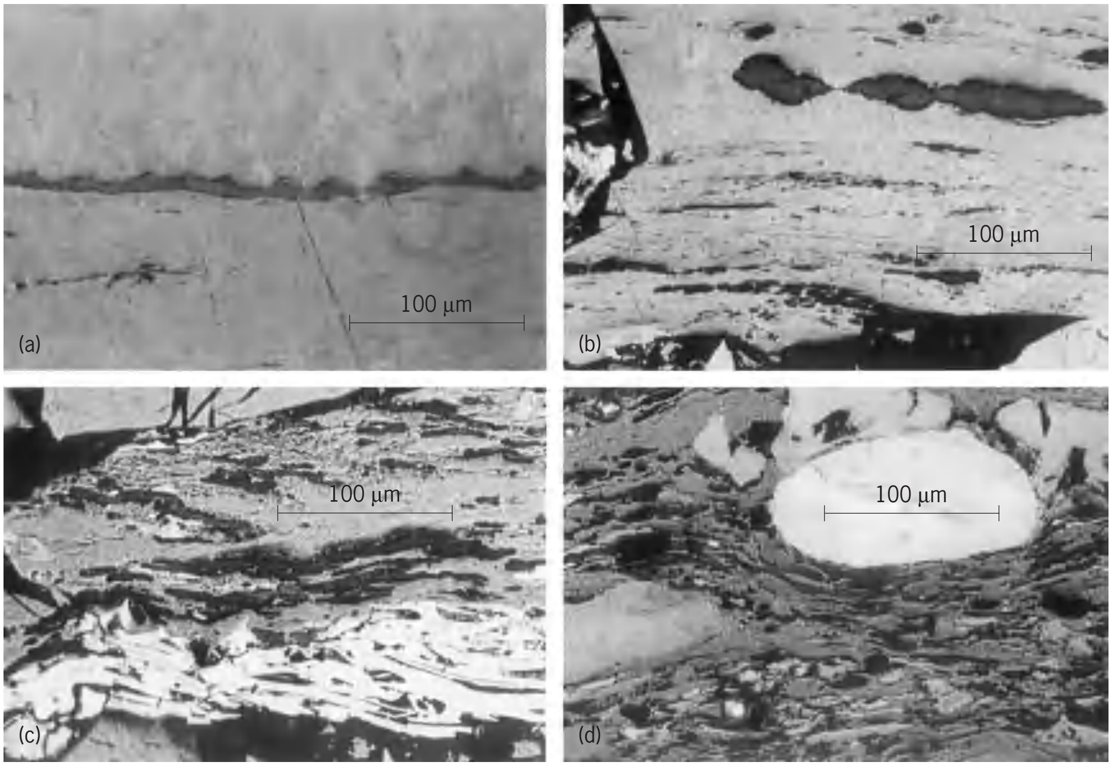
Three major groups of macerals are generally recognized: vitrinites, exinites (or liptinites), and inertinites. These maceral groups are divided into maceral subgroups and, depending on the degree of detail desired, even further (**Table 3** and **illus.**). In polished sections, the macerals are distinguished on the basis of their reflectance and morphology, and to some extent on their size and maceral association.

Vitrinite. This is the predominant group of macerals in most coals (commonly 70–85% by volume). The reflectance of vitrinite is intermediate between the darker exinite and brighter inertinite (see illus.).

TABLE 3. Classification of macerals*

Maceral group	Maceral
Vitrinite	Vitrinite
Exinite (or liptinite)	Sporinite
	Cutinite
	Resinite
	Alginite
Inertinite	Fusinite
	Macrinite
	Micrinite
	Sclerotinite
	Semifusinite
	Inertodetrinite

*After American Society for Testing and Materials, standard D 2796.



Macerals in polished surfaces of bituminous coals in reflected light, under oil immersion. (*a*) Thin, "saw-toothed" cutinite (dark) enclosed in vitrinite. (*b*) Elongate globs of resinite (dark) and other, smaller exinite macerals (dark) enclosed in vitrinite. (*c*) Sporinite (dark lenses) in vitrinite (gray) with fusinite (white) on lower part of photo. (*d*) Large grains of macrinite (white), smaller inertodetrinite (light gray), and sporinite and other exinites (dark gray) interlayered with vitrinite (gray).

Vitrinite generally originated from woody plant parts (tree trunks, branches, roots, and bark). The original cellular plant structure is still more or less visible in many vitrinites. The identifiable cell walls are known as telinite, while the structureless vitrinite is known as collinite. These two are sometimes further subdivided into submacerals for very detailed investigations.

The reflectance of vitrinite is a good indicator of coal rank, especially in higher-rank coals. Viewed under oil immersion, reflectance values range from 0.2–0.3% in low-rank lignites to over 4% in anthracites (Table 2).

Exinite (or liptinite). The macerals of the exinite group reflect light distinctly less than vitrinite (see illus.). Their volatile matter and H contents are significantly higher than those of associated vitrinite. These differences in reflectance, volatile matter, and H contents disappear quickly with increasing rank in coals above about 1% R_{oil}, or about 30% volatile matter (dry ash-free), and converge at about 1.4% R_{oil}, or about 20% volatile matter. The origin of the macerals of the exinite group is clearly implied by their names (Table 3); they are derived from algae, spores, cuticles, resins, waxes, fats, and oils of plants.

Inertinite. Inertinites reflect light significantly more than associated vitrinites (see illus.), except in high-rank anthracites. Inertinites do not become plastic during heating, such as in coke making; they react as inert materials. Fusinite is characterized by well-preserved cell wall structure (sometimes broken by compaction, a characteristic known as bogenstructure). Cell cavities commonly are filled with minerals. Fusinite's general appearance suggests origin by rapid charring in the peat stage (for example, in a forest fire). On the other hand, macrinite and micrinite lack visible cell structure. Particle size is greater than 10 μm for macrinite and less than 10 μm, commonly about 1 μm, for micrinite. Micrinite appears to be a solid by-product of the coalification of liptinite macerals in the bituminous rank range. Sclerotinite occurs as high-reflecting round to oval cellular bodies of varying size (20–300 μm) or as interlaced tissues derived from fungal remains. Semifusinite is transitional between fusinite and associated vitrinite in both reflectance and cell structure. Inertodetrinites are small, angular clastic fragments of other inertinites commonly enclosed in vitrinite or associated with mineral matter.

The presence of inertinites indicates oxidative conditions during the peat stage of coal formation. Inertinite contents of 5–15% are the rule for many coals of the eastern United States and Europe. But some coals have inertinite contents in the 30–40% range (for example, the High Splint and Winefrede coal seams of eastern Kentucky), indicating strong oxidizing conditions during peat formation. The mostly Permian-age Gondwana coals of Australia, India, South Africa, and South America are well known for their high inertinite contents, up to 85%. These coals were formed in a relatively cold climate with alternating dry and rainy seasons, providing

TABLE 4. Minerals frequently occurring in coals and their stoichiometric compositions, relative abundances, and modes of occurrences*

Mineral	Composition	Common minor- and trace-element associations	Frequency of occurrence in coal seams	Concentration in mineral matter	Chief occurrences Physical†	Genetic‡
Clay minerals						
Illite (sericite)	$KAl_2(AlSi_3O_{10})(OH)_2$	Sodium, calcium,	Common	Abundant	D,L	d,s(?)
Smectite (including		iron, lithium,				d,s(?)
mixed layered)	$Al_2Si_4O_{10}(OH)_2 \cdot H_2O$	titanium,	Common	Abundant	D,L	
		manganese, fluorine,				d,e,s(?)
Kaolinite group	$Al_2Si_2O_5(OH)_4$	and other lithophile	Common	Abundant	L,F	d
Chlorite	$Mg_5Al(AlSi_3O_{10})(OH)_8$	elements	Rare	Moderate	L	
Sulfides						
Pyrite	FeS_2 (isometric)		Rare to common	Variable	D,N,F	s,e
Marcasite	FeS_2 (orthorhombic)	Arsenic, cobalt,	Rare to moderate	Trace	D(?)	s(?)
Pyrrhotite	$Fe_{1-x}S$	copper, and other	Rare	Trace	D	s(?)
Sphalerite	ZnS	chalcophile elements	Rare	Minor to trace	F	e
Galena/chalcopyrite	$PbS/CuFeS_2$		Rare	Trace	F	e
Carbonates						
Calcite	$CaCO_3$		Rare to common	Abundant	N,F	e,s
Dolomite (ankerite)	$CaMg(CO_3)_2$	Manganese, zinc,	Moderate	Trace	N,L	s,e
Siderite	$FeCO_3$	strontium	Rare	Minor	N	s,e
Oxides						
Quartz	SiO_2	–	Common	Abundant	D,L,N	d,s(?)
Magnetite/hematite	Fe_3O_4/Fe_2O_3	Manganese, titanium	Common	Minor to trace	N	s
Rutile and anatase	TiO_2	–	Common	Trace	D	d(?)
Others						
Goethite/limonite	FeO(OH)	Manganese, titanium	Common	Trace	N	w
Feldspar	$K(Na)AlSi_3O_8$	Calcium	Moderate	Trace	D,L	d
Zircon	$ZrSiO_4$	–	Moderate	Trace	D	d
Sulfates						
Gypsum	$CaSO_4 \cdot 2H_2O$	–	Moderate	Minor	D,F	w
Barite	$BaSO_4$	Sodium, strontium, lead	Rare	Minor	F	e
Szomolnokite	$FeSO_4 \cdot H_2O$	–	Rare	Trace	D	w
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	Manganese, cerium, strontium, uranium	Moderate	Trace	D	d,s(?)
Halite	NaCl	Potassium, magnesium	Rare	Trace	D	e

* After R. D. Harvey and R. R. Ruch, Mineral matter in Illinois and other U.S. coals, in K. S. Vorres (ed.), *Mineral Matter and Ash in Coal*, Amer. Chem. Soc. Symp. Ser. 301, pp. 10–40, 1986.
† D, disseminated; L, layers (partings); N, nodules; F, fissures (cleat). First listed is the most common occurrence.
‡ d, detrital; s, syngenetic; e, epigenetic; w, weathering. First listed is the most common occurrence. (?) indicates there is divergence of opinion about the genetic occurrence.

ample opportunity for widespread oxidation of the accumulating plant material. In contrast, the Pennsylvanian-age coals of North America and Europe originated in the humid equatorial zone.

Mineral matter. Whether they occur as discrete mineral grains or are disseminated through coal macerals, the inorganic components are referred to collectively as mineral matter. The low-temperature oxygen-plasma ashing technique developed in the mid-1960s has permitted detailed analyses of the minerals found finely dispersed in coal (**Table 4**). Mineral matter occurs in coal seams as discrete layers or partings, as nodules, as fissure fillings, as rock fragments, and as small particles finely disseminated throughout. Genetically, minerals can be classified as inherent (plant-derived), detrital (water- or wind-borne during sedimentation), syngenetic (formed early in the peat stage), and epigenetic (formed during and after lithification and during weathering). There is no sharp boundary between syngenetic and epigenetic origins. Minerals, just as macerals, indicate the environments that prevailed during their incorporation into peat or later during coalification. Similarly, the inorganic major, minor, and trace elements of coal were introduced at various stages of coal formation. Multivariate statistical methods permit attribution of most minor and trace elements to specific mineral phases.

Coal Rank

During burial to greater and greater depth, peat is transformed into brown coal or lignite, subbituminous coal, bituminous coal, and anthracite (coalification series) as a result of increasing overburden pressure and rising temperature. Both physical (pressure, heat) and chemical (biochemical, thermochemical) factors are influential in the transformation of peat into the other members of the coalification series (**Table 5**). The boundaries between the members of the series are transitional and must be chosen somewhat arbitrarily. The term rank is used to identify the stage of coalification reached in the course of coal metamorphism. Rank is a fundamental property of coal, and its determination is essential in the characterization of a coal. Classification of coal by rank generally is based upon the chemical composition of the coal's ash-free or mineral-matter-free organic substance (Table 2), but parameters derived from empirical tests indicative of technological properties, such as agglomerating characteristics (Table 2) or the Free

TABLE 5. Examples of typical proximate and ultimate analyses of samples of each rank of common banded coal in the United States*

	Proximate analysis, % (as-received basis)					Ultimate analysis, % (dry basis)					
Rank	State	Moisture	Volatile matter	Fixed carbon	Ash	Sulfur	Hydrogen	Carbon	Nitrogen	Oxygen	Heating value, Btu/lb† (as-received basis)
Anthracite	Pa.	4.4	4.8	81.8	9.0	0.6	3.4	79.8	1.0	6.2	13,130
Semianthracite	Ark.	2.8	11.9	75.2	10.1	2.2	3.7	78.3	1.7	4.0	13,360
Bituminous coal											
Low volatile	Md.	2.3	19.6	65.8	12.3	3.1	4.5	74.5	1.4	4.2	13,220
Medium-volatile	Ala.	3.1	23.4	63.6	9.9	0.8	4.9	76.7	1.5	6.2	13,530
High-volatile A	Ky.	3.2	36.8	56.4	3.6	0.6	5.6	79.4	1.6	9.2	14,090
High-volatile B	Ohio	5.9	43.8	46.5	3.8	3.0	5.7	72.2	1.3	14.0	13,150
High-volatile C	Ill.	14.8	33.3	39.9	12.0	2.5	5.8	58.8	1.0	19.9	10,550
Subbituminous coal											
Rank A	Wash.	13.9	34.2	41.0	10.9	0.6	6.2	57.5	1.4	23.4	10,330
Rank B	Wyo.	22.2	32.2	40.3	4.3	0.5	6.9	53.9	1.0	33.4	9,610
Rank C	Colo.	25.8	31.1	38.4	4.7	0.3	6.3	50.0	0.6	38.1	8,580
Lignite	N. Dak.	36.8	27.8	30.2	5.2	0.4	6.9	41.2	0.7	45.6	6,960

*After *Technology of Lignitic Coals,* U.S. Bur. Mines Inform. Circ. 769, 1954. Sources of information omitted.
†1000 Btu/lb = 2.326 MJ/kg.

Swelling Index, as well as the ROGA, Gieseler, and Gray-King tests, are commonly used in several countries outside the United States in addition to coal rank parameters. *See* METAMORPHISM.

Coal rank increases with depth at differing rates from place to place, depending primarily on the rate of temperature increase with depth (geothermal gradient) at the time of coalification. Coal rank also changes laterally, even in the same coal seam, as former depth of burial and thus exposure to different pressure and temperature vary. Originally established vertical and regional coalification patterns can be significantly altered by various kinds of geologic events, such as the intrusion of large magma bodies at depth (plutonism), or renewed subsidence of a region. Volcanic activity may cause significant local anomalies in coal rank, but rarely leads to regional changes in coalification pattern. *See* MAGMA.

The chemical parameters customarily used to rank coal may yield misleading results in coals that are not primarily composed of vitrinite. Coals rich in exinite may have significantly higher contents of volatile matter and coals rich in inertinite may have significantly lower contents of volatile matter than associated so-called normal coals. This problem can be minimized by the use of vitrinite reflectance to indicate rank. Reflectance data have the additional advantage of being applicable to small coaly particles that occur dispersed throughout most sediments, permitting rank measurements in strata devoid of coal beds.

As rank increases during maturation, most coal properties change in tandem. This is reflected in the values given in Tables 2 and 5, but can also be represented graphically in correlation charts.

Occurrence and Resources

During geologic history, coal could not form in economic quantities until vascular land plants evolved during the Devonian Period some 400 million years ago and until they conquered the continents during the Carboniferous Period. The Carboniferous (Mississippian and Pennsylvanian of North America) witnessed an explosive development of vast swamp forests along the Euramerican equatorial coal belt, which extended from the North American midcontinent to Russia. The Atlantic Ocean did not exist then, and the North American and European continents were fused together as part of a continent called Laurasia. Another important coal-forming belt stretched over what was then Gondwana of the Southern Hemisphere. Gondwana subsequently drifted north and broke up into South America, Africa, India, and Australia. Most major coal deposits on Gondwana are of Permian age. They formed in a cool, humid climate. Most of the vast coal deposits of the western United States and Canada, along the eastern margin of the Rocky Mountains, originated during the Cretaceous and Tertiary periods. *See* CARBONIFEROUS.

Not all coal deposits are of economic interest. Governments and private industry need to know how much coal exists in the ground (resources) and what portion may be available for development under current economic and legal conditions (reserves). Various classification schemes have been adopted by national and international agencies for determination of coal resources and reserves on comparable bases. However, no universally accepted standard has yet emerged. An international framework for the classification of reserves/resources for solid fuels and mineral commodities has been developed under the auspices of the United Nations to fill the gap.

Two independent factors generally are considered in these assessments: the degree of economic minability, and the degree of geologic assurance of the existence of a coal deposit of given properties. The World Energy Conference (WEC) has attempted to overcome the lack of standardization between countries by adopting carefully worded definitions of resource and reserve categories, and has asked national organizations to interpret their databases in these terms. **Table 6** is a summary of the worldwide compilation by the World Energy Conference.

TABLE 6. World coal resources and reserves, in 10^9 metric tons*

Continent or country	Proved amount in place	Estimated recoverable reserves	Estimated additional reserves in place	Additional recoverable reserves
Africa	134	62	114	0.1
South Africa	121	55	5	0
North America	455	253	1199	2
United States	431	241	1139	0
South and Central America	21	10	46	7
Brazil	10	3	22	6
Asia (excl. former Soviet Union)	562	228	767	198
China	287	115	668	150
India	223	70	90	47
Former Soviet Union	287	241	5200	0
Australia	117	91	704	433
Europe (excl. former Soviet Union)	819	150	552	39
Former CSSR	571	5	5	2
Germany	122	67	186	0
Poland	79	42	144	27
United Kingdom	1.0	2.5	190	0
New Zealand, New Caledonia	0.6	0.1	8	<0.1
World total	2396	1034	8590	680

*After survey by World Energy Council, 1995.

Uses

Coal is used primarily for producing steam in electric power plants [87% of coal consumed in the United States in 1997, 67% in countries of the Organization for Economic Cooperation and Development (OECD) in 1996, and 52% in the world in 1996]. Other important uses are by industry for producing steam and heat (9% United States, 12% OECD), and by the steel industry for coke making (3% United States, 7% OECD). Conversion of coal to synthetic liquid or gaseous fuels does not constitute a major use of coal worldwide or in most countries. However, coal conversion has been important under special circumstances in some countries. During World War II, Germany produced a significant amount of liquid fuels from coal, and South Africa, when it became isolated because of its apartheid policy, established a major coal liquefaction industry to reduce its dependence on oil imports. One large coal gasification plant in the United States produces synthetic natural gas from North Dakota lignite; it was built with government support. It will take a significant rise in the price of oil and natural gas to make conversion into synthetic liquid and gaseous hydrocarbons competitive in the future. *See* SYNTHETIC FUEL.

The massive Clean Coal Technology (CCT) cooperative program between the United States government and private industry that began in 1988 included several large-scale projects where coal is gasified, the gas cleaned and then burned on site, first to drive high-temperature gas turbines, and then to generate steam for steam turbines; this makes for very clean and high-efficiency electric power generation. The CCT program has also demonstrated a wide range of other technologies to produce energy from coal cleanly and efficiently. *See* COAL CHEMICALS; COAL GASIFICATION. **Heinz H. Damberger**

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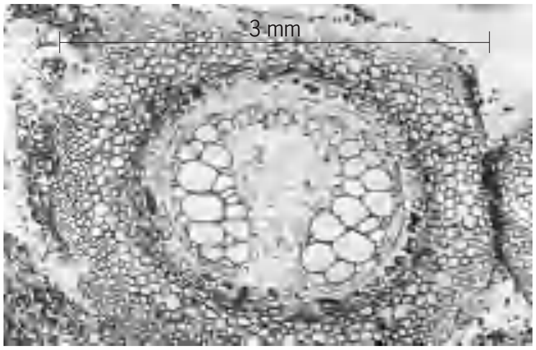
Coal balls

Variously shaped nodules consisting of fossilized peat in which the individual cells and tissue systems of the plant parts are infiltrated by minerals, principally calcium carbonate, along with pyrite, dolomite, and occasionally silica. This type of fossilization, in which the cell walls are filled with minerals, is termed permineralization. Coal balls occur principally in Pennsylvanian (upper Carboniferous) bituminous and anthracite coals, often below black marine shales in North America, but permineralized plants have also been reported in coals from as early as the Devonian and extending well into the Paleocene.

How coal balls formed is not well understood, but some are believed to represent accumulations



Photomicrograph of the peel made from a coal ball containing the petiole of a fern. 1 mm = 0.04 in.

of peat in which the plants were growing in low-lying swampy areas close to the sea. According to this model, seawater provided the high source of calcium carbonate in the permineralization processes. It has also been suggested that the permineralizing fluids were derived from percolating carbonate-rich ground water.

Because the individual plant cells in coal balls have not been crushed, they offer a wealth of information about the structure, morphology, and biology of the plants. Plants are studied by cutting a coal ball with a lapidary saw and then preparing an acetate peel of the surface. That is, the surface is etched with dilute acid that removes mineral material from the cell lumens, and then a thin sheet of acetate is added to the etched surface that has been flooded in acetone. The acetate-acetone mixture flows in and around the cell walls that are standing in relief. When the acetate sheet dries, a thin layer of plant cells can be peeled from the coal ball surface. After lightly grinding the coal ball surface with fine silicon powder, another peel can be prepared. Thus, the paleobotanist can prepare a set of serial sections of a fossil plant organ just as is done in the preparation of living plant and animal tissues. Peels can be observed with a dissecting microscope, or mounted on microscope slides under a cover glass to be examined with a compound microscope (see **illus.**).

Coal balls also contain the reproductive parts of plants. These can be observed on peels, or in the case of pollen grains and spores they can be macerated and studied with scanning and transmission electron microscopy. The preservation is sometimes so good that delicate structures such as nuclei, chromosomes, and membranes can be observed in great detail. *See* COAL PALEOBOTANY; PALEOBOTANY.

Thomas N. Taylor

Coal chemicals

For about 100 years, chemicals obtained as by-products in the primary processing of coal to metallurgical coke were the main source of aromatic compounds used as intermediates in the synthesis of dyes, drugs, antiseptics, and solvents. However, over 97% of the aromatic hydrocarbons, such as benzene, toluene, and xylenes, are now obtained largely from petroleum. Naphthalene, phenanthrene, heterocyclic hydrocarbons such as pyridines and quinolines, and some phenols are still obtained from coal tar.

Coke oven by-products, as a percentage of the coal used, are gas 18.5, light oil 1.0, and tar 3.5. Coke oven gas is a mixture of methane, carbon monoxide, hydrogen, small amounts of higher hydrocarbons, ammonia, and hydrogen sulfide. Most of the ammonia is recovered as about 20 lb (9 kg) of ammonium sulfate per ton (0.9 metric ton) of coal, but only about 10% of the hydrogen sulfide is recovered as elemental sulfur. Most coke oven gas is used as fuel. The composition of a typical coke oven crude light oil is shown in **Table 1**. The unidentified fractions contain very small amounts of a large number of hydrocarbons, and organic compounds containing oxygen and nitrogen.

Although several hundred chemical compounds have been isolated from coal tar, a relatively small number are present in appreciable amounts. These may be grouped as in **Table 2**.

All the compounds in Table 2 except the monomethylnaphthalenes are of some commercial importance. The amounts recovered and sold, however, are only 5–25% of the totals present in the coal tar.

The direct utilization of coal as a source of bulk organic chemicals has been the objective of much research and development. Oxidation of aqueous alkaline slurries of coal with oxygen under pressure yields a mixture of aromatic carboxylic acids. Because of the presence of nitrogen compounds and hydroxy acids, this mixture is difficult to refine. Hydrogenation of coal at elevated temperatures and pressures yields much larger amounts of tar acids and

TABLE 1. Analysis of a typical coke oven crude light oil

Component	% by vol
Forerunnings	
Cyclopentadiene	0.5
Carbon disulfide	0.5
Amylenes, unidentified substances	1.0
Crude benzol	
Benzene	57.0
Thiophene	0.2
Saturated nonaromatic hydrocarbons	3.0
Unsaturates, unidentified substances	3.0
Crude toluol	
Toluene	13.0
Saturated nonaromatic hydrocarbons	0.1
Unsaturates, unidentified substances	1.0
Crude light solvent	
Xylenes	5.0
Ethylbenzene	0.4
Styrene	0.8
Saturated nonaromatic hydrocarbons	0.3
Unsaturates, unidentified substances	1.0
Crude heavy solvent	
Coumarone, indene, dicyclopentadiene	5.0
Polyalkylbenzenes, hydrindene, etc.	4.0
Naphthalene	1.0
Unidentified heavy oils	1.0
Wash oil	
(Used to separate light oil from coke oven gas)	5.0

TABLE 2. Coal tar chemicals

Compound	Fraction of whole tar, %	Use
Naphthalene	10.9	Phthalic acid
Monomethylnaphthalenes	2.5	Organic syntheses
Acenaphthenes	1.4	Dye intermediates
Fluorene	1.6	Organic syntheses
Phenanthrene	4.0	Dyes, explosives
Anthracene	1.0	Dye intermediates
Carbazole (and other similar compounds)	2.3	Dye intermediates
Phenol	0.7	Plastics
Cresols and xylenols	1.5	Antiseptics, organic syntheses
Pyridine, picolines, lutidines, quinolines, acridine, and other tar bases	2.3	Drugs, dyes, antioxidants

aromatic hydrocarbons of commercial importance than are obtained by carbonization.

Synthetic fuels may be produced from coal by either direct or indirect methods. In direct liquefaction processes, pulverized coal is suspended in a solvent, the resultant slurry is heated and exposed to gaseous hydrogen under pressure, and the liquids produced are separated from the ash and distilled to obtain the fuel fractions. In the indirect process, the coal is decomposed thermally to yield combustible gases, which are synthesized to yield gasoline, alcohols, and waxes. *See* COAL LIQUEFACTION; COKE; DESTRUCTIVE DISTILLATION; ORGANIC CHEMISTRY; PYROLYSIS.

Howard W. Wainwright

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Coal gasification

The conversion of coal or coal char to gaseous products by reaction with steam, oxygen, air, hydrogen, carbon dioxide, or a mixture of these. Products consist of carbon monoxide, carbon dioxide, hydrogen, methane, and some other gases in proportions dependent upon the specific reactants and conditions (temperatures and pressures) employed within the reactors, and the treatment steps which the gases undergo subsequent to leaving the gasifier. Similar chemistry can also be applied to the gasification of coke derived from petroleum and other sources. The reaction of coal or coal char with air or oxygen to produce heat and carbon dioxide could be called gasification, but it is more properly classified as combustion. The principal purposes of such conversion are the production of synthetic natural gas as a substitute gaseous fuel and synthesis gases for production of chemicals and plastics. *See* COMBUSTION.

Industrial uses. In all cases of commercial interest, gasification with steam, which is endothermic, is an important chemical reaction. The necessary heat input is typically supplied to the gasifier by combusting a portion of the coal with oxygen added along with the steam. From the industrial viewpoint, the final product is either chemical synthesis gas (CSG), medium-Btu gas (MBG), or a substitute natural gas (SNG). Heating values, compositions, and end uses for these gases are compared in the **table**.

Each of the gas types in the table has potential industrial applications. In the chemical industry, synthesis gas from coal is a potential alternative source of hydrogen and carbon monoxide. This mixture is obtained primarily from the steam reforming of natural gas, natural gas liquids, or other petroleum liquids. Fuel users in the industrial sector have studied the feasibility of using medium-Btu gas instead of natural gas or oil for fuel applications. Finally, the natural gas industry is interested in substitute natural gas, which can be distributed in existing pipeline networks. *See* NATURAL GAS.

There has also been some interest by the electric power industry in gasifying coal by using air to provide the necessary heat input. This could produce low-Btu gas (because of the nitrogen present), which can be burned in a combined-cycle power generation system. *See* ELECTRIC POWER GENERATION.

Gasification processes. In nearly all of the processes, the general process-flow diagram is the same (**Fig. 1**). Coal is prepared by crushing and drying, pretreated if necessary to prevent caking, and then gasified with a mixture of air or oxygen and steam. The resulting gas is cooled and cleaned of char fines, hydrogen sulfide, and CO_2 before entering optional processing steps to adjust its composition for the intended end use.

Thermodynamics. In discussions of the thermodynamics of coal gasification, at least one simplifying assumption is usually made, namely, that coal and coal char can be treated as pure carbon. Coal and coal char are really nonhomogeneous solids containing hydrogen, oxygen, sulfur, nitrogen, and mineral matter, but errors associated with this assumption are not likely to be significant.

The basic chemical reactions common to all coal gasification processes are coal and char reactions (1)–(3) and gaseous reactions (4) and (5). Reaction (2) is highly endothermic, requiring 32 kilocalories/mole (134 kilojoules/mole). The principal thermodynamic issue in most practical gasification processes is how to supply the heat for this reaction. Several methods have been considered, but generally

$$\text{Coal} \xrightarrow{\text{heat}} \text{gases } (CO, CO_2, H_2, CH_4) + \text{char} \quad (1)$$

$$C\text{ (char)} + H_2O \rightarrow CO + H_2 \quad \text{(endothermic)} \quad (2)$$

$$2C\text{ (char)} + {}^3/_2\, O_2 \rightarrow CO_2 + CO \quad \text{(exothermic)} \quad (3)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad \text{(mildly exothermic)} \quad (4)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \text{(exothermic)} \quad (5)$$

Coal gasification products

Product	Higher heating value*	Major constituents	Use
Synthesis gas (CSG)	250–400 Btu/SCF† (9–15 MJ/m^3)	CO, H_2	Chemical feedstock for synthesis of H_2, NH_3, methanol, hydrocarbons, and so forth
Medium–Btu gas (MBG)	300–500 Btu/SCF (11–19 MJ/m^3)	CO, H_2, CH_4	General-purpose fuel for utilities and industries
Substitute natural gas (SNG)	900–1050 Btu/SCF	CH_4	Gaseous fuel

* Based on producing water as a liquid.
†SCF = Standard cubic feet.

heat is supplied by allowing exothermic reactions (3) and (5) to occur in the same vessel as reaction (2). The degree to which one reaction or the other is used depends on the process configuration and the desired product. Reactions (4) and (5) are often carried out in downstream processing blocks in order to tailor the gas composition for particular end uses. In these arrangements it is generally not feasible to return the heat to the gasifier, as the downstream reactions are carried out at much lower temperatures. The heat input methods used in the principal commercial and developing processes are given in the process descriptions below.

Processes. The differences in coal gasification processes principally involve the method of heat input, gasifier type, and ash recovery system. First-generation (commercial) gasifiers include the Lurgi (dry bottom), Koppers-Totzek (K-T), and Winkler gasifiers.

Lurgi. The Lurgi gasifier utilizes a bed of crushed coal moving downward through the reactor with countercurrent flow of gas, and operates at pressures up to 450 lb/in.^{2} gage (3100 kilopascals). Crushed coal, screened to remove fines, is fed to the top of the gasifier through a coal lockhopper, and passes downward through the drying pyrolysis, gasification, and combustion zones. Steam and oxygen are admitted through a revolving grate at the bottom of the gasifier which also removes the ash produced. After burning a portion of the coal to provide the heat required, the hot combustion gas passes upward through the zones of the coal bed. Steam is used as a reactant to gasify the coal, and is also added to keep the temperature below the ash melting point. Although the predominant source of methane (CH_4) is devolatilization, some methane comes from coal hydrogenation, releasing heat which is transferred to the coal and minimizing the oxygen requirements. As the coal moves down through the gasifier, the temperature initially rises slowly. Further down in the gasifier, it rises dramatically as the coal approaches the combustion zone where the temperature exceeds 2200°F (1200°C). The Lurgi reactors commonly used are of the general type shown in **Fig. 2**. Because of the countercurrent flow in the gasifier, high carbon utilization and good heat recovery are obtained.

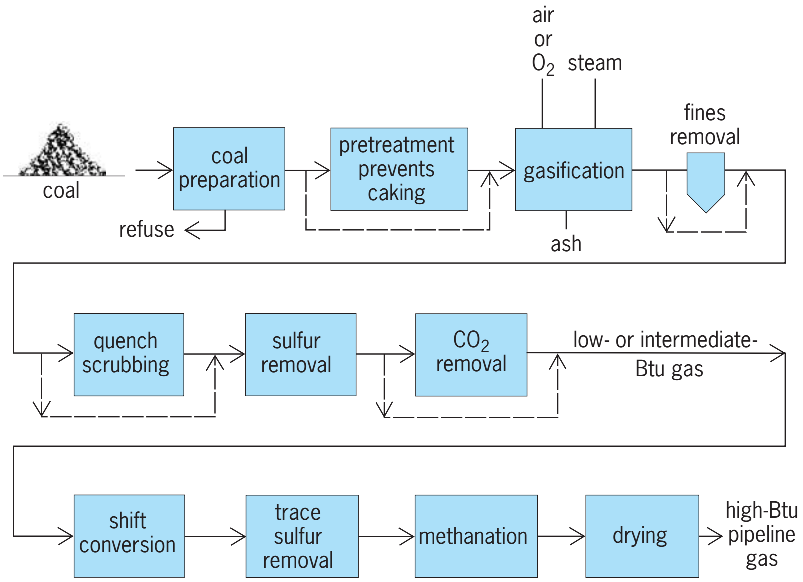

Fig. 1. Schematic representation of the processing steps in coal gasification.

The dry-bottom Lurgi process is generally applicable to subbituminous coals and lignites because the gasifiers operate best with noncaking, nonfriable coals with high reactivity and high ash melting points. The internal design and operating conditions of these reactors may be altered for coals of different caking characteristics and reactivities. Dry-bottom Lurgi gasifiers are used in the Great Plains coal gasification project in North Dakota and also in the world's largest gasification facilities at the SASOL coal-to-oil plants in South Africa.

Koppers-Totzek. The K-T gasifier is an atmospheric, entrained reactor. Dried and pulverized coal is mixed with steam and oxygen and fed to coaxial burners. The pulverized coal is gasified as it is carried in the flow of gas and as a portion of the coal is combusted. Practically every type of coal can be gasified by this technique. The operability of the process is not affected by caking properties of the coal.

The complete entrainment of the feed particles requires high gas velocities to achieve reaction times of only a few seconds; consequently the reaction temperature required is 3300–3500°F (1825–1925°C). At these temperatures, most of the carbon reacts very rapidly with oxygen and steam to produce carbon oxides, hydrogen, and molten slag. Less than 0.1% CH_4 is present in the product gas, and no tars or phenols are produced. More than 50% of the ash flows down the gasifier walls as molten slag into a

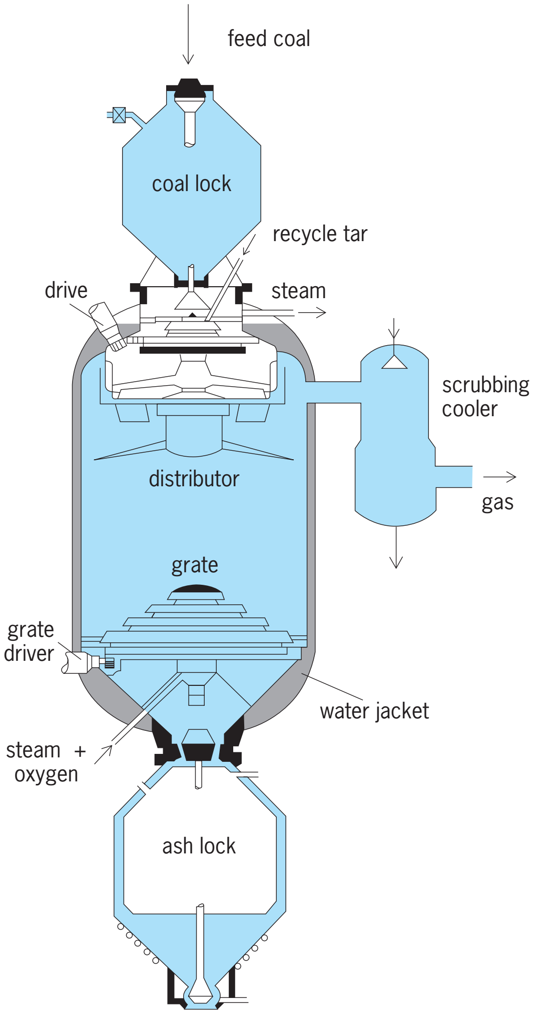

Fig. 2. Diagram of a Lurgi pressure gasifier.

slag quench tank. The rest leaves as entrained fly ash in the exit gas. The gasifier has a double-walled shell and a thin refractory lining. Water is circulated in the vessel jacket to protect the refractory. Most of the operating plants utilizing K-T gasifiers have been for the production of a H_2-rich gas for NH_3 manufacture.

Winkler. The Winkler gasifier is an atmospheric, fluidized-bed reactor that was developed in Germany in the 1920s. The vessel is cylindrical and refractory-lined, with nozzles for injecting a mixture of steam and oxygen at the bottom of the gasifier and above the top of the char bed to control fines. Crushed, dried coal is fed to the gasifier by means of a screw conveyor. The gasification temperature is controlled around 1800–2000°F (1000–1100°C) by adjusting the ratio of oxygen and steam to coal, and thus the portion of the coal being combusted. Gas is removed overhead, cooled, and dedusted. Product gas is low in CH_4 and contains no tars. Heavy char particles, which contain ash, settle to the bottom of the fluidized bed and are withdrawn from the gasifier by a screw conveyor. Most of the Winkler gasifiers that have been built are in eastern Europe and Asia.

Research and development. Most process research and development is directed toward increasing the efficiency of certain process steps, gasifying a wider range of coals or lowering plant costs. Important programs in the United States include work on partial oxidation, gasification with controlled ash agglomeration, and catalytic gasification. Major European efforts include work on the slagging gasifier and partial oxidation.

Slagging gasifier. The British Gas/Lurgi slagging gasifier is a modification of the commercial dry-bottom Lurgi design. It uses less steam and is less coal-sensitive than the dry-bottom Lurgi. These modifications are achieved by incorporating a high-temperature slagging zone at the bottom of a gasifier. Coal is screened and crushed before being introduced via lock-hoppers into the top of the reactor. As the coal moves downward through the reactor as a slowly moving bed, it passes through the drying, pyrolysis, gasification, and combustion zones. The coal ash is melted in the combustion zone and collects in a pool, from which it is tapped and quenched with water before being withdrawn from the gasifier. The oxygen and steam for the reaction are supplied through tuyeres in the bottom of the reactor. Tar, oil, and some of the coal fines produced in the crushing step can also be injected through the tuyeres and gasified. Some quantity of dusty tar can also be distributed at the top of the bed. The gas moving upward countercurrently through the moving bed of coal supplies the heat for the various gasification reactions and for drying the coal. The gas exits the reactor at approximately 1000°F (540°C), and is quenched in a scrubber to remove heavy tars and fines before being cooled in a waste heat boiler. This process is considered to be more attractive than the dry-bottom Lurgi for caking coals, such as bituminous coals of the eastern United States.

Partial oxidation. Both Texaco and Shell have pursued partial-oxidation process development. The Texaco gasifier is a pressurized (up to about 1000 $lb/in.^2$ absolute or 6800 kPa), entrained reactor. Coal is pulverized in a wet mill and slurried (50–70 wt % solids) in water. The slurry is then pumped to pressure and injected with oxygen and steam into the downflow entrained gasifier. The hot gas and slag exit the bottom of the gasifier and pass through a radiant cooler. Most of the ash is collected at the bottom of the radiant section. The gas that contains some fly ash passes through a convective cooler and a scrubber. Both the radiant and convective coolers generate high-pressure, saturated steam. An alternate design involves cooling the hot gas from the reactor by water quench. In this case, no steam is generated, but the gas produced contains sufficient water for subsequent conversion of the carbon monoxide to hydrogen.

The Shell process is similar, but utilizes a dry feed system rather than a water slurry. In this process, ground coal is metered into an entrained gasifier where it reacts with oxygen and steam.

Gasification with controlled agglomeration. Both Westinghouse and the Institute of Gas Technology have pursued gasification under conditions which result in controlled ash agglomeration. The Westinghouse gasifier is a pressurized (about 250 lb/in.^{2} absolute or 1600 kPa), fluidized-bed reactor. Coal is crushed before pressurizing via lockhoppers. The coal is injected with steam and oxygen into the fluid bed through an axial lift pipe. The higher temperature at the outlet of the lift pipe gives controlled ash agglomeration in the fluid bed. Larger particles of ash concentrate at the bottom of the gasifier and are removed and rejected. Steam and recycled gas are also injected in the lower portion of the reactor in order to fluidize the bed and control ash particle size. The resulting gas product is removed overhead, dedusted by cyclones, and cooled in waste heat boilers. The cooled gas is scrubbed to remove fines, and a portion is recycled to provide fluidization gas.

Catalytic coal gasification. The Exxon catalytic coal gasification process is intended for substitute natural gas production, and differs significantly from other gasification methods in that it uses a potassium catalyst to accomplish steam gasification [reaction (2)] and methanation [reaction (5)] in the same vessel. The catalyst enables the gasifier to operate at mild process conditions of 1300°F (700°C) and 500 lb/in.^{2} gage (3550 kPa). A major advantage of this "one-step" approach is that the overall reaction is almost thermally neutral. The gasification heat requirement is essentially supplied by the methanation heat release. Therefore, the catalytic coal gasifier does not require a large heat input by means of oxygen or other methods. The gasifier off-gas is treated by commercially available acid-gas–removal technology, and the methane product is cryogenically separated, with H_2 and CO recycled to the gasifier. The catalyst-char-ash material which is removed from the gasifier is washed countercurrently with water to recover most of the potassium catalyst for reuse. *See* HETEROGENEOUS CATALYSIS.

Underground gasification. Only about one-fifth of the total coal in the ground can be recovered by mining. The remainder is either too deep or in seams that are too thin to be mined. Long-term underground gasification is a promising possibility for utilizing this unminable coal. This process involves drilling wells into coal deposits, preparing a rubbled bed of coal through which gas can flow, and initiating gasification in the bed by using steam and air or oxygen. Such underground field tests have been conducted in the United States, but problems with underground gasification include process control, land subsidence, and ground-water pollution. *See* COAL MINING.

Several organizations have been active in this field, emphasizing work on the nature and direction of subsurface fracture systems, the means to calculate fluid movement underground, and environmental impacts. Directional drilling techniques and fracturing of the underground formations with chemical explosives have been studied. *See* COAL. W. R. Epperly

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Coal liquefaction

The conversion of most types of coal (with the exception of anthracite) primarily to petroleumlike hydrocarbon liquids which can be substituted for the standard liquid or solid fuels used to meet transportation, residential, commercial, and industrial fuel requirements. Coal liquids contain less sulfur, nitrogen, and ash, and are easier to transport and use than the parent (solid) coal. These liquids are suitable refinery feedstocks for the manufacture of gasoline, heating oil, diesel fuel, jet fuel, turbine fuel, fuel oil, and petrochemicals.

Liquefying coal involves increasing the ratio of hydrogen to carbon atoms (H:C) considerably—from about 0.8 to 1.5–2.0. This can be done in two ways: (1) indirectly, by first gasifying the coal to produce a synthesis gas (carbon monoxide and hydrogen) and then reconstructing liquid molecules by Fischer-Tropsch or methanol synthesis reactions; or (2) directly, by chemically adding hydrogen to the coal matrix under conditions of high pressure and temperature. In either case (with the exception of methanol synthesis), a wide range of products is obtained, from light hydrocarbon gases to heavy liquids. Even waxes, which are solid at room temperature, may be produced, depending on the specific conditions employed. **Table 1** lists potential uses for coal liquefaction products and indicates the additional processing which would likely be required.

Indirect liquefaction. Indirect coal liquefaction consists of three important steps: first, the coal is gasified; second, the composition of the resulting gas is adjusted (shifted, if necessary, to increase H_2 content; and H_2S and CO_2 are removed); and third, the CO and H_2 in the resulting synthesis gas are catalytically reacted to form the liquids. Commercial processes for catalytically reacting CO and H_2 to form the indirect coal liquids include Fischer-Tropsch synthesis and methanol synthesis. In addition, a Mobil process for conversion of methanol to gasoline is expected to be an important commercial operation.

Fischer-Tropsch synthesis. The synthesis processes based on the Fischer-Tropsch chemistry are represented by reaction (1). This reaction represents a

$$2nH_2 + nCO \rightarrow (\text{—}CH_2\text{—})_n + nH_2O \qquad (1)$$

polymeric addition of methylene (—CH_2—) groups to form a distribution of linear paraffins. In practice, a broad range of molecular weights is produced, and the product includes branched, olefinic, and oxygenated compounds, depending on reactor type,

TABLE 1. Potential uses for coal liquefaction products

Product	Commercial uses	Additional processing required
Light hydrocarbons		
Methane and ethane	Pipeline gas	None
C_3–C_4 hydrocarbons	Liquefied petroleum gas (LPG)	None
C_2–C_4 hydrocarbons	Ethylene and propylene manufacture	Steam cracking
Naphtha		
C_4–160°F (71°C) naphtha	Motor gasoline	Hydrotreating
160–350°F (71–180°C) naphtha	Motor gasoline	Hydrotreating and reforming
	Chemicals (benzene, toluene, xylene)	Extraction
350–430°F (180–220°C) naphtha	Motor gasoline	Hydrotreating
Middle distillate	Turbine fuel	Direct use or hydrotreating
350–650°F (180–340°C) or 430–650°F (220–340°C)	Low- or medium-speed diesel fuel	Direct use
	No. 6 fuel oil blendstock	Direct use
	Home heating oil	Direct use (with burner adjustment) or hydrotreating
	Auto diesel blendstock	Moderate hydrotreating
	Jet, auto diesel, No. 2 fuel oil	Severe hydrotreating or hydroconversion
Heavy distillate		
650–1000°F (340–540°C) vacuum	Fuel oil blendstock	Direct use or hydrotreating
Gas oil	Fluid catalytic cracking or hydroconversion feed	Hydrotreating
Other products		
Solvent refined coal (solid)	Boiler fuel	Direct use
Methanol	Motor fuel, distillate fuel	Direct use (with special distribution system)
Fischer-Tropsch liquids	Gasoline, diesel oil, jet fuel, wax	Hydrotreating, reforming, isomerization, polymerization

operating conditions, and catalyst type. The average molecular weight of the product mixture can be adjusted to some extent by the selection of process conditions.

Two synthesis processes (ARGE and Synthol) are used in the commercial coal liquefaction plants of the South African Coal, Oil, and Gas Company (Sasol) in the Republic of South Africa. The ARGE process utilizes a fixed-bed reactor and a precipitated-iron catalyst to produce a high-boiling, linear paraffin product, including a range of waxes. The Synthol process uses an entrained-bed reactor and a fused-iron catalyst to produce a somewhat lower-boiling hydrocarbon product which contains more isoparaffins and olefins.

The Sasol I commercial coal liquefaction plant started operations in 1955 and utilizes both the ARGE fixed-bed and the Synthol entrained-bed processes. Sasol II operation was initiated in 1980, when a site was also prepared for Sasol III. Both Sasol II and Sasol III are modified and enlarged versions of Sasol I. Each is designed to include seven of the Synthol entrained-bed reactors. Production of nonfuel products will be minimized in Sasol III.

Modified process techniques and conditions can have a significant impact on the Fischer-Tropsch product distribution. New catalyst formulations can improve activity and tailor the product distribution to meet fuel and chemical product demands. Engineering research to define better reactor designs and optimum operating conditions for more economic processes have also been undertaken. *See* FISCHER-TROPSCH PROCESS.

Methanol synthesis. The methanol synthesis processes are based on the chemistry represented by reactions (2) and (3).

$$CO + 2H_2 \rightarrow CH_3OH \qquad (2)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (3)$$

Commercial processes use copper- and zinc-based catalysts and fixed-bed reactors operating at high pressure (100 atm or 10 megapascals) and low conversion per pass with high recycle ratios. Crude methanol can be utilized in three ways: as a neat fuel in fleet applications, as a gasoline blendstock, or as a feed to the Mobil methanol-to-gasoline process. *See* METHANOL.

Mobil methanol-to-gasoline process. In the Mobil process, a complex sequence of reactions occurs over a zeolite catalyst. Methanol is the first dehydrated to an equilibrium mixture of dimethyl ether, methanol, and water. This mixture is then fed to catalytic reactors where the remaining methanol is dehydrated to dimethyl ether, which reacts to form olefins that polymerize to form aromatic gasoline components. A fixed-bed version of this process is commercially available and has been applied in a New Zealand natural gas-to-gasoline project. A fluid-bed version of the methanol-to-gasoline process is used in a pilot plant in Germany, which started up in late 1982. *See* ZEOLITE.

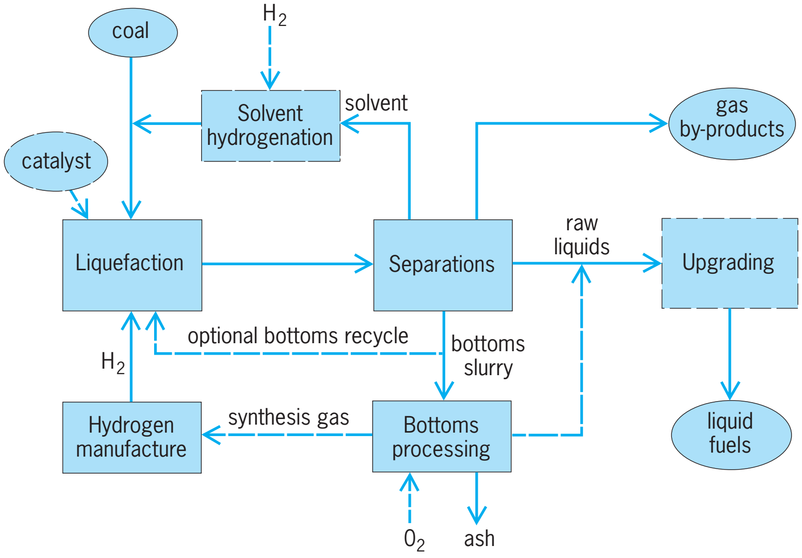
TABLE 2. Leading direct coal liquefaction technologies*

	EDS	H-Coal	SCR II	Modified Bergius-Pier
Demonstration plant	250 tons/day (230 Mg/day), Baytown, Texas	200 tons/day (180 Mg/day), Catlettsburg, Kentucky	35 tons/day (32 Mg/day), Fort Lewis, Washington	220 tons/day (200 Mg/day), Bottrop, Germany
Recycle solvent	Hydrogenated distillate	Distillate	Product slurry	Distillate
Pressure, atm (MPa)	140–170 (14–17)	210 (21)	140 (14)	300 (30)
Bottoms recycle	Optional	No	Essential	No
Catalyst	Ni-Mo in solvent hydrotreater (none in liquefaction)	Co-Mo (in ebullating bed reactor)	None (relies on catalytic activity in recycled coal ash)	$FeSO_4$ as red mud
Types of coal	Bituminous Subbituminous Lignite	Bituminous Subbituminous	Bituminous	Bituminous

*Mg = megagrams.

Direct liquefaction. Direct liquefaction or hydrogenation of coal was developed in Germany in the 1920s by F. Bergius, who received the Nobel Prize in chemistry for his work. This technology was later modified by M. Pier and commercially proved during World War II. However, this technology operated at extremely high pressure (almost 700 atm or 70 MPa) and in small reactors (3-ft or 1-m diameter) and was too costly to be economically justified in peacetime.

Since the war, interest in direct coal liquefaction has periodically been revived, generally in response to projected shortages of petroleum, but no commercial plants have been built. However, four second-generation liquefaction technologies have been demonstrated in large pilot plants, and these are compared in **Table 2**. These technologies were an outgrowth of the Bergius-Pier process, but operate at much lower pressure (140–300 atm or 14–30 MPa). Other technologies have also benefited from major advances in reactor design since the 1940s, which will allow much larger (and therefore more economical) plants to be built. However, notwithstanding the technical improvements which have been made, the basic processing steps in coal liquefaction (see **illus.**) have not changed conceptually.



Processing steps in direct coal liquefaction. Broken lines represent optional steps or flow streams.

Coal is first crushed and slurried in a process-derived solvent and then heated and pumped to typical reaction conditions, in the range of 800–930°F (425–500°C) and 140–300 atm (14–30 MPa). Depending on the process, a catalyst may be added to the liquefaction step, or the solvent may be hydrogenated to improve hydrogen transfer to the coal. As the coal is heated to reaction temperatures and held there for 40–80 min nominal residence time, thermal cracking (thermolysis) occurs. At liquefaction temperature, chemical bonds are broken, that is, cracked, generating free-radical fragments which can participate in secondary reactions—combining with hydrogen to produce stable liquids, reacting further to form lighter liquids, or polymerizing to form high-molecular weight, high-boiling-point bottoms. Control of these secondary reactions is important in achieving high conversions and good selectivity to distillable liquid products. During liquefaction, heteroatoms in the coal (oxygen, nitrogen, and sulfur) are also liberated, principally as carbon oxides, water, ammonia, and hydrogen sulfide.

After liquefaction, products must be separated from bottoms (ash, heavy coal liquids, and unconverted coal) and solvent recovered. The most common technique for separation is distillation, although hydroclones, which separate by centrifugal force, have been used in Hydrocarbon Research's H-Coal and extraction in Gulf solvent-refined coal (SRC) for removal of ash and coal residues. Gulf's SRC II process, which evolved from SRC, recycles bottoms to increase the ash level in the liquifaction reactor and improve conversion. The EDS process has operated with and without bottoms recycling, and employs recycling to increase conversion and produce a lower-molecular-weight product slate. Product slate refers to the end products that are actually sent to the market from the plant. It has been shown that the bottoms contain high-boiling asphaltenes and preasphaltenes which can be readily converted to lighter products through recycling.

The net bottoms product is sent to a bottoms processing step, where the carbon is utilized and coal ash is separated. Carbon utilization can involve recovery of additional liquids by coking or extraction, partial oxidation to produce plant fuel or hydrogen, or combustion to provide plant heat. Hydrogen generation is frequently the preferred bottoms-processing step. In this case, bottoms would be sent to a partial oxidation unit and gasified with oxygen to produce a synthesis gas for hydrogen production. Alternatively, hydrogen could be produced by partial oxidation of coal or by conventional steam reforming of light gases as in present-day petroleum refineries and chemical plants. *See* COAL GASIFICATION; PETROLEUM PROCESSING AND REFINING; SOLVENT EXTRACTION.

Upgrading of coal liquids. In most cases, coal liquids require upgrading prior to use. The type and severity of upgrading depends on the initial characteristics of the liquids and the desired product properties (Table 1). In general, however, the upgrading processes are similar to those employed for petroleum liquids. Hydrotreating (mild hydrogenation) is commonly selected for removal of nitrogen, sulfur, or oxygen in coal liquids. Direct coal liquids are rich in cycloparaffins and aromatics. In the gasoline fraction, the cycloparaffins can be dehydrogenated by catalytic reforming to aromatics, which have a high octane rating. In the middle distillate fraction, the aromatics can be hydrogenated to cycloparaffins, which have improved performance in diesel and jet engines. In addition, catalytic cracking or hydroconversion of heavy distillates can be used to increase the yield of gasoline and middle distillate.

Indirect coal liquids are primarily paraffins and olefins. Polymerization of the propane-butane fraction can be used to increase the yield of gasoline. Reforming of the gasoline fraction increases octane rating by producing aromatics via cyclization of paraffins and subsequent dehydrogenation. Isomerization of linear paraffins also increases octane. Heavy, waxy streams can be cracked to gasoline and middle distillate. *See* HYDROCRACKING.

The severity of product upgrading typically decreases with increasing severity of direct liquefaction. The reason for this lies in the basic chemistry of converting high-carbon coal (H:C atomic ratio of about 0.8) into naphtha and light distillate (H:C of 1.2–1.9). Since the overall reaction involves hydrogen addition, it can be seen that a low level of hydrogenation in the liquefaction section would yield a high percentage of high-boiling components which require extensive hydrotreating to produce salable products. On the other hand, a liquefaction process of relatively high severity would yield liquids which require less extensive treatment to achieve the same salable products. As a result, yield comparisons of different coal liquefaction processes are usually closer on a finished product basis than on an intermediate product basis. It is generally agreed that a commercial coal liquefaction plant will produce approximately 3 barrels (0.5 m^3) of liquid product for every ton (0.9 metric ton) of dry, ash-free coal feed.

Continuing research. Research on improving coal liquefaction processes is concentrated in the general areas of staged liquefaction and catalysis. The principal goal of this work is to increase the yield of distillate products while reducing the amount of gas produced. In staged processes, the conditions in each stage are selected to optimize production of the desired liquid products. In catalytic processes, a catalyst which promotes formation of the desired molecular species is selected. Most emerging technologies incorporate elements of both staging and catalysis to obtain the advantages of each approach.

Staged liquefaction processes utilize two or more distinct stages to promote coal conversion or to improve the product slate. Though processes with many stages are theoretically possible, all of the staged liquefaction concepts use only two stages. Their essential features include a coal dissolver section (first stage), a deashing section to remove solids, and a catalytic hydroconversion section (second stage) to upgrade the heavy liquids. The dissolver section could range between a plug-flow reactor and a short-contact-time preheater. Deashing may be accomplished with hydroclones or by using proprietary antisolvent or critical-solvent deashing techniques. The hydroconversion section is typically operated at a lower temperature than the dissolver section (to prevent thermal cracking of liquids into gases) and contains catalyst in either a fixed bed, expanded bed, or ebullating bed.

In addition to these process differences, several variations in processing sequence are possible improvements to the two-stage technology. For example, the degree to which process streams from the hydroconversion section are recycled to the dissolver section may be adjusted to yield an integrated, partially integrated, or nonintegrated operation. Another option is placement of the second stage; since some hydroconversion processes are less sensitive to solids concentration, it may be possible to locate the deashing section downstream of both liquefaction stages. Finally, within the framework of any given processing sequence, the number of recycle streams, the cut points of these streams, and the severity of hydrotreating can also be changed.

The major two-stage liquefaction processes employ catalysts for additional conversion of heavy liquids. The two-stage process of the Electric Power Research Institute and the U.S. Department of Energy and the integrated two-stage liquefaction (ITSL) process of Lummus, both have high-temperature, plug-flow first stages and solvent-extraction deashing followed by lower-temperature, catalytic hydroconversion. In addition, ITSL uses a short-contact time preheater. The Chevron Coal Liquefaction process uses the same process sections but employs solids separation after both of the liquefaction stages. Overall, direct liquefaction is a fertile area for continuing research. *See* CATALYSIS; COAL; HETEROGENEOUS CATALYSIS.

W. R. Epperly

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Coal mining

The technical and mechanical activities involved in removing coal from the earth and preparing it for market. Coal mining in the industrialized countries is characterized by the integration of a number of complex systems into a production methodology that varies for surface versus underground mining. *See* COAL.

The basic systems of the production methodology are the following. (1) Extraction systems: the methods and techniques used to break out or "win" the coal. (2) Materials-handling systems: the transport of coal and waste products away from the active production area, and the transport of the necessary materials, equipment, supplies, and workers to service the extraction system. (3) Ventilation: the development and operation of an air distribution system to provide the quantity, quality, and velocity of air where and when needed, to meet health and safety requirements. (4) Ground control: the control of the behavior of underground and surface openings developed by the extraction of coal. (5) Reclamation: the restoration of the mined area to its approximate original state or to an approved state.

To properly plan, design, and engineer a production system, knowledge of the geology of the deposit and the chemical and physical properties of the coal must be assembled and assessed. Basic information on the geology of the deposit is obtained from surface prospecting and mapping, and borehole drilling. This information is used to determine the size and shape of the coal area, the geologic column above and below all minable seams, the continuity and persistence of geologic features throughout the deposit, the presence of water or methane gas, and other special conditions. Proximate chemical analyses are made to determine coal characteristics, which affect its utilization. Tests are made to determine the cleaning, grinding, and handling properties of the coal. Ultimate chemical analyses are made to determine the fundamental chemical constituents of the coal. Maps are drawn to summarize this information, and are used for scheduling and sequencing production. *See* ANALYTICAL CHEMISTRY; ENGINEERING GEOLOGY; PROSPECTING; ROCK MECHANICS; SOIL MECHANICS; SPECTROSCOPY.

Surface Mining

When a coal seam lies sufficiently close to the ground surface, a surface mining method may be employed. The geographic location and geologic column—in particular, the ratio of the thickness and quality of the overburden and interseam waste to be removed, to the thickness and quality of the coal to be produced—are the initial considerations. Site conditions, which affect the production method,

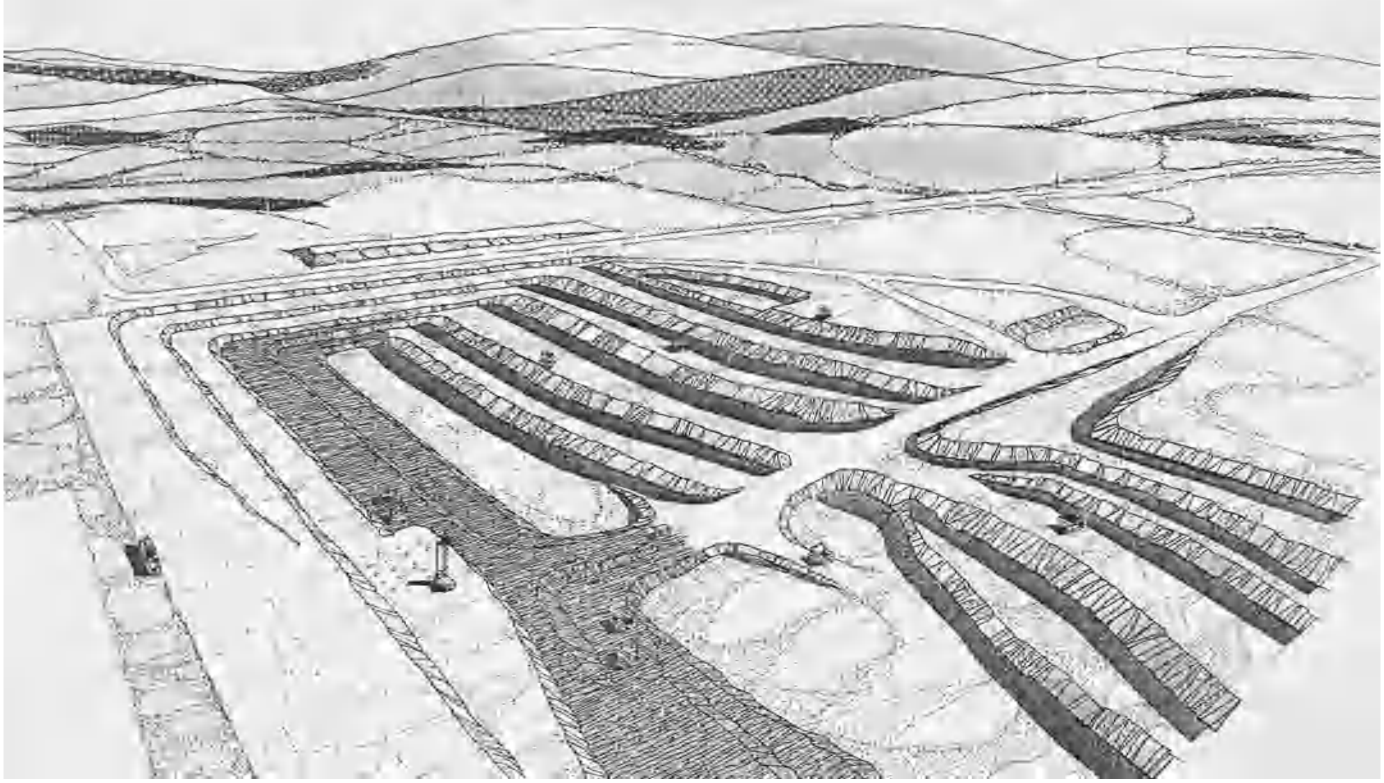

Fig. 1. Diagram of a terrace pit coal mine, showing terrace pit stripping and reclamation. (*After U.S. Department of Energy, The Development of Optimal Terrace Pit Coal Mine Systems, DOE Rep. FE/10023-1, January 1971*)

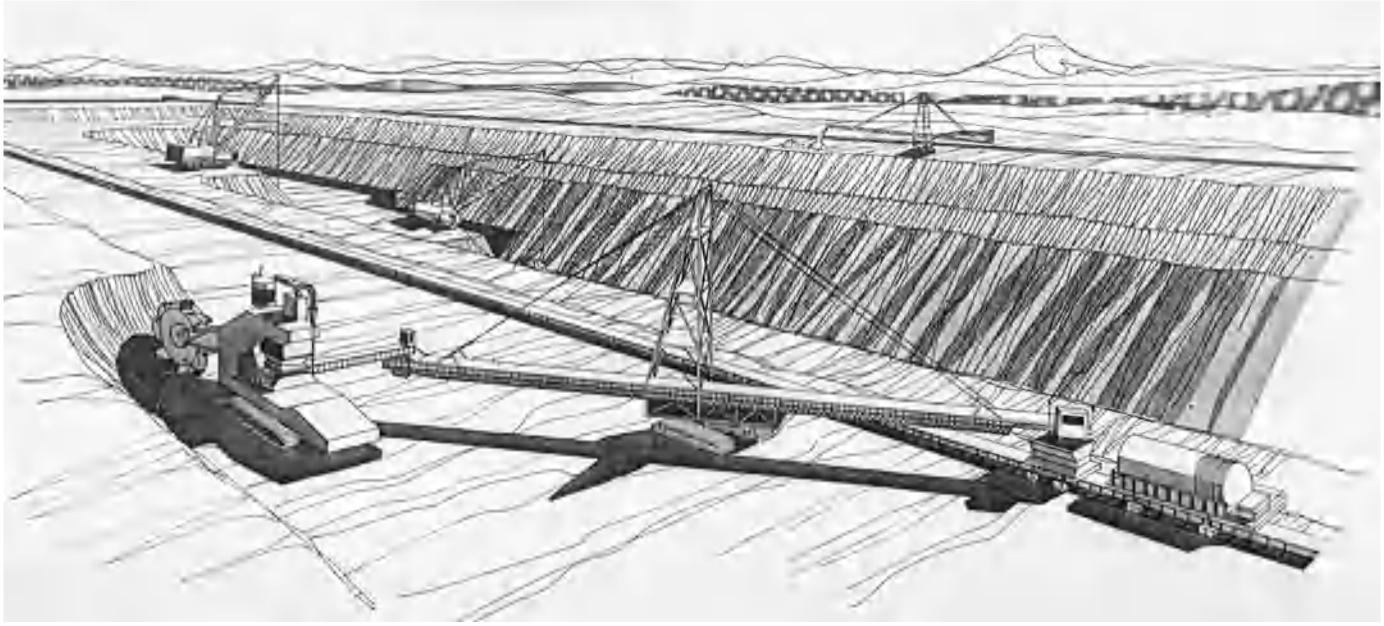

Fig. 2. Diagram of a strip coal mine, showing bucket-wheel excavator prestripping for draglines. (*After U.S. Department of Energy, The Development of Optimal Terrace Pit Coal Mine Systems, DOE Rep. FE/10023-1, January 1971*)

include types of terrain, temperature range, altitude, and rainfall and snowfall. Overburden and interseam waste characteristics affecting the production methods are material weight, stickiness, and swell; ability to form a stable highwall and spoil pile; ratio of rock and other material requiring blasting, to soil in the overburden; and need for special handling of waste materials for reclamation purposes. The presence of thicker and good-quality coal that commands higher prices can justify the removal of thick overburden.

Surface coal mines involve area mining or modified open pit mining, contour mining and mountaintop removal, and auger mining. Removal of overburden is called stripping, and hence the term "strip mining" is often applied to surface coal operations (**Figs. 1** and **2**). Area mining is applicable in relatively flat to gently undulating terrain where coal seams are of considerable area and may be at various dips. Contour mining and mountaintop removal are used in hilly and mountainous country and can be modified to handle coal seams at any dip. Auger mining follows the other surface methods when overburden removal becomes uneconomic, and is generally limited to more or less horizontal coal seams. *See* SURFACE MINING.

Area or modified open pit. In a typical area mine the layout is roughly rectangular with adjustments made to fit the boundaries of the property. The length of the pit varies depending on the rate of planned production, but may range to about 2 mi (3 km) or more. Extraction operations involve topsoil and subsoil removal, overburden removal, and coal loading. Drilling and blasting or ripping of the overburden and coal may be required.

The equipment used in topsoil and subsoil removal and in stripping overburden is selected based on the characteristics of the soil and rock to be removed. In soft digging, bulldozers, wheel loaders, and elevating scrapers may be used to excavate the soil and overburden and to load it into trucks (**Fig. 3**). In many parts of Europe, where the geologic column consists of soft-digging materials, bucket wheel excavators, used singly and in tandem, excavate and convey the soil and overburden to storage areas. Pan scrapers are found to be useful both in soil and overburden removal and in reclamation. When rock is present, drilling and blasting or ripping are required to loosen and break out the overburden. Draglines (**Fig. 4**) and power shovels (**Fig. 5**) are used to dig the harder and more consolidated materials.

Since outcrops rarely occur where area surface mining is practiced, mining begins with an opening or box cut, with the spoil from the cut being

Fig. 3. Front-end loader.

Fig. 4. Small dragline.

cast to one side or removed to a stockpile, and the uncovered coal is mined. Then an adjoining parallel cut of overburden is removed and deposited in the previous excavation, and the exposed coal is mined. Mining proceeds in this fashion until an economic, technologic, or property limit is reached.

The box cut is usually taken where the coal has the least overburden and in an orientation which allows the pit to advance toward coal with the greatest overburden. In a single-bench operation the box cut is designed to allow for a pit floor width which will accommodate the in-pit equipment and the initial overburden spoil used in backfilling, which must lie at a safe angle of repose. In a dragline or stripping shovel operation the toe of the spoil is adjacent to the coal seam in order to minimize the required operating radius for the equipment. Where multiple benches or terraces are developed for overburden and coal removal, the box cut width varies at each bench or terrace level.

In a single-bench, simple sidecasting dragline operation, there is no rehandling of material, and it is therefore a widely practiced and economical method for overburden excavation. Coal is mined by loading shovels or wheel loaders and is hauled by truck. The dragline may be operated so as to make a rough separation between soil and overburden and hence aid in reclamation of the mined area. Large power shovels are also used for stripping overburden in this type of operation.

Draglines have been used exclusively since the 1960s. The superiority of the dragline (**Fig. 6**) is its long reach and dumping, which permits thicker overburden to be mined and the spoil to be placed at a greater distance and in higher piles; and the large capacity of its buckets, which determines the productivity of the machine.

Multiple bench or terraced pits may be developed by using different combinations of equipment, but a shovel-truck combination or a shovel-truck-dragline combination is usually high on the list of feasible options. In a typical shovel-truck combination, overburden is removed with power shovels and loaded into trucks. A bulldozer works with each power shovel for cleanup, leveling, and bench preparation. The overburden benches are about 50 ft (15 m) in height and are mined in 200-ft (60-m) pushbacks. Shovels advance the pushback on the top level first and then proceed to the lower benches. Trucks haul the overburden up ramps on the highwall side of the

Fig. 5. Power shovel loading coal trucks.

Fig. 6. Dragline working from the surface of the ground. (*Morrison Knudsen Co.*)

pit, then around the pit on the spoil side, advancing the spoil dump at the same rate as the highwall. Spoil from the box cut is stockpiled for later use in reclamation.

Overburden drilling is done by rotary drills with bits of 6.78–12.12-in. (17.5–31.8-cm) diameter. Coal drilling is done with truck-mounted rotary drills using 6-in.-diameter (15-cm) bits. Blastholes are loaded with ANFO (ammonium nitrate–fuel oil) explosive, usually from bulk mixing trucks, which mix and meter the amount of explosive for each hole. After blasting, coal is loaded, with either power shovels or wheel loaders, onto bottom dump trucks of 100–150-ton (90–135-metric ton) capacity which are favored for coal hauling because of their low body height. Coal benches are about 30 ft (9 m) high and 200 ft (60 m) wide, and are advanced in 100-ft (30-m) pushbacks. *See* DRILLING AND BORING, GEOTECHNICAL.

A dragline may be added to the shovel-truck combination after the box cut is excavated and backfilling with spoil has begun. A bench is excavated for the dragline at the appropriate level above the seam. Operating from this bench, the dragline excavates the overburden above the seam and sidecasts it into the pit floor area from which coal has been extracted.

A number of variations on the shovel-truck combination are possible. For example, an around-the-pit conveyor transport system may be used to reduce or eliminate truck haulage. Excavated overburden may be loaded directly or may be transported by truck to a hopper equipped with a fixed grizzly screen to reject oversize material. From the hopper, the spoil is fed to a shiftable conveyor system, which carries the spoil out of the pit to a stacker-spreader. This in turn spreads the material along a spoil bench in the pit. The conveyor system is shifted forward in 100-ft (30-m) increments as the benches advance.

Bucket wheel excavators are useful in certain mining conditions. Essentially a bucket wheel excavator consists of (1) a large wheel with toothed buckets pinned to the circumference and mounted on the end of a maneuverable boom; (2) a discharge boom supporting a belt conveyor; (3) a revolving frame mounted on crawler supports; and (4) electric motors and control devices. Material is excavated by moving the rotating wheel into the overburden or coal and swinging it on the maneuverable boom through an arc. Material is cut, chopped, or scraped into the buckets, and as the wheel continues to rotate, the buckets are emptied. The excavated material is transported away from the wheel by a system of conveyors, and finally moves up the discharge conveyor to the discharge point. The conveyor system may consist of an around-the-pit conveyor incorporating a shiftable conveyor section. The shiftable conveyor must be periodically moved to keep it within the discharge range of the bucket wheel excavator. A mobile transfer conveyor may be added to the system to improve the continuity of material flow. In all cases, however, material flow is more or less continuous.

Bucket wheel excavators are capable of high production under favorable conditions with outputs in the range of 1600–12,000 yd^3 (1200–9200 m^3) per hour. However, they have difficulty in handling hard, consolidated material even when blasted; alternating the hard and soft formations slows production. Also, large boulders, buried vegetation, and sticky materials clog the buckets, transfer points, and machinery. However, bucket wheel excavators are widely used in Europe for the mining of brown coals. The rock strata, consisting of unconsolidated earth, soft shale, and siltstone overlying thick beds of brown coal, is ideally suited to the capabilities of bucket wheel excavators. The brown coals extend over large areas and may be found in thicknesses of 600 ft (180 m) or more, interbedded with sand and clay zones. Area pit dimensions may be a number of miles, and coal and spoil transport to delivery points is by belt conveyor or rail.

Bucket wheel excavators have found limited application in the United States. *See* OPEN PIT MINING.

Contour mining and mountaintop removal. This method of surface mining is used in the hilly and mountainous areas of the Appalachians, where coal seams are numerous and are generally flat-lying or subhorizontal, outcropping on the steeply sloping valleys and ridges. The geologic column consists of shales, sandstones, and limestones of varying thickness and hardness.

Now illegal, conventional contour mining started with an initial cut along the outcrop line on the mountainside. The overburden was indiscriminately cast over the side of the hill and the coal extracted. This procedure was continued into the mountainside and along the outcrop line until an economic, technical, or property limit was reached. The resulting

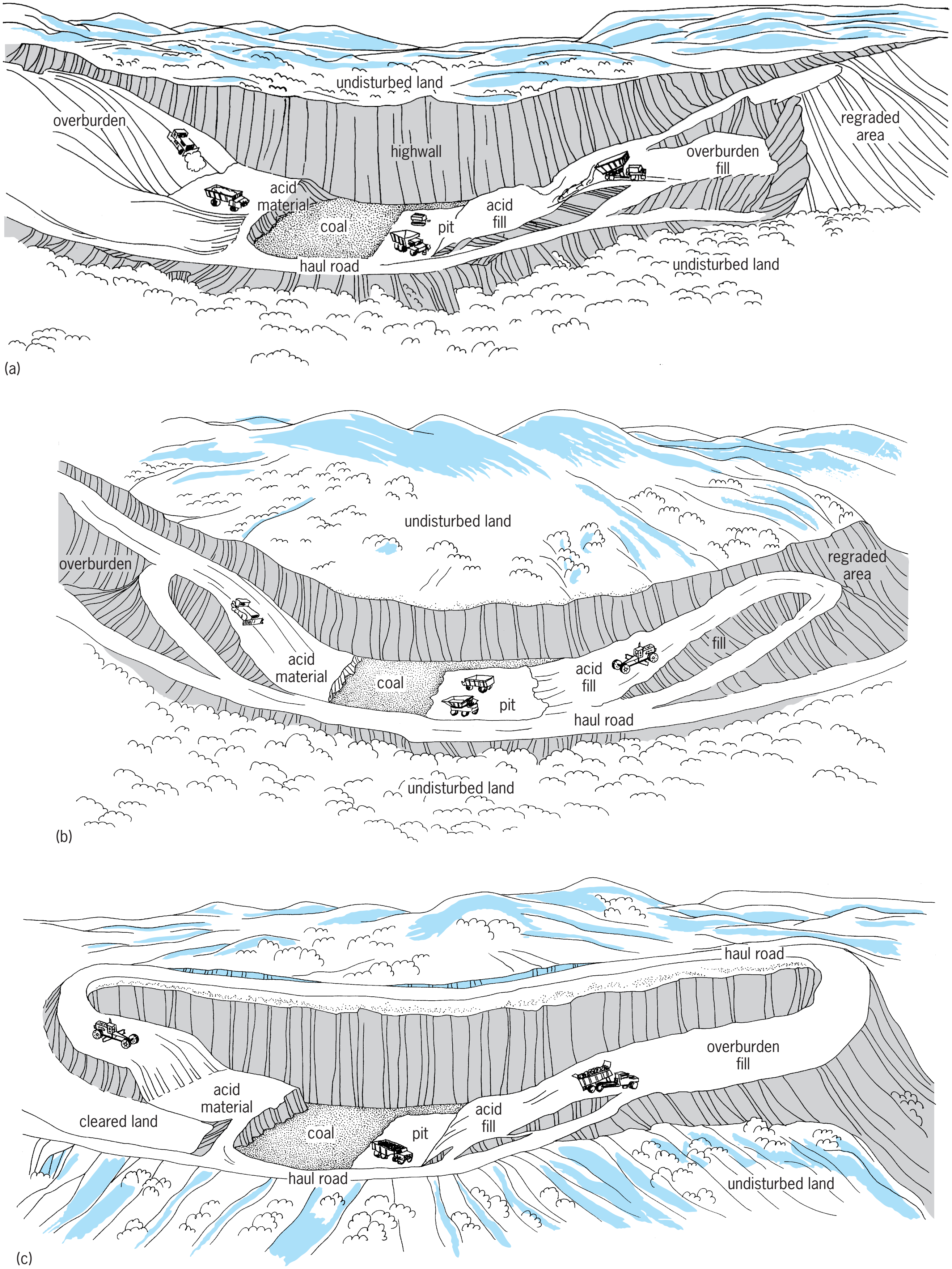

Fig. 7. **Typical haulback or lateral movement methods. (*a*) Truck. (*b*) Scraper. (*c*) Truck and scraper. (*After R. Stefanko, Coal Mining Technology, Theory and Practice, Society of Mining Engineers, AIME, 1983*)**

excavation left a collar around the mountain consisting of a highwall, bench, and castover spoil bank.

The haulback method of contour mining is environmentally sound because it eliminates the casting-over of spoil and provides for concurrent reclamation (**Fig. 7**). The initial cut is made into the mountainside to the highwall limit, and the excavated overburden is hauled to a prepared storage area. The initial cut serves the same purpose as the box cut in area mining. Mining proceeds along the outcrop line, with overburden, subsoil, and topsoil being trucked and placed as coal is removed. The method leads to minimum disturbance of the land and allows for contemporaneous reclamation.

In the haulback method the layout of haul roads and the design and construction of the spoil storage area are critical. Haul roads are designed and situated so as to assist in the control of water flow from the pit and the spillage of spoil on the downslope. Spoil storage areas are generally located in hollow valleys or low areas, and provisions must be made for prevention of contamination of streams by the spoil material and for stability of the material.

The equipment used in the haulback method is small in comparison to that found in an area mine. Wheel loaders, trucks, dozers, and scrapers are used in various combinations, and sometimes power shovels are employed. Drilling and blasting are done with rotary rigs and ANFO. Overburden is drilled and blasted, then wheel-loaded into trucks for haulage to the mined-out pit. Subsoil and topsoil that have been removed by dozers are then placed on top of the overburden, and the spoil materials are graded, seeded, and revegetated.

Mountaintop removal might be considered as an extension of area mining techniques to the mountainous and hilly terrains. A box cut is made across the ridge or mountain, and the spoil from this cut is placed in hollow or valley spoil-storage areas. The pit is advanced from the box cut by excavating parallel slices, with the spoil from the new cut being placed in the adjacent excavated cut. If multiple seams are to be extracted, a bench or terrace pit is developed. The equipment is similar to that in contour mining. The result of mountaintop removal is the transformation of a rugged topography into more level land, but in the process total coal recovery is obtained. Future use of this method will depend upon its perceived advantages in comparison with other techniques.

Auger mining. This method consists of boring large-diameter holes as far as possible into more or less horizontal coal beds, with hole diameter and spacing depending on seam thickness and geologic conditions. The level bench left from a conventional contour mine provides an ideal platform for equipment operation; otherwise a bench must be developed along the coal outcrop line. The auger consists of a cutting head and a set of twisted flights, resembling a carpenter's wood bit or drill. It can be extended by additional flight sections: the drive unit is uncoupled and withdrawn, allowing another flight to be lowered into place for making another advance. As boring proceeds, the coal is moved along the flights and discharged onto an elevating conveyor and then into trucks. Auger mining is attractive because it recovers coal from the highwall side of the contour mine that might otherwise be lost,

Fig. 8. Highwall miner. (*Superior Highwall Miners*)

and it does this with minimal capital and labor cost. Reclamation and environmental problems can significantly affect the cost of auger mining.

A variation in auger mining, called highwall mining, is a system that can be adapted for varying coal seam thickness (**Fig. 8**). Instead of the typical auger cutting head, a continuous miner or a similar arrangement cuts the coal and loads it onto a conveyor. The mined coal is loaded directly on a truck behind the highwall miner, much the same as in the auger mining system.

Future trends. Surface mining has steadily increased its share of the United States market, and this trend is expected to continue into the foreseeable future. The fundamental extraction and materials-handling systems that have evolved present a range of methods that appear capable of coping with future mining problems. Coal lying under deeper and more difficult geologic columns may require some modification in extraction techniques and methods, but it does not appear that a new generation of large equipment needs to be developed. Emphasis will be placed on better planning and managing of the existing methodologies and automation of cyclic operations, where feasible, to obtain highly efficient mines. Moreover, the development of highly productive and efficient underground mines will provide an economic limit to surface mines. *See* LAND RECLAMATION.

Underground Mining

When a coal seam does not lie close to the surface, it must be extracted by underground methods. The methods may be classified as room-and-pillar, longwall, and others. In each method, modifications to the basic techniques are needed to cope with varying geologic conditions and seam factors. Irregular seam thickness, steep dips, changing rock quality, seam partings, and other factors have a marked influence on the mine geometry and equipment specifications. Seams dipping between 0 and 10° and with regular seam thickness are assumed in the following discussion of room-and-pillar and longwall mining.

Mine development. In developing a particular extraction system, development openings and production openings must be driven. Development openings provide the primary access to various parts of the coal deposit and are called mains. In room-and-pillar mining, the production openings are the rooms driven in the panel and the extraction cuts made during pillar retrieval. In longwall mining, the production openings are the longwall faces. In general, the term "development" includes all openings and other work which precedes production.

Main access to a horizontal or near-horizontal coal seam is usually by drift entry when the coal seam outcrops on a mountainside; otherwise, slope and shaft entries are used. Slopes are preferred over shafts when the seam is not too deep because conveyor belt haulage can be used. In addition, mining machinery can usually be brought underground with less disassembling. From the foot of these access openings, a set of parallel main entries (usually 7–10 individual headings) are driven, and when these have advanced 3000–4000 ft (915–1220 m) a set of submain entries are driven to the right and left of the main entries. This entire set of entries divides the coal property into large blocks, which are further divided by panel entries driven off the submains.

Because of ventilation restrictions, mining machinery movements, and ground conditions, connections between entries are made at intervals. These are called crosscuts. The crosscuts divide the coal block between entries into pillars, often called chain pillars, which provide the primary support for the ground overlying the coal deposit. Since main and submain entries must remain open and stable for long periods of time, the design of the pillars and the roof support in the entries is a critical item in mine planning.

Panel entries, up to 17,000 ft (5180 m) or longer, divide the large coal blocks into rectangular blocks (panels) for production mining. Barrier pillars are left between the mains, the submains, and the rectangular panels in order to minimize the effect of the coal extraction associated with production on the stability of the mains.

Room-and-pillar mining. In the room- and-pillar system (**Fig. 9**) the mining methods may be by either continuous or conventional. The essential differences between the two methods are in the equipment spectrum and the cycle of face operations that the equipment dictates.

In continuous mining, the cycle of operations begins with a continuous miner sumping into the coal face. A shuttle car is positioned behind the miner to receive and transport the cut coal to the belt feeder. When the shuttle car is filled, it moves out and is replaced by the next shuttle car. This operation continues until the continuous miner operator reaches the last roof support. The continuous miner is then withdrawn, and safety posts or hydraulic jacks are placed in the excavated opening. The miner then widens the room to its final size (usually 18–20 ft or 5.5–6 m) by cutting the adjacent strip. The miner moves onto the next working place—a room or a crosscut—and roof-bolt support is installed. Continuous miners equipped with roof-bolting capabilities eliminate this intermediate step and continue to widen the room without the installation of hydraulic jacks. The final roof-bolting pattern is completed after the continuous miner moves to the next room. The face ventilation system is adjusted to compensate for the freshly cut room and the new working location of the continuous miner. Electric cables to the equipment, the power center, the belt feeder, and other items must be adjusted and moved forward as the overall mining section advances.

In conventional mining, the breaking out of the coal from the face is done by undercutting, drilling, and blasting operations. First, the cutting machine saws a 10–12-ft-deep (3–4-m) slice horizontally across the room width at the bottom and then moves out to the next place to be cut. Then the drilling machine (**Fig. 10**) moves in and drills holes into the

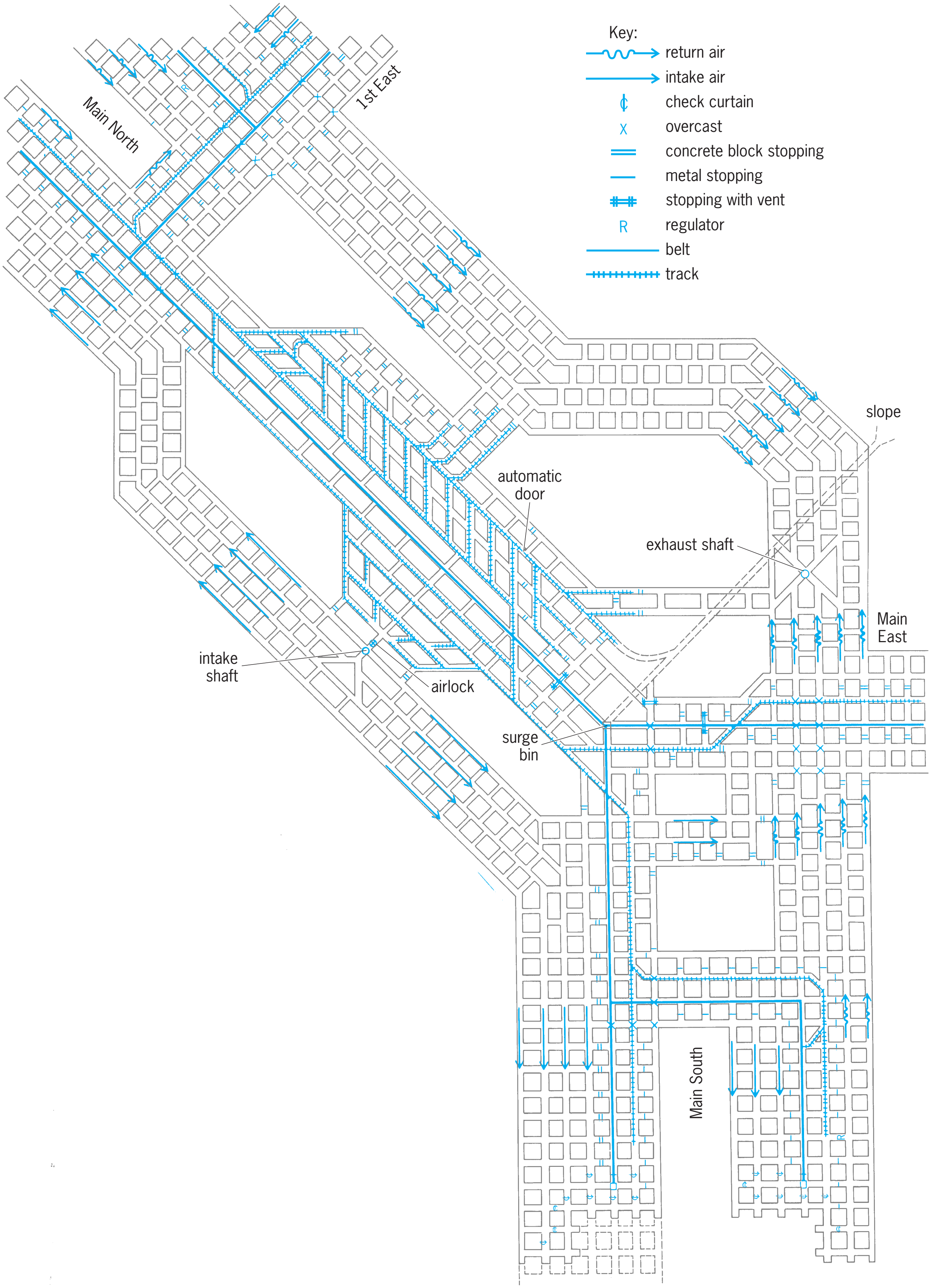

Fig. 9. Plan of a room-and-pillar mining operation. (*After R. Stefanko, Coal Mining Technology, Theory and Practice, Society of Mining Engineers, AIME, 1983*)

Fig. 10. Single-boom face drill operating in low-seam coal. (*Long-Airdox Co.*)

cut face, and this is followed by the blasting operation. After the area is examined for safety, the loading machine and shuttle cars move in and load out the coal. Sufficient working places should be available to minimize the idle time of equipment. Ventilation, electric cables, power center, belt feeder, and other items must be adjusted and moved forward as the overall mining section advances.

Retreat mining. The system of rooms and crosscuts driven in the production panels divides the panel into a series of coal pillars of approximately equal size. These coal pillars are extracted by methods that allow the mining operation to retreat toward the panel entries. As the pillars continue to be extracted, the bridging span of the immediate roof and then of the main roof is exceeded and the ground caves into the opening. This caved rock is called the gob. Since methane gas may accumulate in the gob, a bleeder system of entries is established at the top of the panel to allow a portion of the ventilating air to circulate through the gob.

Fig. 11. Remote-controlled continuous miner.

There are four basic pillar extraction techniques: split-and-fender, pocket-and-wing, outside lift, and open end. The first two are suited for continuous mining methods. Open end is utilized with conventional mining equipment, and outside lift is primarily used to extract long, thin pillars.

In the split-and-fender method, the pillar is split into two fenders of coal by driving a room parallel to the long side of the pillar. Because of roof control restrictions, which do not allow the splitting of the pillar by a single pass of the continuous miner, two pillars are mined simultaneously. The continuous mining unit, operating in an alternating fashion, mines a cut in each pillar. Rock bolts are used for roof support in the splitting operation, but breaker posts and cribs are used for roof control when the fenders of coal are removed. Check curtains are used to direct the ventilating current to the working faces.

The cuts used in the outside lift method are similar to those used in removing a fender of coal.

In the pocket-and-wing method, two working places can be sequenced in the same pillar. The pillar is alternately split transversely, then longitudinally, producing three fenders. These are then removed by using breaker posts for roof control. Ventilation is controlled by check curtains.

In the open-end method of pillar extraction, the sequence of extraction cuts is made adjacent to the gob without a protecting fender of coal.

Equipment. Continuous miners (**Fig. 11**) consist of a cutting head, a coal-gathering system, and a scraper conveyor system; the whole piece of equipment is electrically powered and mounted on a crawler-supported carrier. The cutting heads of various designs rip, bore, or auger the coal from the face. The ripper type of miner is most popular. Rippers have drum cutting heads mounted horizontally and fitted with steel bits. The cutting head, which is supported by arms that allow it to be positioned in a vertical plane, is crowded into the face by moving the carrier forward. Coal is ripped from the face, drops to the floor, and is gathered onto the scraper conveyor by a set of rotating disks or gathering

Fig. 12. Shuttle car for transporting coal within the mine.

Fig. 13. Diesel scoop in operation. (*WVA Mining Equipment Co.*)

arms. The scraper conveyor transports the coal into the positioned shuttle car. Geologic conditions, especially the seam height and the presence of in-seam rock, influence the operation and design of the miner.

A shuttle car is a low-bodied diesel or electrically powered unit (**Figs. 12** and **13**) that carries the coal to a nearby belt conveyor system that takes the coal out of the mine.

Roof bolts are an essential component of both continuous and conventional mining. They are used to provide ground control for the immediate roof strata overlying the mined room, and a means of support that does not obstruct the mine opening. Roof bolters are used to drill the holes and install the bolts. Roof bolting is a prime bottleneck in room-and-pillar mining and a dangerous operation; hence roof-bolting equipment must be fast and efficient and provide temporary support to the mine roof while the operator is installing the bolt.

A cutting machine is a large chain saw mounted on a rubber-tired carrier. A universal cutter can be maneuvered to cut a slice at any angle to the horizontal. Blasthole drilling in coal is done with electrically driven augers. Blasting may be done with special coal mine explosives, compressed air, or carbon dioxide cartridges. The loading machine consists of a gathering system, which sweeps the coal off the mine floor onto an inclined scraper conveyor for transport to the shuttle car. A belt feeder has a toothed roll crusher for sizing the coal, which is then fed at a uniform rate by a scraper conveyor onto the section belt conveyor.

Ventilation. The primary function of mine ventilation is to dilute, render harmless, and carry away the gas and dust produced in the underground mining of coal. Federal law requires the following conditions to be met: (1) Minimum air velocity in the working place must be at least 60 ft (18 m) per minute. (2) Minimum air volume at the last open crosscut must by 9000 ft^3 (255 m^3) per minute. (3) Minimum air volume reaching each working face must be 3000 ft^3 (85 m^3) per minute. (4) Respirable dust levels in the mine air cannot exceed an average of 2 mg/m^3. (5) Air used to ventilate belt conveyors cannot be used to ventilate working faces and must be vented to return airways. (6) Methane accumulations cannot be allowed to exceed 1% in the working area.

The mine ventilation system is composed of three subsystems: (1) the primary distribution system, which consists of main fans and the main intake and return entries; (2) the face ventilation system (**Fig. 14**), which controls airflow throughout the active production area; and (3) control devices to direct the air through the mine. Main fans are required to be installed on the surface, and usually pull air through the mine. They do this by developing a pressure gradient between the intake air entries and the return air entries in the mine. Hence, crosscuts between these two sets of main entries must be closed off by permanent stoppings. Splitting the intake air at each set of submains allows different areas of the mine to have their own independent air, and also serves to minimize power costs. Return air from these splits must be carried over the intake mains by air bridges or overcasts. The flow of air within a split can be controlled by increasing the resistance to flow with regulators placed at strategic locations in various entries and rooms.

The production area of the mine generates the most gas and dust, and hence requires constant

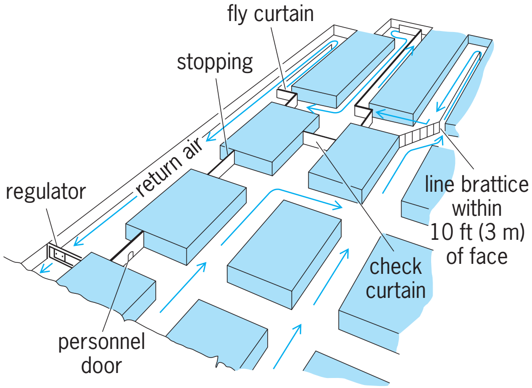

Fig. 14. Diagram of a blower line-brattice face ventilation. Arrows indicate direction of flow of air. (*After R. Stefanko, Coal Mining Technology, Theory and Practice, Society of Mining Engineers, AIME, 1983*)

examination and modification of the airflow pattern to cope with the changing situation developed by the advancing faces. The blind room headings ahead of the last open crosscut may be ventilated by line brattices (nylon-plastic curtains which are installed so as to split the blind room heading longitudinally) or auxiliary fans. Air is then directed up one side and down the other. The line brattices are also used to direct the movement of air throughout the production area by acting as check curtains in certain rooms. In order to do an effective job of diluting and sweeping dust and gas from the working face, line brattices must be kept close to the face. Auxiliary fans and tubing in a push-pull arrangement are alternatives to line brattices, and better diffuse air across the working face but introduce other problems.

Ground control. The rock strata above the coal seam may be divided into an immediate roof and a main roof. The immediate roof responds quickly to the removal of the coal support and collapses unless some artificial support is installed to prevent and control the deformation. The main roof shows stability for long periods of time. In general, the boundary between these two roofs is formed at the contact zone defined by fairly thick competent rocks, such as sandstone and limestone, and thinly bedded incompetent rocks, such as shale and coal. The function of the pillars of coal developed by driving rooms and crosscuts is to provide support for the total roof structure over both the pillars and the mined openings. The ground load immediately over the pillars is transferred directly to the pillars, but the ground load over the rooms and crosscuts must transfer its load to the pillars. This mechanism of load transfer is called the bridging action of the rocks; competent rocks have good bridging action and incompetent rocks have poor bridging action. Artificial support is used to assist, enhance, or develop the bridging action of the rocks in the immediate roof.

Simple posts with cap pieces were the first roof supports used. The concept is to decrease the overall bridging span between posts. More posts with larger cap pieces and three-piece sets are added to control less competent roof strata. Posts for roof control are still used in pillar recovery work or retreat mining. However, for the highly mechanized continuous and conventional mining of entries, rooms, and crosscuts, timber posts and three-piece sets cannot be used because they restrict the movement of equipment and may be knocked down.

Prop-free openings with the immediate roof spanning the full entry width can be developed with the aid of roof bolts. The most commonly used roof bolt is an expansion-shell-anchored, 5/8-in.-diameter (1.6-cm), extrastrength, square-head steel bolt. The law specifies that the bolt must be a minimum of 30 in. (76 cm) in length. The function of the bolt is to bind together the various laminae in the immediate roof and make them act as a unit in developing bridging action. The bolts, when anchored in competent rock, also prevent sagging of the immediate roof. The binding and suspension action of the bolt is developed when tension is produced in the bolt by tightening it into the anchoring shell. A number of variations of this basic bolt are in use.

Ground control in main entries or in areas where roof bolts cannot develop the desired support is done by other means. Room and entry intersections often exceed mandated limits on roof bolts, so steel sets or steel beams resting on wood cribs or concrete blocks are used for the support of the intersections. In some main entries, steel arches or yielding steel arches are used. Where rapid temporary support is required, screw jacks or hydraulic props are easy to install and make excellent supports.

In the United States, federal law mandates that each mine operator have an approved roof control plan, a history of all unintentional roof falls, and a systematic evaluation of the roof control system in use. The roof control plan must show the geologic column, and identify the rock type and thickness above and below the coal seam. Further, the plan must describe the sequence of mining and installation of supports, including temporary supports, and must designate the area of the mine covered by the roof control plan.

Longwall mining. Longwall mining (**Fig. 15**) is the basic underground coal mining method practiced in Europe, and it enjoys wide acceptance throughout the world. It has a greater production potential than room-and-pillar systems, and is safer since mining takes place beneath a complete overhead steel canopy (**Fig. 16**) that moves as the face is mined. Longwall methods were tried in the United States for a number of years, but could not compete with the room-and-pillar system until modern longwall mining was introduced in 1960. Since that time, longwall mining has gained wide acceptance by coal producers in the United States. More coal is being produced now by longwall mining than any other underground mining method in the United States. Longwall systems are classified as retreat or advancing systems based on whether the panel is completely developed by panel entries before panel extraction commences.

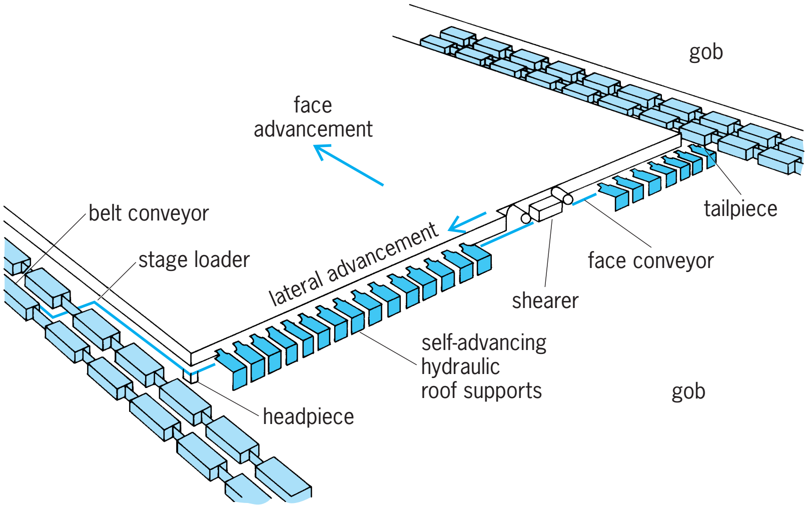

Fig. 15. Diagram showing the basic equipment components on a longwall face. (*After R. Stefanko, Coal Mining Technology, Theory and Practice, Society of Mining Engineers, AIME, 1983*)

Fig. 16. Longwall shearer and hydraulic roof support.

In the modern retreat system, entries (gates or roadways) are driven to block out a coal panel. Coal is then retreat-mined from the far end of the panel back to the submains. In the advancing system, development entries are kept only a short distance ahead of the working face which advances to the far end of the panel. In the United State, panels are usually 600–1100 ft (180–330 m) wide and 3000–17,000 ft (915–5180 m) long.

Regulatory constraints in the United States require longwall panels to be developed by multiple entries similar to those used in room-and-pillar mining. These entries are usually developed by continuous mining methods. Bleeder entries as well as a longwall equipment setup entry are driven across the top of the panel and connect panel entries. The panel entry containing the beltline, electrical and hydraulic equipment, and other items is called the head gate. Its complement on the other side of the panel is called the tail gate. Panels are arranged so that the previous panel's head gate is the new panel's tail gate.

Single head and tail gate entries are common in Europe. When retreat mining is practiced, full-face tunneling machines are used to drive the entries and rock bolts are used for support. These will be supplemented with steel arches or some other method of support as conditions change due to mining. When advance mining is practiced, an in-team miner or stable driving equipment is used. One aspect of longwall mining on the advance is that the head and tail gate must be established and maintained through the gob. This usually means that the roof or floor of these entries must be ripped and the entry cross section reestablished and supported.

Three pieces of equipment are fundamental to modern longwall mining: armored face conveyors, powered supports, and the coal cutting machine. The cycle of face operations is based on the movement of this equipment. The armored face conveyor is erected along the coal face, and is connected to powered supports by means of double-acting hydraulic jacks. The cutter-loader usually slides along the top of the armored conveyor and breaks out a strip of coal 20–30 in. (50–75 cm) wide along the face and then pushes the broken coal onto the conveyor. As the cutter-loader progresses, it leaves a web 20–30 in. (50–75 cm) wide into which the armored conveyor is pushed by the hydraulic jacks on the powered supports. The hydraulic jacks supporting the overhead steel canopy are retracted, freeing the powered supports from roof pressure. These supports are advanced up to the armored conveyor by using the double-acting hydraulic jacks connecting the two, and are then reset. When the cutter-loader completes a pass across the face, it is reset to take a cut as it returns across the face, and the cycle is repeated. As coal is extracted and the powered supports are moved forward, more and more of the roof is left unsupported. The immediate roof collapses and is followed by the main roof collapsing or settling on the broken rock in the gob.

Equipment. An essential element of the modern longwall system is the armored face conveyor, sometimes called a snaking conveyor because in plan it can be curved around behind the cutter-loader into the web that is created as the cutter-loader advances along the face. The face conveyor is a steel trough running the length of the coal face and strong enough to carry the weight of the cutter-loader. One or more endless chains within the trough pull steel flights (paddles) that drag the coal to the head end, where it discharges into the head gate transportation system. The face conveyor may be driven by single or multiple drive units situated at the head and tail gate ends and on either side or both sides of the conveyor. Each drive unit consists of a motor, fluid coupling, and reduction gearing. The overall bulk of these units has an influence on the width of the head and tail gates. The preferred alternative of having drive units at both ends usually cannot be met because the excessive ground pressure on the tail gate makes it difficult to maintain the necessary room for tail drives. Face lengths are limited by the drive arrangements, the chain pull needed to move the coal, and other factors. The face conveyor does not dump directly onto the belt conveyor taking coal out of the panel. Instead it dumps onto a stage loader which serves as a feeder-breaker system for changing the direction and velocity of coal travel and breaking large lumps of coal and rock.

The good roof control developed by powered supports is a key to successful longwall mining. Powered supports have evolved, with a number of different features being introduced as the need arose. A very popular version in the United States is called a shield support. The unit consists of a set of hydraulic props placed between a steel floor beam and a roof beam with the beams pin-connected to a steel caving shield so that the individual members may rotate with respect to each other. Control valves, hydraulic hoses, and a double-acting jack complete the assembly. The caving shield linking the two beams is arranged so that adjacent supports provide skin-to-skin protection against broken rock in the gob flushing into the traveling way and working area of the face. The roof beam cantilevers over the traveling way and working area of the face, completing the steel canopy protecting workers and giving a prop-free front face. The design principles of the shield allow it to cope with both vertical and lateral movements of the immediate roof as it responds to coal extraction. Powered supports have not been designed to work in thin coal seams.

Cutter-loaders are of two types: shearers and plows. A shearer (Fig. 16) consists of a drum fixed to the end of the ranging arm, and the combined unit is connected through gearing to a power unit riding on the conveyor. The drum is a spiral arrangement fitted with picks for breaking out the coal. A cowl is attached to the machine at the back end of the drum, and the combination of spiral drum and cowl acts as a screw conveyor moving the newly mined coal into the face conveyor. A shearer may have two drums mounted at each end of the power unit. Double-drum shearers with cowls that can be repositioned make bidirectional mining feasible as well as allowing the shearer to accommodate to variable seam height. The shearer moves across the face by a rack-and-pinion mechanism between the shearer and the face conveyor.

The coal plow (planer) is pulled back and forth across the face by an endless chain system. It is designed to travel in the space between the face conveyor and the coal, and cuts a layer of coal 2–6 in. (5–15 cm) thick. The coal is deflected or plowed onto the face conveyor. The plow is held against the face by hydraulic jacks located between the conveyor frame and the plow. An operator does not follow the plow along the face, and the plow does not cut as thick a web as the shearer, so planers can probably work under more difficult roof conditions than shearers.

Ventilation and ground control. The speed of coal production and the length of the longwall face give rise to difficulties in face ventilation. Shearers not only produce a fine product and create dust, but also develop a deep web. The net effect of these factors is an increase in methane liberation. Part of the input face ventilation escapes into the gob, and hence is not used to sweep away and dilute these products. Methane that escapes and collects in the gob area may be drained away by a system of boreholes.

Ground control problems usually result from seam factors. Soft floors may have insufficient bearing capacity for support loads. Massive roof strata with long bridging spans will not cave and overload face support. Variations in seam height and uneven floor conditions can unbalance face support systems. Thick seams must be mined by successive lifts. Tail entries are subjected to severe ground pressures and require heavy timbering and hydraulic prop support.

Other methods. Two of the numerous variations on the basic room-and-pillar and longwall methods will be described. Shortwall mining, using equipment from both room-and-pillar and longwall methods, is an attempt to handle the technical and economic alternatives in choosing an extraction system. The shortwall layout is similar to the longwall panels except that the panel width is 150–200 ft (46–60 m) wide. A continuous miner, loading shuttle cars, substitutes for the cutter-loader-face conveyor system, and the roof beams of the powered supports need to give cantilever action over a wider working area. Shortwall mining is considered when the coal seam is relatively shallow but is overlain by massive roof strata; when a large, relatively homogeneous and undisturbed area of coal is not available for longwall panels; or when ventilation difficulties from dust preclude face personnel from working downwind from the cutter-loader.

Hydraulic mining uses large quantities of water at high pressure to break and convey the coal from the working area. It is most effectively applied to a steeply dipping, relatively thick coal seam that is bounded by an immediate roof and floor and breaks into large pieces. Jets of water are directed tangentially along the coal face to break off lumps of coal. The coal is washed into a system of troughs for conveying away from the working area. Subsequently the coal may be dewatered and moved by conveyor belt, or it may remain in troughs or be pumped to its final location. Hydraulic mining is successfully applied in China, Russia, the United States, and Canada.

Remote control and teleoperation. Remote control enables the operation of mining machines at some distance from the operator. In underground coal mining, remote control of continuous mining machines is a common practice. In all cases, the operator keeps visual contact with the machine, particularly with the cutting head. In cases where visual contact would be limited or impossible, this practice would have little or no advantage. In coal mining, other remotely controlled equipment includes loaders, longwall shearers, belt conveyors, highwall mining machines, roof bolters, and mobile roof support systems. Although health and safety improvements have been made using remotely controlled equipment, efficiency improvements are limited since operation of these systems still requires manual control and visual contact.

In teleoperation, mining machinery is controlled from a remote location without direct visual contact. Ideally, the operator is at the surface or at a relatively safe area and does not enter the work area at all. Some examples have been demonstrated for metal mining, but no applications in coal mining have been implemented. *See* REMOTE-CONTROL SYSTEM.

Future trends. New equipment and equipment modifications to meet the challenges of difficult underground mining conditions will dominate the future. Remotely controlled longwall systems and continuous miners are expected to proliferate for their improved safety and higher productivity. How to mine thin seams, thick seams, steeply dipping seams, seams at greater depths, extremely gassy seams, and seams under bodies of water, or combinations of these needs to be solved. Integration of extraction, haulage, ventilation, ground control, and reclamation systems into an economic and ecologically sound plan is the challenge for future mining engineers. *See* MINING; UNDERGROUND MINING.

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Coal paleobotany

A special branch of the paleobotanical sciences concerned with the origin, composition, mode of occurrence, and significance of the fossil plant materials that occur in, or are associated with, coal seams. Information developed in this field of science provides knowledge useful to the biologist in efforts to describe the development of the plant world, aids the geologist in unraveling the complexities of coal measure stratigraphy in order to reconstruct the geography of past ages and to describe ancient climates, and has practical application in the coal, coke, and coal chemical industries. *See* COAL CHEMICALS.

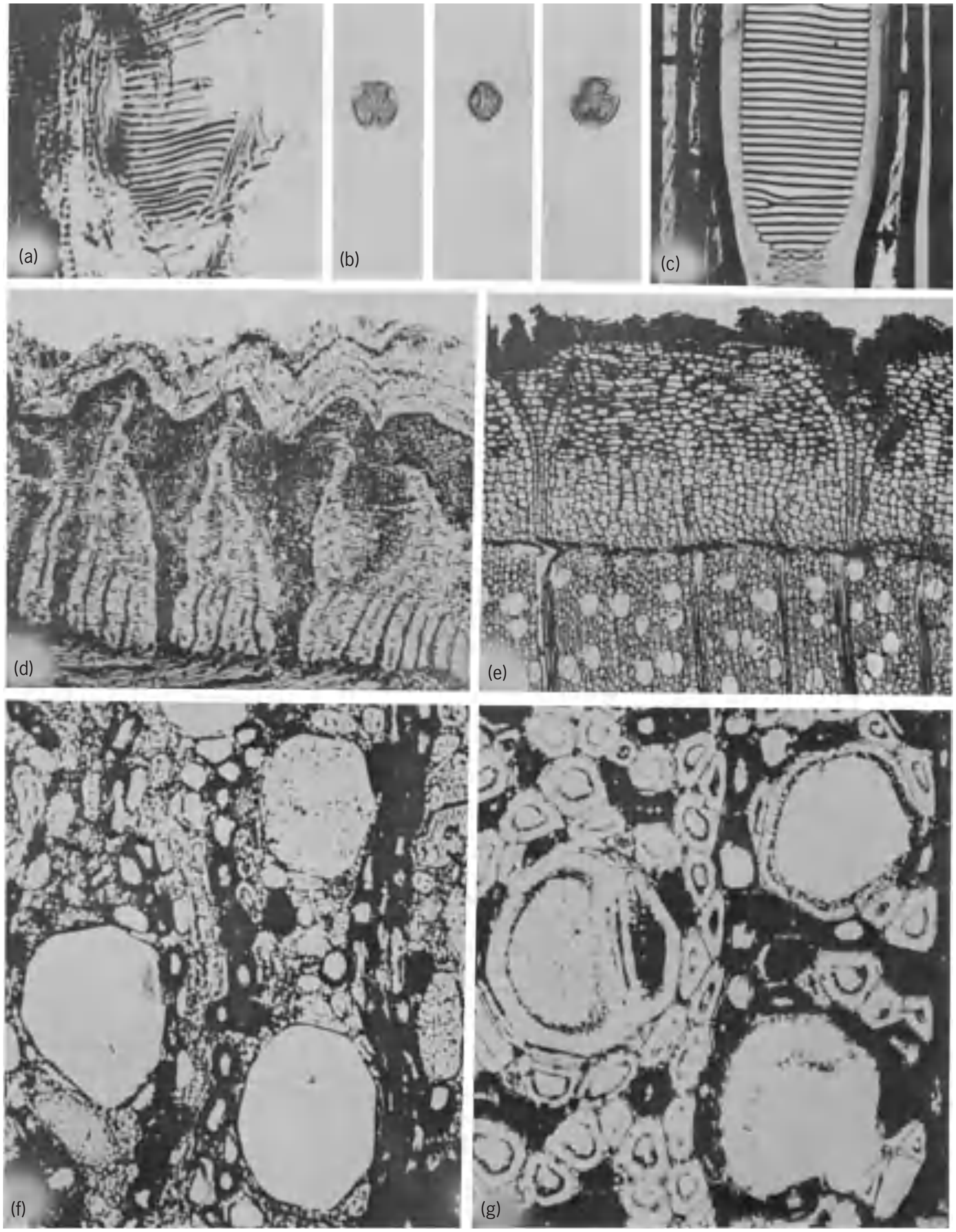
Nature of coal seams. All coal seams consist of countless fragments of fossilized plant material admixed with varying percentages of mineral matter. The organic and inorganic materials initially accumulate in some type of swamp environment. Any chemical or physical alteration experienced by the organic fragments during the course of transportation and deposition is followed by another series of changes effected by the chemical, physical, and microbiological agents characterizing the environment in which the particle comes to rest. Subsequent burial beneath a thick cover of sediment induces further physical and chemical alteration of the particles comprising the coal seam. Usually a consolidated layer of well-bonded fragments results. In some instances, crustal deformation and even volcanism add their modifying effects. Thus, the chemical composition, size, shape, and orientation of the fossilized plant remains are influenced both before and after death by biological processes and by the chemical and physical processes attending their postdepositional history. Even in coal seams that have been metamorphosed to anthracitic rank, certain of the constituents remain recognizable as portions of particular plant organs, tissues, or cells. Such entities are classed as phyterals, and in paleobotanical descriptions of coal seams these are identified as specifically as possible as megaspores, cuticles, periderm, and so on. In seams of peat, lignite, and high-volatile bituminous coal, entities are more readily recognized as particular phyterals than they are in higher-rank deposits. This is partly because fewer are destroyed by the metamorphic processes and partly because of the distinctiveness of the substances composing the entity.

In some instances, the fossilized plant fragments can be recognized as remnants of a plant of some particular family, genus, or species. When this is possible, information can be obtained on the vegetation extant at the time the source peat was formed and such data aid greatly in reconstructing paleogeographies and paleoclimatic patterns. Perhaps the most extensive studies of this type are those conducted on the Tertiary brown coals of the Rhine Valley in Germany. From these, detailed reconstructions have been prepared, describing and illustrating the three major swamp environments that gave rise to the sedimentary layers comprising these spectacular coal seams.

Plant fossils in coal seams. Pollen grains and spores are more adequately preserved in coals than are most other plant parts. Recognition of this fact, coupled with an appreciation of the high degree to which these fossils are diagnostic of floral composition, has led to the rapid development of the paleobotanical subscience of palynology. Fruits, seeds, and identifiable woods also occur as coalified fossils and are deserving of more attention than has been accorded them in the past. Often minute structural details are preserved (see **illus.**). Identifiable leaf fossils are comparatively uncommon, although the coalified cuticles of leaves are frequently encountered and their botanical affinities determined. Occasionally, coal seams contain fossil-rich coal balls. Essentially all types of plant fossil, including entire leaves, cones, and seeds, are encountered in these discrete nodular masses. Within the coal ball, the altered but undistorted plant tissues are thoroughly impregnated with mineral matter, usually with calcite or dolomite. Comparatively few coal seams have been encountered with large concentrations of coal balls, but these seams have provided a wealth of detailed information on the nature of the plants which gave rise to the coals concerned. *See* COAL BALLS; FOSSIL SEEDS AND FRUITS; PALYNOLOGY.

Sedimentary units of coal seams. As implied previously, coal seams generally are composed of several superposed sedimentary layers, each having formed under somewhat different environmental conditions. The coal petrologist and paleobotanist recognize these layers because of their distinctive textural appearance and because each consists of a particular association of organic and inorganic materials. Accordingly, each coal seam usually contains several types of coal. These coal types, or lithotypes, possess characteristic suites of physical properties, and knowledge of these properties is very profitably employed in manipulating coal composition in coal preparation and beneficiation plants.

A given lithotype may form several of the constituent layers of lithobodies of a coal seam. Each lithobody often possesses a characteristic assemblage of botanically identifiable fossil plant fragments rendering the unit recognizable to the coal paleobotanist without reference to its textural or compositional features. Paleobotanical descriptions of coal beds may relate to the entire thickness of the seam



Plant fossils in coal. (*a*) Coalified remnants of scalariform perforation plate in vessel element of piece of lignitized *Cyrilla* wood from Oligocene lignite deposit near Brandon, Vermont. (*b*) Coalified *Cyrilla* pollen grains extracted from Brandon lignite. (*c*) Scalariform perforation plate of vessel in wood of modern *C. racemiflora*. (*d*) Transverse section of lignitized bark of *Cyrilla* from Brandon lignite. (*e*) Transverse section of extant *C. racemiflora* bark with portion of secondary xylem shown in lower half of photo. (*f*) Transverse section of coalified secondary xylem of *Cyrilla* wood from Brandon lignite showing preservation of fine structural detail. (*g*) Transverse section of secondary xylem of *C. racemiflora* showing the structure of vessels, fiber tracheids, wood parenchyma, and rays. Note the coalification effects by making a comparison with *f*.

without regard for the seam's composite nature, or the fossils may be described in relation to the particular lithobody sequence. The more detailed type of description is required if paleoecological interpretations are to be made or if detailed stratigraphic work is involved.

Interrelations with coal petrology. Another facet of coal paleobotany concerns the nature of the substances which compose the coalified plant fragments. When focusing attention upon such matters, the coal paleobotanist is indistinguishable from the coal petrologist and both begin to encroach on the province of the coal chemist. It is noteworthy, however, that the paleobotanist tends to concentrate attention on the genetic relationships of the various coal substances and hence upon the steps in the derivation and subsequent evolution of maceral materials. The initial stages of coalification tend to be ignored by the coal chemist and petrologist, and the study of these has, quite properly, been thought of as an integral part of coal paleobotany. Thus, through the study of the botanical character of coalified fossils and by means of investigating the substances produced by the coalification process, coal paleobotanists extend knowledge of the organically derived sediments of the Earth's crust. *See* COAL.

William Spackman

Coalbed methane

Coalbed methane production, sometimes referred to as coal degasification, is the process of extracting natural gas from underground coal formations (coalbeds or coal seams). This extraction is accomplished with production technology similar to that used in the conventional natural gas industry. The objectives of producing the natural gas from a coal seam are to improve mine safety, to sell the natural gas, or both. *See* COAL; NATURAL GAS.

Coalbed methane production is a leading form of unconventional production in terms of annual gas production and reserves. Other unconventional gas resources include low-permeability sandstones, Devonian shales, geopressured aquifers, and gas-hydrate reservoirs.

Historical development. The behavior of explosive gases in coal seams has been investigated since the inception of the underground coal mining industry. In 1845, Michael Faraday identified the chain of events leading to devastating mine explosions. First, a localized methane outburst generates a cloud of fine coal particles in the mine. This coal dust may then be ignited through the ignition of the original methane outburst, the ignition of a subsequent methane outburst, or continued mine activity. Clouds of fine coal particles can have an explosive force comparable to black powder. Most of the early coalbed methane production was conducted with the objective of improving mine safety.

With the onset of the energy crisis in the 1970s, a second objective of coalbed methane production was identified: the production of a valuable natural resource, gaseous hydrocarbons.

In 1980, nonconventional fuel tax credits were enacted in the United States to provide economic incentives to stimulate the development of new energy resources.

In 1985, approximately 1×10^9 standard cubic feet of gas were produced from United States coal seams. A standard cubic foot is that volume of gas measured at standardized conditions, for example, 14.7 lb/in^2. (1.5 megapascals) at 60°F (16°C). Due to the increased number of coalbed methane wells and to improvements in production technology, approximately 1.6×10^{11} standard cubic feet of gas were produced from domestic coal seams in 2003. With the success of the United States coalbed methane industry in the 1980s, other governments and international energy companies began investigating the viability of producing natural gas from coal seams outside the United States.

Production and reserves. In 2003, coalbed methane production accounted for approximately 8.0% of the United States' annual natural gas production and 10% of its total proven natural gas reserves. In addition, natural gas production from all of the unconventional gas resources accounted for approximately 33% of the United States' total annual production. **Table 1** provides the annual growth of coalbed

TABLE 1. Coalbed methane proved reserves for 1989–2003, in billion cubic feet at 14.7 psia and 60°F

Year	Alabama	Colorado	New Mexico	Utah	Wyoming	Eastern states[*]	Western states[†]	Others[‡]	United States
1989	537	1,117	2,022	NA[§]	NA	NA	NA	0	3,676
1990	1,224	1,320	2,510	NA	NA	NA	NA	33	5,087
1991	1,714	2,076	4,206	NA	NA	NA	NA	167	8,163
1992	1,968	2,716	4,724	NA	NA	NA	NA	626	10,034
1993	1,237	3,107	4,775	NA	NA	NA	NA	1,065	10,184
1994	976	2,913	4,137	NA	NA	NA	NA	1,686	9,712
1995	972	3,461	4,299	NA	NA	NA	NA	1,767	10,499
1996	823	3,711	4,180	NA	NA	NA	NA	1,852	10,566
1997	1,077	3,890	4,351	NA	NA	NA	NA	2,144	11,462
1998	1,029	4,211	4,232	NA	NA	NA	NA	2,707	12,179
1999	1,060	4,826	4,080	NA	NA	NA	NA	3,263	13,229
2000	1,241	5,617	4,278	1,592	1,540	1,399	41	—	15,708
2001	1,162	6,252	4,324	1,685	2,297	1,453	358	—	17,531
2002	1,283	6,691	4,380	1,725	2,371	1,488	553	—	18,491
2003	1,665	6,473	4,396	1,224	2,759	1,528	698	—	18,743

[*] Includes Pennsylvania, Virginia, and West Virginia.

[†] Includes Kansas, Montana, and Oklahoma.

[‡] Includes Oklahoma, Pennsylvania, Utah, Virginia, West Virginia, and Wyoming; these states are individually listed or grouped in Eastern states and Western states after 1999.

[§] N/A, not available.

SOURCE: *U.S. Crude Oil, Natural Gas, and Natural Gas Liquids Reserves: 2003 Annual Report, Advance Summary*, Energy Information Administration, Office of Oil and Gas, U.S. DOE, September 2004.

TABLE 2. Coalbed methane production for 1989–2003, in billion cubic feet at 14.7 psia and 60°F

Year	Alabama	Colorado	New Mexico	Utah	Wyoming	Eastern states[*]	Western states[†]	Others[‡]	United States
1989	23	12	56	NA[§]	NA	NA	NA	0	91
1990	36	26	133	NA	NA	NA	NA	1	196
1991	68	48	229	NA	NA	NA	NA	3	348
1992	89	82	358	NA	NA	NA	NA	10	539
1993	103	125	486	NA	NA	NA	NA	18	752
1994	108	179	530	NA	NA	NA	NA	34	851
1995	109	226	574	NA	NA	NA	NA	47	956
1996	98	274	575	NA	NA	NA	NA	56	1,003
1997	111	312	597	NA	NA	NA	NA	70	1,090
1998	123	401	571	NA	NA	NA	NA	99	1,194
1999	108	432	582	NA	NA	NA	NA	130	1,252
2000	109	451	550	74	133	58	4	NA	1,379
2001	111	490	517	83	278	69	14	NA	1,562
2002	117	520	471	103	302	68	33	—	1,614
2003	98	488	451	97	344	71	51	—	1,600

[*] Includes Pennsylvania, Virginia, and West Virginia.

[†] Includes Kansas, Montana, and Oklahoma.

[‡] Includes Oklahoma, Pennsylvania, Utah, Virginia, West Virginia, and Wyoming; these states are individually listed or grouped in Eastern states and Western states after 1999.

[§] N/A, not available.

SOURCE: *U.S. Crude Oil, Natural Gas, and Natural Gas Liquids Reserves: 2003 Annual Report, Advance Summary*, Energy Information Administration, Office of Oil and Gas, U.S. DOE, September 2004.

methane proven reserves from 1989 to 2003, while **Table 2** provides the annual coalbed methane production during this period.

Coal seam reservoirs. Coal seam reservoirs are generally characterized as a dual-porosity system (**Fig. 1**). That is, most coal seams contain a primary porosity system (micropores) and a secondary porosity system (macropores, cleat system, or natural fracture system). The primary porosity system consists of the void space within the solid coal matrix. This porosity system is a result of the processes that occur during the deposition of the original organic matter which, over the geological time scale, is eventually converted to coal. Due to the dimensions of the pores (diameters range from 0.8 to 2.0 nanometers), the primary porosity system is inaccessible to ground water and, consequently, is fully saturated with gas. *See* GROUND-WATER HYDROLOGY.

The secondary porosity system of the coal seam consists of the void space in the fractures created after deposition. This fracture system is a result of shrinkage during the coalification process (by which organic matter is converted to coal). Natural fracturing may also be induced by localized tectonic forces. In general, the secondary porosity system in coal seams is composed of two types of fractures: the face cleat and butt cleat. The face cleat is continuous throughout the coal seam, while the butt cleat is discontinuous, generally ending at an intersection with the face cleat. Typically, the face cleat and butt cleat intersect at approximately 60–90° angles with a fairly uniform cleat spacing. Both ground water and gas may exist in the secondary porosity system of coal.

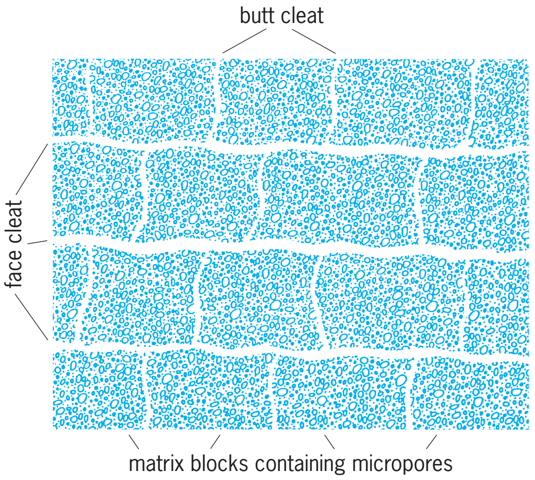


Fig. 1. Plan view of the dual porosity characterization of coal.

Natural gas in coal seams. The natural gas associated with coal is a by-product of the coalification process. Therefore, coal-seam reservoirs are different from conventional natural gas reservoirs; the coal seam is both the source rock and reservoir rock for the gas. Although no universal correlation exists, it has been observed that the original gas content of a coal seam tends to increase with increasing rank (a measure of the maturity and chemical structure of the coal) and increasing depth.

The natural gas associated with coal is composed of low-molecular-weight hydrocarbon gases, predominantly methane, and inorganic gases such as carbon monoxide, carbon dioxide, hydrogen sulfide, and oxygen. The compositions of gases from several coal seams in the United States are listed in **Table 3**. Samples of gas from virgin coal seams have a heat content greater than 950 British thermal units per standard cubic foot, making them of commercial quality with little processing.

Gas storage mechanisms. Gas is stored in coal seams in one of three states: as an adsorbed gas on the pore walls of the coal matrix, as a free gas within the pore structures of the coal, and as gas in solution in resident brine.

TABLE 3. Characteristics of gas from United States coal seams

	Pittsburgh	Pocahontas #3	Mary Lee	Sunnyside	Typical natural gas
Rank:	High-volatile bituminous	Low-volatile bituminous	High-volatile bituminous	High-volatile bituminous	
Geologic era:	Carboniferous (Pennsylvanian)	Carboniferous (Pennsylvanian)	Carboniferous (Pennsylvanian)	Cretaceous	
Gas:					
Methane	90.68*	96.32*	95.97*	99.01*	95.00*
Ethane	0.29	1.39	0.01	0.18	3.50
Propane	—	0.02	—	0.03	0.60
Butane	—	Trace	—	—	0.30
Pentane	—	—	—	—	0.20
Oxygen	0.20	0.17	0.15	0.30	—
Nitrogen	0.59	1.70	3.50	0.48	0.40
Carbon dioxide	8.24	0.36	0.10	—	—
Hydrogen	—	0.01	—	—	—
Helium	—	0.03	0.27	—	—
Heat content, Btu/SCF†:	973	1059	1024	1007	1068

* Chemical composition in mole percent.
† British thermal units/standard cubic foot.

Due to the dimensions of the pores in the primary porosity system and the organic, carbon-rich nature of coal, a large internal surface area containing many potential adsorption sites is present in the coal matrix. The majority of gas stored in coal exists as a physically adsorbed, molecular monolayer on the walls of the primary porosity system. The gas adsorption phenomenon in coal conforms to Langmuir theory and is commonly modeled with a Langmuir adsorption isotherm. *See* ADSORPTION.

In addition to adsorbed gas, free gas may exist in the secondary porosity system of the coal seam. Free-gas storage results from the compressible nature of gas in the presence of the hydrostatic pressure exerted by local ground water. This is the gas storage mechanism that typically dominates in conventional natural gas reservoirs. Free-gas storage is generally modeled with the real gas law.

To a lesser extent, gas is stored in solution in the ground water within the secondary porosity system. The amount of gas dissolved in connate water is dependent on the water salinity and on the temperature and pressure of the coal seam.

Gas transport mechanisms. With gas and water production and the resulting pressure depletion, gas is desorbed from the pore walls of the coal matrix and migrates through the primary porosity system to the natural fractures. The gas is then transported, along with ground water, through the natural fracture system to the production wells. Thus, the natural fracture system acts both as a low-pressure sink to the primary porosity system and as a conduit to the production wells. Gas transport through coal seams is a two-stage process (**Fig. 2**).

Due to low permeability and small pore dimensions, the principal gas-transport mechanism in the primary porosity system is diffusion. Within the primary porosity system, gas can be transported by bulk diffusion (where molecule–molecule interactions dominate), Knudsen diffusion (where molecule–surface interactions dominate), or surface diffusion of the adsorbed gas layer (where molecular movement from adsorption site to adsorption site dominates). Regardless of the dominant diffusion mechanism, gas transport through the primary porosity system obeys Fick's law. The potential that drives the diffusion process is the partial pressure (concentration) gradient. *See* DIFFUSION; RAREFIED GAS FLOW.

Within the secondary porosity system of the coal seam, gas and water are transported by Poiseuille, or forced, flow. For porous media such as the secondary

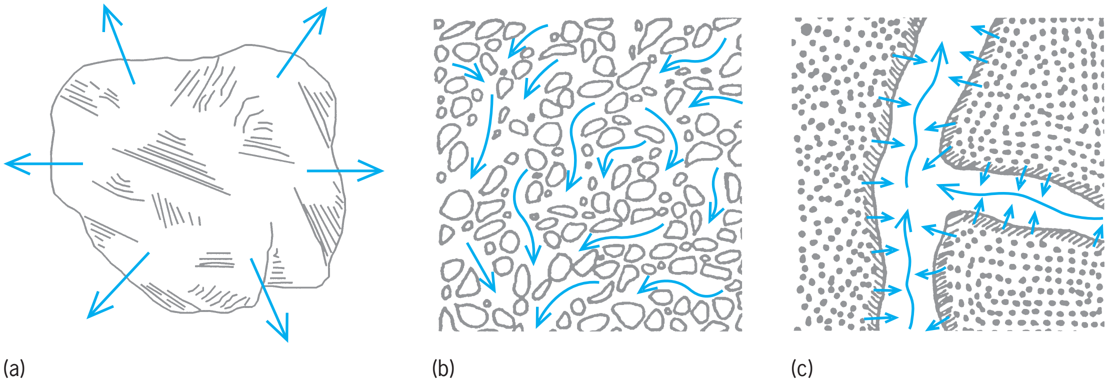

(a) (b) (c)

Fig. 2. Transport of gas through coal. (*a*) Gas desorption from coal grains in the coal matrix. (*b*) Step 1: diffusion through the primary porosity system to the cleat system. (*c*) Step 2: Poiseuille flow through the cleat system to production wells.

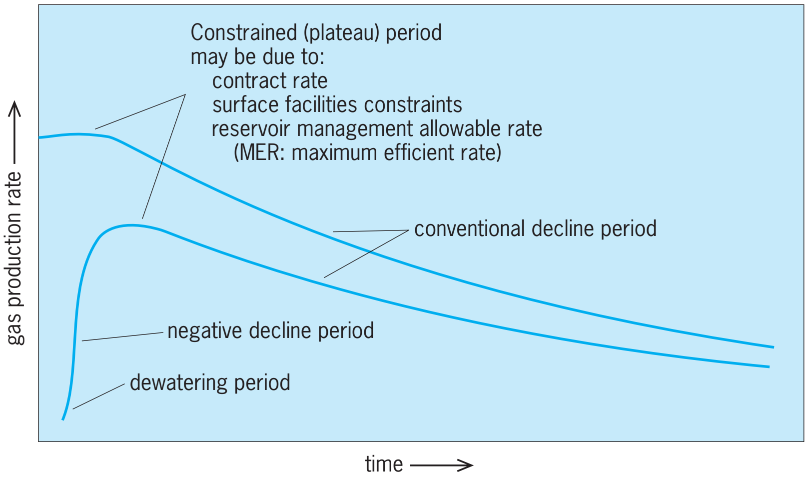


Fig. 3. Comparision of typical gas production rates of a coalbed methane well and a conventional natural gas well.

porosity system in a coal seam, Poiseuille flow is typically modeled with Darcy's law. The potential that drives Poiseuille flow is the total pressure gradient. This is the transport mechanism that normally dominates in conventional natural gas reservoirs. *See* SOIL MECHANICS; VISCOSITY.

Production technology. The drilling technology used for coalbed methane wells is identical to the technology used for conventional natural gas wells. The production technologies, however, do differ in well completions. The well completion is the portion of the well that connects the wellbore to the reservoir. Specialized well completions are required for coalbed methane wells because of the unique mechanical properties of coal.

There are two well completions commonly used in coalbed methane wells: open-hole cavity completions and hydraulically stimulated completions. In the open-hole cavity completion, the well is injected with high-pressure gas and water and is then rapidly depressurized. This process is repeated several times to break down the coal in order to create a large effective well radius, or cavity, in the coal seam.

In the hydraulic stimulation process, a high-pressure fluid (usually a gelled liquid, foam, or gas) is injected into the well along with a proppant (generally sand). The injection of the fracturing fluid either creates and propagates a fracture from the well into the coal seam, or opens preexisting, near-wellbore fractures. The proppant is used to keep the fractures open once the well is put into production. The hydraulic stimulation process used for coalbed methane wells differs from the hydraulic fracturing process used for conventional natural gas wells in that stimulation treatment must be optimized for the low-bulk modulus of coal. Most of the conventional hydraulic fracture technology has been developed for high-bulk modulus clastic and carbonate reservoirs.

Two characteristics distinguish gas production from coalbed methane wells: (1) a dewatering period, which may take up to several months, is often required to initiate the desorption process and, eventually, gas production; and (2) a "negative" gas-decline period, during which the gas production rate increases with time. This is in contrast to the conventional behavior in which gas production normally decreases with time. The dewatering and negative gas-decline periods are a direct result of the unique mechanisms of gas storage and transport in coal seams (**Fig. 3**).

Gregory R. King

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Coastal engineering

A branch of civil engineering concerned with the planning, design, construction, and maintenance of works in the coastal zone. The purposes of these works include control of shoreline erosion; development of navigation channels and harbors; defense against flooding caused by storms, tides, and seismically generated waves (tsunamis); development of coastal recreation; and control of pollution in nearshore waters. Coastal engineering usually involves the construction of structures or the transport and possible stabilization of sand and other coastal sediments.

The successful coastal engineer must have a working knowlege of oceanography and meteorology, wave mechanics, geomorphology, soil mechanics, statistics, and structural mechanics. Tools that support coastal engineering design include analytical theories of wave motion, wave-structure interaction, diffusion in a turbulent flow field, and so on; numerical and physical hydraulic models; basic experiments in wave and current flumes; and field measurements of basic processes such as beach profile response to wave attack, and the construction of works. Postconstruction monitoring efforts at coastal projects have also contributed greatly to improved design practice.

Environmental forces. The most dominant agent controlling coastal processes and the design of coastal works is usually the waves generated by the wind. Wind waves produce large forces on coastal structures, they generate nearshore currents and the alongshore transport of sediment, and they mold beach profiles. Thus, a primary concern of coastal engineers is to determine the wave climate (statistical distribution of heights, periods, and directions) to be expected at a particular site. This includes the annual average distribution as well as long-term extreme characteristics. In addition, the nearshore effects of wave refraction, diffraction, reflection, breaking, and runup on structures and beaches must be predicted for adequate design. *See* OCEAN WAVES.

Other classes of waves that are of practical importance include the astronomical tide, tsunamis, and waves generated by moving ships. The tide raises and lowers the nearshore water level and thus establishes the range of shoreline over which coastal processes act. It also generates reversing currents in inlets, harbor entrances, and other locations where water motion is constricted. Tidal currents which often achieve a velocity of 3–6 ft/s (1–2 m/s) can strongly affect navigation, assist with the maintenance of channels by scouring sediments, and dilute polluted waters. *See* TIDE.

Tsunamis are quite localized in time and space but can produce devastating effects. Often the only solution is to evacuate tsunami-prone areas or suffer the consequences of a surge that can reach elevations in excess of 33 ft (10 m) above sea level. Some attempts have been made to design structures to withstand tsunami surge or to plant trees and construct offshore works to reduce surge velocities and runup elevations. *See* TSUNAMI.

The waves generated by ships can be of greater importance at some locations than are wind-generated waves. Ship waves can cause extensive bank erosion in navigation channels and undesirable disturbance of moored vessels in unprotected marinas.

On coasts having a relatively broad shallow offshore region (such as the Atlantic and Gulf coasts of the United States), the wind and lower pressures in a storm will cause the water level to rise at the shoreline. Hurricanes have been known to cause storm surge elevations of as much as 16 ft (5 m) for periods of several hours to a day or more. Damage is caused primarily by flooding, wave attack at the raised water levels, and high wind speeds. Defense against storm surge usually involves raising the crest elevation of natural dune systems or the construction of a barrier-dike system. *See* STORM SURGE.

Besides the cyclic variations in the mean sea level along the coast that are caused by the tide, tsunamis, and storm surge, there are longer-term sea-level variations owing to land uplift or subsidence with a superimposed rise in water levels that has been associated with atmospheric warming trends. The result in most coastal locations is a net sea-level rise relative to the land. In turn, there is a slow recession of the shoreline owing to the raised water level and to the beach profile's response to this raised mean sea level.

Other environmental forces that impact on coastal works include earthquake disturbances of the sea floor and static and dynamic ice forces. Direct shaking of the ground will cause major structural excitations over a region that can be tens of kilometers wide surrounding the epicenter of a major earthquake. Net dislocation of the ground will modify the effect of active coastal processes and environmental forces on structures. *See* EARTHQUAKE.

Ice that is moved by flowing water and wind or raised and lowered by the tide can cause large and often controlling forces on coastal structures. However, shore ice can prevent coastal erosion by keeping wave action from reaching the shore.

Coastal processes. Wind-generated waves are the dominant factor that causes the movement of sand parallel and normal to the shoreline as well as the resulting changes in beach morphology. Thus, structures that modify coastal zone wave activity can strongly influence beach processes and geometry.

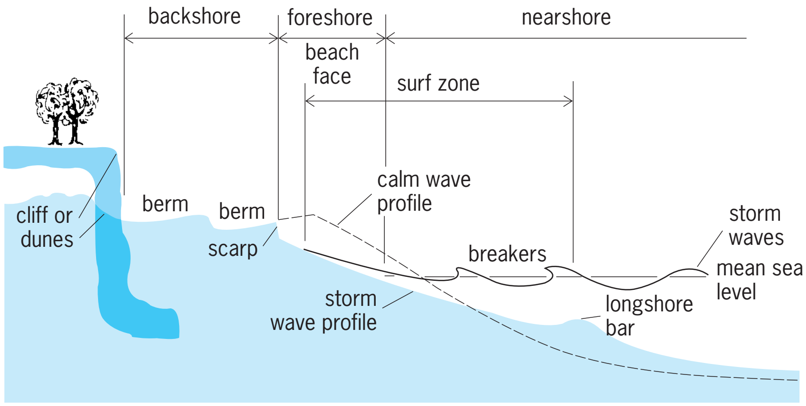

Fig. 1. Typical beach profiles (vertical scale is exaggerated).

Active beach profile zone. In typical beach profiles found at a sandy shoreline (which may be backed by a cliff or a dune field), the backshore often has one or two berms with a crest elevation equal to the height of wave runup during high tide (**Fig. 1**). When low swell, common during calm conditions, acts on the beach profile, the beach face is built up by the onshore transport of sand. This accretion of sand adds to the seaward berm. On the other hand, storm waves will attack the beach face, cut back the berm, and carry sand offshore. This active zone of shifting beach profiles occurs primarily landward of the 33-ft (10-m) depth contour. If the storm tide and waves are sufficiently high, the berms may be eroded away to expose the dunes or cliff to erosion. The beach profile changes (Fig. 1) are superimposed on any longer term advance or retreat of the shoreline caused by a net gain or loss of sand at that location.

Any structure constructed along the shore in the active beach profile zone may retain the sand behind it and thus reduce or prevent erosion. However, wave attack on the seaward face of the structure causes increased turbulence at the base of the structure, and usually increased scour which must be allowed for or prevented, if possible, by the placement of stone or some other protective material.

It is desirable to keep all construction of dwellings, recreational facilities, and other such structures landward of the active beach profile zone, which usually means landward of the frontal dunes or a good distance back from retreating cliffs. It is also desirable to maintain and encourage the growth of the frontal dune system by planting grass or installing sand fencing.

In addition to constructing protective structures and stabilizing the dune system, it is common practice to nourish a beach by placing sand on the beach face and nearshore area. This involves an initial placement of sand to develop the desired profile and periodic replenishment to make up for losses to the profile. Often shore stabilization structures are constructed along with beach nourishment to increase the stability of the nourished beach section. A common source for sand, which should be clean and at least as coarse as the native sand, is the offshore area near the nourishment site. Sand for beach nourishment has also been obtained from bays and estuaries and from land quarries.

Alongshore current and transport. Waves arriving with their crest oriented at an angle to the shoreline will generate a shore-parallel alongshore current in the nearshore zone. The current flows in the direction of the alongshore component of wave advance and has the highest velocity just inside the breaker line. It may be assisted or hindered by the wind and by tidal action, particularly along sections of the shore adjacent to tidal inlets and harbor entrances. There is a continuous accumulation of flow in the downcoast direction which may be relieved by seaward-flowing jets of water known as rip currents.

The alongshore current transports sand in suspension and as bed load, and is assisted by the breaking waves, which place additional sand in suspension. Also, wave runup and the return flow transports sand particles in a zigzag fashion along the beach face. Coastal structures that obstruct these alongshore transport processes can cause the deposition of sand. They do this by blocking wave action from a section of the shore and thus removing the wave energy required to maintain the transport system; by interfering with the transport process itself; or by directly shutting off a source of sand that feeds the transport system (such as a structure that protects an eroding shoreline).

The design of most coastal works requires a determination of the volumetric rate of alongshore sand transport at the site—both the gross rate (upcoast plus downcoast transport) and the net rate (upcoast minus downcoast transport). The most reliable method of estimating transport rates is by measuring the rate of erosion or deposition at an artificial or geomorphic structure that interrupts the transport. Also, field studies have developed an approximate relationship between the alongshore transport rate and the alongshore component of incident wave energy per unit time. With this, net and gross transport rates can be estimated if sufficient information is available on the annual wave climate. Typical gross transport rates on exposed ocean shorelines often exceed 500,000 yd^3 (382,000 m^3) per year.

Primary sources of beach sediment include rivers discharging directly to the coast, beach and cliff erosion, and artificial beach nourishment. Sediment transported alongshore from its sources will eventually be deposited at some semipermanent location or sink. Common sinks include harbors and tidal inlets; dune fields; offshore deposition; spits, tombolos, and other geomorphic formations; artificial structures that trap sand; and areas where beach sand is mined.

By evaluating the volumetric transports into and out of a segment of the coast, a sediment budget can be developed for the coastal segment. If the supply exceeds the loss, shoreline accretion will occur, and vice versa. When a coastal project modifies the supply or loss to the segment, geomorphic changes can be expected. For example, when a structure that traps sediment is constructed upcoast of a point of interest, the shoreline at the point of interest can be expected to erode as it resupplies the longshore transport capacity of the waves.

Harbor entrance and tidal inlet control structures built to improve navigation conditions, stabilize navigation channel geometry, and assist with the relief of flood waters will often trap a large portion of the alongshore sand transport. This can result in undesirable deposition at the harbor or inlet entrance and subsequent downcoast erosion. The solution usually involves designing the entrance structures to trap the sediment at a fixed and acceptable location and to provide protection from wave attack at this location so a dredge can periodically pump the sand to the downcoast beach. *See* NEARSHORE PROCESSES.

Computer models. Computer modeling of wave and coastal processes has greatly enhanced the ability of coastal engineers to more realistically and accurately define the effects of these processes. Specific examples of computer models in common use are models for the forecasting of wind-generated wave action caused by hurricanes and extratropical storms; prediction of wave transformation as waves propagate from deep water to the shore; prediction of related surge levels during storms; and prediction of beach morphology changes over a coastal segment caused by incident wave action. Computer models are also available that will predict the changing wave characteristics as the tide and tsunami waves enter the coastal zone, as well as the resulting resonant response of harbors and estuaries to these waves.

Coastal structures. Coastal structures can be classified by the function they serve and by their structural features. Primary functional classes include seawalls, revetments, and bulkheads; groins; jetties; breakwaters; and a group of miscellaneous structures including piers, submerged pipelines, and various harbor and marina structures.

Seawalls, revetments, and bulkheads. These structures are constructed parallel or nearly parallel to the shoreline at the land-sea interface for the purpose of maintaining the shoreline in an advanced position and preventing further shoreline recession. Seawalls are usually massive and rigid, while a revetment is an armoring of the beach face with stone rip-rap or artificial units. A bulkhead acts primarily as a land-retaining structure and is found in a more protected environment such as a navigation channel or marina.

A key factor in the design of these structures is that erosion can continue on adjacent shores and flank the structure if it is not tied in at the ends. Erosion on adjacent shores also increases the exposure of the main structure to wave attack. Structures of this class are prone to damage and possible failure caused by wave-induced scour at the toe. In order to prevent this, the toe must be stabilized by driving vertical sheet piling into the beach, laying stone on the beach seaward of the toe, or maintaining a protective beach by artificial nourishment. Revetments that are sufficiently porous will allow leaching of sand from behind the structure. This can lead to structure slumping and failure. A proper stone or cloth filter system must be developed to prevent damage to the revetment. In an attempt to develop low-cost shore protection, a number of novel materials have been used for shoreline revetments, including cinder blocks, tires, sand-filled rubber tubes, woven-fiber mattresses, and soil-cement paving. *See* REVETMENT.

Groins. A groin is a structure built perpendicular to the shore and usually extending out through the surf zone under normal wave and surge-level conditions. It functions by trapping sand from the alongshore transport system to widen and protect a beach or by retaining artificially placed sand (**Fig. 2**). Typical groin alongshore spacing-to-length ratios vary from 1.5:1 up to 4:1.

There may be erosion downcoast of the groin field, the volume of erosion being approximately equal to the volume of sand removed by the groins from the alongshore transport system. Groins must be sufficiently tied into the beach so that downcoast erosion superimposed on seasonal beach profile fluctuations does not flank the landward end of a groin. Even the best-designed groin system will not prevent the loss of sand offshore in time of storms.

Jetties. Jetties are structures built at the entrance to a river or tidal inlet to stabilize the entrance as well as to protect vessels navigating the entrance channel. Stabilization is achieved by eliminating or reducing the deposition of sediment coming from adjacent shores and by confining the river or tidal flow to develop a more uniform and hydraulically efficient channel. Jetties improve navigation conditions by eliminating bothersome crosscurrents and by reducing wave action in the entrance.

At many entrances there are two parallel (or nearly parallel) jetties that extend approximately to the seaward end of the dredged portion of the channel. However, at some locations a single updrift or downdrift jetty has been used, as have other arrangements such as arrowhead jetties (a pair of straight or curved jetties that converge in the seaward direction). Jetty layouts may also be modified to assist sediment-bypassing operations. A unique arrangement is the weir-jetty system in which the updrift jetty has a low section or weir (crest elevation about mean sea level) across the surf zone. This allows sand to move over the weir section and into a deposition basin for subsequent transport to the downcoast shore by dredge and pipeline.

Breakwaters. The primary purpose of a breakwater is to protect a shoreline or harbor anchorage area from wave attack (**Fig. 3**). Breakwaters may be located completely offshore and oriented approximately parallel to shore, or they may be oblique and connected to the shore where they often take on some of the functions of a jetty. At locations where a natural inland site is not available, harbors have been developed by the construction of shore-connected breakwaters that cover two or three sides of the harbor.

The offshore breakwater intercepts incident waves, thus trapping the predominantly southeastern longshore sand transport; it provides a protected area where a dredge can operate to bypass sediment; and it provides protection to the harbor entrance. A series of shore-parallel offshore breakwaters (with or without artificial nourishment) has been used for shore protection at a number of locations. If there is sufficient fill or trapped material, the tombolo formed in the lee of each breakwater (Fig. 3) may grow until it reaches the breakwater.

Breakwaters are designed to intercept waves, and often extend into relatively deep water, so they tend to be more massive structures than are jetties or groins. Breakwaters constructed to provide a calm anchorage area for ships may have a high crown elevation to prevent overtopping by incident waves and subsequent regeneration of waves in the lee of the breakwater.

Rubble mound structures. Groins, jetties, and breakwaters are most commonly constructed as rubble mound structures (**Fig. 4**). The breakwater has an outer armor layer consisting of the largest stones or, if sufficiently large stones are not available, the armor units may be molded of concrete with a special shape. Stone sizes decrease toward the core and base in order to develop a filter system so that the fine core stone and base sand are not removed by wave and current action. The core made of fine stone sizes is provided to diminish wave transmission through

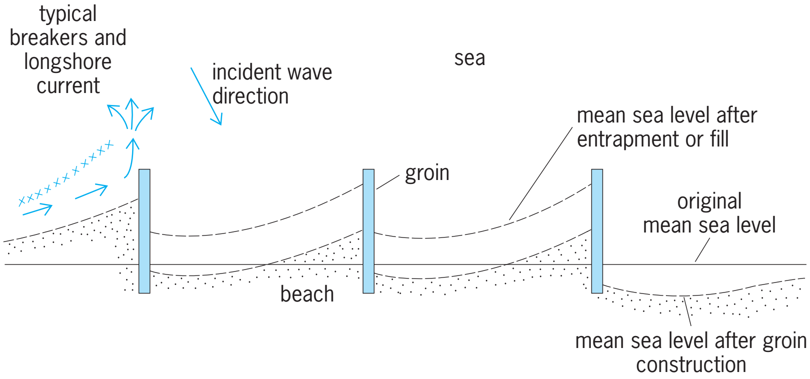

Fig. 2. Groin system and beach response.

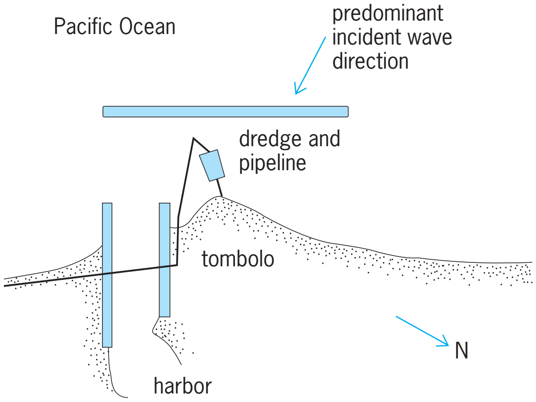

Fig. 3. Overhead view of breakwater and jetty system at the entrance to Channel Islands Harbor, California.

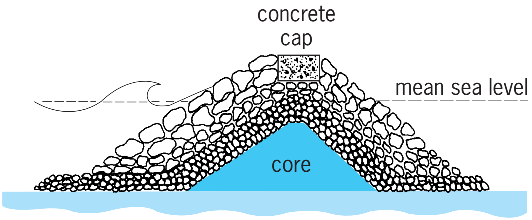

Fig. 4. Cross section of a typical rubble mound breakwater placed on a sand foundation.

the structure. Jetties and groins have a simpler cross section, consisting typically of only armor and core layers. Breakwaters, groins, and jetties have also been constructed of steel or concrete caissons with sand and gravel fill; wood, steel, and concrete sheet piles; and sand-filled bags.

A different type of breakwater that can be effective where incident wave periods are short and large water-level fluctuations occur (as in a reservoir marina) is the moored floating breakwater. This type has been constructed of hollow concrete prisms, scrap tires, logs, and a variety of other materials.

Economic, environmental, and esthetic considerations have resulted in some changes in the types of rubble mound structures being constructed along the coast. Rather than structures with several defined layers (Fig. 4) including an armor layer of large stone designed to remain stable during wave attack, berm breakwaters and revetments have been constructed in regions where large stones are not readily available. The armor layer in these structures consists of smaller stones with a larger size variation that is expected to remold itself to a stable profile in the same manner that a beach profile responds to wave attack. This armor layer must be thicker to allow for this remolding action.

Also, there has been a trend in offshore shore-parallel breakwaters to build the structure with its crest below sea level. This approach saves on stone costs and is visually more acceptable. During calm wave conditions, most of the wave action reaches the shore, a positive condition for shore recreation. However, the larger storm waves are broken and reflected by the structure so that storm-induced beach erosion is reduced. Robert M. Sorensen

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Coastal landforms

The characteristic features and morphology of the land in the coastal zone. They are subject to processes of erosion and deposition as produced by winds, waves, tides, and river discharge. The interactions of these processes and the coastal environments produce a wide variety of landforms. Processes directed seaward from the land are dominated by the transport of sediment by rivers, but also include gravity processes such as landslides, rockfalls, and slumping. The dominant processes on the seaward side are wind, waves, and wave-generated currents. Mixed among these locations are tidal currents which also carry large volumes of sediment.

All of these processes are relatively continuous or rapid. Some processes that influence coastal development are much slower. Changes in sea level are important over centuries and millennia with rates of a few millimeters per year. Over thousands of years these changes have resulted in an increase or decrease in sea level of as much as 100 m (330 ft). Another process that influences coastal development is plate tectonics, which has a time frame of millions of years. Although not a process, the geologic framework and geomorphology both seaward and landward of the shoreline are also factors in the development of coastal landforms. *See* GEOMORPHOLOGY; PLATE TECTONICS.

Subcontinental- to continental-scale coastal landform patterns are related to plate tectonics. A landmark paper by D. Inman and C. Nordstrom relating coastal development to plate tectonics provided a simple but useful approach to classification of coasts on this scale. It showed that there are three general geologic framework types into which all coasts can be classified. Some coasts are associated with plate boundaries and others are not. The three major tectonic coastal types are leading-edge, trailing-edge, and marginal sea coasts. Leading-edge coasts are associated with colliding plate boundaries where there is considerable tectonic activity. Trailing-edge coasts are on stable continental margins, and marginal seas have fairly stable coasts with plate margins, commonly characterized by island arcs and volcanoes, that form their seaward boundaries. *See* CONTINENTAL MARGIN.

Leading-edge coasts. The primary characteristic of these coasts is the rugged and irregular topography, commonly displaying cliffs or bluffs right up to the shoreline (**Fig. 1**). Seaward, the topography reflects this with an irregular bottom and deep water near the shoreline. The geology is generally complex with

Fig. 1. Rugged, high-relief coast in central Oregon, an example of a leading-edge coast.

Fig. 2. Central Atlantic coastal plain and coast of the United States, showing large estuaries bounded on the seaward side by a system of long barrier islands. (*NASA*)

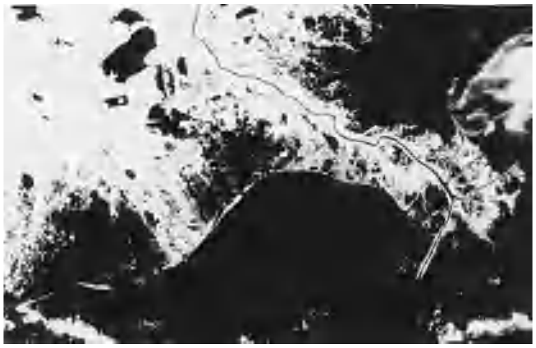

Fig. 3. Mississippi Delta, an example of a large muddy coast landform in a marginal sea.

numerous faults and folds in the strata of the coastal zone. These coasts tend to be dominated by erosion with only local areas of deposition, typically in the form of small beaches or spits between headlands. Waves tend to be large because of the deep nearshore water, and form wave-cut platforms, terraces, notches, sea stacks, and caves.

Trailing-edge coasts. The most diverse suite of coastal landforms develops along trailing-edge coasts. These coasts are generally developed along the margin of a coastal plain, they are fed by well-developed and large river systems, and they are subjected to a low-to-modest wave energy because of the gently sloping adjacent continental shelf. The overall appearance is little topographic relief dominated by deposition of mud and sand. The spectrum of environments and their associated landforms includes deltas, estuaries, barrier islands (**Fig. 2**), tidal inlets, tidal flats, and salt marshes. *See* BARRIER ISLANDS; COASTAL PLAIN; DELTA; FLOODPLAIN; SALT MARSH.

Although there is typically only low-to-moderate wave energy along such coasts, there is potential for considerable change in landforms through the passage of intense storms, including hurricanes. It is common for such events to cause more change in the coast in one or two days than might take place in a century or more under so-called normal conditions.

These trailing-edge coasts are subdivided into three categories based upon the maturity of the continental margin: neo-trailing-edge coasts, Afro-trailing-edge coasts, and Amero-trailing-edge coasts. The neo-trailing-edge coast develops only a short time after the splitting and spreading apart of a landmass. There has been insufficient time for development of a coastal plain, and the continental margin is narrow and steep but not tectonically very active. The Red Sea that separates Africa from the Middle East is an excellent example of this type. The Afro-trailing-edge coast has a significant level of maturity and a well-developed continental margin and is characterized by both the west coast and southeast coast of Africa. The Amero-trailing-edge coast is one where a very long geological time has passed since the plates separated. Both the continental margin and the coastal plain are wide and well developed. The east coasts of North and South America are excellent examples.

Marginal sea coasts. Some coastal settings are along a stable continental mass and are protected from open ocean processes, commonly an island arc system or other form of a plate boundary. The consequence is a coastal zone that tends to be subjected to small waves and where considerable mud is allowed to accumulate in the coastal zone. Many coastal landforms are present in much the same fashion as on the trailing-edge coasts. Marginal sea coasts tend to have large river deltas (**Fig. 3**). Examples are the eastern margin of Asia along the Gulf of Korea and the China Sea, the entire Gulf of Mexico, and the Mediterranean Sea. *See* DEPOSITIONAL SYSTEMS AND ENVIRONMENTS; NEARSHORE PROCESSES.

Richard A. Davis, Jr.

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Coastal plain

An extensive, low-relief area that is bounded by the sea on one side and by some type of relatively high-relief province on the landward side. The geologic province of the coastal plain actually extends beyond

Fig. 1. Coastal plains of the United States.

the shoreline across the continental shelf. It is only during times of glacial melting and high sea level that much of the coastal plain is drowned. *See* CONTINENTAL MARGIN.

The coastal plain is a geologic province that is linked to the stable part of a continent on the trailing edge of a plate. The extent and nature of the coastal plains of the world range widely. Some are very large and old, whereas others are small and geologically young. For example, the Atlantic and Gulf coasts of the United States are among the largest in the world. They extend continuously from the New Jersey area beyond the border with Mexico (**Fig. 1**). In some areas the coastal plain is hundreds of kilometers wide. In the United States it extends back about 100 million years. By contrast, local coastal plains in places like the east coast of Australia and New Zealand are only 1 or 2 million years old and extend only tens of kilometers landward from the shoreline.

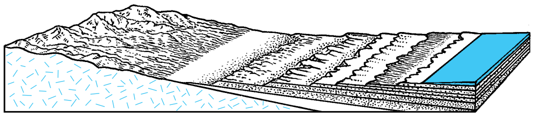

Fig. 2. Block diagram of a coastal plain showing the gentle dip of the strata and the erosional ridges.

The typical character of a coastal plain is one of strata that dip gently and uniformly toward the sea. There may be low ridges that are essentially parallel to the coast (**Fig. 2**) and that have developed from erosion of alternating resistant and nonresistant strata. These strata are commonly a combination of mudstone, sandstone, and limestone, although the latter is typically a subordinate amount of the total. These strata resulted from deposition in fluvial, deltaic, and shelf environments as sea level advanced and retreated over this area. Coastal plain strata have been a source of considerable oil and gas as well as various economic minerals. Although the coastal plain province is typically stable tectonically, there may be numerous normal faults and salt dome intrusions. *See* COASTAL LANDFORMS; DELTA; GEOMORPHOLOGY; PLAINS. Richard A. Davis, Jr.

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Coati

Any of three species of carnivorous mammals assigned to the raccoon family Procyonidae. The common or ring-tailed coati (*Nasua nasua*) ranges through the forests of Central and South America (see **illustration**), the mountain coati (*Nasuella olivacea*) is found only in South America, while *Nasua nelsoni* is confined to Cozumel Island in Central America.

The coatis are characterized by their elongated snouts, body, and tail, which is held erect when they walk. They are adept at climbing trees in search of birds and lizards, and their diet also includes fruit, insects, and larvae. *Nasua nasua* roams in bands of females and young during the day in search of food. The males are excluded from the band except during the brief breeding season, when a single male is allowed to join. He is aggressive toward any other male but subordinate to the females. After mating, the male leaves and the female builds an isolated nest in a tree. Here, following a gestation period of 11 weeks, a litter of about five young are born and cared for by the female away from the group. After about 1 month the female and her young rejoin the band. *See* CARNIVORA. Charles B. Curtin

Ring-tailed coati (*Nasua nasua*). (*Photo © by Lisa Kostich*)

Coaxial cable

An electrical transmission line comprising an inner, central conductor surrounded by a tubular outer conductor. The two conductors are separated by an electrically insulating medium which supports the inner conductor and keeps it concentric with the outer conductor. One version of coaxial cable has periodically spaced polyethylene disks supporting the inner conductor (**Fig. 1**). This coaxial is a building block of multicoaxial cables used in L-carrier systems. *See* TRANSMISSION LINES.

The symmetry of the coaxial cable and the fact that the outer conductor surrounds the inner conductor make it a shielded structure. At high frequencies, signal currents concentrate near the inside surface of the outer conductor and the outer surface of the inner conductor. This is called skin effect. The depth to which currents penetrate decreases with increasing frequency. Decreased skin depth improves the cable's self-shielding and increases transmission loss. This loss (expressed in decibels per kilometer) increases approximately as the square root of

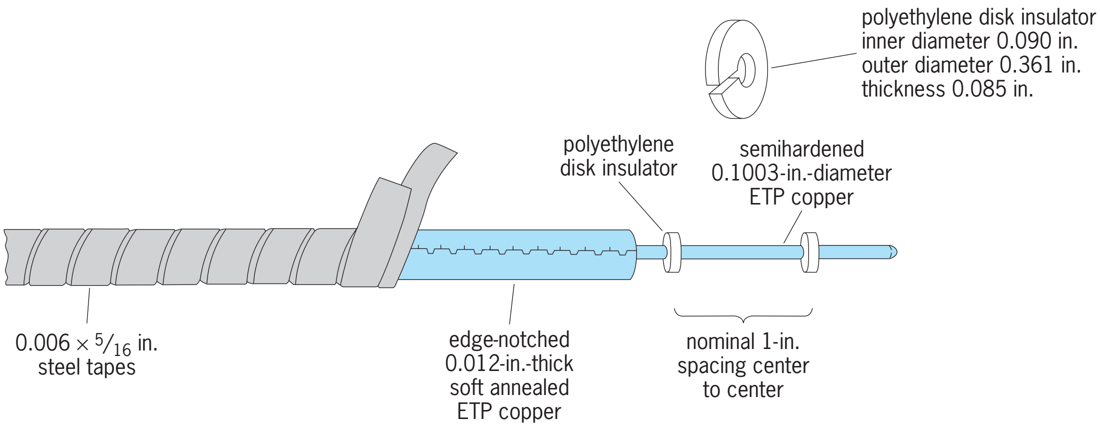


Fig. 1. Air dielectric disk-insulated coaxial cable. 1 in. = 25 mm.

frequency because of the skin effect. *See* ELECTRICAL SHIELDING; SKIN EFFECT (ELECTRICITY).

Coaxial cables can carry high power without radiating significant electromagnetic energy. In other applications, coaxial cables carry very weak signals and are largely immune to interference from external electromagnetic fields.

A coaxial cable's self-shielding property is vital to successful use in broadband carrier systems, undersea cable systems, radio and TV antenna feeders, and community antenna television (CATV) applications.

Coaxial units are designed for different mechanical behavior depending upon the application. Widely used coaxials are classified as flexible or semirigid.

Materials. Conductors for coaxial cable are generally made of copper or aluminum. The low resistivity of these metals results in low cable loss. A typical dielectric material is polyethylene; special grades are made with very low dielectric loss. Where mechanical factors allow, much of the space between inner and outer conductor is occupied by air. This may be done by using spaced insulating disks (Fig. 1) or expanded or spiraled insulation. *See* ALUMINUM; CONDUCTOR (ELECTRICITY); COPPER; POLYOLEFIN RESINS.

Flexible coaxials. These generally have a braided outer conductor and a stranded inner conductor. Insulation is made of solid or expanded plastic of a low-loss electrical grade. Since a single layer of braid has some air gaps between intersecting wires, a second layer of braid is placed over the first when shielding requirements are severe.

Flexible coaxials are used for high-frequency patch cords and intra- and interbay cabling. Very small-diameter coaxials are used to interconnect components on printed wiring boards. Since runs are short in these applications, loss is not generally important.

Semirigid coaxials. This class of coaxials finds the most extensive use in communications systems, such as cables used in long-distance terrestrial and undersea communications. Also, CATV and closed-circuit television often use semirigid coaxials. To minimize cable loss, the insulation may be of expanded plastic, effectively using air bubbles for up to 80% of the dielectric.

Terrestrial coaxials. The coaxial unit in the L3, L4, L5, and L5E carrier systems uses polyethylene disks spaced 1 in. (2.5 cm) apart to keep the inner conductor centered (Fig. 1). The outer conductor is then precision-formed around the disk-insulated inner conductor. Two layers of steel tape are overlapped to complete the unit. The tapes give the assembly mechanical stability and provide added shielding at low frequencies.

Such a coaxial unit has low loss and excellent impedance characteristics. In the L5E system a pair of such coaxial units can carry 13,200 telephone calls. Cables carrying 20 of these coaxial units are used in L-carrier systems (**Fig. 2**), and a 22-unit coaxial

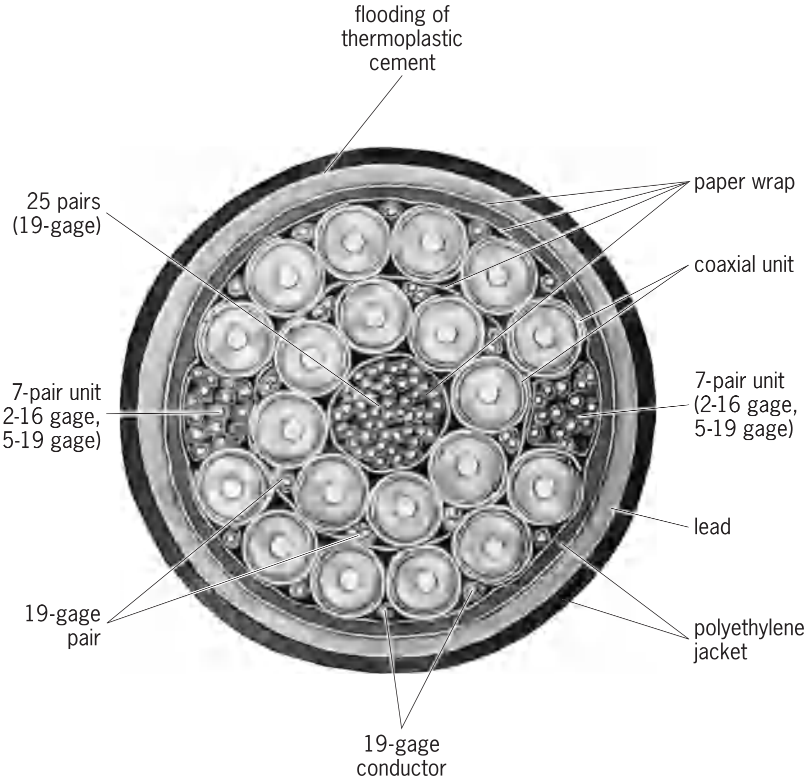


Fig. 2. Construction of multicoaxial transmission line with twenty 0.375-in. (9.5-mm) coaxial units.

version of this cable was used in later L5E installations. Fully equipped, this cable provides 132,000-telephone-channel capacity over the 10 working coaxial pairs. The eleventh pair provides service protection for the 10 working pairs.

Two coaxial cables span the United States from east to west, with many intermediate and shorter installations. For current and future use, optical fiber cables are playing the key role earlier played by coaxial cables.

Undersea coaxials. To function reliably in a high-performance system in the ocean environment, undersea coaxials must meet severe requirements. Some of these are (1) stable dimensions and predictable transmission characteristics under pressures of up to 11,000 lb/in.^{2} (76 megapascals); (2) 25-year service lifetime; and (3) ability to withstand handling and scuffing. A solid polyethylene core withstands ocean pressure which would crush a cable with any air fill. The use of inert materials that resist attack by marine organisms assures the desired lifetime. The high-strength (300,000-lb/in.^{2} or 2-gigapascal) steel strand and high-density jacket assure survival and continuity despite severe handling.

In coaxial cables used in fourth-generation analog undersea cable systems, the high-tensile steel strand provides longitudinal strength needed to lay or recover the cable in ocean depths of up to 4 nautical miles (7 km). The inner conductor is a high-conductivity copper tube, 0.48 in. (12 mm) in diameter, which is formed and swaged over the steel strand. Low-loss polyethylene is extruded over the inner conductor assembly to form the 1.7-in.-diameter (43.2-mm) cable core. To achieve an accurate (±0.001 in. or 0.025 mm) core diameter, the core is extruded slightly oversize and mechanically shaved.

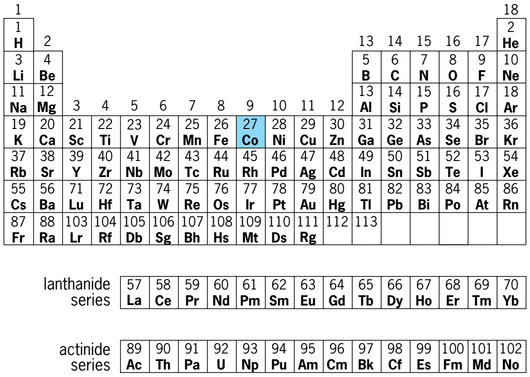
In a further manufacturing operation, the 10-mil-thick (0.010-in. or 0.25-mm) copper outer conductor is formed over the cable core with an overlapped seam. A high-density polyethylene jacket, 2 in. (50 mm) in diameter, is extruded over the outer conductor to complete the cable. *See* COMMUNICATIONS CABLE; SUBMARINE CABLE.

S. Theodore Brewer

Cobalt

A lustrous, silvery-blue metallic chemical element, Co, with an atomic number of 27 and an atomic weight of 58.93. Metallic cobalt was isolated in 1735 by the Swedish scientist G. Brandt, who called the impure metal cobalt rex, after the ore from which it was extracted. The metal was shown to be a previously unknown element by T. O. Bergman in 1780.

Cobalt is a transition element in the same group as rhodium and iridium. In the periodic table it occupies a position between iron and nickel in the third period. Cobalt resembles iron and nickel in both its free and combined states, possessing similar tensile strength, machinability, thermal properties, and electrochemical behavior. Constituting 0.0029% of the Earth's crust, cobalt is widely distributed in nature, occurring in meteorites, stars, lunar rocks, seawater, fresh water, soils, plants, and animals. *See* PERIODIC TABLE; TRANSITION ELEMENTS.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H**																	2 **He**
3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
55 **Cs**	56 **Ba**	71 **Lu**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	103 **Lr**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112	113					

lanthanide series	57 **La**	58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**
actinide series	89 **Ac**	90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**

Cobalt and its alloys resist wear and corrosion even at high temperatures. The most important commercial uses are in making alloys for heavy-wear, high-temperature, and magnetic applications. Small amounts of the element are required by plants and animals. The artificially produced radioactive isotope of cobalt, ^{60}Co, has many medical and industrial applications.

Cobalt, with a melting point of 1495°C (2723°F) and a boiling point of 3100°C (5612°F), has a density (20°C; 68°F) of 8.90 g·cm^{-3}, an electrical resistivity (20°C) of 6.24 microhm·cm, and a hardness (diamond pyramid, Vickers; 20°C) of 225. It is harder than iron and, although brittle, it can be machined. The latent heat of fusion is 259.4 joules/g, and the latent heat of vaporization is 6276 J/g; the specific heat (15–100°C; 59–212°F) is 0.442 J/g · °C. Cobalt is ferromagnetic, with the very high Curie temperature of 1121°C (2050°F). The electronic configuration is $1s^22s^22p^63s^23p^63d^74s^2$. At normal temperatures the stable crystal form of cobalt is hexagonal close-packed, but above 417°C (783°F) face-centered cubic is the stable structure. Although the finely divided metal is pyrophoric in air, cobalt is relatively unreactive and stable to oxygen in the air, unless heated. It is attacked by sulfuric, hydrochloric, and nitric acids, and more slowly by hydrofluoric and phosphoric acids, ammonium hydroxide, and sodium hydroxide. Cobalt reacts when heated with the halogens and other nonmetals such as boron, carbon, phosphorus, arsenic, antimony, and sulfur. Dinitrogen, superoxo, peroxo, and mixed hydride complexes also exist. In its compounds, cobalt exhibits all the oxidation states from −I to IV, the most common being II and III. The highest oxidation state is found in cesium hexafluorocobaltate(IV), Cs_2CoF_6, and a few other compounds.

There are over 200 ores known to contain cobalt; traces of the metal are found in many ores of iron, nickel, copper, silver, manganese, and zinc. However, the commercially important cobalt minerals are the arsenides, oxides, and sulfides. Zaire is the chief producer, followed by Zambia. Russia, Canada, Cuba, Australia, and New Caledonia produce most of the rest. Zaire and Zambia together account for just over 50% of the world's cobalt reserves. Nickel-containing laterites (hydrated iron oxides) found in the soils of the Celebes, Cuba, New Caledonia, and many other tropical areas are being developed as sources of cobalt. The manganese nodules found on the ocean floor are another large potential reserve of cobalt. They are estimated to contain at least 400 times as much cobalt as land-based deposits. *See* MANGANESE NODULES.

Since cobalt production is usually subsidiary to that of copper, nickel, or lead, extraction procedures vary according to which of these metals is associated with the cobalt. In general, the ore is roasted to remove stony gangue material as a slag, leaving a speiss of mixed metal and oxides, which is then reduced electrolytically, reduced thermally with aluminum, or leached with sulfuric acid to dissolve iron, cobalt, and nickel, leaving metallic copper behind. Lime is used to precipitate iron, and sodium hypochlorite is used to precipitate cobalt as the hydroxide. The cobalt hydroxide can be heated to give the oxide, which in turn is reduced to the metal by heating with charcoal.

Cobalt ores have long been used to produce a blue color in pottery, glass, enamels, and glazes. Cobalt is contained in Egyptian pottery dated as early as 2600 B.C. and in the blue and white porcelain ware of the Ming Dynasty in China (1368–1644).

An important modern industrial use involves the addition of small quantities of cobalt oxide during manufacture of ceramic materials to achieve a white color. The cobalt oxide counteracts yellow tints resulting from iron impurities. Cobalt oxide is also used in enamel coatings on steel to improve the adherence of the enamel to the metal. Cobalt arsenates, phosphates, and aluminates are used in artists' pigments, and various cobalt compounds are used in inks for full-color jet printing and in reactive dyes for cotton. Cobalt blue (Thenard's blue), one of the most durable of all blue pigments, is essentially cobalt aluminate. Cobalt linoleates, naphthenates, oleates, and ethylhexoates are used to speed up the drying of paints, lacquers, varnishes, and inks by promoting oxidation. In all, about a third of the world's cobalt production is used to make chemicals for the ceramic and paint industries. *See* CERAMICS; DYE; INK; METAL COATINGS.

Cobalt catalysts are used throughout the chemical industry for various processes. These include hydrogenations and dehydrogenations, halogenations, aminations, polymerizations (for example, butadiene), oxidation of xylenes to toluic acid, production of hydrogen sulfide and carbon disulfide, carbonylation of methanol to acetic acid, olefin synthesis, denitrogenation and desulfurization of coal tars, reductions with borohydrides, and nitrile syntheses, and such important reactions as the Fisher-Tropsch method for synthesizing liquid fuels and the hydroformylation process. Cobalt catalysts have also been used in the oxidation of poisonous hydrogen cyanide in gas masks and in the oxidation of carbon monoxide in automobile exhausts. *See* CATALYTIC CONVERTER.

Although cobalt was not used in its metallic state until the twentieth century, the principal use of cobalt is as a metal in the production of alloys, chiefly high-temperature and magnetic types. Superalloys needed to stand high stress at high temperatures, as in jet engines and gas turbines, typically contain 20–65% cobalt along with nickel, chromium, molybdenum, tungsten, and other elements.

In parts of the world where soil and plants are deficient in cobalt, trace amounts of cobalt salts [for example, the chloride and nitrate of Co(II)] are added to livestock feeds and fertilizers to prevent serious wasting diseases of cattle and sheep, such as pining, a debilitating disease especially common in sheep. Symptoms of cobalt deprivation in animals include retarded growth, anemia, loss of appetite, and decreased lactation.

The principal biological role of cobalt involves corrin compounds (porphyrin-like macrocycles). The active forms contain an alkyl group (5′-deoxyadenosine or methyl) attached to the cobalt as well as four nitrogens from the corrin and a nitrogen from a heterocycle, usually 5,6-dimethylbenzimidazole. These active forms act in concert with enzymes to catalyze essential reactions in humans. However, the corrin compounds are not synthesized in the body; they must be ingested in very small quantities. Vitamin B_{12}, with cyanide in place of the alkyl, prevents pernicious anemia but is itself inactive. The body metabolizes the vitamin into the active forms. Although the cobalt in corrins is usually Co(III), both Co(II) and Co(I) are involved in enzymic processes. Roughly one-third of all enzymes are metalloenzymes. Cobalt(II) substitutes for zinc in many of these to yield active forms. Such substitution of zinc may account, in part, for the toxicity of cobalt. *See* ENZYME; VITAMIN B_{12}.

L. Marzilli; Patricia A. Marzilli

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Coca

Shrubs of the genus *Erythroxylum* in the coca family (Erythroxylaceae). The genus contains over 200 species, most in the New World tropics. Two species, *E. coca* (*see* **illus.**) and *E. novogranatense*, are cultivated for their content of cocaine and other alkaloids. Leaves of cultivated coca contain 14 alkaloids, chiefly cocaine, and significant amounts of vitamins and minerals. The cocaine content averages 0.5%, rarely exceeding 1.0%.

Millions of South American Indians "chew" coca every day as a mild stimulant by placing dried leaves in the mouth and masticating with various alkalies such as lime or plant ashes to promote the release of the alkaloids, which are swallowed. Coca is

Flowering branch of coca (*Erythroxylum coca*).

important in the folk medicine of Andean Indians, especially as a treatment for gastrointestinal disorders. It may regulate carbohydrate metabolism in a useful way and supplement an otherwise deficient diet. Coca also has great magical and religious significance in Andean societies. Although it has long been the focus of political debate, especially in Peru, ritualized use of the leaf in traditional cultures is not inconsistent with good physical health and social productivity. *See* COCAINE; COLA; LINALES.

Andrew T. Weil

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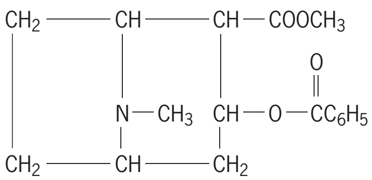
Cocaine

The principal alkaloid of coca leaves, a topical anesthetic and stimulant, and popular illicit drug. The molecular formula is given below. Cocaine was first



isolated by A. Niemann in 1860. In 1884 C. Koller demonstrated its efficacy as an anesthetic in eye surgery, introducing the age of local anesthesia. For the next decade cocaine enjoyed the status of a wonder drug and panacea. It fell into disfavor with increasing reports of acute toxicity and long-term dependence. Today it is used as a topical anesthetic in the eye, nose, mouth, and throat; for injection anesthesia it has been replaced by synthetic drugs with fewer central nervous system effects. *See* ANESTHESIA; COCA.

Cocaine increases heart rate and blood pressure and causes feelings of alertness and euphoria. It stimulates noradrenergic pathways by blocking reuptake of norepinephrine at the synapse, and also stimulates dopaminergic pathways. In animals it can be shown to be strongly reinforcing. It does not produce physical dependence, as alcohol and opiates do, but many people find it hard to use in a stable and moderate fashion if they have access to it in quantity. Although it is quite active orally, most users of illicit cocaine take it intranasally by snuffing; few inject it intravenously. Aside from local irritation of the nasal membranes, occasional users suffer few adverse effects. The psychological consequences of frequent use can be devastating. The soluble hydrochloride salt is the common form. Insoluble cocaine free base, that is, the free alkaloid form of the drug, may be smoked, a practice that increases the toxicity of the drug and is more likely to be associated with dependence. *See* ADDICTIVE DISORDERS; ALKALOID; NORADRENERGIC SYSTEM.

Andrew T. Weil

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Coccidia

A subclass of the class Telosporea. These protozoa are typically intracellular parasites of epithelial tissues in both vertebrates and invertebrates. The group is divided on the basis of life cycles into two orders, the Protococcida (in which there is only sexual reproduction) and the Eucoccida (in which there is both sexual and asexual reproduction). There are only a few species in Protococcida, and all are parasites in marine invertebrates. There are hundreds of species in Eucoccida; these are parasites in both invertebrates and vertebrates. The Eucoccida contains three suborders: Adeleina, which occur mostly in invertebrates and in which there is usually one host for the sexual stages and a different host for the asexual stages (an example is *Hepatozoon muris*, found in rats and transmitted by mites); Haemosporina, which occur mainly in vertebrates and which have their sexual stages in invertebrates (an example is *Plasmodium falciparum* which causes malaria in humans and is transmitted by mosquitoes); and Eimeriina, which occur mostly in vertebrates and in which the sexual and asexual stages occur in the same host (an example is *Eimeria*, species of which cause coccidiosis in many domestic animals and wildlife, and which are transmitted by filth). The malaria parasites and coccidia are of direct importance to humans, and also cause important losses in chickens, cattle, sheep, and other domesticated animals. *See* EUCOCCIDA; PROTOCOCCIDA; PROTOZOA; SPOROZOA; TELOSPOREA.

Elery R. Becker; Norman D. Levine

Coccolithophorida

A group of unicellular, biflagellate, golden-brown algae characterized by a covering of extremely small (1–35 micrometers) interlocking calcite (the hexagonal form of calcium carbonate) plates called coccoliths. The plates show extinction crosses in a polarizing light microscope; however, detailed study requires the use of electron transmission or electron scanning microscopes. The Coccolithophorida are usually considered plants but possess also some animal characteristics. Botanists assign them to the class Haptophyceae (based on the possession of a haptonema, a threadlike organ of attachment) of the phylum Chrysophyta, and zoologists to the class Phytamastigophorea, superclass Mastigophora, subphylum Sarcomastigophora of the phylum Protozoa. *See* CILIA AND FLAGELLA; PHYTAMASTIGOPHOREA; PROTOZOA.

Classification. The Coccolithophorida are mainly classified by the shape of their coccoliths into two groups: the holococcoliths, with simple rhombic or hexagonal crystals arranged like a mosaic; and the heterococcoliths, with complex crystals arranged into boat, trumpet, basket, or collar-button shapes. Classification is complicated by the presence of polymorphism (more than one type of coccolith per cell) and complex life cycles involving alternation of generations either with different types of coccoliths or with none at all (see **illus.**).

Life cycle. Reproduction occurs mostly by fission. Haploid and diploid phases, motile versus nonmotile phases, resting spores, and ameboid and filamentous stages have been noted but their interrelationships require further study.

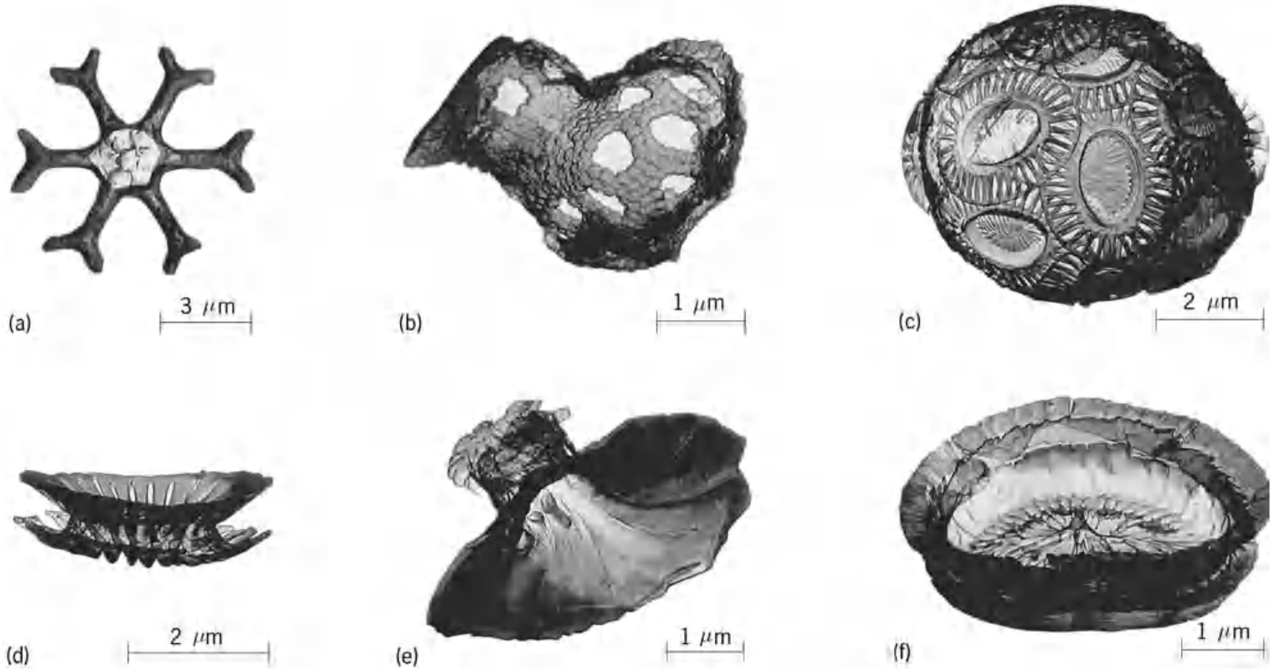
Ecology. Chiefly photosynthetic, although epiphytism, phagotrophism, and saprophytism have also been shown, the Coccolithophorida form a significant percentage of the nannoplankton (plankton of less than 74-μm size) of the tropic through subarctic-subantarctic waters of all oceans; a few brackish and fresh-water species also exist. Together with the diatoms they constitute the primary producers of the open ocean food chain. *See* BACILLARIOPHYCEAE; PHYTOPLANKTON.

Coccoliths. Ease of culture makes these organisms a prime choice for studying biologic calcification. Research shows that coccoliths are extruded to the cell surface after being formed intracellularly on an organic matrix located between the nucleus and a “reticular body,” which plays some yet undiscovered but essential role, and that the process is light-dependent and linked to photosynthesis. Coccolith formation has been introduced in naked cells by lowering the nitrogen content of the culture medium, and coccolith-bearing cells have lost their covering with the addition of carbon dioxide to their medium.

The function of coccoliths is unknown, but one worker suggests that they serve as a shield against excessive sunlight.

Fossil record. Coccoliths preserve well and have a fossil record dating back into the Jurassic, 180,000,000 years ago. They make up limestone and chalk deposits such as the White Cliffs of Dover on land and up to 30% of the sediments underlying tropical to arctic-antarctic ocean waters.

Their long and involved evolutionary record makes them useful for dating ancient sediments. The onset of the Pleistocene, or glacial, period is marked by the appearance of new coccolith species and



Examples of Coccolithophorida. (*a*) *Discoaster*; (*b*) a holococcolith; (*c*) a coccosphere; (*d*) a coccolith; (*e, f*) heterococcoliths. (*A. McIntyre, Lamont-Doherty Geological Observatory of Columbia University*)

the disappearance of older forms, including the discoasters, a group of star-shaped members prominent during the Tertiary. Extinction of the latter in a sedimentary sequence is a classic marker of the Pliocene-Pleistocene boundary.

Because they live in surface waters, coccoliths are under direct climatic control. Thus many modern species with relatively long fossil records are excellent temperature indicators. Research indicates that these can be used to unravel the climatic variations of the Pleistocene period that evolved into present weather patterns. *See* MICROPALEONTOLOGY.

Andrew McIntyre

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Cocoa powder and chocolate

Products derived from the seeds of the tropical tree *Theobroma cacao*, which grows within a narrow belt along both sides of the Equator. There are three basic varieties: Criollo, which was native to Central and South America; Forastero, which constitutes the bulk of the world supply and is mostly cultivated in West Africa and Brazil; and Trinitario, consisting of various hybrids. *See* CACAO.

The seeds, contained in pods which grow on the trunks and lower branches of the trees, are surrounded by a mucilaginous pulp. They are whitish in color and have no normal chocolate flavor. Each mature bean is about $^3/_4$–1 in. (2–2.5 cm) in length with an average weight not less than 0.04 oz (1 g). The shell (testa) is about 12% of the total bean weight, the nib (cotyledon) 87%, and germ 1%—the last being the point at which germination would have commenced in the live bean. The main constituents of the dried nib are approximately the following: fat (cocoa butter) 54%; protein 12–14%; starch, other carbohydrates, and mucilage 20%; tannins 6%; theobromine 1.3%; caffeine 0.2%; and moisture 3–5%. Good-quality beans show a brown or purplish-brown color and striations in the sliced cotyledon. Unfermented beans have a dense structure and slaty color. *See* SEED.

Processing. To develop a chocolate flavor, the beans are first subjected to a fermentation process. The pods are split open and the seeds and pulp placed in heaps surrounded by plantain leaves or in "sweat boxes." Under these conditions microbiological and enzymatic action occurs, with a rise in temperature to about 120°F (50°C).

After 4–6 days, during which the beans are turned over, they develop a purplish-brown color, and the outer shell and nib become more distinct. The pulp liquefies and drains away, and precursors of the true chocolate flavor are formed. After fermentation the beans are sun-dried in shallow trays that are protected from rainstorms by sliding canopies; in very wet climates, such as that found in Cameroon, various forms of artificial drying are used. After drying, the product is described commercially as cocoa or cocoa beans and should have a moisture content of 6–7%.

A series of well-defined operations are used to produce good-quality cocoa or chocolate.

Cleaning. Machines, by a combination of sieving and air elutriation, remove stones, sand, bag fiber, stalks, and immature beans. Without this treatment, grit would pass to subsequent processes, resulting in machine damage and poor-quality products.

Roasting. In this essential process the chocolate flavor is fully developed from the precursors, the shell loosened from the nib, and the moisture content reduced.

There are many roaster designs. One type is a rotating drum with external heating, which may handle single batches or have a continuous throughput. Other roasters use high-temperature air passing through a continuous stream of beans. Roasting temperatures vary greatly, ranging from 200 to 300°F (95 to 150°C). The temperature used is related to the time of roasting and the type of product required. The shell should never be burned.

In two-stage roasting, the beans are heated at a low temperature in a closed, moist atmosphere, and then a higher temperature and drying follow.

Winnowing. After roasting, the winnowing process separates the shell from the nib. The ideal is complete separation with full recovery of the nib, but in practice this is not possible. Winnowing machines have been greatly improved. A modern system uses a bank of vibrating sieves with an air lift to remove shell pieces at the discharge end of each sieve (**Fig. 1**). At the machine entry the beans are broken by hexagonal impact rollers which minimize the production of fine dust. The shell is a waste product that is used as a boiler fuel and an agricultural mulch.

Liquor milling. The roasted nibs are ground at a temperature above the melting point of the cocoa butter constituent (93–95°F or 34–35°C) to produce a dark brown liquid called liquor, mass, or unsweetened chocolate. Finely ground liquor is the basis for manufacture of cocoa powder and chocolate.

Different machines are used for this purpose. Pin and hammer mills in conjunction with roller refiners are frequently used. Other machines include horizontal disk mills with three stages and the vertical ball mill. In the ball mill partially ground liquor is fed through a vertical cylinder containing hard steel or ceramic balls rotated at high speed by means of a central spindle and attached plates.

Cocoa powder manufacture. To manufacture cocoa powder, liquor is subjected to hydraulic pressing, which separates some of the cocoa butter from the solid cocoa matter. The pressing machine consists of a number of pots arranged horizontally, each provided with a filter and linked to a hydraulic ram capable of providing pressures of over 6000 lb/in.^{2} (10^8 pascals). The pots are filled automatically with hot liquor, and when the ram operates liquid cocoa

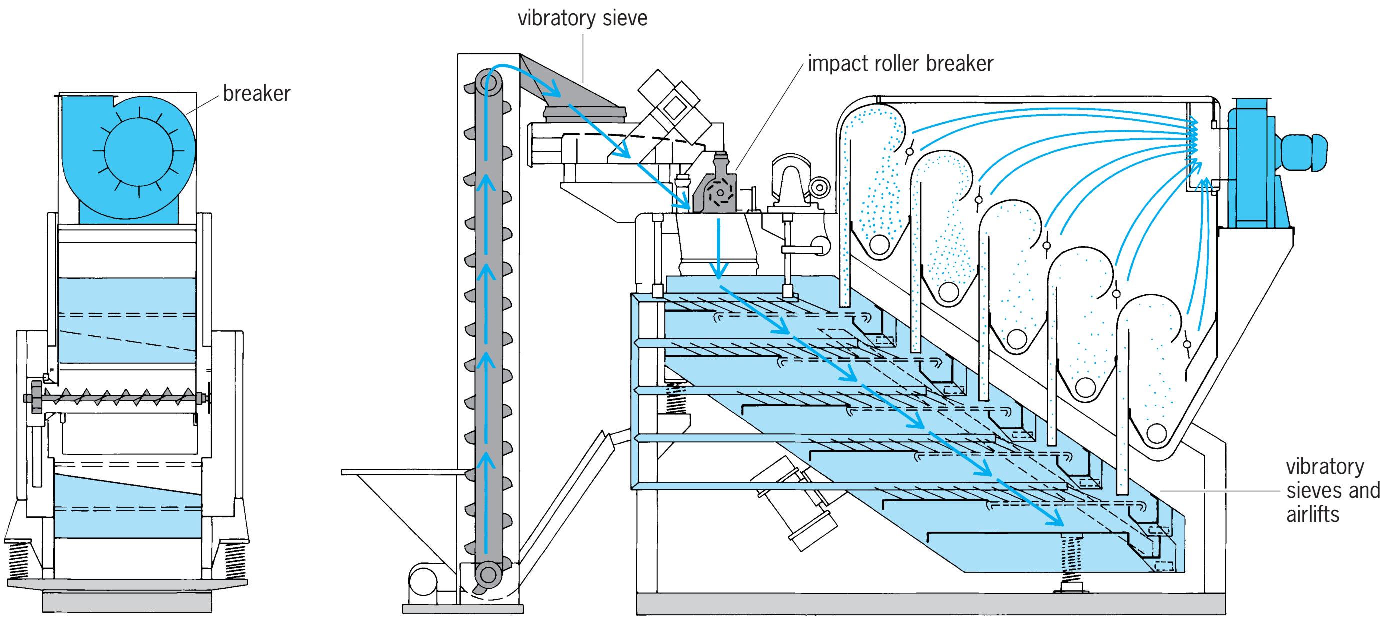

Fig. 1. **Two views of winnowing machine. (*Bauermeister Maschinen Fabrik*, *Hamburg*, *Germany*)**

butter is forced through the filters and into a common channel at the base of the press. The amount of cocoa butter pressed out is determined by control of time and pressure.

At the end of the pressing cycle the ram is reversed, thus opening the pots and releasing compressed cocoa cakes. To make cocoa powder, these cakes are first mechanically broken into small pieces called kibbled cake and then put through pulverizers which, in conjunction with air separators, produce a very fine powder. Such cocoa powder is called natural cocoa.

Additionally, if dark brown or reddish-brown cocoas are required, the liquor, kibbled cake, or preferably the nibs are subjected to a process called alkalization or dutching. This consists of saturating the nibs (or other intermediate) with a solution of potassium or sodium carbonate followed by drying and roasting. In most countries, the amount of added alkali permitted is limited to 3% of the nib.

Color is controlled by the degree of roast of the nib and the quantity and concentration of the alkali used. Alkalization also serves to neutralize the natural acidity of the nib.

Commercial cocoa powders may have a residual cocoa butter content of 10–22%. They are used extensively as ingredients in cookies, biscuits, chocolate syrups and spreads, and vegetable fat coatings.

Chocolate manufacture. Dark, bitter, or sweet chocolate is manufactured from liquor (or nibs), sugar, and cocoa butter—the cocoa butter being obtained from cocoa powder manufacture. Cocoa butter is a very stable, natural fat; it melts just below body temperature and has a narrow melting range. It displays good contraction on solidifying from the liquid state, which enables chocolate to be molded into various shapes. Its melting properties impart good texture in the mouth and flavor release.

Milk chocolate is made from liquor, sugar, milk solids, and cocoa butter. The milk solids are derived from liquid milk, usually by a spray-drying process. Another milk product often used, called milk crumb, is prepared by concentrating and drying liquid milk in the presence of sugar and liquor. This gives a caramelized milk flavor which has proved very popular. *See* MILK.

Refining. In the manufacture of chocolate, the solids are mixed mechanically with liquor and some cocoa butter to give a plastic paste. This paste is fed to refiners, which consist of five steel rolls mounted vertically with the bottom feed roll offset to enable the paste to be delivered continuously from the mixers. The rolls work on a system in which the speed of rotation increases from the bottom to the top roll, thereby obtaining a grinding shear between the roll surfaces and enabling the paste to travel upward from one roll to the next. The refined paste is scraped off the top roll by a sharp blade. In some instances refining is done in two stages. **Figure 2** shows a mixing and double refining system.

Conching. The final process in chocolate making is called conching, which removes moisture and volatile substances that would produce acid and harsh flavors. Conching also reduces viscosity and contributes a smoothness to the eating qualities of the chocolate.

At one time conching was carried out in machines which consisted of a heated tank with a flat bottom over which a roller traveled backward and forward through the liquid chocolate. While these were effective, much time was necessary to produce good chocolate; the process also took much energy, and extra cocoa butter was needed to give fluidity.

Later it was shown that with more powerful machinery it was possible to directly conche the friable

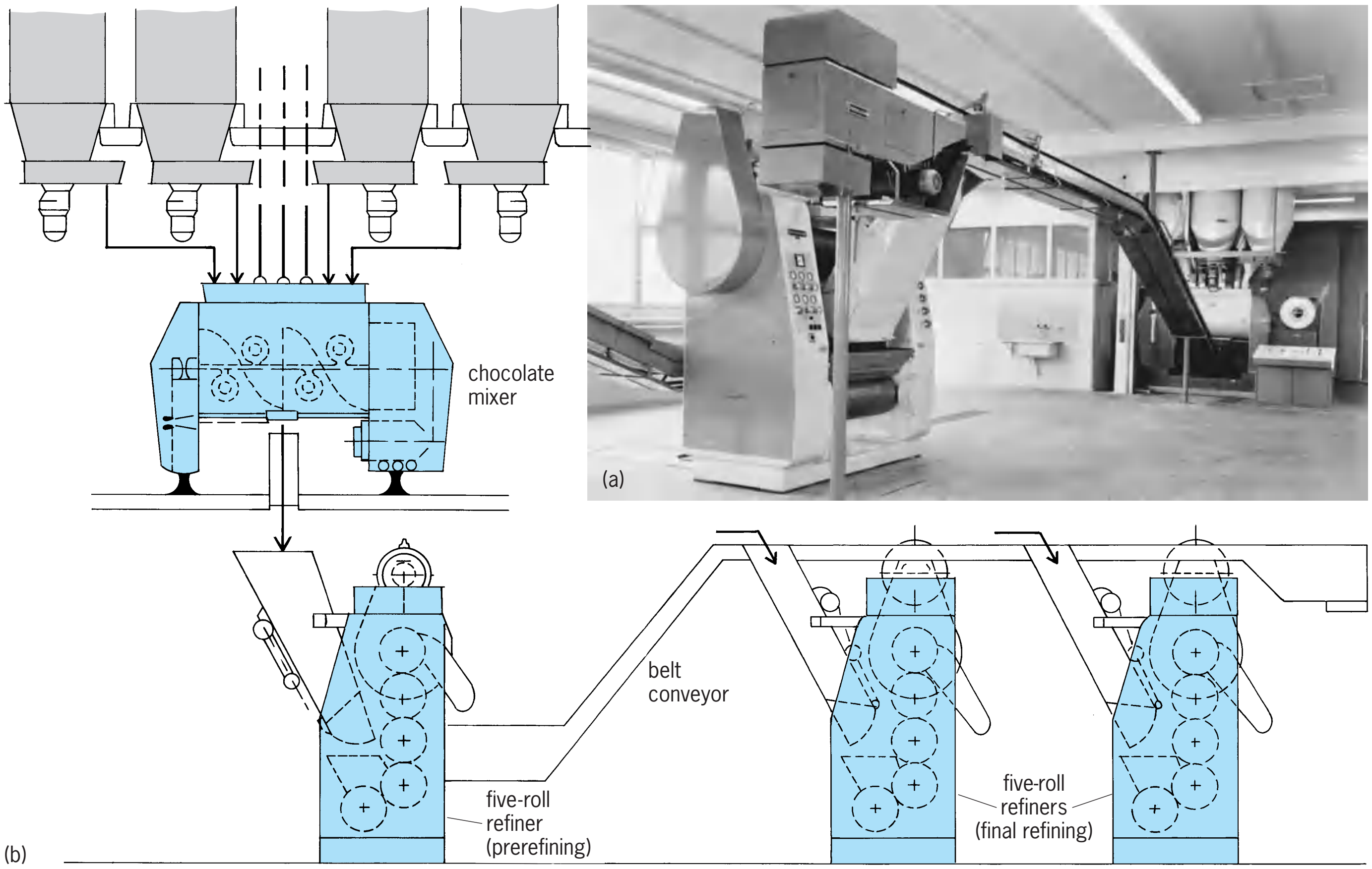

Fig. 2. Modern chocolate-making plant. (*a*) Mixer, conveyor, and refining rolls. (*b*) Diagram of operation of this equipment. (*Buhler-Miag*, *Uzwil*, *Switzerland*)

flake from the refining rolls. This is known as dry conching, a process which removes the volatiles in a much shorter time. Extra fluidity is obtained by mechanical mixing alone. Dry conching is now mostly done in rotary conches (**Fig. 3**), taking about 4 h. Then extra cocoa butter is added and the speed of rotation increased for a further period of 6–12 h depending on the type of chocolate desired.

Fig. 3. Modern rotary conche. (*Petzholdt*, *Frankfurt*, *Germany*)

Besides mechanical improvements, the use of emulsifiers has reduced costs by obtaining the correct fluidity with less cocoa butter. The universally used emulsifier is natural lecithin obtained from the soya bean; in most countries the amount permitted by law is limited to 0.5% of the final chocolate product. About 1 h before the end of the conching period, the emulsifier is added, and the viscosity is checked and adjusted by the addition of more cocoa butter. The final viscosity depends on whether the chocolate is to be used for molding bars or coating confectionery centers.

Tempering. In both refining and conching, the chocolate must be subjected to tempering before it is applied to confectionery centers or deposited into molds. Cocoa butter is polymorphic, which means it crystallizes in several forms on solidifying. Some forms are unstable, and these will transform to the stable form slowly if the chocolate is not tempered, resulting in an unsightly grayish surface film called bloom.

To temper chocolate it is necessary to seed the liquid chocolate with the stable form of crystal. There are several ways of doing this. The most common way is to reduce the temperature of the liquid chocolate from about 100 to 84°F (38 to 29°C), with constant stirring, until cocoa butter seed is formed, and then raising the temperature again to 90–91°F (32–33°C), which will melt out the remaining unstable forms and render the chocolate sufficiently fluid for application. Modern machines called enrobers or coaters carry out this process. *See* FOOD MANUFACTURING. Bernard W. Minifie

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Coconut

A large palm, *Cocos nucifera* (in the family Areacaceae), widely grown throughout the tropics and valuable for its fruit and fiber. Usually found near the seacoast, it requires high humidity, abundant rainfall (60 in. or 1.5 m), and mean annual temperature of about 85°F (31°C). Southern Florida, with mean temperature of 77°F (25°C), is at the limit of successful growth. The origin of the coconut has been in dispute, but strong evidence points to southern Asia with wide dispersal by ocean currents and human migrations. *See* ARECALES.

The fruit, 10 in. (25 cm) or more in length, is ovoid and obtusely triangular in cross section (**Fig. 1**). The tough, fibrous outer husk (exocarp) encloses a spherical nut consisting of a hard, bony shell (endocarp) within which is a $^1/_2$-in. (1.25-cm) layer of fleshy meat or kernel (endosperm). The meat is high in oil and protein and, when dried, is the copra of commerce.

Production and culture. Principal commercial producers are the Philippines, Indonesia, Malaya, Ceylon, and Oceania. Although many trees grow along the seashore and in native villages without special care, the crop lends itself to plantation culture with control of weeds, fertilization, and protection from diseases, insects, and animal pests.

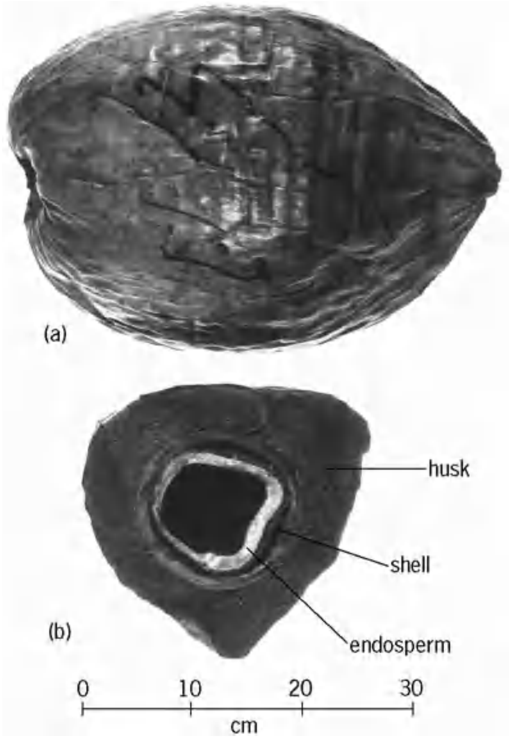

Fig. 1. Coconut. (*a*) Fruit. (*b*) Cross section of fruit showing husk, shell, and endosperm (meat). 2.5 cm = 1 in.

Palms begin to bear nuts the sixth year after planting and reach full bearing about the eighth year. Individual nuts mature about a year after blossoming and normally fall to the ground. In plantation culture, clusters of mature nuts are cut from the trees with knives on long poles just before maturity. Picking individual nuts by climbing the trees is sometimes practiced.

Processing and products. The thick husks are removed from the nuts, which are then split open with a heavy knife and partially dried to loosen the meat. This is pried out of the shell and dried to about 7% moisture either in the sun, if conditions are favorable, or in kilns with additional heat often furnished by burning the husks and shells.

The oil from the dried coconut meats, or copra, is widely used for margarine, soap, and industrial purposes. High-quality copra may be shredded for confectionery and the baking trade. The residue, after oil removal, is used for animal feed.

Coconut husks are an important source of fiber called coir. In coir production, mostly limited to India, the nuts are harvested about a month before maturity and the husks retted in brackish water for 8–10 days to rot away the soft tissues between the fibers. The fiber is cleaned and washed by hand and dried. Recently the industry has become partially mechanized. The various grades of coir are used for ropes, mats and matting, and upholstery filling. *See* COIR.

In the tropics of both the Orient and the Occident the coco palm is the most useful of all plants to the native population. An important source of food and drink, it also furnishes building material, thatch, hats, dishes, baskets, and many other useful items. *See* NUT CROP CULTURE. Laurence H. MacDaniels

Diseases. Cadang-cadang (**Fig. 2**), a disease confined to certain islands of the Philippines, is caused by a viroid. This same agent is also present in the African oil palm and in the Buri palm. No vector is yet known. Since the disease affects mature palms, control is based on replanting with early maturing palms.

Red ring is caused by the nematode *Rhadinaphelenchus cocophilus* and is confined to tropical America. Transverse sections of stems from diseased palms show a typical ring. The disease is always lethal, causing death shortly after infection. The nematode is spread by a palm weevil (*Rhyncophorus palmarum*) which in turn is attracted by damaged palm tissues. Control is effected through sanitation and by the application of insecticides.

Heart rot is confined to tropical America and is caused by a trypanosomatid flagellate protozoon of the genus *Phytomonas*. This organism also attacks the African oil palm. Many of the symptoms resemble lethal yellowing. No effective control is known.

Bud rot is worldwide and is caused by the fungus *Phytophthora palmivora*, which attacks the

Fig. 2. Midstage symptoms of cadang-cadang. Fronds assume an erect position in the crown, and no nuts are being produced.

growing point and causes it to rot. There is no effective control.

Kerala wilt is a debilitating disease of coconut palms in southern India. It results in production of fewer buttons and nuts, reduction of nut size, and thinner husks. The cause is unknown.

Blast and dry bud rot affect young palms in the nurseries and right after planting. Both diseases seem most serious in newly released hybrids. Mycoplasma organisms have been suggested as the cause of blast in the Ivory Coast, where the insect *Ricelia mica* is the vector. *See* PLANT PATHOLOGY.

Luigi Chiarappa

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Coelacanthiformes

An order of lobefin fishes placed in the subclass Coelacanthimorpha and well known as fossils. Coelacanthiformes and the fossil suborders Rhizodontimorphi and Osteolepimorpha (rhipidistians) were once grouped as the subclass Crossopterygii. However, since it is now believed this assemblage is artificial, the coelacanth fraction was elevated to the subclass Coelacanthimorpha, with one order (Coelacanthiformes), four fossil families, and one extant family (Coelacanthidae).

Members are easily recognized by the two dorsal fins, by the paired pectoral and pelvic fins, and the anal fin, and by their symmetrical caudal fin with small central prolongation (**Fig. 1**). The only living fish with such features is *Latimeria chalumnae*; it is also the only extant fish with an intracranial joint, which otherwise occurs only in fossil rhipidistians. In 1952 its habitat was discovered to be the deep waters around the Comoro Islands. A new population of *Latimeria* was discovered in 1998 north of Sulawesi in the Indonesian archipelago.

Anatomy. The Coelacanthiformes (or Actinistia) are the only fishes with a special rostral organ, a deep postcoronoid in the lower jaw, a tandem double articulation of the lower jaw, a postspiracular bone, and an additional bone, the extracleithrum, in the shoulder girdle. Like lungfish, coelacanths lack the marginal upper jaw bone, the maxilla, and possess a short dentary. Except for two Devonian (*Miguashaia* and *Gavinia* with heterocercal tail) and a Carboniferous (*Allenypterus* with diphycercal tail) genus, coelacanths have a caudal fin with equal-sized upper and lower lobe of unbranched fin rays separated by an axial notochordal lobe (triphycercal tail).

On the snout are the three paired openings of the rostral organ in addition to the two paired openings of the nasal sacs (**Fig. 2**). The rostral organ has a central chamber from which three tubes diverge to both sides. It is an electroreceptive organ, unique in its shape and concentration of electroreceptors among fishes.

The lateral side of the lower jaw is formed by angular and splenial bones; a short toothed dentary lies above the splenial bone. The coronoid bones on the dorsal margin of the lower jaw and the prearticular on the inner side of the jaw carry small pointed teeth. The deep postcoronoid reaches high above the dorsal margin of the lower jaw and does not carry teeth. The posterior end of the lower jaw forms a double groove for the articulation (joint) of the double condyle (the rounded process at the end of a bone) of the quadrate and another groove for the symplectic bone (**Fig. 3**).

The posterior moiety (otico-occipital region) of the endocranium carries the brain with labyrinth (the hollow in the temporal bone); a long extension of the pituitary gland (pituitary foot) surpasses the articulation between posterior and anterior moieties and reaches to the base of the anterior. Below the brain cavity the notochord extends in a tube to the posterior end of the anterior moiety. A paired basicranial muscle connects ventrolaterally the anterior with the posterior moiety. The basicranial muscle together with jaw and gill arch muscles acts in the movement of the anterior moiety against the posterior (lifting the snout) and in the opening of the mouth (**Fig. 4**).

The shoulder girdle is composed of anocleithrum, cleithrum, clavicle, and extracleithrum (**Fig. 5**). An unpaired interclavicle unknown in *Latimeria* is

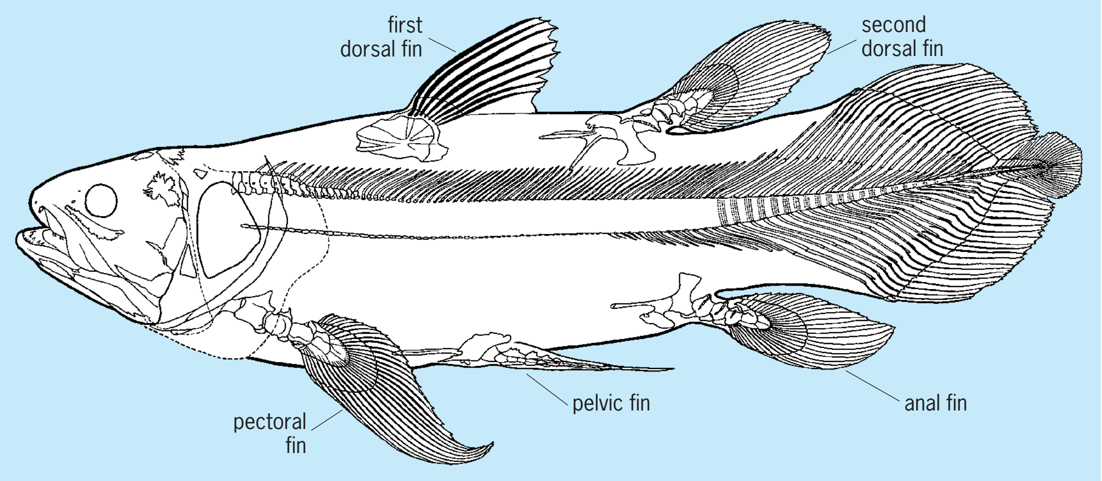

Fig. 1. Overall shape and internal structures of *Latimeria chalumnae*.

known from at least two fossil forms. The endoskeletal scapulocoracoid forms a knob on which the first mesomer of the axial endoskeletal elements of the pectoral fin articulates. Superficial muscles reach from the scapulocoracoid to the distal end of the axial skeleton and the bases of the fin rays; muscles connect internally the axial elements. This fleshy lobe is covered by small scales. The pelvic, second dorsal, and anal fins show the same structure. The first dorsal fin lacks axial elements and the fleshy lobe. The fin rays are articulated but not branched except for one Devonian genus. The exposed surface of the round scales is covered by ridges or tubercles converging toward the median posterior tip of the scales. The vertebral column is formed by an unrestricted notochord with neural arches and spines dorsally and with hemal arches and spines ventrally in the caudal region; ribs occur in some fossil forms. The notochordal fluid is considered by some Far Eastern people to be a life-prolonging elixir. The lung of *Latimeria* is an elongated oil organ well adapted to a deep-water existence. In contrast, fossil coelacanths were shallow-water dwellers with a much larger ossified lung. The intestine is formed as a scroll or longitudinal valve. The rectal gland is a salt-excreting organ which developed in parallel to that of cartilaginous fishes and serves for osmoregulation with high retention of urea. Coelacanths are carnivorous; fish are known to be stomach content in the extant *Latimeria* and in fossil forms.

Reproduction. *Latimeria* shows sexual dimorphism; the female is longer (measuring up to 1.8 m or 6 ft) than the male (up to 1.4 m or 5 ft). Reproduction is by internal fertilization even though the male has no intermittent organ. *Latimeria* has the largest eggs (9 cm or 3.6 in. in diameter) of any bony fish. It is ovoviviparous; up to 30 developing juveniles have been found in one female. Ovovivipary occurs also in Mesozoic coelacanths. Yolk-sac-carrying juveniles of comparatively small Paleozoic coelacanths have been found fossilized; these finds, in addition to the occurrence of unhatched specimens, indicate egg-laying early coelacanths.

Fossil record. Coelacanths are known since the Middle Devonian. They reach high diversity in the Early Triassic and Late Jurassic. Coelacanths acquired their common structure in the Carboniferous. The number of morphological changes is minor thereafter. There is no fossil record for the last 80 million years. The last known fossil coelacanths from the Upper Cretaceous of North America are also the largest known (estimated length of 3.5 m or 11 ft for *Megalocoelacanthus*). Fossil coelacanths are distributed worldwide; Paleozoic forms are known exclusively from the Northern Hemisphere, whereas Mesozoic forms have been found also in southern continents. Most fossil records refer to marine forms;

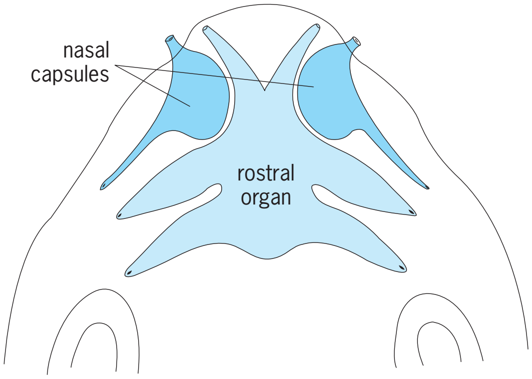

Fig. 2. Snout of *Latimeria*.

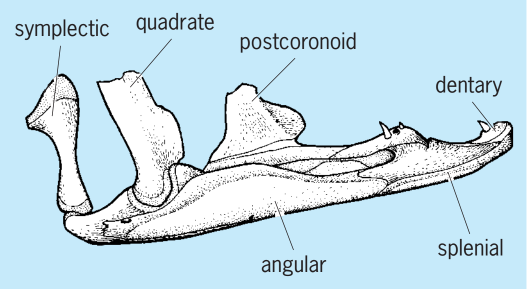

Fig. 3. Lower jaw of *Latimeria* with external bones.

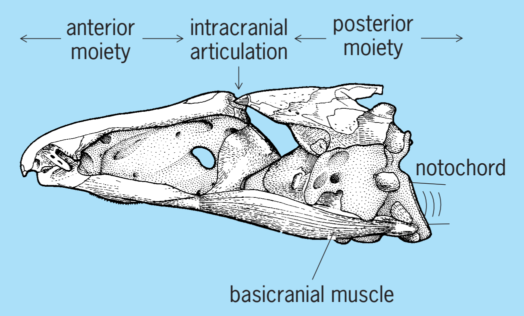

Fig. 4. Endocranium of *Latimeria*.

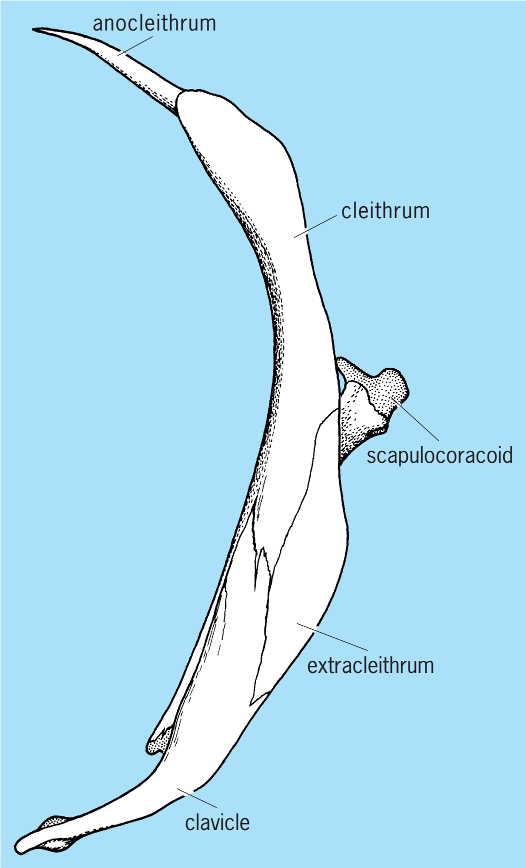

Fig. 5. Shoulder girdle of *Latimeria*.

nevertheless, some coelacanths were able to enter fresh water. *See* FOSSIL.

Relationship. The phylogenetic position of the coelacanthiforms within sarcopterygian fishes is debated. Within extant fishes, they may be closer to tetrapods than to the lungfish, or vice versa. Even the possibility that both coelacanthiforms and lungfish are more closely related to each other than each is to tetrapods is postulated. In any case, both are not close relatives of tetrapods; the latter are related to rhipidistian fishes, especially Elpistostegalia. The living coelacanth is not, as often written, a survivor of human ancestry. *See* OSTEICHTHYES; SARCOPTERYGII.

Hans-Peter Schultze

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Coelom

The coelom is the mesodermally lined body cavity of most animals above the flatworms and nonsegmented roundworms. Its manner of origin provides one basis for classifying the major higher groups.

Annelida. Annelids, arthropods, and mollusks have a coelom which develops from solid mesodermal bands. Within the trochophore larva of annelids, a single pole cell proliferates two strips of mesoblast lying on either side of the ventral midline. These bands subdivide transversely into bilateral solid blocks, the somites. Each somite then splits internally to form a hollow vesicle, the cavity of which is the coelom. The somitic vesicles of each side expand until their surfaces become apposed above and below the gut, thus forming its supporting mesenteries. The anteroposterior surfaces of contact between somites form the septa between segments of the body. In some of the annelids which have developed a parasitic mode of life, as the leeches, septa disappear between segments, and the coelom is much reduced by encroachment of mesenchymatous tissue. *See* ANNELIDA.

Mollusca. The mollusks also form bands of mesoderm from a single pole cell, but these bands do not segment. They split internally to form single right and left coelomic sacs, but the cavities are soon reduced and the surrounding mesoblast disperses as separate cells, many of which become muscle. The only remnants of the coelom in the adult are the pericardial cavity and the cavities of the gonads and their ducts. *See* MOLLUSCA.

Arthropoda. In arthropods paired bands of mesoblast may proliferate from a posterior growth center or may separate inward from a blastoderm, a superficial layer of cells, on the ventral surface of the egg. These bands divide into linear series of somites which then hollow out. Their cavities represent the coelom. The upper wall of each somite moves dorsally to meet its partner from either side and fuse into a longitudinal tube, the heart. The outer and inner somitic walls give rise to muscles of the body wall and gut, respectively. The lower wall may form fat body or move into the appendages to form excretory organs or glands. In adult arthropods the coelom persists only as small cavities within the segmental excretory organs or glands and as the cavities of the gonads and gonoducts. *See* ARTHROPODA.

Echinodermata and Chordata. Echinoderms and chordates constitute a second major group, characterized by the origin of the coelom from outpocketings of the primitive gut wall. In echinoderms one pair of bilateral pouches evaginates and separates from the archenteron or primitive digestive cavity. Each pouch constricts into three portions, not homologous to the metameres of other animals. Of these the left middle coelom assumes major importance, giving rise to the water-vascular system and primordia of the radii of the adult. Contributions to the stone canal and axial sinus are made by the left anterior coelom. The rearmost cavities are converted into the main perivisceral coelom of the adult. *See* CHORDATA; ECHINODERMATA.

Protochordata. The protochordates of the groups Hemichordata and Cephalochordata exemplified by *Balanoglossus* and *Branchiostoma*, respectively, have three coelomic pouches formed by separate evaginations of the archenteral roof. The first or head cavity is single and median in origin, the other bilateral and paired. In hemichordates the head cavity remains single as the cavity of the proboscis and has a pore to the exterior on each side. The second pouches form cavities within the collar and also acquire external pores. The third pair is contained within the trunk and forms the major perivisceral cavity.

Cephalochordata. In cephalochordates the head cavity divides into lateral halves. The left side communicates, by a pore, to an ectodermal pit called the wheel organ. The second pair of pouches forms the pair of mesoblastic somites, and the third pouches subdivide transversely to give rise to the remainder of the linear series of somites. The upper or myotomic portion of each somite remains metameric and forms the segmental muscles. As it enlarges, the coelomic space is displaced ventrally and expands above and below the gut to form the perivisceral cavities and mesenteries, as described for annelids. However, the transverse septa perforate and disappear between adjacent somites, so that a continuous anteroposterior body cavity is formed on either side of the gut.

Vertebrata. In vertebrates the mesoderm arises as a solid sheet from surface cells that have been involuted through the blastopore. Lateral to the notochord, beginning at about the level of the ear, the mesoderm subdivides into three parts: (1) the somites; (2) the nephrotomic cord, temporarily segmented in lower vertebrates, which will form excretory organs and ducts; and (3) the unsegmented lateral plate. The coelom arises as a split within the lateral plate. In lower vertebrates the split may continue through the nephrotome into the center of the somite, thus resembling the condition in *Branchiostoma*. Such dorsal extensions are soon lost. The lateral plate expands to meet its partner of the other side, thus forming the body cavity and mesenteries of the gut. *See* GASTRULATION; INVERTEBRATE EMBRYOLOGY.

Howard L. Hamilton

Coelomycetes

Filamentous fungi that reproduce asexually by making spores inside microscopic fruiting bodies. Estimates of the number of genera range up to 1000, with the number of species between 7000 and 10,000. They are especially numerous on living or decomposing plants, but they can occur on several other substrata. Many are plant pathogens. A few have been isolated in clinical or veterinary settings. Although all members of the group reproduce asexually by making their spores (conidia) via mitosis, some species also have known sexual states (teleomorphs) which produce spores via mating and meiosis.

Taxonomy and identification. The group Coelomycetes was accorded formal status in traditional fungal taxonomy, but it has long been recognized that this group is artificial (nonphylogenetic, that is, encompassing multiple evolutionary lineages). Most members are asexual states of fungi traditionally classed as ascomycetes (Ascomycota), and a very few are asexual states of basidiomycetes (Basidiomycota). Some mycologists now prefer to write the name in lowercase (coelomycetes) to accentuate the nonphylogenetic nature of the group. The coelomycetes are one of three groups of fungi (coelomycetes, hyphomycetes, and mycelia sterilia) reproducing asexually and collectively referred to as imperfect fungi or deuteromycetes. Other names for this collective group are anamorphic fungi or, for those producing conidia, mitosporic fungi. By convention, asexual states of ascomycetes and basidiomycetes are included in deuteromycetes, and asexual states of Zygomycetes are usually excluded. *See* ASCOMYCOTA; BASIDIOMYCOTA; ZYGOMYCETES.

The traditional orders are Melanconiales, Sphaeropsidales, and Pycnothyriales, which correspond to coelomycetes producing fruiting bodies that are disklike with wide apical openings (acervuli, **Fig. 1**), globose with restricted apical openings (pycnidia, **Fig. 2**), or flattened with small apical openings (pycnothyria). Members of the first two orders are much more common and more important as plant pathogens than members of the third order. Each order is also nonphylogenetic, so

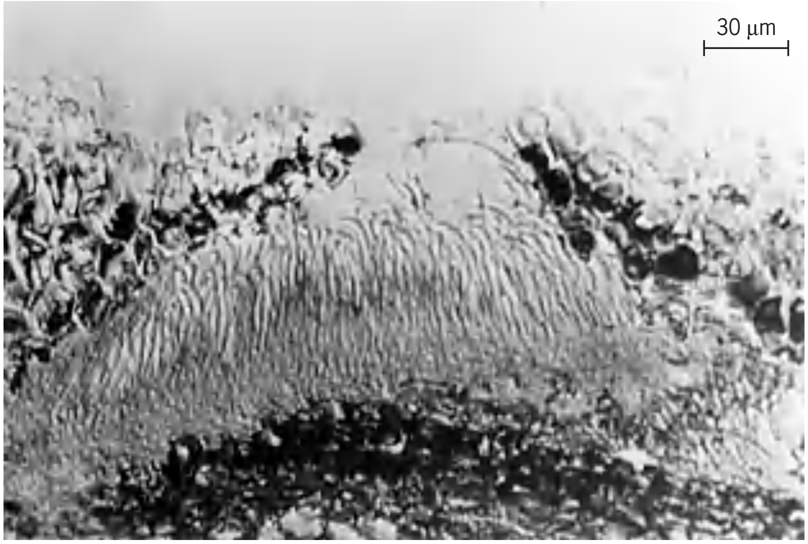

Fig. 1. Section of a typical acervulus, produced by the fungus *Cryptosporiopsis curvispora*, a cause of branch canker and fruit rot of apple.

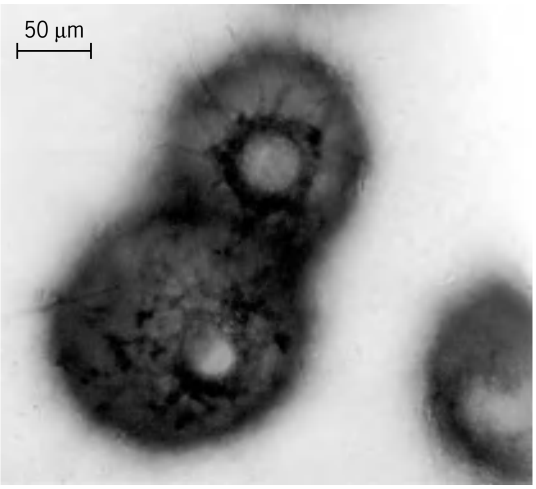

Fig. 2. Surface view of typical pycnidia, produced by the fungus *Ascochyta pinodella*, a cause of stem and leaf spot of pea.

contemporary mycologists often abandon the formal names of the orders and simply refer to acervular, pycnidial, or pycnothyrial fungi. For some fungi, the morphology of the fruiting bodies (conidiomata) is variable or otherwise nonconforming to the above terminology. In such instances, all the above terms may be discarded, and the conidiomata are described in terms of the number of cavities (locules), shape and dimension, wall construction, color, and so on. Of equal or greater importance in modern classification is the structure of the cells that produce the conidia (conidiogenous cells). This approach, first formulated for hyphomycetes by S. J. Hughes, was applied to the coelomycetes by B.C. Sutton, whose name became synonymous with coelomycete taxonomy. Contemporary identification relies on structure and color of the conidia, conidiogenous cells, conidiomata, and proper identification of the host plant. Routine diagnosis still depends on taxonomic keys and descriptions, especially those of Sutton, or the taxonomically more conservative keys of J. A. von Arx, plus literature specific to a given host. Increasingly, DNA sequence data are used in research. Commercial identification kits utilizing molecular-genetic technology are available for a small number of coelomycetes. *See* HYPHOMYCETES.

Cultivation and preservation. Most common coelomycetes can be grown on a variety of artificial, agar-based media. However, the ability to produce conidia or other reproductive structures (such as thick-walled spores called chlamydospores or multicellular structures called sclerotia) may be enhanced by the proper choice of medium. Some coelomycetes may not produce in culture the structures that characterize their growth on plants, and this is especially true of fungi that are acervular *in planta*. Prolonged growth and repeated transfers on artificial media may impair formation of structures or pathogenic abilities. Coelomycetes producing abundant conidia on artificial media usually can be preserved for many years by lyophilization, in glycerol in ultralow-temperature freezers, or in liquid nitrogen vapor. Alternatively, some species will produce conidia on sterilized filter paper squares placed on top of an agar medium. The squares can be removed, desiccated, placed in sterile envelops, and stored in a conventional freezer (approximately −15 to −20°C).

Biology, economic importance, and control. Plant pathogenic genera from temperate and tropical climates have received the greatest attention. Among those with highest impact are *Ascochyta, Colletotrichum*, and *Phoma* species on fruits and vegetables, and *Septoria* and *Stagonospora* species on cereal grains. A given species may parasitize leaves, stems, or fruits of the growing plant, or may be a postharvest pathogen on stored produce. Several genera (for example, *Cryptosporiopsis, Marssonina, Phomopsis*) cause stem cankers on berry bushes or on trees producing fruits or nuts. *Diplodia, Macrophoma*, and *Phomopsis* cause diseases on grape vines or grapes. Species in some genera (such as *Phomopsis, Sphaeropsis*) attack forest trees. *Colletotrichum, Cryptocline, Phomopsis*, and *Sphaceloma* present disease problems for the ornamental flower industry. *Ascochyta, Selenophoma, Septoria,* and *Stagonospora* afflict turf grasses. Fiber crops are attacked by *Colletotrichum* (on cotton, flax, and jute) and *Ascochyta* and *Phomopsis* (on hemp). For important species in which the teleomorph is abundant, much research has focused on the implications that sexual recombination of genes has for generation of new races, fungicide resistance, or enhanced aggressiveness. Sometimes epidemics in field crops are initiated by wind-blown sexual spores (ascospores), in which case control of the sexual stage becomes as important as control of the conidial state. Conidia are usually produced later in the season, are more abundant than ascospores, and tend to be produced in sticky masses dispersed by rain splash or irrigation. Control may be via breeding of resistant plant cultivars, fungicide applications, or cultural practices. In clinical situations, infection by coelomycetes usually occurs through wounds. Itraconazole, an antifungal compound, has been used successfully for therapy. A few coelomycetes are parasitic on lower animals; for example, *Aschersonia* is known as a pathogen of scale insects and whiteflies. Species with saprophytic capabilities can become destructive if colonizing manufactured materials, such as occurs with some *Phoma* species on carpet, paper, or plastics. However, coelomycetes are also recovered in studies of decaying plant litter, where they probably play a beneficial role. Frank Dugan

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Coenopteridales

True ferns which span the Late Devonian through Permian time between the recognizable beginnings of fernlike morphology and the earliest-appearing extant filicalean families (Gleicheniaceae, Osmundaceae). A true fern is a relatively advanced type of vascular land plant with distinct stem, fronds, roots, and foliarborne annulate sporangia. Coenopterid ferns are mostly small and simple in contrast to late Paleozoic tree ferns of the Marattiales. All well-known genera of the Coenopteridales in the Pennsylvanian Period exhibit fronds with circinate vernation (croziers), laminate vegetative foliage, and annulate sporangia. Their stems are mostly protostelic with a few siphonostelic species, and one genus (*Zygopteris*) has secondary growth. These ferns are better from anatomically preserved specimens, especially from peat beds, than from coalified compressions, but they occurred in a variety of habitats mostly known on Northern Hemisphere continents. Their fronds have distinct vascular strands, useful in identifying genera (**Fig. 1**).

There are two major distinct groups. Zygopterid ferns are the most ancient and diverse, and apparently a dead-end evolutionary line; they differ the most from other ferns. *Zygopteris* (Zygopteridaceae: Etapteroideae) had dichotomous rhizomes with distantly spaced erect fronds exhibiting three-dimensionally arranged primary pinnae in four rows. Sessile sori of elongate multiseriate sporangia with paired annuli and with sclerotic nests in their interannular walls were borne abaxially on laminate foliage in *Corynepteris* or trailed from pinnae on slender stalks in *Biscalitheca* (**Fig. 2**). Coenopterid ferns are usually placed in the Anachoropteridaceae and Botryopteridaceae, or in one of several extinct families assigned to the Filicales. Coenopterid ferns *sensu stricto* are probably ancestral to, and consequently form an imperceptible transition with, the Filicales. The best-known genera, *Anachoropteris* and *Botryopteris*, commonly have semierect (like *Osmunda*), protostelic rhizomes with closely spaced fronds bearing two rows of branched pinnae, occasional to frequent buds or vegetative shoots, laminate foliage except on some fertile pinnae, and small to large clusters of uniannulate sporangia. Some of the Pennsylvanian-age fern genera (*Sermaya, Doneggia*) with *Anachoropteris*-like anatomy have been assigned to the filicales as members of an extinct family, Sermayaceae.

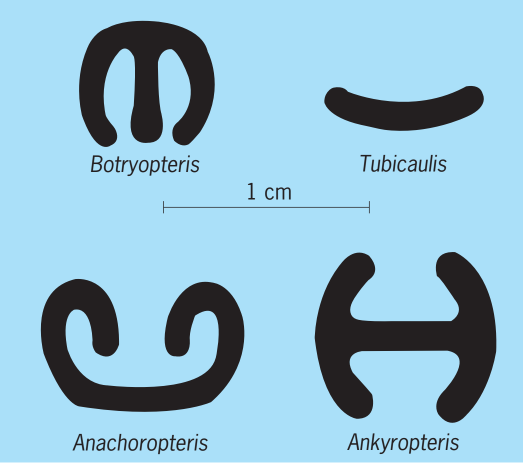

Fig. 1. Diagrammatic cross sections of petiolar vascular strands of representative coenopterid genera, oriented so the parent stem would appear below each diagram.

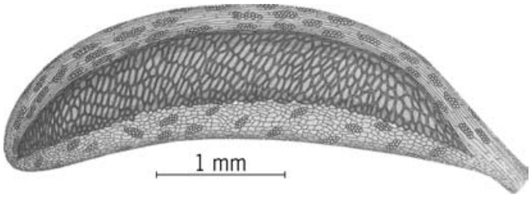

Fig. 2. Side-view reconstruction of ***Biscalitheca musata***, a zygopterid sporangium with dorsiventral symmetry, two lateral multiseriate annuli, and small nests of thickened cells in the sporangial wall. (***After S. H. Mamay, Amer. J. Bot., 44(3):236, 1957***)

Evolution of stelar morphology from protostelic to siphonostelic, with or without leaf gaps, is demonstrated in the Anachoropteridaceae and Botryopteridaceae in the Pennsylvanian. Sporangia of various coenopterid genera are osmundoid, gleichenioid, or schizaeoid, generalized and simple morphological types.

The Zygopteridaceae appear in Late Devonian time, the Botryopteridaceae in Visean (Mississippian), the Anachoropteridaceae in the lower Westphalian A (Pennsylvanian), and all families extend into the Permian. *See* PALEOBOTANY.

Tom L. Phillips

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Coenurosis

The infection by the larval stage of several species of *Taenia* from canids, such as *T. multiceps, T. serialis*, and *T. brauni*. It is rare in humans. A bladder as large as a hen's egg and containing scolices (protoscolices) forms and daughter bladders bud off either internally or externally, attached by stalks. In subcutaneous or ocular locations the bladders are unilocular, but in the central nervous system they are frequently multilocular (racemose). Symptoms are the result of toxic and allergenic metabolites and pressure effects. Surgery may be attempted; chemotherapy may be effective, but secondary effects still render a poor prognosis.

Herbivores feeding on grass contaminated by the parasite's eggs also develop coenurosis. If the central nervous system is involved (as is frequent in sheep) neurological signs appear and the animal staggers and circles. Such an animal is said to be giddy (thus the origin of the term "gid tapeworm"). Economic losses in sheep-raising regions due to coenurosis are considerable. The disease could be controlled by treatment of shepherd dogs. *See* CYCLOPHYLLIDEA.

José F. Maldonado-Moll

Coenzyme

An organic cofactor or prosthetic group (nonprotein portion of the enzyme) whose presence is required for the activity of many enzymes. In addition, many enzymes need metal ions, such as copper, manganese, and magnesium, for activation. The prosthetic groups attached to the protein of the enzyme (the apoenzyme) may be regarded as dissociable portions of conjugated proteins. The conenzymes usually contain vitamins as part of their structure. Neither the apoenzyme nor the coenzyme moieties can function singly, since dissociation of the two results in inactivation. In general, the coenzymes function as acceptors of electrons or functional groupings, such as the carboxyl groups in α-keto acids, which are removed from the substrate. Some of the well-known coenzymes are mentioned below. *See* PROTEIN; VITAMIN.

The pyridine nucleotides, nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP), function as hydrogen acceptors for a large number of dehydrogenase enzymes. Thiamine pyrophosphate (TPP), or cocarboxylase, the prosthetic group of carboxylase, is responsible for the decarboxylation of α-keto acids in the body. Flavin mononucleotide (FMN) and flavinadenine dinucleotide (FAD) act as hydrogen acceptors in aerobic dehydrogenases. Pyridoxal phosphate, also known as codecarboxylase and cotransaminase, serves as coenzyme for various racemases in reactions involving the decarboxylation of α-amino acids, and also functions in transamination.

Iron protoporphyrin (hemin) acts as coenzymes of catalase, peroxidases, and cytochromes. The uridine phosphates are involved in carbohydrate metabolism. Uridine diphosphate (UDP) is the chief transferring coenzyme for carbohydrates. UDP-glucose is responsible for the interconversion of glucose and galactose, is used in the synthesis of glycogen, and can be oxidized to UDP-glucuronate for the synthesis of glucuronides and chrondroitin or converted to UDP-galactose for the synthesis of lactose and chrondroitin.

Adenosine triphosphate (ATP), adenosine diphosphate (ADP), and adenosine monophosphate (AMP), the phosphorylated derivatives of adenylic acid, can be active in phosphate transport or transphosphorylation or both. Lipoic acid functions in acyl-generating and in acyl-transfer reactions. In combination with TPP and NAD, it functions in oxidative decarboxylation of α-keto acids. Coenzyme A (CoA), a coenzyme in certain condensing enzymes, acts in acetyl or other acyl group transfer and in fatty acid synthesis and oxidation. Folic acid coenzymes are involved in the metabolism of one carbon unit. Biotin is the coenzyme in a number of carboxylation reactions, where it functions as the actual carrier of carbon dioxide. *S*-Adenosylmethionine, active methionine, functions is transmethylation reactions. *See* ADENOSINE DIPHOSPHATE (ADP); ADENOSINE TRIPHOSPHATE (ATP); BIOCHEMISTRY; BIOLOGICAL OXIDATION; BIOTIN; CARBOHYDRATE METABOLISM; CYTOCHROME; ENZYME; HEMOGLOBIN; NICOTINAMIDE ADENINE DINUCLEOTIDE (NAD); NICOTINAMIDE ADENINE DINUCLEOTIDE PHOSPHATE (NADP); URIDINE DIPHOSPHOGLUCOSE (UDPG).

Mary B. McCann

Coesite

A naturally occurring mineral of wide interest, the high-pressure polymorph of SiO_2. Coesite was first discovered and identified in various meteorite impact craters and in some tektites. Because it requires a unique physical condition, extremely high pressure, for its formation, its occurrence is diagnostic of a special natural phenomenon, in this case, the hypervelocity impact of a meteorite.

Coesite occurs in grains that are usually less than 5 micrometers in size and are generally present in small amounts. The properties of the mineral are known mainly from studies of synthesized crystals. It is colorless with vitreous luster and has no cleavage. It has a specific gravity of 2.915 ± 0.015 and a hardness of about 8 on Mohs scale. It is biaxial positive with $2V$ about 64°. Its indices of refraction are α 1.5940, β 1.5955, and γ 1.5970 ± 0.0005. Its dispersion is horizontal, with r less than v (weak). The optical orientation is $X = b$, $Z \angle C = 4\text{–}6^\circ$, and $\beta = 120^\circ$. Synthetic crystals occur as euhedral to subhedral hexagonal platelets, and laths with positive elongation. Simple contact twins occur with (021) as twin and composition plane.

Natural coesite can be identified from thin sections of rocks by its peculiar habit and high index of refraction. However, its positive identification must rest on the x-ray powder diffraction technique.

Coesite has as yet no evident commercial use and therefore has no obvious economic value. As a stepping-stone in scientific research, it serves in at least two ways: where it occurs naturally, coesite is diagnostic of a past history of high pressure; the natural occurrence of coesite suggests that shock as a process can transform a low-density ordinary substance to one of high density and unique properties.

Coesite has been found in materials ejected from craters formed by the explosion of 500,000 tons (450,000 metric tons) of TNT. The study of coesite and craters is important to the understanding of the impact craters on the Earth as well as those on the Moon. Edward C. T. Chao

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Coffee

A tropical evergreen shrub or small tree of the genus *Coffea* (Rubiaceae), a native of northeast Africa and adjacent southwest Asia. The beverage known as coffee is made by the hot-water extraction of solubles from the ground roasted beans (seeds) of the shrub. *Coffea* grows mainly between the Tropic of Cancer and Tropic of Capricorn at elevations of 2000–6000 ft (600–1800 m) above sea level, at temperatures near 70°F (21°C), and with annual rains near 60 in. (150 cm).

Annual international commerce is about 75 million bags (standard of 130 lb or 60 kg per bag) of green coffee beans, that is, coffee beans that have been cultivated, harvested, and are ready for commercial processing. The supply generally is a third each from Brazil, Africa, and all other countries. The United States and Europe consume 85% of all world exports. Coffee beverage has no nutritive value and is consumed for its flavor and stimulating effects. The stimulating ingredient in coffee is caffeine. The two main coffee varieties are Arabica with about 1.1% caffeine and Robusta with 2.2%. *See* CAFFEINE.

History. The *C. arabica* shrub (**Fig. 1**) is native to Ethiopia, where it grows wild in rainforests, and its seeds have been used by the native populations since before recorded time. The *C. robusta* shrub grows taller (to 20 ft or 6 m) than the Arabica shrub and is more productive and hardy. It grows in warmer climates and is native to the Congo area south of Ethiopia. About A.D. 900, Arabs planted the Ethiopian coffee shrub in Yemen, and for 700 years coffee propagation was limited to this area.

Fig. 1. *Coffea arabica* branch.

Commercial coffee cultivation was started by the Dutch in Java and Ceylon in the late 1600s; by the French, English, and Spanish in the West Indies in the early 1700s; in Mexico, Central America, and Hawaii in the early 1800s; in Colombia about 1900; and in Africa in the late 1940s. Brazil had been the dominant supplier since the early 1800s, but its dominance receded in favor of African coffee. However, Brazil has become a large producer of soluble coffee powder, producing over 60 million pounds (27 million kilograms) per year.

Green coffee cultivation. The coffee plant is a shrub or relatively small tree, often controlled to a height of 15–18 ft (4.5–5.5 m). *Coffea arabica* (milds) accounts for 69% of world production; *C. canephora* (robustas), 30%; and all others, 1%. Each species includes several varieties.

After the spring rains, the plant produces white flowers. About 6 months later the flowers are replaced by fruit the size of a small cherry (Fig. 1). The cherries can be underripe, ripe (red, yellow, and purple color), and overripe; and they can be selectively picked to harvest only ripe ones, or strip-picked to yield mostly ripe but also some over- or underripe fruit. The green coffee beans are the two halves of the seed derived from the processed cherries. Franklin Kramer

Diseases. There are more than 350 known diseases of coffee, and new ones are still being discovered on *C. arabica*, *C. robusta*, *C. liberica*, and *C. excelsa* in widely separated tropical lands. Probably no crop grows under more varied conditions or is subjected to so many unknown diseases.

Leaf rust (caused by *Hemileia vastatrix*), one of the most important diseases of the crop worldwide, was described as early as 1869 in Ceylon, where there were once flourishing coffee plantations. Rust became so damaging that, in the absence of control measures, coffee production had to be abandoned. In Eastern and African coffee-producing countries, rust restricted cultivation of coffee to particular altitudes and districts, rendering cultivation more expensive and difficult. As a consequence, the center of the world's potential coffee production shifted to Brazil and other South and Central American countries, where leaf rust was unknown until 1970. Control of the disease can be achieved by fungicidal sprays, but this inevitably increases production costs. Development of resistant varieties is complicated because of the existence of many different races of the coffee rust fungus, but some new introductions show promise.

Other diseases, which are less widespread than leaf rust, have also been extremely damaging. In East Africa, bark disease (caused by *Fusarium stilboides*) destroyed the once-flourishing coffee

Fig. 2. Coffee berry disease (caused by *Colletotrichum coffeanum*). Berries, which may be infected at any stage of development, are completely destroyed.

industry of Malawi and, in the late 1960s, berry disease (caused by *Colletotrichum coffeanum*; **Fig. 2**) devastated the crop in Kenya and threatened the viability of the coffee production. Fungicidal sprays now give control. Berry disease spread from Kenya to all other African coffee-producing countries, but is unknown outside the African continent.

American leaf spot (caused by *Mycena citricolor*) is very serious but is found only in the Americas, whereas Cercospora leaf spot and the leaf rot caused by *Pellicularia koleroga* occur in both hemispheres. The last two diseases are controlled by spraying.

Fruit, stem, and branch infections are injurious. Wilts and trunk cankers, caused by *Gibberella, Nectria*, and *Ceratocystis*, are troublesome. Probably six *Rosellinias*, a few *Fusaria*, two *Armillarias*, and fungi like *Fomes, Ganoderma*, and *Polyporus* attack roots. Root and trunk infections are reduced by good cultural practices. Coffee is also affected by some half dozen viruses, a few bacteria, and numerous parasitic mistletoes. *See* FUNGISTAT AND FUNGICIDE; PLANT PATHOLOGY; PLANT VIRUSES AND VIROIDS.

Ellis Griffiths

Coffee cherry processing. Coffee cherries are processed by either dry or wet methods. Dry-method products are so-called natural coffees, while wet-method products are usually the more uniform and higher-quality washed coffees.

The dry method is used in Brazil and in other countries where water is scarce in the harvesting season. The cherries from strip picking are spread on open drying ground and turned frequently to permit thorough drying by the sun and wind. Sun drying usually takes 2–3 weeks, depending on weather conditions. Some producing areas use hot air, indirect steam, and other machine-drying devices. When the coffee cherries are thoroughly dry, they are transferred to hulling machines that remove the skin, pulp, parchment shell, and silver skin (a thin cellulosic layer that envelops the coffee bean) in a single operation. In Colombia, freshly picked ripe coffee cherries are fed to a tank for initial washing and removal of stones and other foreign material. The cherries are then transferred to depulping machines that remove the outer skin and most of the pulp, although some pulp mucilage clings to the parchment shells that encase the coffee beans. This is removed in fermentation tanks, usually containing water, a process that may last from 12 h to several days. Because prolonged fermentation may cause undesirable flavors and odors in the beans, enzymes may be used to speed up the process.

The beans are then dried, either in the sun or in mechanical dryers. Machine drying has become more popular in spite of higher costs, because it is faster and independent of weather conditions. After drying, the coffee is further processed in machines that remove silver skins, producing green coffee beans. The coffee beans are then machine graded by screens, oscillating tables, and airveying (pneumatic conveying) into large, medium, and small beans. Damaged beans or foreign materials are removed by hand or by mechanical sorting devices. The beans are then further graded according to appearance, color, and cupping of roasted samples. After processing, the green beans have 10–12% moisture and maintain acceptable quality for about a year.

Coffee chemistry. Chemical analysis of green coffee reveals a complex chemical composition (**Table 1**). The main differences between milds and robustas are caffeine content (higher for robusta coffee), lipids (higher for milds), chlorogenic acid (higher for robusta), trigonelline (higher for milds), and sucrose (higher for milds).

Green coffee has no desirable taste or aroma—these qualities result from roasting. Many complex physical and chemical changes occur during roasting, including the change in color from green to brown. In the first stage of roasting, free water is removed. In the second stage, chemical reactions lead to the formation of compounds associated with aroma and flavor.

Some reactions during roasting are exothermic. These produce a rapid rise in temperature, usually accompanied by a sudden expansion or puffing of the beans, with a volume increase from 50 to 100% depending on the bean variety and roasting conditions. The relatively high value of caffeine in brewed and instant coffee solids (**Table 2**) is due to the very high solubility of caffeine in hot water compared to the other constituents in the roasted beans. The total solids content in a brewed cup of coffee is 0.7–1.2%; espresso coffee has about 3–5% solids. Most aromatic compounds are lost or changed in the instant coffee

TABLE 1. Typical analyses of green coffee, %

Constituent[*]	Type[†]	
	C. canephora (robustas)	*C. arabica* (milds)
Moisture	11 (10–13)	12.5 (10–13)
Lipids	10 (7–11)	15 (14–17)
Ash	4.2 (3.9–4.5)	4.0 (3.5–4.5)
Caffeine	2.0 (1.5–2.6)	1.3 (1.1–1.4)
Chlorogenic acid	9 (7–10)	7 (5–8)
Carboxylic acids	2 (1–3)	2.5 (1.5–3.5)
Trigonelline	0.7 (0.3–0.9)	1.1 (0.9–1.2)
Protein	11 (9–13)	11 (9–13)
Free amino acids	0.8	0.5
Sucrose	4 (3–6)	8 (5–9)
Reducing sugars	0.5 (0.4–0.6)	0.1 (0.1–0.2)
Others[‡]	8.8 (5–10)	5.5 (3–8)
Polymeric carbohydrate		
Mannan	22	22
Arabinogalactan	17 (16–18)	15 (14–16)
Cellulose	8 (7–9)	7 (7–8)

[*] Dry basis (ex moisture; as-is basis).
[†] Typical value (range).
[‡] Others by difference.

processing steps. Instant coffee producers are particularly interested in the nature of these compounds and how to capture and include them in the final product.

Green-bean processing. A series of basic bean processing steps is required to produce the major types of commercial coffee products (**Fig. 3**). First, the green beans are weighed and cleaned, and then they are stored in silos, each containing a single bean type. Green coffee beans to be used for decaffeinated coffee products are processed separately to remove the required amount of caffeine (usually 97% in the United States) and then stored in special silos before further processing.

Roasting and grinding technology. Roasting and grinding are key steps in producing all coffee products.

Roasting. The roasting step, including the type of beans, roasting machinery, and operating parameters (particularly temperature and time), is the most important operation in defining the final product characteristics. Roasting is performed with individual bean types, blended beans, decaffeinated beans, and beans with additional ingredients—for example, sugar and chicory may be added to form specialized flavored coffees.

Roasting is usually conducted by use of hot combustion gases in rotating cylinders or fluidized-bed systems. Infrared and microwave energy has been used to a limited extent in the Far East. The hot-gas roasters are designed for batch and continuous operations. Batch cylinder roasters, which continue to be used only by smaller producers and for specialty products, traditionally have had roasting times of 10–20 min. Fluidized-bed batch roasters roast beans for 2–5 min. Continuous roasters, which are available in cylinder and fluidized-bed form and can achieve very short roasting times, are best suited for large producers that are roasting a consistent blend.

After moisture has been eliminated and the bean

TABLE 2. Approximate analyses of roasted, brewed, and instant coffee, %[*]

Constituent[†]	Roasted	Brewed	Instant
Moisture	4 (1–5)		3.5 (2–5)
Oil	17 (16–20)	0.8 (0.2–1.0)	(0.1–0.6)
Ash	4.5 (4–5)	14	9 (7–11)
Caffeine	1.2 (1.0–1.6)	4.8	3.5 (2–5)
Chlorogenic acid	1.5 (1–3.5)	14.8	(3–9)
Carboxylic acids	3 (2–4)	3.0	5.5 (4–8)
Trigonelline	0.5–1.0	1.6	(0.5–2)
Protein	8–10	6	(1–6)
Reducing sugar	0.2	0.4	(1–5)
Sucrose	0.2 (0–0.5)	0.8	(0.6–0)
Aroma compounds	0.1	0.1–2	0.05
Browning products and others	(22–11)	29.4	(20–35)
Polymeric carbohydrate	38	24	(30–50)
Mannan	20		
Arabinogalactan	12		
Cellulose	6		

[*] Typical value (range).
[†] Dry basis (ex moisture; as-is basis).

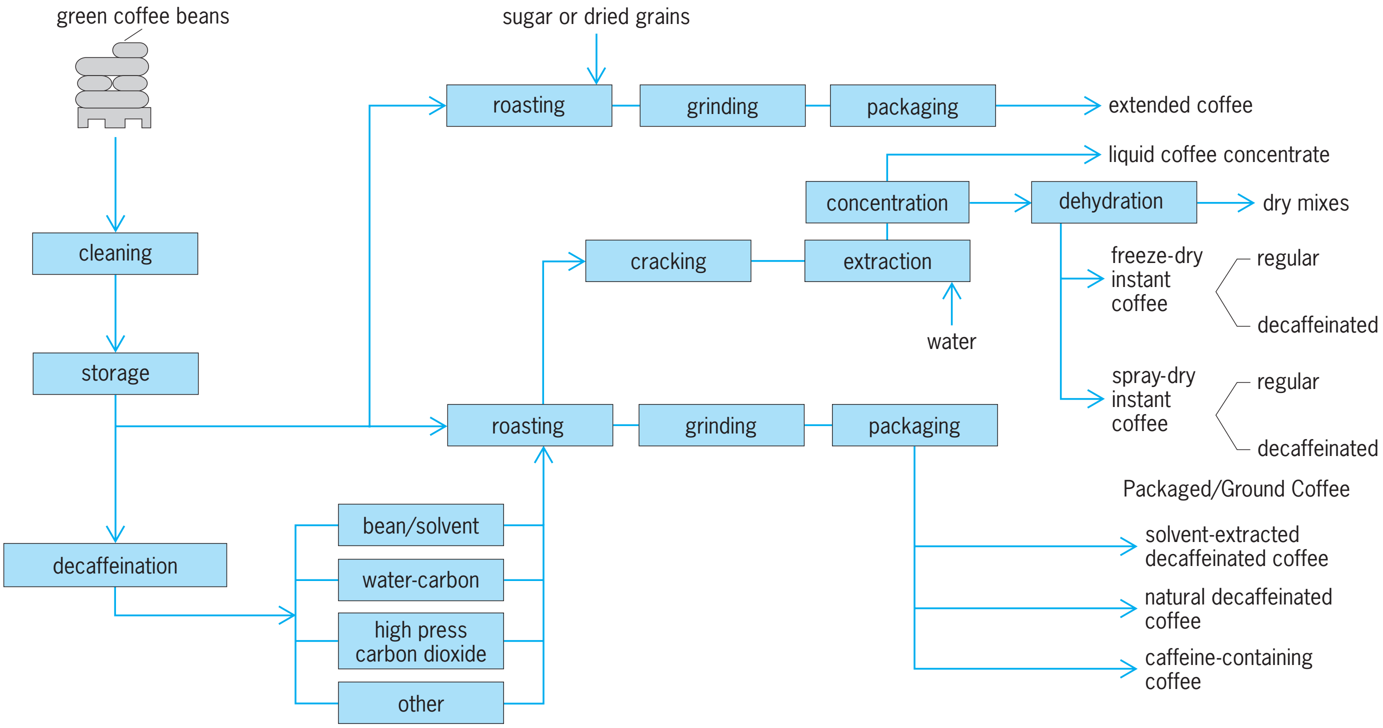

Fig. 3. Flow chart showing the basic processing steps for producing coffee products from green coffee beans.

temperature has reached 330°F (166°C), the reaction changes from endothermic to exothermic, and the required features of the roasted product begin to develop while the beans swell to as much as twice their original size. When the bean temperature reaches 375–475°F (190–246°C), roasting is terminated by rapidly adding a water quench. The final roast temperature is the critical control point that fixes the flavor and color of the product, and it must be consistent for good quality control. Periodic photometric reflectance tests on a ground sample are used for fine-tuning the required bean temperature just before quenching. The water quench adds moisture (usually 2–4%) to the roasted beans.

The faster fluidized-bed roasters are used for producing high-yield coffee. This method provides faster roasting with significantly lower combustion gas temperatures, resulting in more uniform temperature within the beans and hence a larger percentage of soluble solids. Such coffees lend themselves to the low-weight packaged roast and ground coffee, and offer higher yield opportunities for instant coffee processes. Roasting gas temperatures range from 450 to 750°F (230 to 400°C). The exhausted roaster gas normally requires afterburners to remove particulates to conform with environmental regulations. *See* FLUIDIZATION.

The quenched beans are air cooled and conveyed to storage bins for moisture and temperature equilibration prior to grinding. Residual foreign material (mostly stones) that has passed through the initial cleaning step is removed in transit to the storage bins by means of a high-velocity air lift, which leaves the heavier debris behind. The separation is much more efficient at this point because bean density has been reduced by the roasting step.

Grinding. Grinding of the roasted coffee beans is tailored to the requirements of the intended beverage preparation. For example, only coarse cracking of the beans is needed for instant coffee, whereas finer grinds are required for packaged roast and ground coffee.

The most commonly used grinder is a multistep steel roll mill. After passing through a pair of coarse cracking rolls, the broken beans pass through two successive sets of paired longitudinally scored rolls that are operated at speeds designed to cut, rather than crush, the particles. The second set of rolls are more finely scored and operate at higher speeds. The final part of the roll grinder is the normalizer mixing section, to provide a uniform distribution. Particle size is controlled by regulation of roll separation.

Instant coffee processing. Instant coffee comprises the dried solids made from water extraction of the soluble solids in roasted and partially ground (cracked) coffee. The extraction process follows the same principle as home brewing using a filter-drip percolator, except that it is much more efficient and results in very high solid-extraction yields. The countercurrent staged extraction system consists of a battery of 5–10 vertical columns connected by appropriate manifolds of pipes and valves. The water, heated under pressure to 300–350°F (150–180°C), circulates countercurrent to the cracked roasted coffee by intermittent column stage position changes. The columns do not move, but by valve changes the flow of water is stepwise from the final fresh column to the fully extracted first position, each step lasting 30–45 min. The flowing extract is cooled just prior to the final fresh column so that the finished extract is collected at 150–180°F (66–85°C). Yields of 40–60% by weight of roasted coffee are achieved, depending on the flow rates, type of coffee used, and heat input. *See* EXTRACTION.

The coffee extract is concentrated from about 20–35% to 50% by using multiple-effect vacuum evaporators or freeze concentration, or a combination of both. The flavor of the final dry product can be enhanced by recovering the aroma and flavor compounds prior to, or as part of, the concentration process and then introducing these to the concentrated extract just before drying. The method of drying defines the instant coffee as either spray dried or freeze dried. Spray drying involves spraying the concentrated aroma-enhanced extract into a concurrently flowing stream of hot combustion gases. The amount of flavor retained is greater as the concentration of sprayed droplets increases. The dry product is collected at the bottom of the dryer as a powder of spherical particles. Its appearance and solubility are improved by forming agglomerates of the particles, usually by mixing them with a flow of steam that condenses on them to provide adhesive. The excess moisture is then removed by air drying.

Freeze drying uses special high-vacuum equipment to remove water from the frozen extract by sublimation. The vacuum has to be maintained below 0.5 mmHg (67 pascals). The very low temperature maintained during the drying period minimizes flavor changes and aroma losses. Freeze-dried coffee is more expensive to produce and requires a much higher investment than the spray-dried product. *See* DRYING.

Decaffeinated coffees. Decaffeinated coffees represent about 18% of the total coffee consumption in the United States. Decaffeinated coffee was commercially developed in Europe about 1900. The early process involved direct contact of water-moistened beans with a solvent. The principle of moisturizing green coffee before decaffeination remains a key process step for all decaffeination processes, because it facilitates transport of caffeine through the cell walls. The older European process requires removing the solvent from beans by steam distillation, followed by air drying to remove the water. The caffeine that is removed, after refining to United States Phamacopeia (USP) standards, is a valuable by-product for pharmaceuticals and soft drinks. Though solvent decaffeination has been considered undesirable, solvents not found harmful by various government laboratories continue to be used. In fact, much of the commercial decaffeinated coffee is made from processes closely resembling the original European method. Other processes have been developed to improve coffee quality as well as to minimize solvent residues.

A water extraction process was developed in the United States in 1943 which provided a decaffeinated coffee with improved flavor and with very low solvent residues, in the parts-per-million range. This process used water to extract solids from green beans in a countercurrent staged column system. The green extract was then decaffeinated by extraction with a non-water-miscible solvent, such as methylene chloride, which had solubility characteristics that favored caffeine over the other soluble solids. The decaffeinated green extract was steam stripped to remove residual solvent and then returned to the extraction system. The caffeine-rich solvent extract was concentrated and recovered for reuse.

Natural decaffeination processes were invented and commercialized from the mid-1970s through the 1980s in response to increasing demand for

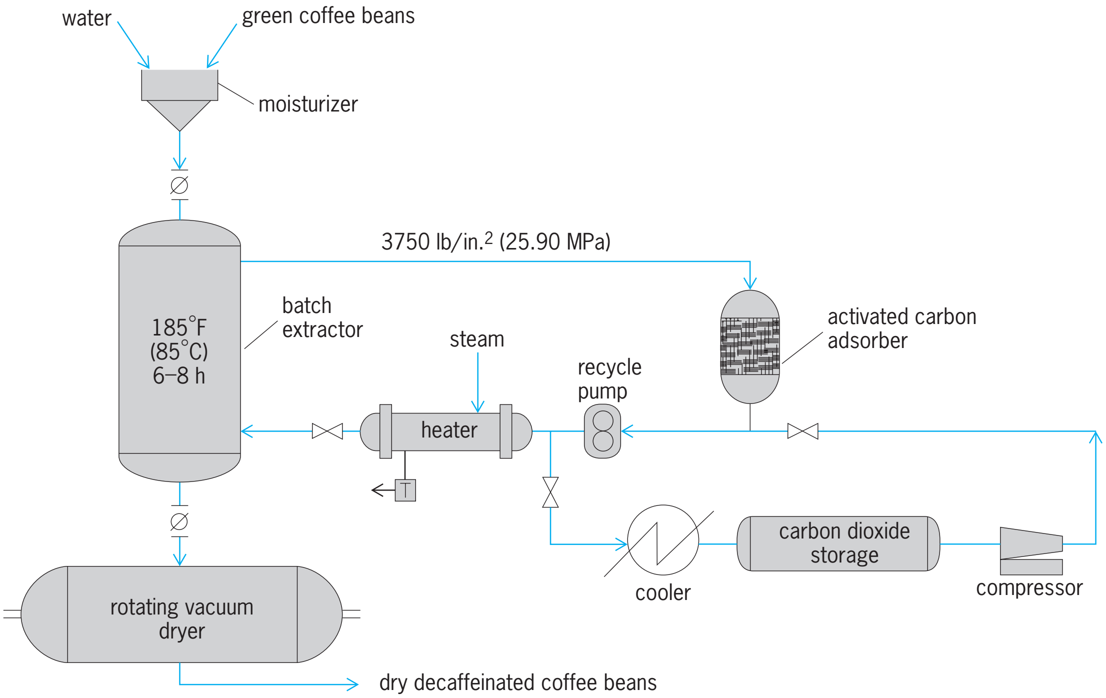

Fig. 4. Flow chart for coffee decaffeination with supercritical carbon dioxide.

decaffeinated coffee that had the same characteristics and quality as regular brewed coffee. Also, decaffeinating solvents, even in trace amounts, were considered to be harmful. Three processes for natural decaffeinated products are commercially available.

Water-carbon process. Referred to as the water process, this method is in many ways the same as the earlier water extraction process. However, instead of using a solvent to remove caffeine from a green coffee extract, the extract is decaffeinated by adsorption using activated carbon. The attraction by the carbon for many of the noncaffeine solids is partially reduced by sugar-coating the carbon. One disadvantage of this process is the inability to recover the caffeine. *See* ACTIVATED CARBON; ADSORPTION.

Supercritical CO_2 processes. Carbon dioxide (CO_2) above its critical temperature (supercritical CO_2) can be used to remove caffeine from green coffee beans (**Fig. 4**). It is a batch operation requiring pressures of about 3500 lb/in. (25.9 megapascals). Supercritical CO_2 is a very specific solvent for caffeine in moistened green beans, but few noncaffeine compounds are removed. Activated carbon adsorbs all the caffeine in the recirculating gas. Even at moderate extraction temperatures, times of 5–8 h are sufficient to obtain the desired degree of caffeine removal. After saturation, the carbon can be regenerated, but the caffeine cannot be recovered. An improved version of the supercritical CO_2 process features two major differences: (1) It simulates a continuous process by intermittently (15-min intervals) removing decaffeinated coffee from the bottom of an extraction tower and then filling space formed at the top of the tower with fresh green coffee. (2) Water is used instead of carbon to remove caffeine from the recirculating supercritical CO_2. The caffeine is then recovered, purified, and dried for reuse.

Other processes. Other so-called natural processes are similar to older solvent processes but use solvents (such as ethyl acetate) considered to be natural, based on the designation "generally regarded as safe" (GRAS) by the U.S. Food and Drug Administration.

Standards. Regulations for decaffeinated coffee differ. The European Economic Community requires that roasted decaffeinated coffee contain no more than 0.1% caffeine (dry basis). This differs from the United States standard, which states "97% caffeine removed," meaning less than 0.03% caffeine in milds and 0.06% in robustas. The United States standard is actually more rigorous, and more difficult to achieve and control.

Product stability and quality. All types of coffee products get stale rapidly when exposed to air, specifically oxygen. Therefore, raw materials, process materials, and the final product must have minimal exposure to oxygen. Although green beans are stable for long periods of time, once roasted, they grow stale in about 7–10 days. Ground coffee becomes stale very rapidly in air and therefore requires vacuum or modified atmospheric packaging (less than 1% oxygen). Once consumer coffee packages are opened, they should be kept refrigerated or in a freezer for extended shelf life.

The instant coffees are less subject to staling but require some of the same packaging and use concerns. The main concern is moisture adsorption due to their hygroscopic nature. Because so-called jar aroma is frequently added, it is desirable to minimize exposure to oxygen. Aromatized instant coffees for consumer sales are normally packaged in nitrogen-flushed jars. *See* FOOD ENGINEERING; FOOD MANUFACTURING.

Franklin Kramer

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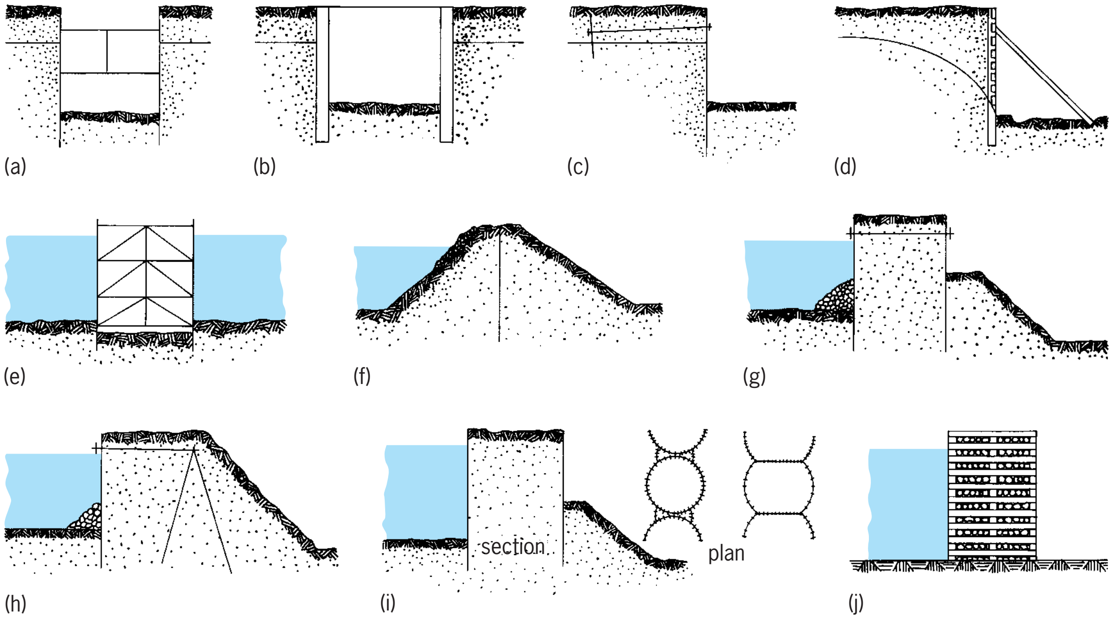
Cofferdam

A temporary wall-like structure which keeps water and soil out of a building site so that construction can proceed under dry conditions. Cofferdams are used in the construction of foundations, bridge piers, dams, dry docks, and similar structures which require dewatering and excavation of an area. The dewatered area can be completely surrounded by a cofferdam structure or a combination of earth slopes and cofferdam structure. The type of construction is dependent on the site depth, soil conditions, fluctuations in water level, availability of materials, working conditions inside the cofferdam, and location either on land or in water. In most situations, since safety, ease of construction, and convenience are the most important considerations, and economy of materials is less important, refined methods of analysis may not be justified. However, an understanding of soil and water pressure against the cofferdam walls is necessary for even the most approximate design. Other important considerations in cofferdam design are the hydraulic analysis of seepage conditions (including filtering), and erosion of the bottom (scour) in streams and rivers.

Where the cofferdam structure can be built on a layer of low-permeability soil (which minimizes the passage of water), the area within the cofferdam can be essentially sealed off. Where the foundation soils are pervious, flow of water into the cofferdam cannot be stopped economically, and the water must be pumped out to maintain dry working conditions.

Types. The **illustration** shows the types of cofferdam construction: *a*, *b*, and *e* are used to enclose small areas, such as individual bridge piers where cross bracing, consisting of steel, wood, or concrete beams and struts, to the opposite wall is practical; the other types are for large areas such as dams,



Types of cofferdams. For use on land: (*a*) cross-braced sheet piles; (*b*) cast-in-place concrete cylinder; (*c*) anchored sheet piles; (*d*) braced vertical piles with horizontal sheeting. For use in water: (*e*) cross-braced sheet piles; (*f*) earth dam; (*g*) tied sheet piles; (*h*) anchored sheet piles with earth berm; (*i*) steel sheet-pile cellular cofferdam; (*j*) rock-filled crib.

river locks, or large buildings, where cross bracing is impractical or undesirable. Cross bracing can be replaced with steel or concrete rings acting in compression when a circular form is used for *a* and *e*.

Sheeted cofferdams are made of sheets of steel, timber, or concrete, driven vertically or placed horizontally. The sheeting may be made reasonably watertight by using interlocking, overlapping, or grouted joints. In gravel or boulders, where sheeting cannot be driven to the required depth, steel H piles are driven vertically into the ground and timber sheeting is placed horizontally between or against the vertical piles (illus. *d*) as the excavation progresses. Watertight cofferdams are designed for a full hydrostatic head of water, plus the pressure of earth when they are on land. Nonwatertight cofferdams have a reduced hydrostatic pressure because of seepage.

Another type of cofferdam suitable for use in gravel or boulders is constructed of cast-in-place concrete. Illustration *b* shows this type in a cylindrical form.

Most sheet-pile cofferdams, with the exception of the cellular type (illus. *i*), require a foundation soil into which the sheets are embedded to give the walls stability. A cellular cofferdam, consisting of interlocking steel sheet piling driven as a series of interconnecting cells, is independently stable when filled and may be constructed on either rock or soil. The cells of the circular type may be filled individually. The cells of the straight-wall diaphragm type must be filled systematically to avoid a differential height of fill that would deform the diaphragms.

The filled crib (illus. *j*) is an open, boxlike structure of timber, precast concrete, or fabricated steel sections, filled with a suitable material. A rock-filled crib is suitable for construction on a rock bottom in swiftly flowing waters. Sheeting or an impervious core provides the necessary watertightness. Earth dams (illus. *f*) can be constructed of soil or rock, but if pervious, a cutoff is required to control seepage.

Another type of cofferdam for a large open building area is a slurry wall anchored back to the earth (illus. *c*). The slurry wall is constructed by pouring a concrete mix into a trench dug along the proposed wall before excavating the cofferdam area.

Uses. When cofferdams are required for year-round construction in waters subject to flooding, they are made sufficiently high to exclude the flood waters. To guard against instability, scour must be prevented along the stream side of cofferdams in swiftly flowing waters by protecting the stream bed. A rock fill, shown in illus. *g* and *h* on the stream side, may be used to provide such protection. In addition, the berms shown in illus. *g*, *h*, and *i* on the dewatered side furnish additional stability and reduce seepage of water under the cofferdam.

The cofferdam in illus. *b* has been used to form a mine shaft 220 ft (66 m) deep. Type *d* was used extensively in subway construction in New York City.

A nautical application of the term cofferdam is a watertight structure used for making repairs below the waterline of a vessel. The name also is applied to void tanks which protect the buoyancy of a vessel. *See* BRIDGE; DAM; FOUNDATIONS.

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Cogeneration systems

Systems in which combined production of electrical power and useful thermal energy is achieved by the sequential use of a fuel or fuels. The electrical power is produced by a generator that is most often powered by a prime mover such as a steam turbine, gas turbine, or reciprocating (piston) engine. Examples of useful thermal energy include hot exhaust gases, hot water, steam, or chilled water. Other names for cogeneration systems are combined heating and power (CHP), district heating, and total energy. *See* DISTRICT HEATING; ELECTRIC POWER GENERATION; GENERATOR; PRIME MOVER; STEAM TURBINE; TURBINE.

The use of cogeneration systems has a number of benefits, including energy efficiency, monetary savings, and reduced environmental emissions. Cogeneration systems may have overall efficiencies of up to about 90%, depending on the application. Because of these high efficiencies, less fuel is consumed and less pollution is generated relative to conventional power plants. Any facility that uses electrical power and has thermal energy needs is a candidate for cogeneration. The basic consideration in determining the feasibility of cogeneration for a particular facility is whether the savings on thermal energy costs is sufficient to justify the capital expenditure. Facilities that may be considered for cogeneration include those in the industrial, commercial, and institutional sectors.

The technology for cogeneration exists for sizes ranging from less than 100 kilowatts to over 100 megawatts. The major equipment requirements include a prime mover, electrical generator, electrical controls, heat-recovery systems, and other typical power-plant equipment. These components are well developed, and the procedures to integrate them into cogeneration systems are well established.

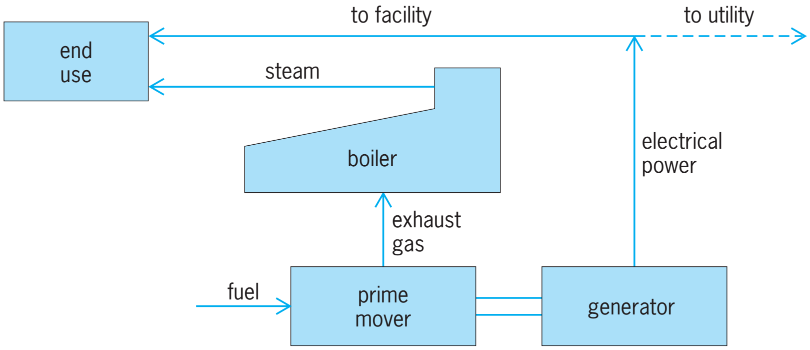

Fig. 1. Cogeneration topping-cycle system.

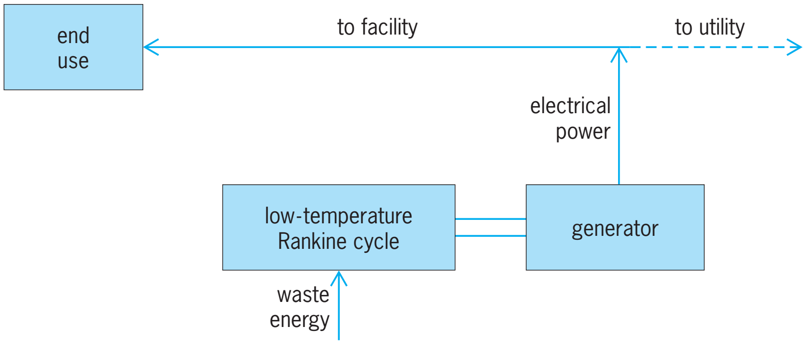

Fig. 2. Cogeneration bottoming-cycle system.

Cogeneration is not new. In the early twentieth century, many industrial facilities generated their own electrical power and often supplied power to nearby communities. They used the thermal energy that was available during the electrical power production to provide or supplement process or building heat. These industrial facilities were the first "cogenerators." As electricity became widely available and less expensive, facilities often stopped generating their own electrical power. It is estimated that from 1954 to 1976 industrial cogenerated electrical power decreased from about 25% to 9% of the total electrical power generated in the United States. Since about the mid-1980s, cogenerated electrical power has been fairly constant at about 5%.

Although arguments for cogeneration technology are persuasive, a number of obstacles constrain the implementation of these systems, including the relatively low cost of electricity, high cost of fuels, high cost of capital investment, environmental regulations, and difficulties working with local utilities. In many cases, these obstacles can be minimized or eliminated, and cogeneration facilities can be developed.

Topping and bottoming cycles. A cogeneration system may be classified as either a topping cycle system (**Fig. 1**) or a bottoming cycle system (**Fig. 2**). For topping-cycle systems, a prime mover uses fuel to power an electrical generator to produce electricity. In one configuration, the hot exhaust gases are directed to a heat-recovery steam generator (HRSG) to produce steam or hot water. This cogeneration system is classified as a topping cycle because the electrical power is generated first at the higher (top) temperature associated with the fuel combustion process, and then the rejected or exhausted energy is used to produce useful thermal energy (such as the steam or hot water in this example). The majority of cogeneration applications are based on topping-cycle systems.

In bottoming-cycle systems (Fig. 2), the high-temperature combustion gases are used first in a high-temperature thermal process (such as high-temperature metal treatment), and then the lower-temperature gases are used in a special low-temperature cycle to produce electrical power. Bottoming-cycle cogeneration systems have fewer applications than topping-cycle systems, and must compete with waste-heat-recovery systems, such as feedwater heaters, recuperators, and process heat exchangers. One of the difficulties with bottoming-cycle systems is the low-temperature electrical power–producing cycle. These cycles are generally much less efficient than conventional-power cycles, often involve special equipment, and use working fluids that are more expensive.

Combined cycles. One power-plant configuration, known as a combined cycle, is based on a form of a topping cycle and is widely used in industry and by electrical utilities. Typically, a gas turbine generates electrical power, and the exhaust gas is ducted to a partially fired heat-recovery boiler. The produced steam drives a steam turbine that produces additional electrical power. In this example, the majority of the steam is then condensed and pumped back to the boiler. To classify as a cogeneration application, some steam would need to be used to satisfy a thermal requirement.

Heat-recovery equipment. Several configurations of heat-recovery devices, or heat-recovery steam generators (HRSGs), are available. HRSGs are often divided into unfired, partially fired, and fully fired. An unfired HRSG is essentially a convective heat exchanger. A partially fired HRSG may include a "duct burner," which often uses a natural-gas burner upstream of the HRSG to increase the exhaust gas temperature. A fully fired HRSG is a boiler that simply uses the exhaust gas as preheated air. These devices can produce hot water, saturated steam, or superheated steam at a range of pressures and temperatures, depending on the need. *See* CONVECTION (HEAT); HEAT EXCHANGER; HEAT TRANSFER.

For chilled water (such as for building cooling), absorption chillers may be used. Absorption chillers use special fluids and a unique thermodynamic cycle to produce low temperatures without the requirement of a vapor compressor that is used in mechanical chillers. Instead of the vapor compressor, an absorption chiller uses liquid pumps and energy from low-temperature sources, such as hot water, steam, or exhaust gas.

Governmental regulations. In 1978 the United States government passed the National Energy Act (NEA), which included the Public Utility Regulatory Policies Act (PURPA). PURPA defined cogeneration systems to include those power plants that supplied a specified fraction of their input energy as useful thermal output in addition to a mechanical or electrical output. For a cogenerating facility to qualify for the privileges and exclusions specified in PURPA, the facility must meet or exceed certain legislated standards. A qualified facility is eligible to use the provisions outlined in PURPA regarding nonutility electrical power generation. In particular, these provisions enhance the interactions between cogenerators and utilities.

Other regulatory legislation directed at managing air and water quality significantly affects the installation of cogeneration systems. Based on the type of fuel and generation process incorporated, the air pollutants regulated for a specific project include nitrogen oxides (NOx), sulfur oxides (SOx), hydrocarbons (HC), carbon monoxide (CO), and particulates. The regulation of emissions from power generation is determined by several different agencies at the federal, state, and local levels. The regulations in some geographical areas have become complex and numerous. For example, certain regions may need to meet limits imposed by new source review or by prevention of significant deterioration.

In addition to air quality standards, most facilities must meet water-quality and solid waste–disposal standards. Generally for these standards, compliance is routine. *See* AIR POLLUTION; WATER POLLUTION.

Pollution control. The reduction of emissions for power-generating equipment may be accomplished by a number of methods depending on the level of reductions required, the pollutant of concern, and the specific equipment. Generally, emissions control equipment either reduces the initial amount of the pollutants generated, referred to as combustion modification control, or reduces the amount of pollutants in the combustion exhaust gas, known as postcombustion control. For gas turbines, combustion modification methods to reduce nitric oxides include steam or water injection, lean premixed combustion, and combustion designs known as "low NOx burners." An example of postcombustion control is selective catalytic reduction, which uses a catalyst and the injection of an ammonia species in the exhaust gas. At the appropriate temperature and conditions, the catalyst reduces nitric oxide to molecular nitrogen (N_2).

Project development/financing. Even with a reliable technical design and favorable economics, the successful completion of a cogeneration project often depends on acceptable financial arrangements. Financing is critical to the success of a cogeneration project, and it is best to determine early on the financial arrangement to be used. The selected financial arrangement will be intimately linked to the ownership structure. The ownership may be structured in a variety of ways. By increasing the number of participants in the project, the individual risk decreases, but the venture is more difficult to organize and the individual potential gains decrease. A cogeneration system may be owned by the facility, by a third-party entity, or by a partnership. In this context, the facility refers to the entity with the electrical and thermal loads. This is sometimes called the thermal consumer, heat consumer, or thermal host. A third party refers to an entity separate from the thermal load owner (first party) and from the local utility (second party).

The thermal and electrical loads of a facility are the items that might motivate others to be involved in developing a cogeneration system. In one respect, these loads represent the opportunity for financial gains. There are a number of potential project participants that could conceivably have an interest in the development of the cogeneration system. These potential participants include equipment manufacturers, power-plant operators, investors (such as banks, insurance companies and pension funds), electrical utilities, fuel suppliers, engineering firms, and governmental agencies. In general, the ownership structure and the financial arrangement are selected to provide the highest profits, lowest risks, and greatest tax benefits.

External participants, partners, and investors will examine a number of issues before deciding to be involved in the project. These issues include the overall economics, the revenue from thermal and electricity sales, the accuracy of the capital costs and operating expenses, the experience of the participants, the projected availability of the plant, the previous success of the proposed technology, the assurance that permits, contracts, and agreements will be obtained on a timely basis, and the availability and cost of fuel. A net positive assessment of these issues will be necessary for any external participation. Jerald A. Caton

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Cognition

The internal structures and processes that are involved in the acquisition and use of knowledge, including sensation, perception, attention, learning, memory, language, thinking, and reasoning. These behaviors are studied by cognitive scientists, a group that includes, but is not limited to, researchers in the areas of cognitive psychology, philosophy, linguistics, computer science, and cognitive neuroscience. Cognitive scientists propose and test theories about the functional components of cognition based on observations of an organism's external behavior in specific situations.

Sensation, perception and attention. Cognition throughout life can be broadly described as an interaction between top-down, knowledge-driven processes and bottom-up, sensory processes, and between controlled processes and automatic processes. When environmental input impinges on an organism's sensors, such as eyes or ears, that sensory information is used to construct an internal representation of the object or event causing the input. This representation undergoes several transformations as more knowledge is activated to make sense of an event. Over time, there is a trade-off between the amount of surface information that is retained in the representation (bottom-up processing) and the amount of meaning that is incorporated (top-down processing).

Following exposure to a stimulus, a sensory representation (sometimes called an image, icon, or echo) is constructed that encodes nearly all the surface characteristics of the stimulus (for example, color, shape, location, pitch, and loudness). The information is short lived, lasting less than a second. Much evidence suggests that extraction of information from this veridical representation takes place in two stages, a feature analysis stage and an object recognition stage. *See* MEMORY; PERCEPTION.

The first stage, sometimes called a preattentive stage, involves the segregation of pattern subcomponents into figures and background by feature analysis. This process is sometimes called parsing the input. A small number of primitive features are extracted from the sensory patterns, including color, size, contrast, tilt, curvature, line ends, movement, stereoscopic depth, and closure. These features are extracted independently by different parts of the visual system, and only in the second stage are they combined to form complete images of three-dimensional objects. For example, if a matrix of T's is juxtaposed next to a matrix of tilted T's, the boundary between the vertical and tilted T's stands out for the viewer. The boundary between juxtaposed matrices of T's and L's, however, does not. These different effects indicate that line orientation (vertical or tilted) is an important feature in early visual processing but the conjunctions of lines (that is, the way vertical and horizontal lines are combined to make up T's and L's) are not. A more surprising feature of object recognition and feature analysis is closure. When jumbles of tilted lines and angles are presented very briefly (200 ms) to viewers, they seldom report seeing triangles. But if small circles (that is, closed geometric figures) are distributed among the lines and angles, the viewers frequently report seeing triangles. When parsing normal triangles, the visual system apparently detects tilted lines, angles, and the abstract feature "closed" (a triangle is a closed geometric figure). The circles in the latter display provide this feature to the viewers' visual systems, along with the lines and angles, allowing them to see illusory triangles. These primitive features, once extracted from the visual input, are combined in the second stage to form objects. It is during this stage that attention (controlled processing) and previous knowledge come into play. For example, the time it takes to indicate whether a slide of O's also contains a Q increases linearly with the number of O's in the display. This relationship suggests that viewers scan the slide serially, focusing attention on each object or location in turn in order to identify each object. Viewers can complete these tasks faster and more accurately when familiar rather than unfamiliar objects are used, demonstrating the influence of top-down processes. Selecting particular objects from among others requires selective attention, that is, the ability to focus on certain inputs and ignore or inhibit processing of others.

Learning and memory. Information from the second-stage image rapidly decays. Typically, no more than five to nine pieces of information can be identified and maintained from the stimulus presented. Aspects of this short-term memory representation that become permanent constitute long–term memory. These aspects include items that mark the beginning and end of events, repeated events, and events that are particularly meaningful to the individual.

There are two independent memory systems. The first is called explicit or declarative memory. It comprises memories that can be consciously recollected, such as facts, episodes, and images. Explicit memories have the self as the agent or experiencer of the event in question and require controlled processing in order to be formed and retrieved. Implicit or nondeclarative memories, in contrast, constitute information acquired during skill learning, habit formation, classical conditioning, emotional learning, and priming. Implicit memories are expressed through performance rather than through conscious recollection. They do not necessarily depend on awareness or attention for their formation or retrieval (automatic processing). While learning to drive a car, a person focuses attentional resources on each subcomponent, such as depressing the clutch, shifting gears, and checking mirrors and blind spots. Once each skill is mastered, however, driving proceeds almost effortlessly, requiring few attentional resources. Such automatic skills or procedures are easier to do than to describe because they consist of memorized sequences of interconnected motor commands that are coordinated for action and executed as a single, fluid movement. *See* LEARNING MECHANISMS.

Conceptual knowledge. Conceptual knowledge is needed to classify objects and events in the world. Some aspects of conceptual knowledge are innate or emerge very early in development, while others are acquired through learning and inference. Advances in the understanding of innate knowledge have come about through an experimental procedure called the habituation technique. In this technique, a preverbal infant or animal is presented with a novel stimulus, which usually elicits a change in some observable behavior, such as directed looking, electrical skin conductance, brain wave activity, or changes in heart rate and blood pressure. The stimulus is presented repeatedly until the response in question declines to half of its initial value. At this point, the subject is said to have habituated to the stimulus. A new, similar stimulus is then presented. If the subject dishabituates and response levels of the subject return to their prehabituation levels, the subject is said to have detected the difference between the old and new stimuli.

By using this technique, human infants have been found to be able to detect differences in small numerosities shortly after birth, indicating innate sensitivity to the concept of number. Six-month-olds have been shown to recognize numerical equivalence across sense modalities, and infants as young as 5 months are capable of adding and subtracting small numbers. By 3 months, infants realize that solid objects cannot occupy the same location at the same time, cannot pass through each other, continue to exist even when out of sight, and cannot influence the trajectory of other objects without direct contact (no action at a distance). In contrast, they do not seem to appreciate the properties of gravity or inertia until about 9 months of age.

Also early to emerge is a sensitivity to ontological category. Studies that explore this type of knowledge typically employ verbal tasks, so it is not clear how early such knowledge develops. By the age of 2 years, however, infants make clear distinctions in their inductive generalizations between objects and substances; by 3 or 4 years, sensitivity is evidenced to distinctions among plants, animals, nonliving natural objects, and human-made artifacts. For example, 4-year-olds believe that a coffee pot can become a bird feeder with a little surgery, but they do not believe that a porcupine can become a cactus. Similarly, if they are told that the human body contains an omentum, they believe that dogs are likely to have one, too, but not human-looking dolls, flowers, or rocks.

Categorization learning is augmented by bottom-up processes, such as grouping together objects that share detectable common features or uses. These groupings typically show graded structure, with objects containing many typical features forming the core, or prototype, of the category. For example, when subjects are asked to list features that typify birds, sparrows, and penguins, the lists generated for sparrow and bird are found to have more features in common than the lists generated for penguin and bird, indicating that sparrows are more typical of the category "bird" than penguins. Because sparrows are closer to the prototype for a bird, people typically classify sparrows as birds more quickly and with fewer errors than they classify penguins as birds. Early on, individuals become sensitive to the ontological distinctions among living things, but learn to form precise categories for members within these distinctions by detecting common features.

Communicating, reasoning, and problem solving. A primary cognitive function of all social species is communication, which can be accomplished by a combination of vocal, gestural, and even hormonal signals. Of all species on Earth, only humans have developed a communication system based on abstract signs. This evolutionary development is closely tied to the greater reasoning capacity found among members of the species as well. All reasoning can be broadly described as pattern recognition and search. People search their conceptual knowledge for relevant information in order to draw a conclusion, solve a problem, or guide behavior. Thinking often takes the form of a chain of associations among concepts in long-term memory, with one thought retrieving others to which it is related. The most common reasoning strategies include direct retrieval, imaging, means-ends analysis, analogy, classification, deduction, and formal procedures.

Reasoning by direct retrieval involves retrieving a known fact from memory to solve a problem, such as determining how much three times three is or where something is located. Reasoning imagistically involves constructing or retrieving images from conceptual memory and examining or manipulating them to solve a problem. For example, individuals reason imagistically when they determine how many windows there are in their living rooms by retrieving an image of the room and counting the windows in the image.

Means-ends analysis is typically employed when solving problems in unfamiliar domains. When a solution is not immediately apparent, reasoners typically compare the goal to the current situation and select means with which to reduce the differences between the two situations. A simple example is getting into a car. The current situation involves an individual standing outside a car with the door locked. The goal situation involves sitting inside the car. The primary difference between the two is the individual's position, inside versus outside the car. To reduce this difference requires opening the car door. If the door is locked, a subgoal is generated to unlock the door. The goal state is an unlocked door, and the current state is a locked door. A search is made for an operator, that is, a means to achieve the end of opening the door. Possible operators includes keys, coat hangers, and bricks. Applying the operator (such as the car key) accomplishes the subgoal of opening the door.

Insight involves the restructuring of a problem representation that allows an available means to be used in a novel way or a seemingly unrelated bit of knowledge to be accessed to solve the problem. For example, scissors can be used not just to cut a string in half but also to serve as a weight to set one of the pieces swinging like a pendulum—a handy solution if a person needs to pass the string or scissors to someone standing out of arm's reach.

Reasoning by analogy is used when a current situation allows an individual to recall another, similar situation that has a known solution or other information relevant to the task at hand. It is a technique that is powerful but error prone. Without proper constraints on the analogy process, irrelevant or incorrect information can be transferred between the target and source analogs. For example, if told "The structure of the atom is like the solar system," the reasoner might also conclude that the nucleus of the atom is hot, just like the Sun.

Reasoning by classification involves making inferences about an object or event based on its category membership. For example, when asked to estimate the likelihood that each of a series of descriptions refers to an engineer or a lawyer, people have been found to base their estimates on the similarity of the descriptions to stereotypes for these professions—regardless of the base rates for the two types of professionals in the pool. Persons described as being interested in mathematical puzzles and reserved in manner were assigned a high likelihood of being engineers, regardless of whether the percentage of engineer descriptions in the pool was reported to be 30% or 70%. Neutral descriptions, such as successful or average weight and height, were judged to have a 50% probability of being an engineer, again regardless of whether subjects were told the percentage of engineers in the pool was 30% or 70%. Judgments like these are called reasoning fallacies because they violate formal rules of reasoning. Ignoring base rates violates Bayes' theorem, a formal model for computing conditional probabilities.

Deductive reasoning involves drawing a conclusion based on its logical relation to one or more premises. A common example is Modus Ponens (If p, then q/p/Therefore, q). Sufficient evidence exists that the Modus Ponens reasoning rule is part of cognitive architecture. Errors on this type of argument rarely occur, judgments are extremely rapid even when other tasks are performed concurrently, and evidence of use of Modus Ponens emerges early in development and independently of formal training. Such unequivocal and converging evidence exists for a scant few other formal rules of deduction.

A second common use for deduction is testing hypotheses. Naive reasoners typically commit a reasoning fallacy termed confirmation bias when testing their hypotheses. For example, when asked to determine the rule used to generate the number series 2, 4, 6, most subjects hypothesized that the rule was even ascending numbers. Importantly, they tested this hypothesis by seeking to confirm their hypothesis rather than trying to disprove it. They did so by generating only instances that were consistent with their hypothesis (8, 10, 12; 22, 24, 26). The correct rule was any ascending sequence. Discovering this required testing a sequence that disconfirmed their hypothesis.

Formal procedures for reasoning and for solving problems have been developed over the centuries. These include logic, mathematics, probability theory and statistics, and scientific investigation. Understanding of the behavior and properties of physical, biological, and cognitive systems has been greatly enhanced through the use of these techniques. *See* PSYCHOLINGUISTICS.

Cognition and the brain. By using noninvasive techniques such as positron emission tomography (PET scan), magnetic resonance imaging, electrical skin conductance, invasive surgical and chemical investigations of animal brains, and data from clinically observed syndromes associated with brain injury, cognitive neuroscientists have pieced together a good deal of information concerning the role that specific brain regions play in the processing of emotional and cognitive events. High-level visual processing, such as object recognition, takes place in the occipital lobes of the cortex (back of the head), although recognition of certain highly complex visual stimuli, such as faces, is handled by the right cerebral hemisphere. Auditory stimuli in general are processed by the temporal lobes of the cortex (near the ears), and written and spoken word recognition and syntactical components of language processing are handled by certain regions of the left hemisphere of the cerebral cortex, notably Broca's and Wernicke's areas; while emotional, idiomatic, and prosodic aspects of language are handled by corresponding regions in the right hemisphere. Higher cognition, such as reasoning and problem solving, involves the frontal lobes of the cortex. Memory and the processing of emotional stimuli are handled by the combined effort of the cortex (notably the anterior and frontal regions) and subcortical structures (notably the limbic system).

One particular subcortical structure—the hippocampus—plays a major role in the formation of new explicit memories. By using positron emission tomography scanning, conscious recollection of events can be seen to involve increased blood flow to the hippocampal region, while implicit memory tasks produce increased blood flow to posterior, extrastriate areas of the cerebral cortex. Damage to the hippocampal region and the medial temporal lobe produces profound amnesic syndrome in which the patient displays normal perceptual linguistic and intellectual functioning but cannot consciously remember recent events (such as having lunch or playing a round of golf). Such patients do, however, show implicit memory for recent events, including the acquisition of new motor skills, habits, and emotional preferences. It is believed that an intact hippocampus is needed to temporarily bind together distributed sites of activation in the cortex that together make up a whole, explicit memory for an event. *See* BRAIN; COMPUTERIZED TOMOGRAPHY.

Computer models. Theories of cognition are often tested by building computer models that embody the theories and then comparing the model's performance with human performance on selected tasks. These models tend to be of two types. Rule-based models simulate cognition as the execution of condition-action rules. The models consist of a long-term memory containing rules which specify actions to take in the presence of particular input patterns, a short-term memory that encodes input patterns and temporarily stores data structures constructed by the rules, and a control structure that guides the process and resolves conflicts when more than one rule applies to the current input. Rule-based models have successfully simulated expert performance in a variety of domains. Neural network models simulate cognition as a strengthening and weakening of associations among cognitive events. They are called neural networks because they learn in a way that is analogous to the way in which brains learn (by modifying synaptic connections among neurons) and have proven to be excellent models of perception and memory. Neural networks consist of a network of interconnected nodes, a mathematical formula for modifying the connections, and a mathematical formula for propagating activation through the network. *See* EXPERT SYSTEMS; INFORMATION PROCESSING (PSYCHOLOGY); INTELLIGENCE; NEURAL NETWORK; PROBLEM SOLVING (PSYCHOLOGY).

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Coherence

The attribute of two or more waves, or parts of a wave, whose relative phase is nearly constant during the resolving time of the observer. The concept has been developed most extensively in optics, but is applicable to all wave phenomena.

Coherence of two beams. Consider two waves, with the same mean angular frequency ω, given by Eqs. (1) and (2). These expressions as they stand

$$\Psi_A(x,t) = A\ \exp\{i[k(\omega)x - \omega t - \delta_A(t)]\} \quad (1)$$

$$\Psi_B(x,t) = B\ \exp\{i[k(\omega)x - \omega t - \delta_B(t)]\} \quad (2)$$

could describe de Broglie waves in quantum mechanics. For real waves, such as components of the electric field in light or radio beams, or the pressure oscillations in sound, it is necessary to retain only the real parts of these and subsequent expressions. Assume that the frequency distribution is narrow, in the sense that a Fourier analysis of Eqs. (1) and (2) gives appreciable contributions only for angular frequencies close to ω. This assumption means that, on the average, $\delta_A(t)$ and $\delta_B(t)$ do not change much per period. For any actual wave, however, they must undergo some change; only waves that have existed forever and that fill all of space can have absolutely fixed frequency and phase. *See* ELECTROMAGNETIC RADIATION; QUANTUM MECHANICS; SOUND.

Suppose that the waves are detected by an apparatus with resolving time T; that is, T is the shortest interval between two events for which the events do not seem to be simultaneous. For the human eye and ear, T is about 0.1 s, while a fast electronic device might have a T of 10^{-10} s. If the relative phase $\delta(t)$, given by Eq. (3), does not, on the average, change

$$\delta(t) = \delta_B(t) - \delta_A(t) \quad (3)$$

noticeably during T, then the waves are coherent. If during T there are sufficient random fluctuations for all values of $\delta(t)$, modulus 2π, to be equally probable, then the waves are incoherent. If during T the fluctuations in $\delta(t)$ are noticeable, but not enough to make the waves completely incoherent, then the waves are partially coherent. These distinctions are not useful unless T is specified. Two waves for which the relative phase changes appreciably in 0.01 s would seem incoherent to unaided human perception, but would seem highly coherent to a fast electronic device.

The degree of coherence is related to the interference patterns that can be observed when the two beams are combined. The following variations of Young's two-slit interference experiment illustrate several possibilities. *See* INTERFERENCE OF WAVES.

Young's two-slit experiment. In the usual Young's experiment (**Fig. 1**) beams A and B come from the same point source and pass through separated slits in a screen. Near a point P equidistant from the slits, for linear wave phenomena, the resultant wave $\Psi(x,t)$ is the sum of $\Psi_A(x,t)$ and $\Psi_B(x,t)$. The observable

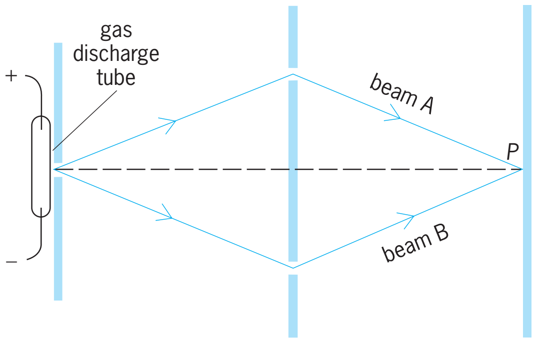

Fig. 1. Young's experiment. If beams *A* and *B* come from the same point source and traverse the same distance, they are coherent around *P* and produce there an interference pattern that has high visibility.

intensity is proportional to $|\Psi|^2$, the square of the magnitude of Ψ. This observable intensity is the energy density or the mean photon density for electromagnetic waves, the energy density for acoustic waves, and the mean particle density for the wave functions of quantum mechanics. With the wave forms of Eqs. (1) and (2), for real A and B, it is given by Eq. (4). The first term gives the intensity of beam A

$$\begin{aligned} |\Psi|^2 &= |\Psi_A + \Psi_B|^2 \\ &= A^2 + B^2 + 2AB\ \cos\ \delta(t) \end{aligned} \qquad (4)$$

alone, the second gives the intensity of B alone, and the third term depends on the relative phase, given by Eq. (3).

The mean life of a typical excited atomic state is about 10^{-8} s. Collisions and thermal motion reduce the effective time of undisturbed emission to around 10^{-10} or 10^{-11} s in standard discharge tubes. The phase $\delta_\mathrm{A}(t)$ of beam A therefore dances about erratically, with substantial changes occurring perhaps 10^{11} times per second. However beam B comes from the same atoms and travels nearly the same distance, and the changes in $\delta_\mathrm{B}(t)$ are the same as those in $\delta_\mathrm{A}(t)$. The relative phase is always zero at the exact midpoint P and takes on other time-independent values in the neighborhood of P. For each point in that neighborhood, $|\Psi|^2$ has a constant value that satisfies inequality (5). A clear interference pattern

$$|A - B|^2 \leq |\Psi|^2 \leq |A + B|^2 \qquad (5)$$

is observed even with a large-T detector such as a photographic plate.

Independent sources. Instead of a single source, two independent sources can be used to produce the two beams (**Fig. 2**). If the two sources are standard discharge tubes, $\delta_\mathrm{A}(t)$ and $\delta_\mathrm{B}(t)$ independently change erratically around 10^{11} times per second. Equation (4) is still valid, but the observed quantity is $|\Psi|^2$ averaged over the resolving time T, denoted by $\langle|\Psi|^2\rangle_\mathrm{T}$. When the average of Eq. (4) is formed, the last term on the right contributes nothing because $\cos\,\delta(t)$ randomly takes on values between $+1$ and -1 and thus obeys Eq. (6). The two beams are incoherent, the observed intensity is simply the sum of the separate intensities, and the superposition does not produce a visible interference pattern. In general, if incoherent waves Ψ_A, Ψ_B, Ψ_C, ... , are combined, much the same argument applies because the average over T of each cross term is zero, so that the observed intensity is given by Eq. (7).

$$\langle\cos\delta(t)\rangle_T = 0 \qquad (6)$$

$$\langle|\Psi|^2\rangle_T + \langle|\Psi_A|^2\rangle_T + \langle|\Psi_B|^2\rangle_T + \langle|\Psi_C|^2\rangle_T + \cdots \qquad (7)$$

The argument that results in Eq. (6) depends on there being random independent changes in the separate phases during times much shorter than T. If the discharge tubes are replaced by very well stabilized lasers, or by loudspeakers or radio transmitters, then the separate phases $\delta_A(t)$ and $\delta_B(t)$ can be made nearly constant during 0.1 s. The relative phase $\delta(t)$ is then also nearly constant, an interference pattern is visible, and the two waves can be called coherent. *See* LASER.

Effect of path length difference. In another arrangement (**Fig. 3**), the two beams are again emitted by the same

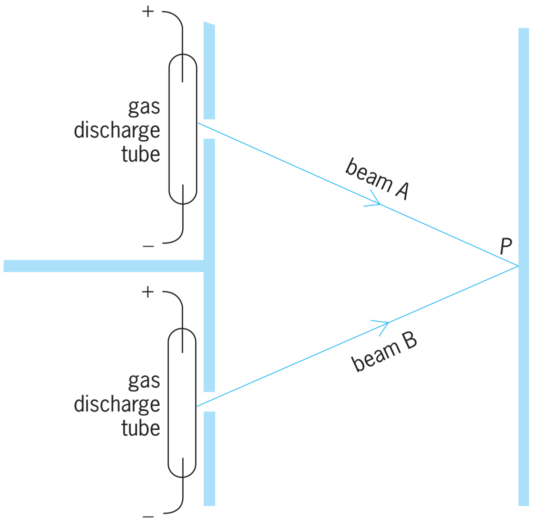

Fig. 2. Independent sources that change their phases frequently and randomly during the resolving time *T* are incoherent, and their superposition does not produce a visible interference pattern.

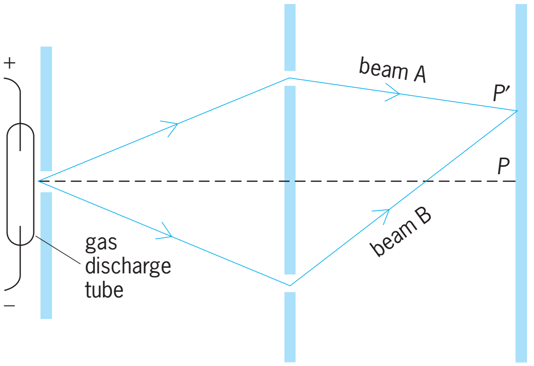

Fig. 3. If the difference between the distances traversed by beams *A* and *B* is of the order of the coherence length, then the beams are partially coherent at *P* ′.

point source and are therefore coherent at their origin. Here, however, the distance from the source to the point P' of wave addition is larger along beam B than along beam A by an amount l. In this arrangement, the path length difference is due to the observation point P' not being near the central axis, but it could equally well be caused by the insertion of different optical devices in the two beams.

The waves that arrive at P' via path B at any instant must have left the source earlier by a time $\tau = l/c$, where c is the wave speed, than those that arrive via path A. Suppose again that the source is a standard discharge tube, so that the phase changes randomly about 10^{11} times per second. For $\tau < 10^{-11}$ s, the coherence between A and B at P' is not spoiled by the path length difference, and there is a visible interference pattern around P'. For $\tau > 10^{-11}$ s, the light that arrives via A left the source so much later than that which arrives via B at the same instant that the phase changed many times in the interim. The two beams are then incoherent, and their superposition does not produce a visible interference pattern around P'. For $\tau \simeq 10^{-11}$ s, perfect coherence is spoiled but there is less than complete incoherence; there is partial coherence and an interference pattern that is visible but not very sharp. The time difference that gives partial coherence is the coherence time Δt. The coherence time multiplied by the speed c is the coherence length Δl. In this example, Δl is given by Eq. (8).

$$\Delta l \simeq 10^{-11}\text{s} \times 3.0 \times 10^{10}\ \text{cm/s} = 0.3\ \text{cm} \quad (8)$$

Effect of extended source. The original arrangement can also be modified by making a large hole in the collimator in front of the discharge tube, so that there is an extended source rather than a point source (**Fig. 4**). Consider two regions of the source, S near the center and S' near one end, separated by a distance y. During times longer than the coherence time, the difference between the phases of the radiation from the two regions changes randomly. Suppose that, at one moment, the radiation from S happens to have a large amplitude while that from S' happens to be negligible. The waves at the two slits are then in phase because S is equidistant from them, and interference at P gives a maximum. Suppose that a few coherence times later the radiation from S happens to be negligible while that from S' happens to have a large amplitude. If the path length along A' differs from that along B' by half of the wavelength λ, then the waves at the two slits are out of phase. Now interference at P gives a minimum, and the pattern has shifted in a few coherence times. If the resolving time T is much larger than the coherence time Δt, the consequence is that beams A and B are not coherent at P.

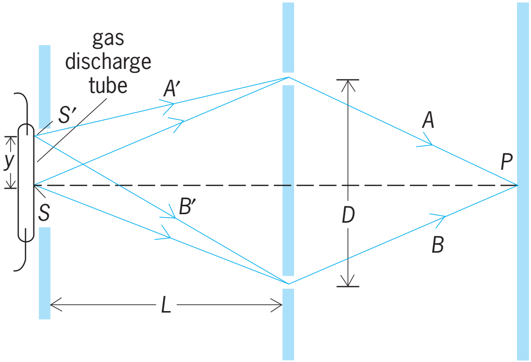

Fig. 4. If the lateral extent *y* of the source is of the order of *L*λ/*D*, then the beams are partially coherent at *P*.

The condition that there be a path length difference of $\lambda/2$ between B' and A' is given by Eq. (9),

$$\sqrt{L^2 + (y + D/2)^2} - \sqrt{L^2 + (y - D/2)^2} = \lambda/2 \quad (9)$$

and for D and y both much smaller than L, expansion of the square roots gives Eq. (10). This argument is

$$2Dy = L\lambda \quad (10)$$

rather rough, but it is clear that a source that satisfies Eq. (11) is too large to give coherence and too

$$y \simeq \frac{L\lambda}{D} \quad (11)$$

small to give complete incoherence; it gives partial coherence.

Coherence of a single beam. Coherence is also used to describe relations between phases within the same beam. Suppose that a wave represented by Eq. (1) is passing a fixed observer characterized by a resolving time T. The phase δ_A may fluctuate, perhaps because the source of the wave contains many independent radiators. The coherence time Δt_W of the wave is defined to be the average time required for $\delta_A(t)$ to fluctuate appreciably at the position of the observer. If Δt_W is much greater than T, the wave is coherent; if Δt_W is of the order of T, the wave is partially coherent; and if Δt_W is much less than T, the wave is incoherent. These concepts are very close to those developed above. The two beams in the arrangement with independent sources are incoherent with respect to each other if one or both have $\Delta t_W < T$, but are coherent with respect to each other if both have $\Delta t_W > T$ (Fig. 2).

The degree of coherence of a beam is of course determined by its source. Discharge tubes that emit beams with Δt_W small compared to any usual resolving time are therefore called incoherent sources, while well-stabilized lasers that give long coherence times are called coherent sources.

Consider two observers that measure the phase of a single wave at the same time. If the observers are close to each other, they will usually measure the same phase. If they are far from each other, the phase difference between them may be entirely random. The observer separation that shows the onset of randomness is defined to be the coherence length of the wave, Δx_W. If this separation is in the direction of propagation, then Δx_W is given by Eq. (12), where

$$\Delta x_W = c\Delta t_W \quad (12)$$

c is the speed of the wave. Of course, the definition of Δx_W is also applicable for observer separations perpendicular to the propagation direction.

The coherence time Δt_W is related to the spectral purity of the beam, as is shown by the following argument. The wave can be viewed as a sequence of packets with spatial lengths around Δx_W. A typical packet requires Δt_W to pass a fixed point. Suppose that n periods of duration $2\pi/\omega$ occur during Δt_W, as expressed in Eq. (13). The packet can be

$$\Delta t_W \frac{\omega}{2\pi} = n \tag{13}$$

viewed as a superposition of plane waves arranged to cancel each other outside the boundaries of the packet. In order to produce cancellation, waves must be mixed in which are in phase with the wave of angular frequency ω in the middle of the packet and which are half a period out of phase at both ends. In other words, waves must be mixed in with periods around $2\pi/\omega'$, where Eq. (14) holds. The difference

$$\Delta t_W \frac{\omega'}{2\pi} = n \pm 1 \tag{14}$$

of Eqs. (13) and (14) gives Eq. (15), where the spread

$$\Delta t_W \Delta\omega = 2\pi \tag{15}$$

in angular frequencies $|\omega - \omega'|$ is called $\Delta\omega$. This result should be stated as an approximate inequality (16). A large Δt_W permits a small $\Delta\omega$ and therefore

$$\Delta t_W \Delta\omega \gtrsim 1 \tag{16}$$

a well-defined frequency, while a small Δt_W implies a large $\Delta\omega$ and a poorly defined frequency.

Quantitative definitions. To go beyond qualitative descriptions and order-of-magnitude relations, it is useful to define the fundamental quantities in terms of correlation functions.

Self-coherence function. As discussed above, there are two ways to view the random fluctuations in the phase of a wave. One can discuss splitting the wave into two beams that interfere after a difference τ in traversal time, or one can discuss one wave that is passing over a fixed observer who determines the phase fluctuations. Both approaches concern the correlation between $\Psi(x,t)$ and $\Psi(x, t + \tau)$. This correlation is described by the normalized self-coherence function given by Eq. (17). The brackets

$$\gamma(\tau) \equiv \frac{\langle \Psi(x, t+\tau)\Psi^*(x, t)\rangle}{\langle \Psi(x, t)\Psi^*(x, t)\rangle} \tag{17}$$

$\langle\,\rangle$ indicate the average of the enclosed quantity over a time which is long compared to the resolving time of the observer. It is assumed here that the statistical character of the wave does not change during the time of interest, so that $\gamma(\tau)$ is not a function of t.

With the aid of the self-coherence function, the coherence time of a wave can be defined quantitatively by Eq. (18). That is, Δt_W is the root-mean-squared

$$(\Delta t_W)^2 \equiv \frac{\displaystyle\int_{-\infty}^{+\infty} \tau^2 \, |\gamma(\tau)|^2 \, d\tau}{\displaystyle\int_{-\infty}^{+\infty} |\gamma(\tau)|^2 \, d\tau} \tag{18}$$

width of $|\gamma(\tau)|^2$. The approximate inequality (16) can also be made precise. The quantity $|g(\omega')|^2$ is proportional to the contribution to Ψ at the angular frequency ω', where $g(\omega')$ is the Fourier transform of Ψ, defined by Eq. (19). The root-mean-squared width

$$g(\omega') \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(0, t) e^{-i\omega' t} dt \tag{19}$$

$\Delta\omega$ of this distribution is given by Eq. (20), where ω

$$(\Delta\omega)^2 = \frac{\displaystyle\int_0^{\infty} (\omega' - \omega)^2 \left|g(\omega')\right|^2 d\omega'}{\displaystyle\int_0^{\infty} \left|g(\omega')\right|^2 d\omega'} \tag{20}$$

is again the mean angular frequency. With these definitions, one can show that inequality (21) is satisfied.

$$\Delta t_W \Delta\omega \geq {}^1/_2 \tag{21}$$

The symbol $\gtrsim$ has become $\geq$; no situation can lead to a value of $\Delta t_W \Delta\omega$ that is less than $^1/_2$. Relation (21) multiplied by Planck's constant is the Heisenberg uncertainty principle of quantum physics, and can in fact be proved in virtually the same way. *See* NONRELATIVISTIC QUANTUM THEORY; UNCERTAINTY PRINCIPLE.

Complex degree of coherence. To describe the coherence between two different waves Ψ_A and Ψ_B, one can use the complex degree of coherence $\gamma_{AB}(\tau)$, defined by Eq. (22), where the averaging process $\langle\,\rangle$

$$\gamma_{AB}(\tau) \equiv \frac{\langle \Psi_A(t+\tau)\Psi_B{}^*(t)\rangle}{\left[\langle \Psi_A{}^*(t)\Psi_A(t)\rangle \langle \Psi_B{}^*(t)\Psi_B(t)\rangle\right]^{1/2}} \tag{22}$$

and the assumptions are the same as for the definition of $\gamma(\tau)$. If beams A and B are brought together, interference fringes may be formed where the time-averaged resultant intensity $\langle|\Psi|^2\rangle$ has maxima and minima as a function of position. The visibility of these fringes, defined by Eq. (23), can be shown, for

$$V = \frac{\langle|\Psi|^2\rangle_{\max} - \langle|\Psi|^2\rangle_{\min}}{\langle|\Psi|^2\rangle_{\max} + \langle|\Psi|^2\rangle_{\min}} \tag{23}$$

the usual interference studies, to be proportional to $|\gamma_{AB}(\tau)|$.

Examples. The concept of coherence occurs in a great variety of areas. The following are some application and illustrations.

Astronomical applications. As is shown in the above discussion, extended sources give partial coherence and produce interference fringes with visibility V [Eq. (23)] less than unity. A. A. Michelson exploited this fact with his stellar interferometer (**Fig. 5**), a modified double-slit arrangement with movable mirrors that permit adjustment of the effective separation D' of the slits. According to Eq. (11), there is

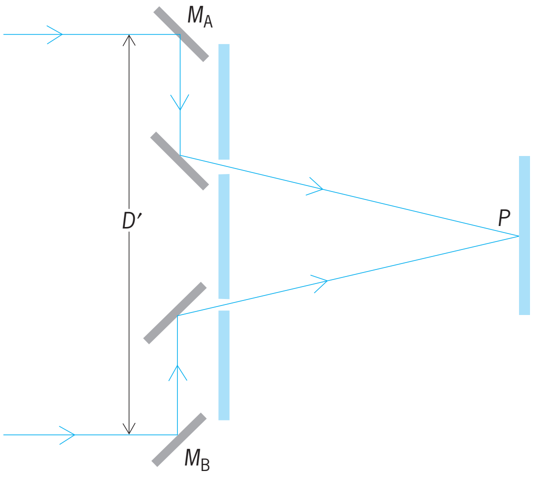

Fig. 5. Michelson's stellar interferometer. The effective slit separation D' can be varied with the movable mirrors M_A and M_B. The angular size of the source can be calculated from the resulting change in the visibility of the interference fringes around P.

partial coherence if the angular size of the source is about λ/D'. It can be shown that if the source is a uniform disk of angular diameter Θ, then the smallest value of D' that gives zero V is $1.22\lambda/\Theta$. The interferometer can therefore be used in favorable cases to measure stellar diameters. The same approach has also been applied in radio astronomy. A different technique, developed by R. Hanbury Brown and R. Q. Twiss, measures the correlation between the intensities received by separated detectors with fast electronics. *See* INTERFEROMETRY; RADIO ASTRONOMY.

Lasers and masers. Because they are highly coherent sources, lasers and masers provide very large intensities per unit frequency, and double-photon absorption experiments have become possible. As a consequence, atomic and molecular spectroscopy were revolutionized. One can selectively excite molecules that have negligible velocity components in the beam direction and thus improve resolution by reduction of Doppler broadening. States that are virtually impossible to excite with single-photon absorption can now be reached. *See* LASER SPECTROSCOPY; MASER.

Musical acoustics. Fortunately, for most musical instruments the coherence time is much less than human resolving time, so that the separate contributions in an orchestra are perceived incoherently. Equation (7) applies, and 20 violins seem to provide 20 times the intensity of 1 violin. If human resolving time were much shorter, the perceived intensity would drift between 0 and 400 times the intensity of a single violin. *See* MUSICAL ACOUSTICS.

Thermodynamic treatment of radiation. Coherence must be considered in thermodynamic treatments of radiation. As one should expect from the connection between entropy and order, entropy is reduced by an increase in coherence. The total entropy of two beams that are coherent with respect to each other is less than the sum of the entropies of the separate beams, because coherence means that the beams are not statistically independent. *See* ENTROPY; THERMODYNAMIC PRINCIPLES.

Quantum physics. In quantum physics, a beam of particles can for some purposes be described by Eq. (1) without the phase $\delta A(t)$. If the wavelength is well defined, measurables such as barrier transmission coefficients and scattering cross sections of sufficiently small targets do not depend on phases and coherence. If, however, the scattering object is large, these aspects may have to be considered.

Electrons emitted by hot filaments show coherence times of roughly 10^{-14} s. In low-energy electron diffraction, where speeds on the order of 10^8 to 10^9 cm/s are used, the coherence length is then on the order of 10^{-5} cm, and the structure can be seen clearly only if the region being studied does not introduce a path length difference greater than this distance. *See* ELECTRON DIFFRACTION.

Most nuclear and particle physics experiments deal with energies so high that the wavelengths of the projectiles are less than 10^{-12} cm, far less than the amplitudes of motions of the scattering nuclei. The many nuclei therefore contribute to the scattered beam incoherently. Equation (7) applies, and the intensity of the scattered beam is proportional to the scattering cross section per nucleus times the number of nuclei. Rolf G. Winter

Photon statistics. Photon statistics is concerned with the probability distribution describing the number of photons incident on a detector, or present in a cavity. By extension, it deals with the correlation properties of beams of light.

According to the quantum theory of electromagnetism, quantum electrodynamics, light is made up of particles called photons, each of which possesses an energy E of $\hbar\omega$, where $\hbar$ is Planck's constant divided by 2π and ω is the angular frequency of the light (the frequency multiplied by 2π). In general, however, the photon number is an intrinsically uncertain quantity. It is impossible to precisely specify both the phase $\phi = \omega t$ of a wave and the number of photons $n \approx E/(\hbar\omega)$ that it contains; the uncertainties of these two conjugate variables must satisfy $\Delta n \Delta\phi \geq {}^1/_2$. For a beam to be coherent in the sense of having a well-defined phase, it must not be describable in terms of a fixed number of particles. (Lacking a fixed phase, a single photon may interfere only with itself, not with other photons.) *See* PHOTON; QUANTUM ELECTRODYNAMICS.

The most familiar example of this uncertainty is shot noise, the randomness of the arrival times of individual photons. There is no correlation between photons in the coherent state emitted by a classical source such as an ideal laser or radio transmitter, so the number of photons detected obeys Poisson statistics, displaying an uncertainty equal to the square root of the mean. The shot noise constitutes the dominant source of noise at low light levels, and may become an important factor in optical communications as well as in high-precision optical devices (notably those that search for gravitational radiation). *See* DISTRIBUTION (PROBABILITY); ELECTRICAL NOISE.

Instead of considering light in terms of phase and photon number, one may equivalently discuss the amplitudes of the two quadrature components, cos *ωt* and sin *ωt*. Another uncertainty relation applies between these conjugate variables, implying that even in the so-called vacuum state (zero photons) these two field amplitudes cannot both be precisely zero. Shot noise may be seen as a relic of these ever-present vacuum fluctuations.

Coherent states (in which the two quadratures are determined to equal accuracy) and states in which the photon number is known precisely may both seem somehow ideal. Until the invention of the laser, essentially all light sources fell far from this ideal: In stars, candles, and light bulbs, the randomness of thermal fluctuations leads to more noise than the minimum required by the uncertainty principle. This noise may be described in terms of bunching. To every process in which a photon can be emitted spontaneously, there corresponds a process in which an already-present photon can stimulate the emission of a second photon, with probability equal to that of the spontaneous process. Once a photon is observed in a thermal beam, the probability of detecting another photon is thus twice the mean probability of photon detection in the beam as a whole. *See* BOSE-EINSTEIN STATISTICS.

Antibunching effects, in which detection of one photon makes detection of subsequent photons less likely, cannot be explained by any classical wave theory. Such behavior is precisely what would be expected for a beam of a fixed number of particles. If a single photon is incident on a beam splitter, it may be detected at either output, but never both. Single-photon states have been created in the laboratory, and their indivisibility has been observed.

So-called squeezed states are those in which the uncertainty of a given variable (for example, the number, phase, or a given quadrature) is smaller than it would be for a coherent state, while the uncertainty for the conjugate variable is larger. The noise in certain measurements is thus reduced below the so-called standard quantum limit, while the uncertainty principle is still obeyed. *See* SQUEEZED QUANTUM STATES.

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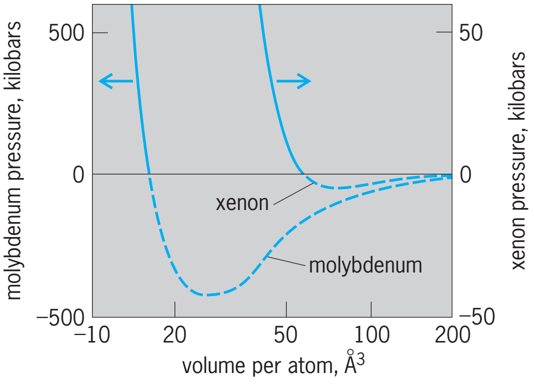
Cohesion (physics)

The tendency of atoms or molecules to coalesce into extended condensed states. This tendency is practically universal. In all but exceptional cases, condensation occurs if the temperature is sufficiently low; at higher temperatures, the thermal motions of the constituents increase, and eventually the solid assumes gaseous form. The cohesive energy is the work required to separate the condensed phase into its constituents or, equivalently, the amount by which the energy of the condensed state is lower than that of the isolated constituents. The science of cohesion is the study of the physical origins and manifestations of the forces causing cohesion, as well as those opposing it. It is thus closely related to the science of chemical bonding in molecules, which treats small collections of atoms rather than extended systems. *See* CHEMICAL BONDING; INTERMOLECULAR FORCES.

When the constituent atoms or molecules are far separated, an attractive force is present. This force is due, directly or indirectly, to the electrostatic interactions of the negatively charged electrons and the positively charged ions. However, when the distances between the constituents become very short, a strong repulsive force results, which is due to the quantum-mechanical kinetic energy of the electrons. The competition between the attractive and repulsive forces determines the equilibrium density for the condensed state (see **illus.**). A positive pressure at a given volume means that pressure must be applied to the solid to keep it at this volume; thus the forces between the atoms are predominantly repulsive. Similarly, the pressure is negative when the forces are predominantly attractive. Both molybdenum and xenon have attractive interactions at large volumes. As the volume drops, the attractive forces reach a maximum and then begin to be canceled by the repulsive forces. The equilibrium volume of the solid is that for which the cancellation is complete, or the pressure vanishes. The equilibrium point actually occurs when the pressure equals the atmospheric pressure, which is approximately 1 bar (100 kilopascals). However, this pressure is effectively zero on the pressure scale of the illustration. *See* COULOMB'S LAW; QUANTUM MECHANICS.



Calculated pressure-volume curves for molybdenum and xenon at absolute zero. Negative-pressure portions of curves are represented by broken lines because they cannot be directly measured. 1 kilobar = 0.1 GPa; 1 Å^3 = 0.001 nm^3.

Attractive forces. The origin and magnitude of the attractive forces depend on the chemical nature of the constituent atoms or molecules. Strong attractive interactions are usually associated with constituents having valence electron shells which are partly filled or open; if the valence electron shells are completely filled or closed, the interactions are weaker. *See* VALENCE.

Open-shell constituents. This is most easily understood for atomic systems. As the atoms approach, the electron energy levels on different atoms begin to interact, forming a complex of energy levels in the solid. Some of these are below the atomic energy levels and some above. Since the atomic shells are partly filled, the lower energy levels in the solid are filled, but at least some of the higher levels are empty. Thus the average energy of the occupied levels in the solid is lower than that in the isolated atoms, resulting in an attractive force. Bonding in open-shell systems can be approximately divided into three categories, although most cases involve a combination *See* BAND THEORY OF SOLIDS; FERMI-DIRAC STATISTICS; SOLID-STATE PHYSICS; VALENCE BAND.

1. *Covalent bonding*. This type of bonding is most similar to the molecular bond. The electron energy levels in the solid are split into a lower and a higher portion, with the states in the lower one filled and the higher one empty. Covalent bonds are strongly directional, with electron charge accumulating around the bond centers. Materials bonded in this fashion typically form structures with low coordination numbers, prototypical materials elements in group 14 of the periodic table, the insulator carbon, and the semiconductors silicon and germanium. *See* PERIODIC TABLE; SEMICONDUCTOR.

2. *Metallic bonding*. In this case, there is no split between the lower and higher states of the electrons in the solid; rather, they occupy levels from the bottom up to a cutoff point known as the Fermi level. For example, in transition metals, the electron states in the solid derived from the atomic *d* orbitals form a complex which is gradually filled with increasing atomic number. The bulk of the cohesive energy is due to this complex. The metallic bond is less directional than the covalent bond, with a more uniform distribution of electronic charge. Metals usually form closely packed structures. *See* FERMI SURFACE; FREE-ELECTRON THEORY OF METALS.

3. *Ionic bonding*. This occurs in compounds having at least two distinct types of atoms. One or more of the species of atoms (the cations) have only a small number of electrons in their valence shells, whereas at least one species (the anions) has a nearly filled valence shell. As the atoms approach each other, electrons drop from the cation valence states into holes in the anion valence shell, forming a closed-shell configuration in the solid. The different types of atoms in the solid have net charges; a strong attractive force results from the interaction between unlike charges. For example, in sodium chloride (NaCl), the sodium atoms acquire positive charges, and the chlorine atoms acquire negative charges. The closest interatomic separations in the solid are between sodium and chlorine, so that the attractive electrostatic interactions outweigh the repulsive ones. *See* IONIC CRYSTALS; SOLID-STATE CHEMISTRY.

Closed-shell constituents. In these systems the above effects are greatly reduced because the atomic or molecular shells are basically inert. The constituents retain their separate identities in the solid environment. If the constituents are atomic, as in rare-gas solids, the cohesion is due to the van der Waals forces. The positions of the electrons in an atom fluctuate over time, and at any given time their distribution is far from spherical. This gives rise to fluctuating long-ranged electric fields, which average zero over time, but can still have appreciable effects on neighboring atoms. The electrons on these atoms move in the direction of the force exerted by the electric field. The net result is that the interactions between unlike charges (electrons and nuclei) are increased in the solid, whereas the interactions between like charges are reduced. Thus the solid has a lower energy than the isolated atoms.

In solids made up of molecules, there are additional electrostatic interactions due to the nonspherical components of the molecular charge density. These interactions are strongest if the molecules are polar. This means that the center of the positive charge on the molecule is at a different point in space from that of the negative charge. Polar molecules, such as water (H_2O), form structures in which the positive charge on a molecule is close to the negative charges of its neighbors. For nonpolar molecules, the electrostatic interactions are usually weaker than the van der Waals forces. The nonspherical interactions in such cases are often so weak that the molecules can rotate freely at elevated temperatures, while the solid is still held together by the van der Waals forces.

Repulsive forces. The repulsive forces in the condensed phase are a dramatic illustration of the combined action of two quantum-mechanical principles, the exclusion principle and the uncertainty principle.

The exclusion principle states that the quantum-mechanical wave function for the electrons in the solid must be antisymmetric under the interchange of the coordinates of any two electrons. Consequently, two electrons of the same spin are forbidden from being very close to each other. *See* EXCLUSION PRINCIPLE.

The uncertainty principle states that if the motion of an electron is confined, its kinetic energy must rise, resulting in a repulsive force opposing the confinement. The kinetic energy due to the confinement is roughly inversely proportional to the square of the radius of the region of confinement. According to the exclusion principle, the motion of an electron in a solid is partially confined because it is forbidden from closely approaching other electrons of the same spin. Thus the uncertainty principle in turn implies a repulsive force. *See* UNCERTAINTY PRINCIPLE.

The magnitude of the repulsive force always exceeds that of the attractive force when the volume per atom becomes sufficiently small. This is most readily understood in the simple metals, which are, roughly, metals in groups 1 through 14. In these metals the electrons can be approximately treated as if they were spread uniformly throughout the solid. If the metal is compressed, the repulsive kinetic energy due to the electron confinement is approximately proportional to d^{-2}, where d is the interatomic separation. The energy due to the attractive force, in contrast, is proportional only to d^{-1}. Thus the repulsive force due to the kinetic energy dominates if d is sufficiently small.

Variations between materials. There are enormous variations between materials in the strength of the cohesive forces. For example, the maximal attractive force in molybdenum, an open-shell solid, corresponds to a negative pressure of nearly 500,000 bars (50 gigapascals); that in xenon, a closed-shell solid, is roughly 100 times smaller (see illus.) This is reflected in a much larger equilibrium volume per atom for xenon, even though the size of an isolated molybdenum atom exceeds that of a xenon atom. The variations in the cohesive forces are also reflected in the boiling point, which is the highest temperature at which a condensed state exists. This can be over 5000°C (9000°F) in open-shell systems, and is usually higher than 200°C (400°F). In elemental closed-shell systems, in contrast, the boiling point is usually below 0°C (32°F); in helium it is −269°C (−452°F), or 4°C (7°F) above absolute zero. Many other properties correlate with the strength of the cohesive forces, including the melting point, elastic moduli, and the energies required to form defects such as vacancies and surfaces. The variations in these properties from material to material have a large impact on their technological applications. *See* CRYSTAL DEFECTS.

Weakening of attractive forces. In analyzing the mechanical properties of solids, it is often conceptually useful to think of the force on a particular atom as being the sum of independent forces due to neighboring atoms. Such a picture is justified for solids consisting of closed-shell atoms or molecules, but is often an inaccurate representation of the forces in open-shell systems, particularly in metals. The attractive force in a solid metal can be several times weaker than that in a dimer molecule, because the atoms interact too strongly with each other to maintain their separate identities; the electrons, instead of being localized on individual atoms, are in states that extend throughout the solid. The weakening of the attractive forces in the solid manifests itself in the atomic geometries around defects. For example, the attractive forces in the vicinity of vacancies or surfaces are intermediate in strength between those in the solid and those in the dimer molecule. This usually results in shorter interatomic separations around these defects, if it is possible for the bonds to contract. In addition, a major contribution to the surface tensions of solids results from changes in the attractive forces near the surface. Anders E. Carlsson

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Coining

A cold metalworking process in a press-type die. Coining is used to produce embossed parts, such as badges and medals, and for minting of coins. It is also used on portions of a blank or workpiece to form corners, indentations, or raised sections, frequently as part of a progressive die operation. The work is subjected to high pressure within the die cavity and thereby forced to flow plastically into the die details. The absence of overflow of excess metal from between the dies is characteristic of coining and is responsible for the fine detail achieved. However, because this action requires highly accurate dies and higher-than-usual die pressures, only essential surfaces are coined. *See* METAL FORMING.

Ralph L. Freeman

Coir

A natural fiber, also known as coco fiber, obtained from the husks of the coconut (*Cocos nucifera*). Although coconuts are grown for copra throughout the tropics and into the subtropics, more than 95% of the coir exports are from Sri Lanka and India. Small amounts are exported from Thailand, Tanzania, Mexico, the Philippines, Malaysia, Kenya, Trinidad, and Tobago. A few other countries produce small amounts of fiber for their own use.

The cells of coir average about 0.028 in. (0.7 mm) in length and about 20 micrometers in width. The cells may have either blunt or pointed ends, and the cell wall has numerous pits. The lumen width and the cell wall thickness are about equal. Coir is a highly lignified fiber and becomes more lignified as it matures.

The outstanding characteristic of coir fiber is its resistance to rot. For example, a coir fiber doormat can stay out in the weather for years. Coir is only intermediate in strength among the vegetable fibers, but its elongation at break is greater than any of the bast or hard fibers.

Types. There are three main types of coir—yarn fiber, bristle fiber, and mattress fiber. Nearly all the yarn fiber comes from southern India; much of the mattress fiber and essentially all the bristle fiber come from Sri Lanka.

Only the finest and longest fiber is suitable for spinning into yarn. It is obtained from the husks of unripe nuts and is the main cash crop rather than a byproduct. The bristle fiber and most of the mattress fiber come from mature nuts and are by-products of copra production.

Production. The yarn and bristle fiber and much of the mattress fiber extraction starts with a natural bacteriological process called retting. The loosened fibers are later separated from the nonfibrous material by mechanical action. Immature husks are used for yarn fiber, while mature husks are used to make bristle and mattress fiber.

Yarn fiber. Within a week after harvest the husks are separated from the shell containing the copra and split into four or five pieces which are put into water for retting, to decompose the nonfibrous materials. Retting usually takes 5 to 6 months but sometimes it requires as long as 10 months. The favored retting centers are in the brackish waters of river estuaries, but many husks are retted in tanks, ponds, lakes, and streams. The circulation of water through the husks—either as a result of a tide, the flow of a stream, or changing the water in a tank—improves the quality of the fiber.

After retting, the husks are washed, air-dried, and then beaten with mallets, stones, or sticks to loosen the fiber and remove the nonfiber materials that have decomposed. Some combing is usually done, either by steel combs mounted on wooden wheels or by stationary combs. Then the fiber is spun by hand into single- or two-ply yarn.

Bristle and mattress fiber. For these fibers, the period of retting is much shorter. Before retting, the nuts are frequently allowed to mature further after harvesting so as to even out the quality of the copra produced from them.

The bristle and mattress fiber is usually separated from retted husks by machines, although the separation still requires extensive hand labor. An increasing number of establishments, especially in new areas, are extracting the fiber from green or dry, unretted husks by automatic machines. However, fiber obtained in such a manner is shorter than fiber obtained by traditional processes and is irretrievably mixed so it must be sold as mattress fiber.

Sorting and grading. Coir fiber ranges in color from light tan to dark brown. Bristles are sorted according to length, which ranges from about 6 to 14 in. (15 to 35 cm), and are packed into bundles of about 17.5 oz (500 g) each. Mattress fiber is packed in small bales of about 11 lb (5 kg) each, and yarn is put up in skeins. Before these packages are put into large bales for shipment, the fiber is graded and sometimes resorted. The fiber is graded on the basis of length, stiffness, color, and cleanliness. Long, clean fibers and light color are desirable for any purpose, but stiffness is desirable in bristles and undesirable for yarn.

Uses. In developed countries, yarn fiber is used chiefly in mats and mattings; in the United States, for instance, its best-known use is in light-brown tufted doormats. In Asia it is used extensively for ropes and twines, and locally for hand-made bags. The principal outlet for bristle fiber has been in brush making, but the market has declined and most bristle fiber is now used in upholstery padding. Mattress fiber is used chiefly in innerspring mattresses, though it has found uses as an insulating material. *See* COCONUT; NATURAL FIBER. Elton G. Nelson

Coke

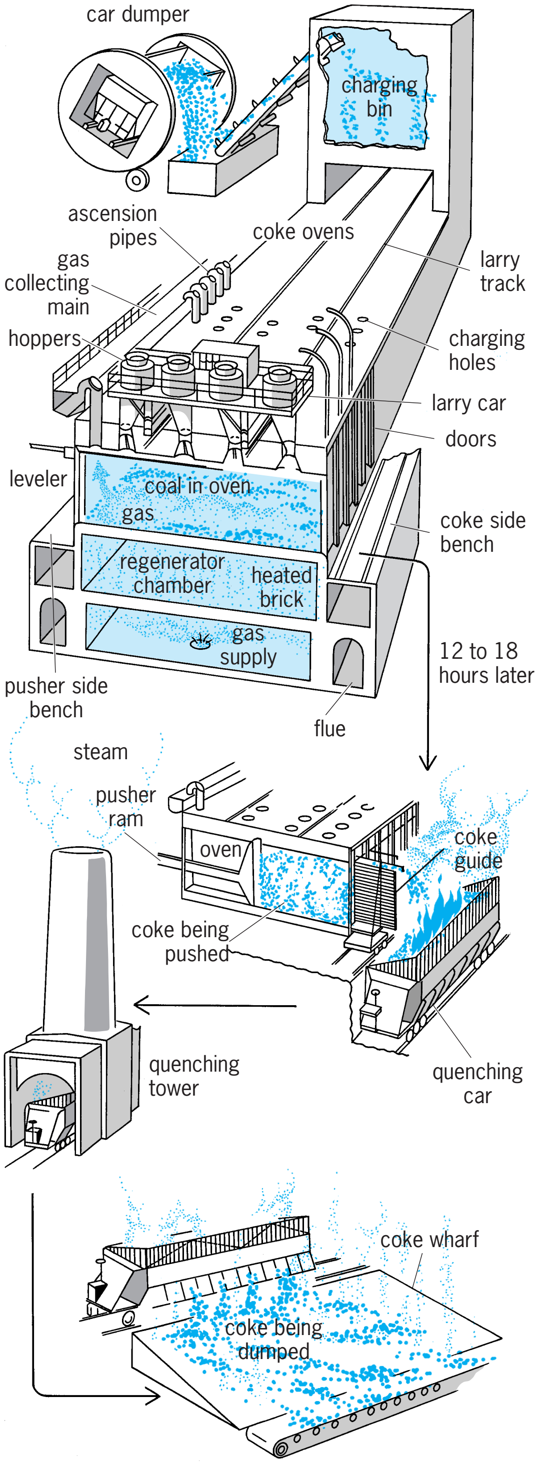
A coherent, cellular, carbonaceous residue remaining from the dry (destructive) distillation of a coking coal. It contains carbon as its principal constituent, together with mineral matter and residual volatile matter. The residue obtained from the carbonization of a noncoking coal, such as subbituminous coal, lignite, or anthracite, is normally called a char. Coke is produced chiefly in chemical-recovery coke ovens (see **illus.**), but a small amount is also produced in beehive or other types of nonrecovery ovens.

Uses and types. Coke is used predominantly as a fuel reductant in the blast furnace, in which it also serves to support the burden. As the fuel, it supplies the heat as well as the gases required for the reduction of the iron ore. It also finds use in other reduction processes, the foundry cupola, and househeating. About 91% of the coke made is used in the blast furnace, 4% in the foundry, 1% for water gas, 1% for househeating, and 3% for other industries, such as calcium carbide, nonferrous metals, and phosphates. Approximately 1300 lb (560 kg) of coke is consumed per ton of pig iron produced in the modern blast furnace, and about 200 lb (90 kg) of coke is required to melt a ton of pig iron in the cupola.

Coke is classified not only by the oven in which it is made, chemical-recovery or beehive, but also by the temperature at which it is made. High-temperature coke, used mainly for metallurgical purposes, is produced at temperatures of 1650–2100°F (900–1150°C). Medium-temperature coke is produced at 1380–1650°F (750–900°C), and low-temperature coke or char is made at 930–1380°F (500–750°C). The latter cokes are used chiefly for househeating, particularly in England. The production of these is rather small as compared to high-temperature coke and usually requires special equipment. Coke is also classified according to its intended use, such as blast-furnace coke, foundry coke, water-gas coke, and domestic coke.

Production. Coke is formed when coal is heated in the absence of air. During the heating in the range of 660–930°F (350–500°C), the coal softens and then fuses into a solid mass. The coal is partially devolatilized in this temperature range, and further heating at temperatures up to 1830–2000°F (1000–1100°C) reduces the volatile matter to less than 1%. The degree of softening attained during heating determines to a large extent the character of the coke produced.

In order to produce coke having desired properties, two or more coals are blended before charging into the coke oven. Although there are some exceptions, high-volatile coals of 32–38% volatile-matter content are generally blended with low-volatile coals of 15–20% volatile matter in blends containing 20–40% low-volatile coal. In some cases, charges consist of blends of high-, medium-, and low-volatile coal. In this way, the desirable properties of each of the coals, whether it be in impurity content or in its contribution to the character of the coke, are utilized.



Steps in the production of coke from coal. After the coal has been in the oven for 12–18 h, the doors are removed and a ram mounted on the same machine that operates the leveling bar shoves the coke into a quenching car for cooling. (*American Iron and Steel Institute*)

The low-volatile coal is usually added in order to improve the physical properties of the coke, especially its strength and yield. In localities where low-volatile coals are lacking, the high-volatile coal or blends of high-volatile coals are used without the benefit of the low-volatile coal. Insome cases, particularly in the manufacture of foundry coke, a small percentage of so-called inert, such as fine anthracite, coke fines, or petroleum coke, is added.

In addition to the types of coals blended, the carbonizing conditions in the coke oven influence the characteristics of the coke produced. Oven temperature is the most important of these and has a significant effect on the size and the strength of the coke. In general, for a given coal, the size and shatter strength of the coke increase with decrease in carbonization temperature. This principle is utilized in the manufacture of foundry coke, where large-sized coke of high shatter strength is required.

Properties. The important properties of coke that are of concern in metallurgical operations are its chemical composition, such as moisture, volatile-matter, ash, and sulfur contents, and its physical character, such as size, strength, and density. For the blast furnace and the foundry cupola, coke of low moisture, volatile-matter, ash, and sulfur content is desired. The moisture and the volatile-matter contents are a function of manner of oven operation and quenching, whereas ash and sulfur contents depend upon the composition of the coal charged. Blast-furnace coke used in the United States normally contains less than 1% volatile matter, 85–90% fixed carbon, 7–12% ash, and 0.5–1.5% sulfur. If the coke is intended for use in the production of Bessemer or acid open-hearth iron, the phosphorus content becomes important and should contain less than 0.01%.

The requirements for foundry coke in analysis are somewhat more exacting than for the blast furnace. The coke should have more than 92% fixed carbon, less than 8% ash content, and less than 0.60% sulfur.

Blast-furnace coke should be uniform in size, about $2^{1}/_{2}$–5 in. (6.4–13 cm), but in order to utilize more of the coke produced in the plant, the practice has been, in some cases, to charge separately into the furnace the smaller sizes after they were closely screened into sizes such as $2^{1}/_{2} \times 1^{3}/_{4}$ in. (6.4×4.5 cm), $1^{3}/_{4} \times 1$ in. (4.5×2.5 cm), down to about $^{3}/_{4}$ in. (1.9 cm) in size. There is now a trend, when pelletized ore is used, to crush and screen the coke to a more closely sized material, such as $2^{1}/_{2} \times {}^{3}/_{4}$ in. (6.4×1.9 cm).

The blast-furnace coke should also be uniformly strong so that it will support the column of layers of iron ore, coke, and stone above it in the furnace without degradation. Standard test methods, such as the tumbler test and the shatter test, have been developed by the American Society for Testing and Materials for measuring strength of coke. Good blast-furnace cokes have tumbler test stability factors in the range of 45 to 65 and shatter indices (2-in. or 5-cm sieve) in the range of 70 to 80%. These are not absolute requirements since good blast-furnace performance is obtained in some plants with weaker coke—but with the ore prepared so as to overcome the weakness.

Foundrymen prefer coke that is large and strong. The coke for this purpose ranges in size from 3 to 10 in. (7.6 to 25 cm) and larger. The size used usually depends upon the size of the cupola and, in general, the maximum size of the coke is about one-twelfth of the diameter of the cupola. High shatter strength is demanded by the cupola operator; shatter indices of at least 97% on 2-in. (5-cm) and 80% on 3-in. (7.6-cm) sieves have been specified.

Other important requirements of foundry coke are high reactivity toward oxygen so that carbon dioxide is produced with high heat evolution, and low reactivity toward carbon dioxide so that the amount of carbon monoxide formed is minimized.

The requirements for coke intended for house-heating vary in different localities. Usually the coke is of a narrow size range, and the size used depends upon the size and type of appliance. In general, a high ash-softening temperature is desirable (more than 2500°F or 1370°C).

Coke intended for water-gas generators should be over 2 in. (5 cm) in size, and should have an ash content below 10% and a moderately high ash-softening temperature. *See* CHARCOAL; COAL; COAL CHEMICALS; DESTRUCTIVE DISTILLATION; FOSSIL FUEL; PYROLYSIS. Michael Perch

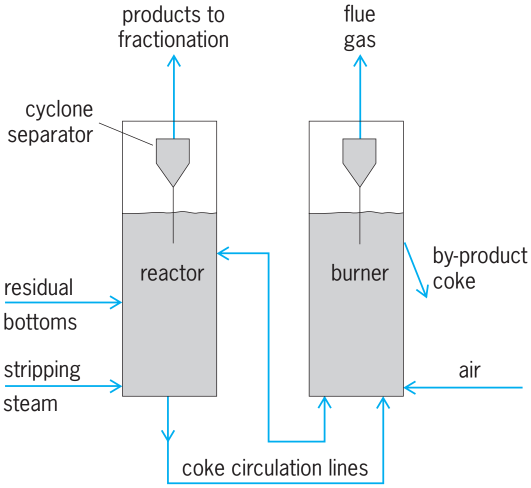
Bibliography. American Society for Testing and Materials, *Petroleum Products, Lubricants, and Fossil Fuels*, vol. 0.505: *Gaseous Fuels: Coal and Coke*, 1993; Commission of the European Communities, *Coke Oven Techniques*, 1983; R. Loison, *Coke*: *Quality and Production*, 2d ed., 1989.

Coking (petroleum)

In the petroleum industry, a process for converting nondistillable fractions (residua) of crude oil to lower-boiling-point products and coke. Coking is often used in preference to catalytic cracking because of the presence of metals and nitrogen components that poison catalysts. There are various coking processes: delayed coking, fluid coking, and flexicoking as well as several others. *See* CRACKING.

Delayed coking. The oldest and most widely used coking process, delayed coking has changed very little in the five or more decades that it has been on-stream in refineries. In the semicontinuous process, the residuum or other heavy feedstock is heated to the cracking/coking temperature (>350°C or 660°F, but usually at temperatures on the order of 480°C or 895°F), and the hot liquid is charged, usually by upflow, to the coke drum, where the coking reactions occur. Liquid and gaseous products pass to the fractionator for separation, and the coke deposits in the drum. The coke drums are arranged in pairs, one on-stream and the other off-stream; and they are used alternately to allow continuous processing. Thus they can be operated on a cycle, typically 24–48 h.

The overhead oil is fractionated into fuel gas (ethane and lower-molecular-weight gases), propane-propylene, butane-butene, naphtha, light gas oil, and heavy gas oil. Yields and product quality vary widely because of the broad range of feedstock types charged to the delayed coking process.



Fluid coking process.

The function of the coke drum is to provide the residence time required for the coking reactions and to accumulate the coke. Hydraulic cutters are used to remove coke from the drum.

Fluid coking. Fluid coking is a continuous fluidized solids process that cracks the feedstock thermally over heated coke particles in a reactor vessel to gas, liquid products, and coke. Heat for the process (see **illus.**) is supplied by partial combustion of the coke, with the remaining coke being drawn as product. The new coke is deposited in a thin fresh layer on the outside surfaces of the circulating coke particles.

Small particles of coke made in the process circulate in a fluidized state between the vessels and serve as the heat transfer medium. Thus the process requires no high-temperature preheat furnace. Fluid coking is carried out at essentially atmospheric pressure and temperatures in excess of 485°C (900°F) with residence times of the order of 15–30 s. The shorter residence time in the fluid coker is in contrast to the residence time of the delayed coker, where the coking reactions are allowed to proceed to completion. This difference is evident from the somewhat higher liquid yields observed in many fluid coking processes. However, the products from a fluid coker may be somewhat more olefinic and slightly less desirable for downstream processing.

Flexicoking. A modification of the fluid coking process, flexicoking also includes a gasifier adjoining the burner/regenerator to convert excess coke to a clean fuel gas with a heating value of about 90 Btu/ft^3 (335 joules/m^3). The coke gasification can be controlled to burn about 95% of the coke to maximize production of coke gas, or at a reduced level to produce both gas and a coke. This flexibility permits adjustment for coke market conditions over a considerable range of feedstock properties and coking processes.

Suitable feedstocks include vacuum residua of all types, asphalt, tar-sand bitumen, and visbreaker bottoms (volatile residues remaining from the viscosity-breaking process).

Uses. The liquid products from the coker, after cleanup via commercially available hydrodesulfurization technology, can provide large quantities of low-sulfur liquid fuels (less than 0.2 wt % sulfur). Another major application for the processes is upgrading heavy low-value crude oils into lighter products.

Petroleum coke is used principally as a fuel or, after calcining, for carbon electrodes. The feedstock from which the coke is produced controls the coke properties, especially in terms of sulfur, nitrogen, and metals content. A concentration effect tends to deposit the majority of the sulfur, nitrogen, and metals in the coke. Cokes exceeding around 2.5% sulfur content and 200 parts per million vanadium are mainly used, environmental regulations permitting, for fuel or fuel additives. The properties of coke for nonfuel use include low sulfur, metals, and ash as well as a definable physical structure. *See* PETROLEUM PROCESSING AND REFINING; PETROLEUM PRODUCTS. James G. Speight

Bibliography. J. G. Gary and G. E. Handwerk, *Petroleum Refining: Technology and Economics*, 3d ed., 1984; J. G. Speight, *The Chemistry and Technology of Petroleum*, 2d ed., 1991; J. G. Speight, *Fuel Science and Technology Handbook*, 1990.

Cola

A tree, *Cola acuminata*, of the family Sterculiaceae and a native of tropical Africa. Its fruit is a star-shaped follicle containing eight hard seeds, the cola nuts of commerce (see **illus.**). These nuts are an important masticatory in many parts of tropical Africa. They have a caffeine content twice that of coffee. The nuts also contain an essential oil and a glucoside, kolanin, which is a heart stimulant. Cola nuts, in combination with an extract from coca, are used in the manufacture of the beverage Coca-Cola. Cola is now cultivated in West Africa, Jamaica, Brazil, India, and other parts of tropical Asia. *See* COCA; MALVALES.

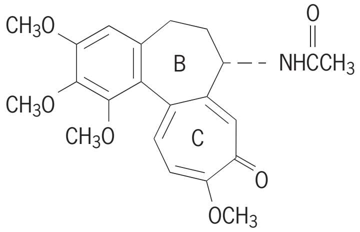
Perry D. Strausbaugh; Earl L. Core

Cola (*Cola acuminata*) branch.

Colchicine

The major alkaloid obtained from the seed capsules, corms, and bulbs of the meadow saffron (autumn crocus; *Colchicum autumnale*). Colchicine is a fairly abundant alkaloid in dried corms (0.03–0.08%) and seeds (0.6–0.9%). It has been isolated also from other species of *Colchicum* and a few related genera, but they are not important sources of alkaloid. *See* ALKALOID; LILIALES.

Colchicine has an unusual structure (shown below) containing two seven-membered rings. Ring C is a tropolone system, present also in some fungal metabolites. The molecule has been synthesized in several ways, by constructing the ring system in either the sequence A → AB → ABC or A → AC → ABC.



The use of the colchicum plant to relieve the pain of gout has been known since medieval times, and colchicine is still the standard treatment for gout, although it is an extremely toxic substance.

An important property of colchicine is its ability to interrupt the mitotic cycle before cell division occurs. This effect leads to cells with multiple chromosomes, which are of value in plant breeding. The antimitotic effect of colchicine is due to strong binding of the alkaloid to the protein tubulin, thus preventing the assembly of microtubules and formation of the mitotic spindle. *See* MITOSIS; POLYPLOIDY.

James A. Moore

Cold hardiness (plant)

The ability of temperate zone plants to survive subzero temperatures. This characteristic is a predominant factor that determines the geographical distribution of native plant species and the northern limits of cultivation of many important agronomic and horticultural crops. For example, plant hardiness zone maps (**Fig. 1**) are frequently used in recommending the selection of various horticultural crops, especially woody ornamentals (see **table**) and fruit trees, for various regions. Further, freezing injury is a major cause of crop loss resulting from early fall frosts, low midwinter temperatures, or late spring frosts. Problems of cold hardiness are of concern to farmers in diverse areas of agriculture—from coffee growers in Brazil to wheat farmers in Canada; from peach growers in Georgia to apple growers in New York; from tropical foliage plant growers in Florida to producers of woody ornamentals in the northeast; from viticulturists (grape growers) in France to citrus growers

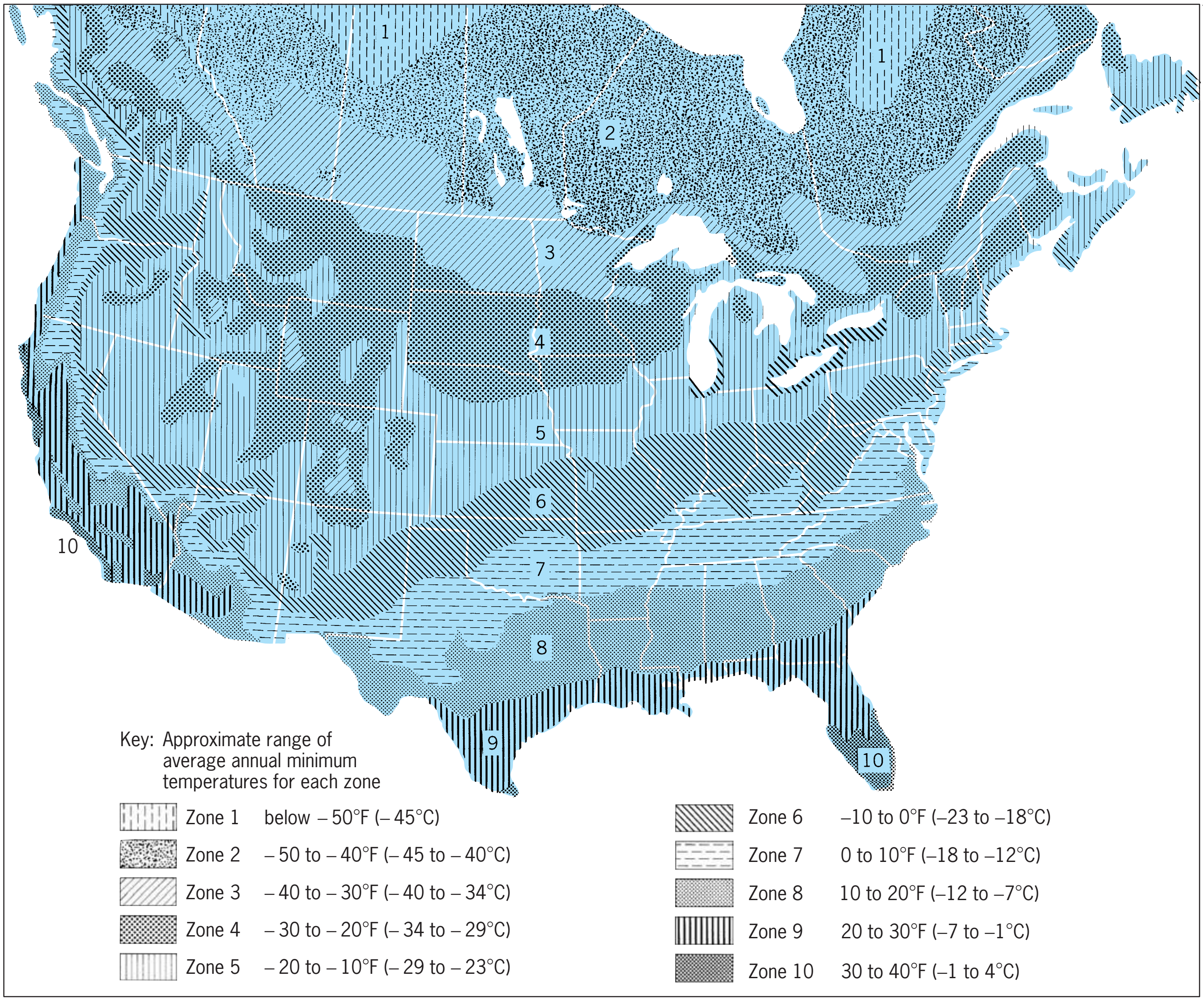


Fig. 1. Plant hardiness zone map of the United States based on isotherms of average minimum winter temperatures.

in Israel. As a result, the development of varieties of cultivated plants with improved cold hardiness is of long-standing concern.

Within the plant kingdom there is a wide range of diversity in low-temperature tolerance—from low levels of hardiness in herbaceous species such as potatoes (27 to 21°F or −3 to −6°C), to intermediate levels of hardiness for winter annuals such as wheat and rye (−4 to −22°F or −20 to −30°C), to extremely hardy deciduous trees and shrubs such as black locust and red osier dogwood that can withstand temperatures of liquid nitrogen (−321°F or −196°C). Within a given species, the range in hardiness can be substantial. For example, the cold hardiness of different varieties of deciduous fruit trees may vary by 18 to 36°F (10 to 20°C). Within a given plant there is a wide range in the cold hardiness of different tissues and organs. For example, roots are much less tolerant of subzero temperatures than shoots; flower buds are more sensitive than vegetative buds.

Environmental effects. The cold hardiness of a given species is an inherent genetic trait that requires certain environmental cues for its expression. With the shorter days and cooler nights of autumn, temperate zone plants become dormant and increase their cold hardiness. This process is referred to as cold acclimation. In the spring, increasing daylength and warmer temperatures result in the resumed growth and development of the plant and a corresponding decrease in cold hardiness. Thus, hardy species such as winter annuals, biennials, and perennials exhibit an annual periodicity in their low-temperature tolerance (**Fig. 2**). In the spring and summer these species are as susceptible to freezing temperatures as are nonhardy species.

Cold hardiness may be influenced by radiation, temperature, photoperiod, precipitation, and stage of development of the plant, with different optimum conditions for different species or cultivars and ecotypes within a species. The various environmental

Representative ornamental plants that will survive in the various hardiness zones

	Scientific name	Common name
Zone 1	*Betula glandulosa*	Dwarf birch
below −50° F (−45° C)	*Empetrum nigrum*	Crowberry
	Populus tremuloides	Quaking aspen
	Potentilla pennsylvanica	Pennsylvania cinquefoil
	Rhododendron lapponicum	Lapland rhododendron
	Salix reticulata	Netleaf willow
Zone 2	*Betula papyrifera*	Paper birch
−50° to −40° F (−45 to −40° C)	*Cornus canadensis*	Bunchberry dogwood
	Elaeagnus commutata	Silverberry
	Juniperus communis	Common juniper
	Picea glauca	White spruce
	Potentilla fruticosa	Bush cinquefoil
Zone 3	*Elaeagnus angustifolia*	Russian olive
−40 to −30° F (−40 to −34° C)	*Lonicera tatarica*	Tatarian honeysuckle
	Malus baccata	Siberian crabapple
	Parthenocissus quinquefolia	Virginia creeper
	Syringa vulgaris	Common lilac
	Thuja occidentails	American arborvitae
Zone 4	*Berberis thunbergi*	Japanese barberry
−30 to −20° C (−34 to −29° C)	*Hydrangea paniculata*	Panicle hydrangea
	Juniperus chinensis	Chinese juniper
	Ligustrum amurense	Amur River privet
	Spiraea vanhouttei	Vanhoutte spirea
	Taxus cuspidata	Japanese yew
Zone 5	*Cornus florida*	Flowering dogwood
−20 to −10° F (−29 to −23° C)	*Deutzia gracilis*	Slender deutzia
	Forsythia ovata	Early forsythia
	Parthenocissus tricuspidata	Boston ivy
	Rosa multiflora	Japanese rose
Zone 6	*Acer palmatum*	Japanese maple
−10 to 0° F (−23 to −18° C)	*Buxus sempervirens*	Common boxwood
	Forsythia suspensa	Weeping forsythia
	Hedera helix	English ivy
	Ilex opaca	American holly
	Ligustrum ovalifolium	California privet
Zone 7	*Azalea Kurume hyb. Hinodegiri*	Red Hussar azalea
0 to 10° F (−18 to −12° C)	*Cedrus atlantica*	Atlas cedar
	Cercis chinensis	Chinese redbud
	Chamaecyparis lawsoniana	Lawson cypress
	Cotoneaster salicifolia	Willowleaf cotoneaster
	Ilex aquifolium	English holly
Zone 8	*Arbutus menziesi*	Pacific madrone
10 to 20° F (−12 to −7° C)	*Choisya ternata*	Mexican orange
	Melia azedarach	Chinaberry
	Olearia haasti	New Zealand daisybush
	Prunus laurocerasus	Cherry laurel
	Viburnum tinus	Laurestinus
Zone 9	*Arbutus unedo*	Strawberry tree
20 to 30° F (−7 to −1° C)	*Eucalyptus globulus*	Tasmanian blue gum
	Grevillea robusta	Silk oak
	Myrtus communis	Myrtle
	Pittosporum tobira	Japanese pittosporum
	Quercus virginiana	Live oak
Zone 10	*Acacia baileyana*	Cootamundra wattle
30° to 40° F (−1 to 4° C)	*Arecastrum romanozoffianum*	Queen palm
	Bougainvillea spectabilis	Bougainvillea
	Casuarina equisetifolia	Horsetail beefwood (Australian pine)
	Eucalyptus citriodora	Lemon eucalyptus
	Ficus macrophylla	Moreton Bay fig

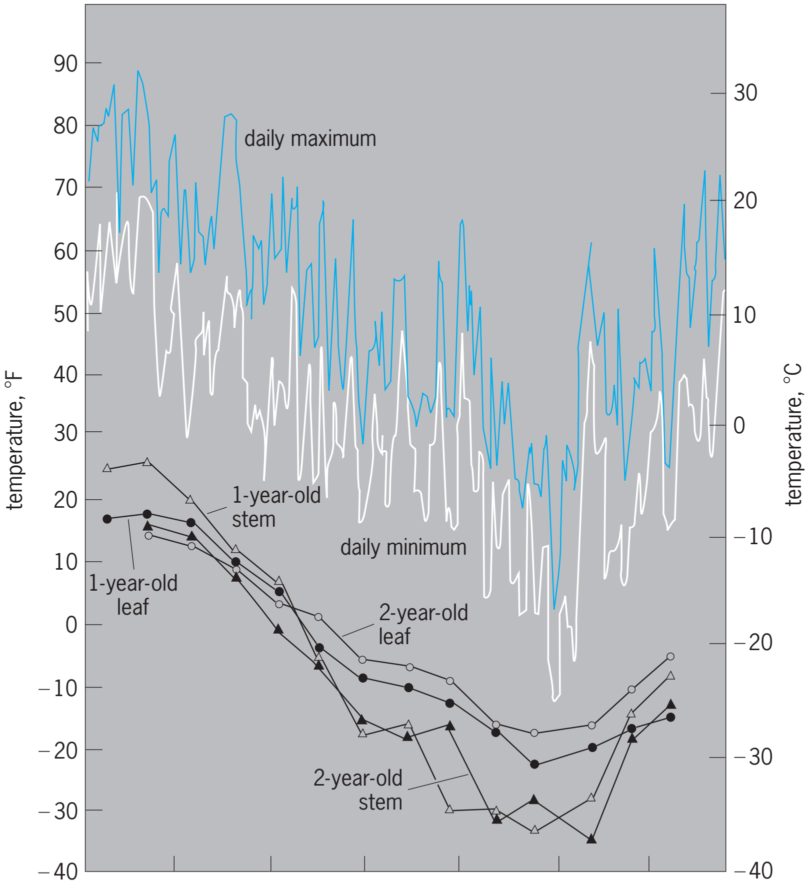


Fig. 2. **Development of cold hardiness of *Hedera helix* (English ivy). The curves show killing points for structures at different ages. (*From P. L. Steponkus and F. O. Lanphear, Factors influencing artificial cold acclimation and artificial freezing of Hedera helix "Thorndale," Proc. Amer. Soc. Hort. Sci., 91:735–741, 1967*)**

cues serve to synchronize plant development with the environment. This synchronization has taken centuries to evolve, and freezing injury in cultivated species can result from any factor that disrupts this synchrony. Some varieties may not be responsive to the prevailing environmental cues or may not respond rapidly enough; some may not develop a sufficient degree of hardiness; and some may deacclimate too rapidly. These factors may arise when individual varieties are introduced into areas that are vastly or even slightly different from their natural habitat, where centuries of selection pressures have evolved those individuals most closely synchronized with the prevailing environment.

Temperature is the key environmental parameter for increasing a plant's capacity to withstand freezing temperatures. Low, above-freezing temperatures are conducive to an increase in hardiness in the fall, and warm temperatures are responsible for the decrease in the spring. Generally, it is considered that most plants will acclimate as temperatures are gradually lowered below 50°F (10°C). However, during acclimation, the progressive decline in temperatures (from the relatively warm temperatures in early fall, followed by low, above-freezing temperatures in late fall and early winter, followed by freezing temperatures in winter) is extremely important. The development of cold hardiness may take 4 to 6 weeks.

Photoperiod is the second major factor influencing cold acclimation, but only in those species that are photoperiodically responsive in relation to growth cessation or induction of dormancy (a true physiological rest period). In other species, light is important only in providing sufficient photosynthetic reserves required for the cold acclimation process. In some cases (for example, germinating seeds), sufficient energy reserves are already present and acclimation can occur in the dark. *See* PHOTOPERIODISM.

There are conflicting reports on the role of moisture in relation to cold hardiness. High soil moisture may reduce the degree of cold acclimation; however, severe winter injury of evergreens will occur if soil moisture levels are too low. Most often tissue moisture levels will influence the survival to a given freeze-thaw cycle rather than directly influencing the process of cold acclimation. Thus, whereas temperature and light effects on hardiness are probably mediated through the development of hardiness (cold acclimation), tissue moisture content directly affects the stresses that are incurred during a freeze-thaw cycle. In addition, various cultural practices can influence the cold hardiness of a given plant. For example, late fall applications of fertilizer or improper pruning practices may stimulate flushes of growth that do not have sufficient time to acclimate. Conversely, insufficient mineral nutrition can also impair the development of maximum cold hardiness.

Freezing of plant tissues. Because plants are poikilotherms and assume the temperature of their surroundings, cold hardiness requires that they tolerate ice formation in tissues. When plant tissues freeze, the water they contain changes both its physical state and location. Ice formation may occur within cells (intracellular ice formation), in the intercellular spaces (extracellular ice formation), or in regions that separate different tissues or organs (extraorgan ice formation). In some organs and cells, such as floral buds or xylem ray parenchyma cells of deciduous forest species, ice formation may be precluded entirely. In these cases, the cytoplasm of the cell remains unfrozen below its freezing point (that is, supercooled) down to temperatures as low as −40°F (−40°C). The location of ice formation (intracellular versus extracellular) is strongly influenced by the rate of cooling, the minimum temperature attained, and the degree of hardiness of the plant.

During cooling, plant tissues initially supercool; that is, ice formation does not occur at the freezing point of the cytoplasm. Instead, ice nucleation occurs on the external plant surfaces because of the presence of foreign nucleating agents, such as ice crystals in the air or, in some cases, bacteria. Ice then propagates through the extracellular spaces, but the plasma membrane (the outer membrane of the cell) prevents seeding of the cytoplasm by the external ice. Because ice has a lower chemical potential than water at the same temperature, a gradient in water potential exists between the unfrozen cytoplasm and the extracellular ice. Water moves in response to

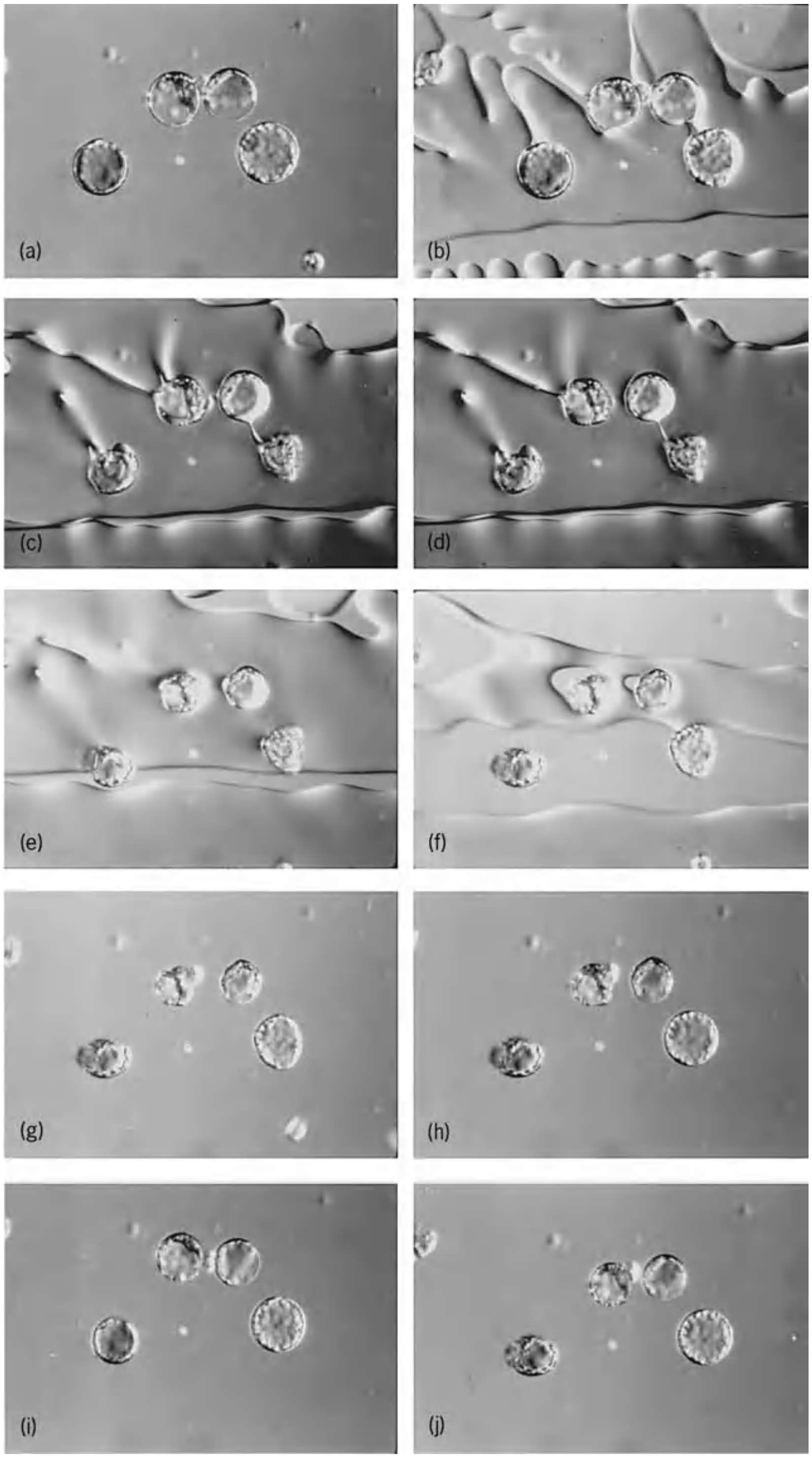


Fig. 3. Cryomicroscopic observations of isolated rye (*Secale cereale*) protoplasts during a freeze-thaw cycle. Cooling: (*a*) 32°F (0°C), (*b*) 28°F (−2°C), (*c*) 23°F (−5°C), (*d*) 14°F (−10°C). Warming: (*e*) 17°F (−8°C), (*f*) 25°F (−4°C), (*g*) 32°F (0°C). (*h–j*) Isothermal at 32°F (0°C). Note the extensive dehydration of the cell that occurs at subzero temperatures. (*Courtesy of Peter L. Steponkus*)

gradients in water potential; hence water will move from the cytoplasm to the extracellular ice and the cell will dehydrate. Because the plasma membrane is a semipermeable membrane that allows for the rapid efflux of water but does not permit the ready efflux of solutes, the cytoplasmbecomes more concentrated. With increasing solute concentration, the freezing point of the cytoplasm is progressively lowered and the intracellular solution remains unfrozen. During warming, the sequence of events is reversed. The extracellular ice melts and the extracellular solution becomes less concentrated than the intracellular solution. As a result, water will flow back into the cell. Thus, during a freeze-thaw cycle, the cells behave as osmometers in response to ice formation in the extracellular spaces. *See* CELL MEMBRANES; CELL WALLS (PLANT).

The osmometric behavior of plant cells depends on the semipermeable characteristics of the plasma membrane that allow for the rapid movement of water while retaining solutes within the cell and excluding extracellular ice crystals. This behavior is readily observed microscopically. Although microscopic observations of biological specimens at subzero temperatures have been reported for over a century, there has been a renaissance in cryomicroscopy since the early 1970s. This has occurred because of the development of sophisticated temperature-control systems and advances in video recording and computer-enhanced video image analysis. As a result, cryomicroscopy has emerged as a very powerful technique for quantifying and understanding cellular behavior during a freeze-thaw cycle. Although it has been nearly 100 years since the cooling-rate dependency of intracellular ice formation was observed in higher plants, quantitative studies of the volumetric behavior of higher plant protoplasts are only now being reported. *See* CRYOBIOLOGY.

Isolated protoplasts are obtained from plant tissues by the enzymatic digestion of the cell walls. The liberated protoplasts behave as ideal osmometers. Their spherical shape over a wide range of solute concentrations facilitates quantitative cryomicroscopic studies of their osmometric behavior. Direct measurements of volumetric behavior during a freeze-thaw cycle (**Fig. 3**) allow for the calculation of water efflux, the extent of supercooling, and water permeability of the plasma membrane. Coupled with a precise time and temperature history, such studies provide considerable insight into the causes and manifestations of freezing injury. Extensive dehydration of the cell occurs at subzero temperatures; following thawing of the suspending medium, the protoplasts rehydrate and osmotically increase in volume. Because the protoplasts in Fig. 3 were isolated from acclimated tissues, they survived the freeze-thaw cycle to a temperature of 14°F (−10°C).

Intracellular ice formation. Whether ice formation is restricted to the extracellular spaces or also occurs within the cells is of utmost importance because intracellular ice formation is invariably associated with lethal injury. In isolated rye protoplasts subjected to rapid cooling rates (9°F or 5°C per minute; **Fig. 4**), intracellular ice formation is manifested as a darkening of the cells (Fig. 4*c* and *d*). This optical darkening or flashing is commonly observed, and was long thought to be the result of the diffraction of light by small ice crystals. High-resolution cryomicroscopy of isolated protoplasts reveals that the optical darkening is due to the formation of gas bubbles following intracellular ice formation. Upon melting of the ice, some of the gas bubbles coalesce (Fig. 4*e*). More importantly, however, intracellular ice formation is associated with lethal injury as manifested by the ruptured protoplasts (Fig. 4*f*). Intracellular ice formation is associated with early frost injury of herbaceous plants, and may also occur when there are sudden temperature changes in deciduous fruit tree buds.

The incidence of intracellular ice formation is strongly dependent on the rate at which the tissue is cooled and the minimum temperature attained. At rapid cooling rates, efflux of water from the cell is limited by the water permeability of the plasma membrane or other impediments to water flux. As a result, concentration of the intracellular solutes and depression of the freezing point will not keep pace with the decreasing temperature, and the intracellular solution will become increasingly supercooled during cooling. With suspensions of isolated plant cells or protoplasts where the cells are surrounded by ice and the only barrier to water efflux is the plasma membrane, excessive supercooling will occur at cooling rates greater than 5°F (3°C) per minute. In intact tissues, rates greater than a few degrees per hour are sufficiently rapid to result in supercooling of the intracellular solution. This is because the ice crystals may be far removed from the intracellular solution and water flow is slowed by impediments resulting from tissue organization, contact of cell walls, or other barriers. Supercooling per se does not result in intracellular ice formation; it only predisposes the cell to this possibility. Nucleation or seeding of the supercooled solution is required for intracellular ice formation. This may occur by either homogeneous or heterogeneous nucleation or by seeding by the extracellular ice.

Homogeneous nucleation is a result of the spontaneous aggregation of water molecules to form ice nuclei and occurs only at temperatures below −38°F (−39°C). Thus, floral buds of some species or xylem ray parenchyma of some deciduous species will tolerate temperatures down to −38°F (−39°C) because they remain supercooled. At lower temperatures, however, intracellular ice formation occurs because of homogeneous nucleation. The sudden and rapid formation of ice is invariably lethal. There is a close relationship between the northern limits of many deciduous forest species that exhibit supercooling of the xylem ray parenchyma cells and the occurrence of temperatures below −40°F (−40°C).

Heterogeneous nucleation may occur at higher temperatures, but it requires the presence of foreign materials that are effective ice-nucleating agents. However, there is little evidence that such compounds are present in the cytoplasm. Instead, there is considerable evidence that intracellular ice formation is a consequence of seeding by extracellular ice as a result of perturbation or penetration of the plasma membrane. Direct cryomicroscopic observations of isolated protoplasts reveal that mechanical failure of the plasma membrane occurs immediately before intracellular ice formation. This occurs in the range of 23 to 5°F (−5 to −15°C) in nonacclimated plants. Thus, intracellular ice formation is a consequence of injury to the plasma membrane rather than a cause of injury.

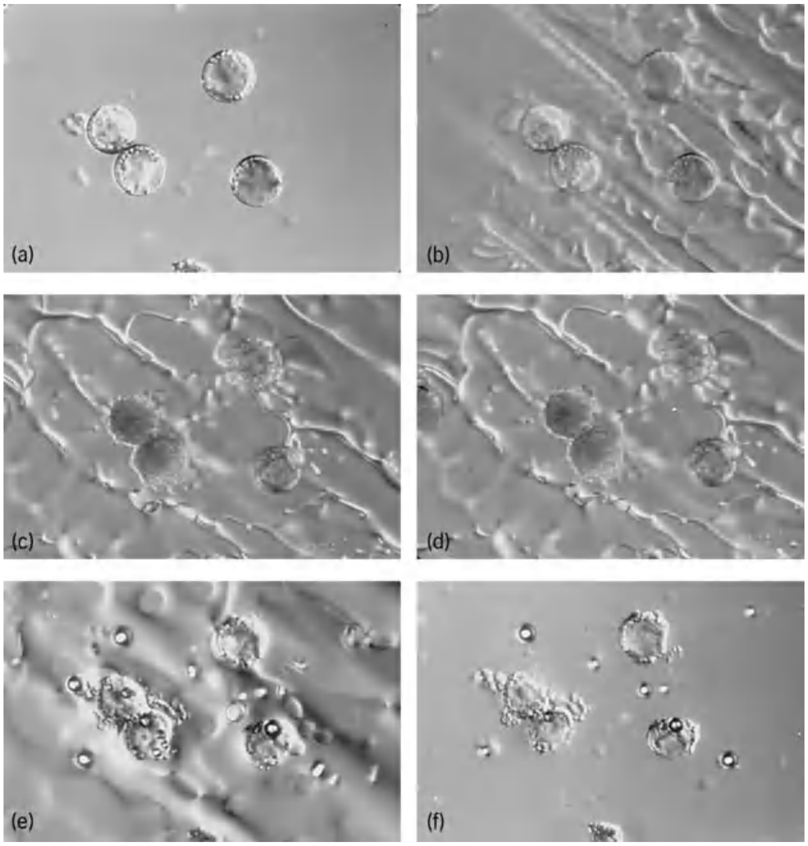


Fig. 4. Intracellular ice formation in isolated rye (*Secale cereale*) protoplasts. Cooling: (*a*) 32°F (0°C), (*b*) 28°F (−2°C), (*c*) 14°F (−10°C), (*d*)14°F (−10°C). Warming: (e) 28°F (−2°C), (*f*) 32°F (0°C). (*Courtesy of Peter L. Steponkus*)

Following cold acclimation, plants are less prone to intracellular ice formation. For many years it was assumed that this was because of an increase in the water permeability of the plasma membrane, which minimized the extent of supercooling. Recently, however, this was shown to be erroneous. Instead, cold acclimation decreases the incidence of intracellular ice formation because the stability of the plasma membrane at lower temperatures is increased and defers seeding by extracellular ice to temperatures as low as −40°F (−40°C).

Freezing injury due to cell dehydration. The visual symptoms of freezing injury—a darkened, water-soaked, flaccid appearance—are apparent immediately following thawing. The rapidity in which injury is manifested indicates that injury is not the result of metabolic dysfunction. Instead, the primary cause of freezing injury is the disruption of the plasma membrane. Manifestations of injury may range from alterations in the semipermeable characteristics to mechanical rupture, and injury can occur at various times during a freeze-thaw cycle (**Fig. 5**). The various forms of injury observed are (1) expansion-induced lysis during warming andthawing of the suspending

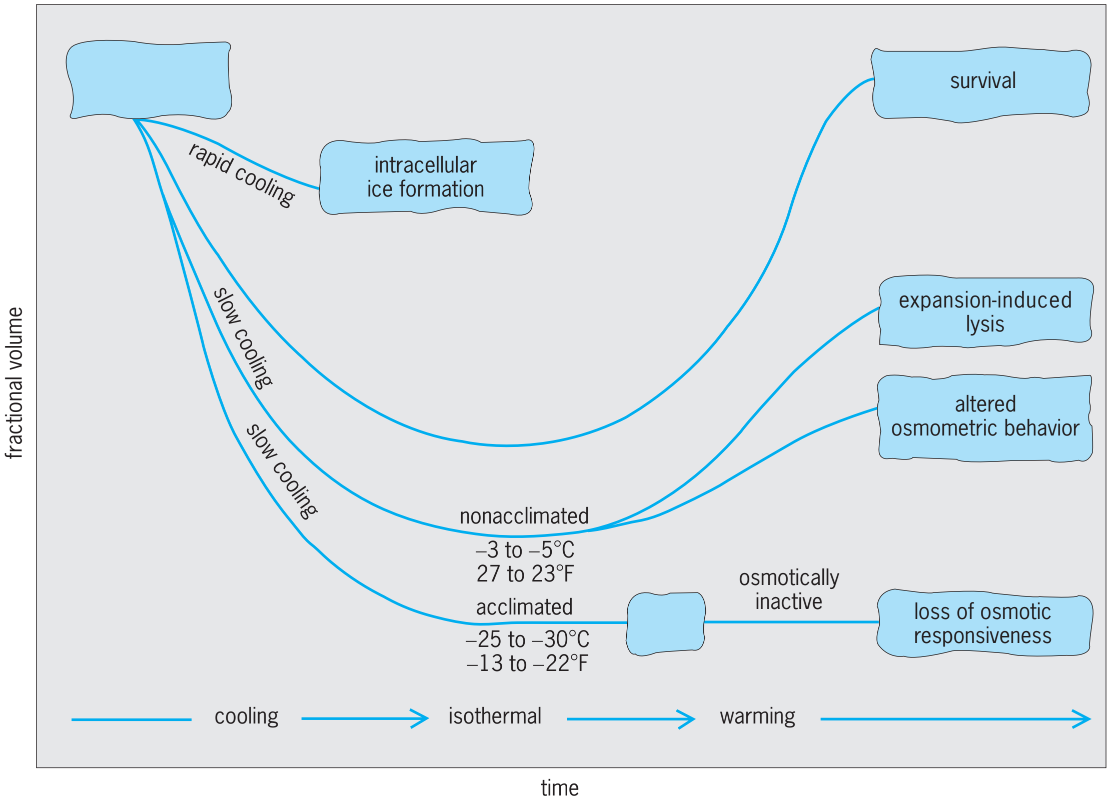


Fig. 5. Manifestations of freezing injury to the plasma membrane.

medium when the decreasing concentration of the suspending medium results in osmotic expansion of the protoplasts; (2) loss of osmotic responsiveness following cooling at slow rates so that the protoplast is osmotically inactive during warming; and (3) altered osmometric behavior during warming, suggestive of altered semipermeable characteristics or leakiness of the plasma membrane.

These symptoms of injury are not consequences of low temperatures per se because low temperatures in the absence of freezing are not injurious to hardy plants. Thus, thermal stresses that may result in membrane phase transitions are unlikely to contribute to freezing injury. Similarly, there is little evidence that injury occurs because of the presence of ice crystals. Instead, injury is primarily a consequence of cell dehydration, and there is a very good correlation between cold hardiness and the ability to withstand dehydration in the absence of freezing. There are, however, several consequences of cell dehydration that can result in injury to the plasma membrane.

In nonacclimated tissues, cell dehydration results in the deletion of membrane material from the plasma membrane in the form of membrane vesicles (**Fig. 6***a*). During contraction of the protoplast, these vesicles are detached from the membrane and become visible in the cytoplasm. Upon thawing, the tissue increases in volume, but the previously deleted membrane material is not reincorporated into the membrane, and rupture of the plasma membrane (lysis) occurs before the cells regain their original size. Hence, this form of injury is referred to as expansion-induced lysis or deplasmolysis injury, and is the predominant form of injury following cell dehydration in nonacclimated herbaceous tissues such as winter cereals (wheat or rye). Injury is largely a consequence of the mechanical stresses imposed on the plasma membrane during cell dehydration and rehydration.

Expansion-induced lysis is not observed in acclimated tissues because membrane deletion does not occur during contraction. Instead, extrusions of the plasma membrane that remain contiguous with the plasma membrane are formed (Fig. 6*b*). These extrusions are readily reincorporated into the plane of the membrane during expansion. Hence, mechanical stresses of the plasma membrane are not responsible for injury in acclimated tissues. Instead, injury is largely the result of chemical stresses associated with cell dehydration.

Loss of osmotic responsiveness occurs in protoplasts isolated from nonacclimated tissues when the protoplasts are cooled to 14°F (−10°C) or lower. At these temperatures severe freeze-induced dehydration occurs with a loss of nearly 90% of the intracellular water, and with a tenfold increase in the concentration of the intracellular solutes. The semipermeable properties of the plasma membrane are disrupted so that following thawing the protoplasts are osmotically unresponsive. In tissues, the cells appear to be plasmolyzed, and therefore this form of injury has been referred to as frost plasmolysis. However, this term is misleading in that the cells cannot be considered plasmolyzed if they are not osmotically responsive.

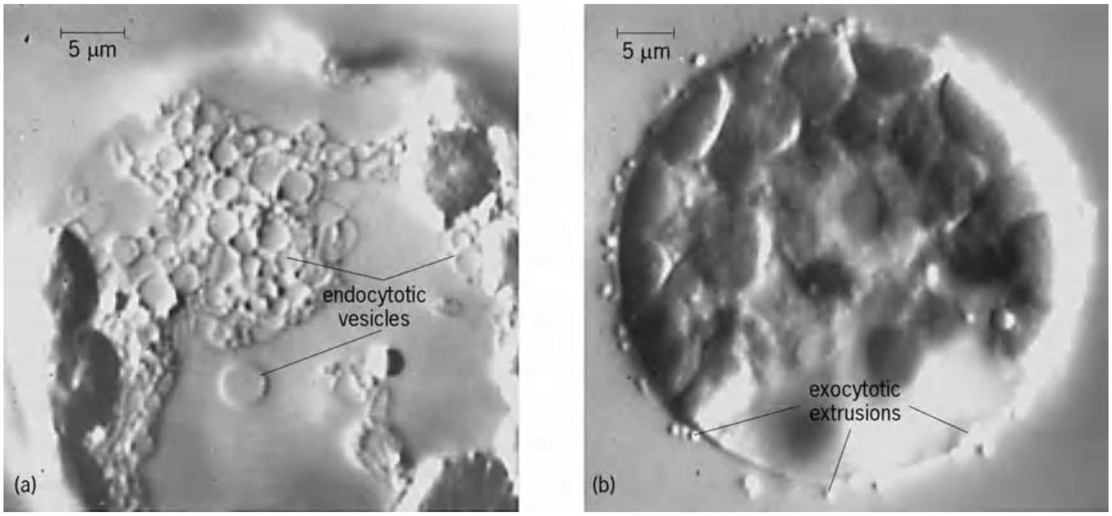


Fig. 6. High-resolution computer-enhanced differential interference contrast micrographs of (*a*) nonacclimated and (*b*) acclimated protoplasts subjected to hypertonic solutions. (*From P. L. Steponkus et al.*, *Destabilization of the plasma membrane of isolated plant protoplasts during a freeze-thaw cycle: The influence of cold acclimation*, *Cryobiology*, *20:448–465*, *1983*)

Loss of osmotic responsiveness is associated with several changes in the ultrastructure of the plasma membrane, including lateral phase separations and bilayer-to-nonbilayer transitions, such as the formation of inverted cylindrical micelles or hexagonal$_{\text{II}}$ phase. These changes occur as a consequence of the close approach (less than 2 to 3 nanometers) of membranes during cell dehydration. Normally, strongly repulsive hydration forces preclude the close approach of two bilayers. However, the high osmotic pressures that occur during freeze-induced dehydration overcome the hydration forces. Dehydration-induced lateral phase separations and the hexagonal$_{\text{II}}$ phase are not observed in protoplasts isolated from cold-acclimated tissues. The increased stability may be a consequence of alterations in the plasma membrane lipid composition that preclude dehydration-induced demixing of the lipids, and the accumulation of cytoplasmic solutes such as sucrose or proline.

Cold acclimation. The process of cold acclimation results in numerous biochemical changes within the plant. These include increases in growth inhibitors and decreases in growth promoters; changes in nucleic acid metabolism; alterations in cellular pigments such as carotenoids and anthocyanins; the accumulation of carbohydrates, amino acids, and water-soluble proteins; increases in fatty acid unsaturation; changes in lipid composition; and the proliferation of cellular membrane systems. Not all of these changes are involved in increased cold hardiness; some are merely changes in response to slower growth rates and decreased photosynthate utilization; others are changes associated with growth at low, above-zero temperatures; and still others are associated with other developmental phenomena, such as vernalization or the induction of dormancy, that also occur during the period of cold acclimation.

As cellular membranes are the primary site of freezing injury, it follows that cold acclimation must involve cellular alterations that allow the membranes to survive lower freezing temperatures. Such alterations may be in the cellular environment so that either the freezing stresses are altered or there is direct protection of the membranes. In addition, cold acclimation may involve changes in the membrane itself, so that its susceptibility to the freezing stresses is decreased.

Large increases in cellular solute concentrations are one of the most universal manifestations of cold acclimation. A doubling of the intracellular solute concentration, most notably sugars, is not uncommon. Such increases have several beneficial effects. First, they serve to depress the freezing point of the intracellular solution. This, however, is of limited advantage because such increases only lower the freezing point to the extent of 1.03°F/osmolal (1.86°C/osmolal).

More important is their effect on the extent of cell dehydration that occurs during freezing. A doubling of the initial intracellular solute concentration will decrease the extent of cell dehydration at any subzero temperature by 50%. An increase in intracellular solutes will also decrease the concentration of toxic solutes at temperatures below 32°F (0°C), because less water will be removed. During dehydration protective compounds, such as sugars, are concentrated along with toxic compounds, such as electrolytes. Because the total concentration of the intracellular solution is a function of the subzero temperature, the toxic compounds will account for only a portion of the total. If the ratio of protective to toxic compounds is initially greater, the final concentration of the toxic compounds at any subzero temperature will be lowered accordingly. In addition, there are some compounds, such as sucrose or proline, that may interact directly with cellular membranes to increase their stability either at low water contents or at high electrolyte concentrations.

Following cold acclimation there are substantial changes in the lipid composition of the plasma membrane. Although there are no lipid molecular species that are unique to the plasma membrane of either nonacclimated or acclimated rye leaves, cold acclimation alters the proportion of virtually every lipid component. This includes an increase in free sterols with corresponding decreases in steryl glucosides and acylated steryl glucosides, a decrease in the glucocerebroside content, and an increase in the phospholipid content. Although the relative proportions of the individual phospholipids (for example, phosphatidylcholine and phosphatidylethanolamine) do not change appreciably, there are substantial differences in the individual lipid molecular species. These include increases in species of phosphatidylcholine and phosphatidylethanolamine that contain two unsaturated fatty acids, whereas species with a single unsaturated fatty acid remain relatively unchanged. The complexity of the plasma membrane lipid composition and the numerous changes that occur during cold acclimation preclude the possibility that any simple correlative analysis of the changes will establish their role in the cold acclimation process; instead, a mechanistic analysis is required.

One approach has been to demonstrate that the differential behavior of the plasma membrane observed in protoplasts isolated from nonacclimated and cold-acclimated leaves (that is, the formation of endocytotic vesicles versus exocytotic extrusions during osmotic contraction and the differential propensity for dehydration-induced bilayer-to-nonbilayer phase transitions) is also observed in liposomes formed from plasma membrane lipid extracts of nonacclimated and acclimated leaves. Thus, the increased cryostability of the plasma membrane following cold acclimation is a consequence of alterations in the lipid composition. However, there are over 100 different lipid molecular species present in the plasma membrane, so that the problem is to determine which of the changes are responsible for the differential cryobehavior. In studies that have used a protoplast–liposome fusion technique to enrich the plasma membrane with specific lipids, it has been established that increases in the proportion of phosphatidylcholine species composed of one or two unsaturated fatty acids increase the freezing tolerance of protoplasts isolated from nonacclimated rye leaves. The increase in freezing tolerance is the result of a transformation in the cryobehavior of the plasma membrane during osmotic contraction so that exocytotic extrusions are formed rather than endocytotic vesicles. As a result, expansion-induced lysis is precluded. Thus, these studies demonstrate that although there are over 100 lipid molecular species in the plasma membrane, altering the proportion of a single species dramatically alters the cryobehavior of the plasma membrane. Similar membrane engineering studies have been undertaken for the other forms of freezing injury (for example, loss of osmotic responsiveness) and should ultimately provide a molecular understanding of the role of plasma membrane lipid alterations in increasing the cryostability of the plasma membrane. *See* ALTITUDINAL VEGETATION ZONES; PLANT PHYSIOLOGY; PLANT-WATER RELATIONS.

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Cold storage

Keeping perishable products at low temperatures in order to extend storage life. Cold storage vastly retards the processes responsible for the natural deterioration of the quality of such products at higher temperatures. Time and temperature are the key factors that determine how well foods, pharmaceuticals, and many manufactured commodities, such as photographic film, can retain properties similar to those they possess at the time of harvest or manufacture.

Food that is placed in cold storage is protected from the degradation that is caused by microorganisms. At 80°F (27°C), bacteria will multiply 3000 times in 12–24 h; at 70°F (21°C), the rate of multiplication is reduced to 15 times; and at 40°F (4°C), it is reduced to 2 times. The lower limit of microbial growth is reached at 14°F (−10°C); microorganisms cannot multiply at or below this temperature. *See* BACTERIAL GROWTH; FOOD MICROBIOLOGY.

Cold storage through refrigeration or freezing makes it possible to extend both the seasons of harvest and the geographic area in which a product is available. In the past, food products were grown locally and had to be marketed within a short period of time. Modern cold storage technology makes virtually any product available year-round on a global basis. Other technologies have been combined with refrigeration to further improve this availability. For example, in controlled-atmosphere storage of apples, controlled temperatures above freezing are maintained in a sealed room where the air is also modified to increase its nitrogen content (20.9% oxygen, 0.03% carbon dioxide, and 78.1% nitrogen with other gases) to keep apples orchard-fresh from one fall harvest through the next.

The cold storage food chain begins at the farm or packing plant where the product is chilled by three principal methods: hydrocooling (immersion in chilled water), forced-air cooling, and vacuum cooling (placing the product in a sealed chamber and creating a vacuum, causing evaporation of some of the water in the product, and subsequent cooling).

If the product is to be frozen, one of five methods is used: (1) air blast freezing (cold air at high velocity is passed over the product); (2) contact freezing (the product is placed in contact with metal plates and heat is drawn off by conduction); (3) immersion freezing (the product is immersed in low-temperature brine); (4) cryogenic freezing [the product is exposed in a chamber to temperatures below −76°F (−60°C) by using liquid nitrogen or liquid carbon dioxide]; and (5) liquid refrigerant freezing (the product is immersed and sprayed with a liquid freezant at atmospheric pressure).

The next step in the cold storage food chain is transport by railroad cars, trucks, airplanes, or boats fitted with refrigeration units that maintain temperatures to critical specifications. Electronic technology permits monitoring of temperature and location by satellite transmission from the transport vehicle to a land-based monitoring station.

Refrigerated warehouses and distribution centers maintain the temperatures required to assure continued maintenance of quality before the product makes its last commercial move to supermarkets or to food-service-industry outlets. Typically, a refrigerated warehouse is a fully insulated structure fitted with refrigeration equipment capable of precise maintenance of specific temperatures in rooms holding up to several million pounds of product. For example, individual rooms may be set to maintain refrigerated storage temperatures of 34°F (1°C) or freezer-room temperatures of 0°F (−18°C). Some food products are being marketed that may require storage temperatures as low as −20°F (−29°C) to maintain texture and to preclude separation of ingredients. *See* REFRIGERATION.

Anhydrous ammonia is the principal refrigerant used in refrigeration systems for cold storage. A number of systems had been introduced that used chlorofluorocarbon refrigerants. However, they are being phased out because of concern about the ozone layer. It is anticipated that such systems will be converted to ammonia or other refrigerants. Most engine rooms are computer-controlled in order to allow optimum use of energy and to transmit alerts if temperatures stray out of the programmed range. *See* GREENHOUSE EFFECT; HALOGENATED HYDROCARBON.

Handling of foods through distribution and cold storage is done by using pallets loaded with 1400–3000 lb (630–1350 kg) of product. Modern freezer rooms are 28–32 ft (8.5–10 m) high for conventional forklift operation, and up to 60 ft (18 m) high when automated or specialized materials-handling equipment is used. *See* FOOD MANUFACTURING; FOOD PRESERVATION; MATERIALS HANDLING.

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Colemanite

One of the more common minerals of the borate group (in which boron is chemically bonded to oxygen).

Physical properties. Colemanite is white to gray with a white streak, is transparent to translucent, and has a vitreous luster. It occurs either as short highly modified prismatic crystals or as massive to granular aggregates. It has perfect cleavage in one direction, parallel to the sheet nature of its crystal structure. Colemanite has hardness of 4–$4^{1}/_{2}$ on Mohs scale and a specific gravity of 2.42. *See* HARDNESS SCALES.

Crystal structure. Colemanite is a hydroxy-hydrated calcium borate with the chemical formula $Ca[B_3O_4(OH)_3](H_2O)$. [Ca = calcium, B = boron, O = oxygen, OH = hydroxyl, H_2O = water]. The fundamental building block of the structure is a ring of one triangular ($B\phi_3$) group ($\phi = O^{2-}, OH^-$) and two tetrahedral ($B\phi_4$) groups that is conventionally symbolized as 1Δ2□:⟨Δ2□⟩. Here 1Δ2□ denotes that there is one ($B\phi_3$) group (Δ) and two ($B\phi_4$) groups (2□), the delimiters ⟨⟩ indicate the presence of a ring of linked polyhedra, specified between the delimiters (**Fig. 1**). This fundamental building block also occurs in many other borate minerals. In colemanite, the ⟨Δ2□⟩ rings share two vertices between triangles and tetrahedra of adjacent rings to form a chain extending along one axis [100]. There is one unique calcium atom coordinated by eight anions in an irregular dodecahedral arrangement.

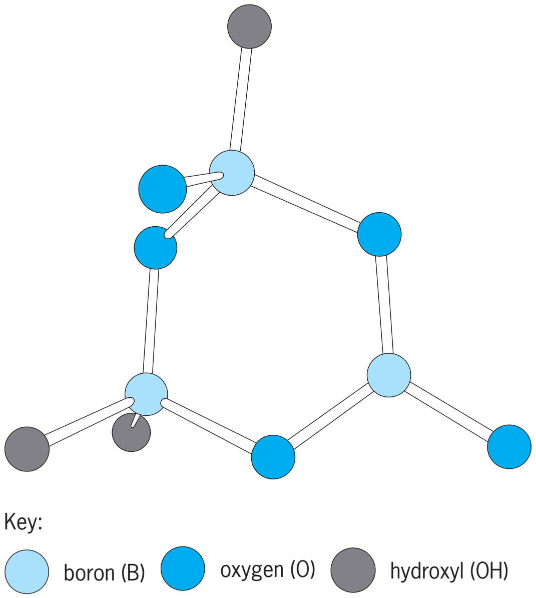

Fig. 1. Fundamental building block in the crystal structure of colemanite.

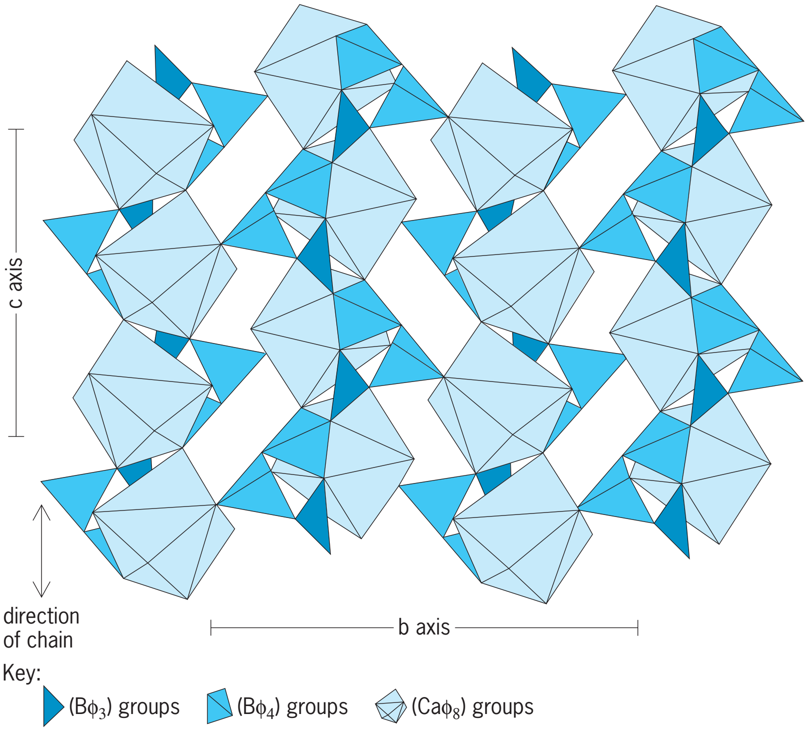

Fig. 2. Crystal structure of colemanite viewed down the *a* axis. The ⟨Δ2□⟩ rings link to form chains of borate polyhedra parallel to the *c* axis.

The (Caϕ_8) polyhedra share corners to form chains parallel to {100} (**Fig. 2**). The [Caϕ_7] chains cross-link the borate chains into a heteropolyhedral sheet of composition [$Ca_2B_3O(OH)(H_2O)$] parallel to {010}. These sheets, seen edge-on in Fig. 2, link via corner-sharing between (BO_4) tetrahedra and (Caϕ_8) dodecahedra, and through an extensive network of hydrogen bonds.

Occurrence. Colemanite typically occurs in lacustrine evaporite deposits of Tertiary age. It forms by thermal diagenesis of primary borate minerals, such as ulexite, $NaCa[B_5O_6(OH)_6](H_2O)_6$, and borax, $Na_2[B_4O_5(OH)_4](H_2O)_8$ (Na = sodium). Both ulexite and borax contain fundamental building blocks that are finite borate clusters consisting of two ⟨Δ2□⟩ rings linked together. During diagenesis, the chemical bonds between these finite borate clusters and the interstitial cations break, and the ⟨Δ2□⟩ rings then polymerize to form chains, as in colemanite. *See* BORATE MINERALS; DIAGENESIS; SALINE EVAPORITES.

Industrial uses. Colemanite is a principal source of boron, together with borax and ulexite, and is mined extensively in California and Nevada, Turkey, and Argentina. Boron is used in a wide variety of industrial commodities: soaps and washing powders, glasses and ceramics, specialty alloys, and fillers in many products. *See* BORON.

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Coleoidea

The cephalopod subclass in the phylum Mollusca that includes living octopods, squids, cuttlefish, and sepiolids (bob-tail squids), and the extinct belemnites. *See* CEPHALOPODA; MOLLUSCA.

General characteristics. The group is defined by the possession of five arm pairs (which are reduced to four in octopods; see **illustration**); arm suckers or hooks with which prey are subdued; chromatophore organs in the skin; a muscular mantle that typically provides jet propulsion; and an internal shell that, although lost in most extant cephalopods, provided buoyancy to the common ancestor.

The shell of belemnites, thought to have been internal because of its unusual microstructure, has a clear buoyancy-regulating structure known as a phragmocone; its discrete chambers are sealed off as the animal grows. As they are emptied of fluid, gas fills them to allow the animal to become neutrally buoyant. The cuttlebone of cuttlefish and the internal shell of the Rams' horn squid, *Spirula spirula*, may be modified from the primitive phragmocone. Most extant coleoids, however, have further reduced the internal support; squids have a thin gladius, and among octopods, only the deep-sea finned taxa have a sizable internal fin cartilage.

Taxonomy and phylogeny. The fossil record of Coleoidea dates back to the Carboniferous. Orders of the extinct belemnite coleoids include the Aulacocerida, Belemnoteuthina, Belemnitida, Diplobelida, and Phragmoteuthida. Phylogenetic relationships among extant coleioids and between living taxa and the extinct belemnites remain unresolved. Although the greatest taxonomic and morphologic diversity of squids and octopods occur in the deep sea, these taxa remain largely unknown. Living coleoids number over 725 species, with many more suspected to remain undiscovered. Squids constitute the order Teuthida (also known as Teuthoidea), which is sometimes recognized as two orders, Myopsida (nearshore squids) and Oegopsida (oceanic squids). The three orders Spirulida (Ram's horn squid), Sepiida (cuttlefish), and Sepiolida (bob-tail

Octopus *Benthoctopus* photographed by the deep-submergence vehicle *ALVIN* at a depth of 2770 m (9140 ft), Gorda Ridge, Northeast Pacific Ocean.

squid) are sometimes treated as the single order Sepioidea. The Vampire squid constitutes the order Vampyromorpha, and order Octopoda contains deep-sea finned octopods, argonauts, midwater pelagic octopus, and the familiar benthic octopuses. *See* BELEMNOIDEA; OCTOPODA; OCTOPUS; SEPIOIDEA; TEUTHOIDEA; VAMPYROMORPHA.

Ecology. Coleoids occupy virtually every habitat in the world's oceans; they are important predators to which many animal taxa potentially fall prey, at least during part of their lives. Several factors, including well-developed brains and large eyes (which are prime examples of evolutionary convergence with vertebrates), contribute to coleiods' effectiveness as predators as well as their defense against predation.

The skin of coleoids is unique in that it contains chromatophore organs, which allow these animals to change color in milliseconds. Coleoids use camouflage to hide from potential predators as well as to sneak up on unsuspecting prey. Chromatophore organs are composed of pigments held in an enervated muscular sac. A section of the coleoid brain controls the animal's coloration by expanding or relaxing the chromatophore organs. *See* CHROMATOPHORE.

The hooks on belemnite arms, the suckers with thorny rings in squids and cuttlefish (secondarily evolved into hooks in some groups), and the muscular gripping suckers in octopods provide excellent prey-handling ability. The ancestral coleoid likely had five arm pairs of equal length. Octopods, having lost one arm pair, likely use stealth (assisted by their elaborate chromatophore-enabled camouflage) and their numerous suckers to secure their prey before injecting it with potent venom. Most other extant coleoids snatch unsuspecting prey from a distance and then draw it to their mouth by using their tentacles, a modified fourth arm pair that are highly extensible, are capable of extremely rapid movement, and have specialized hooks and/or suckers at the tips.

Reproduction and development. Intensive study of a relatively few species indicates that extant coleoids generally live short lives, typified by extremely rapid growth early in the life cycle, which slows with full sexual maturity. In most taxa, egg production occurs only near the end of the life cycle, after which both males and females begin to senesce. Although squids generally leave their eggs to survive unattended, benthic and epipelagic octopuses, such as argonauts, exhibit maternal care of their eggs through development.

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Coleoptera

An order of Insecta (generally known as beetles) with a complete metamorphosis (with larva and pupa stages), the forewings forming hard protective elytra under which the hindwings are normally folded in repose, and the indirect flight muscles of the mesothorax having been lost. The head capsule is characterized by a firm ventral (gular) closure, the antennae are basically 11-segmented, and mouthparts are of the biting type with 4-segmented maxillary palpi. The prothorax is large and free. The abdomen has sternite I normally absent, sternite II usually membranous and hidden, and segment X vestigial, with cerci absent. The female has one pair of gonapophyses, on segment IX. There are four or six malpighian tubules, which are often cryptonephric. True labial glands are nearly always absent (**Fig. 1**).

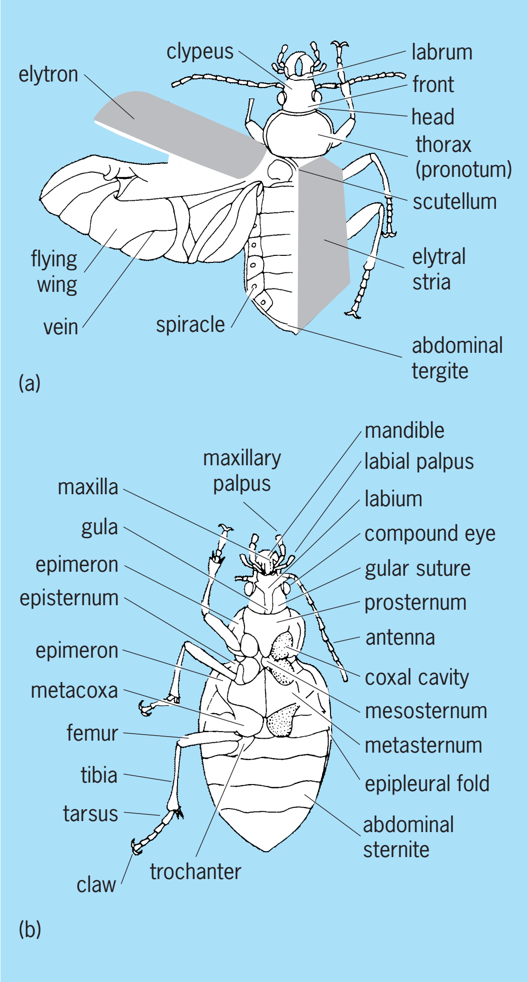

Fig. 1. Diagrammatic sketch of Carabidae member. (*a*) Dorsal view. (*b*) Ventral view.

General Biological Features

The order has well over 250,000 described species, more than any comparable group, showing very great diversity in size, form (**Fig. 2**), color, habits, and physiology. Some Ptiliidae have body lengths as small as 0.01 in. (0.25 mm), and some Cerambycidae may exceed 4 in. (100 mm). Beetles have been found almost everywhere on Earth (except as yet for the Antarctic mainland) where any insects are known, and species of the order exploit almost every habitat and type of food which is used by insects. Many species are economically important.

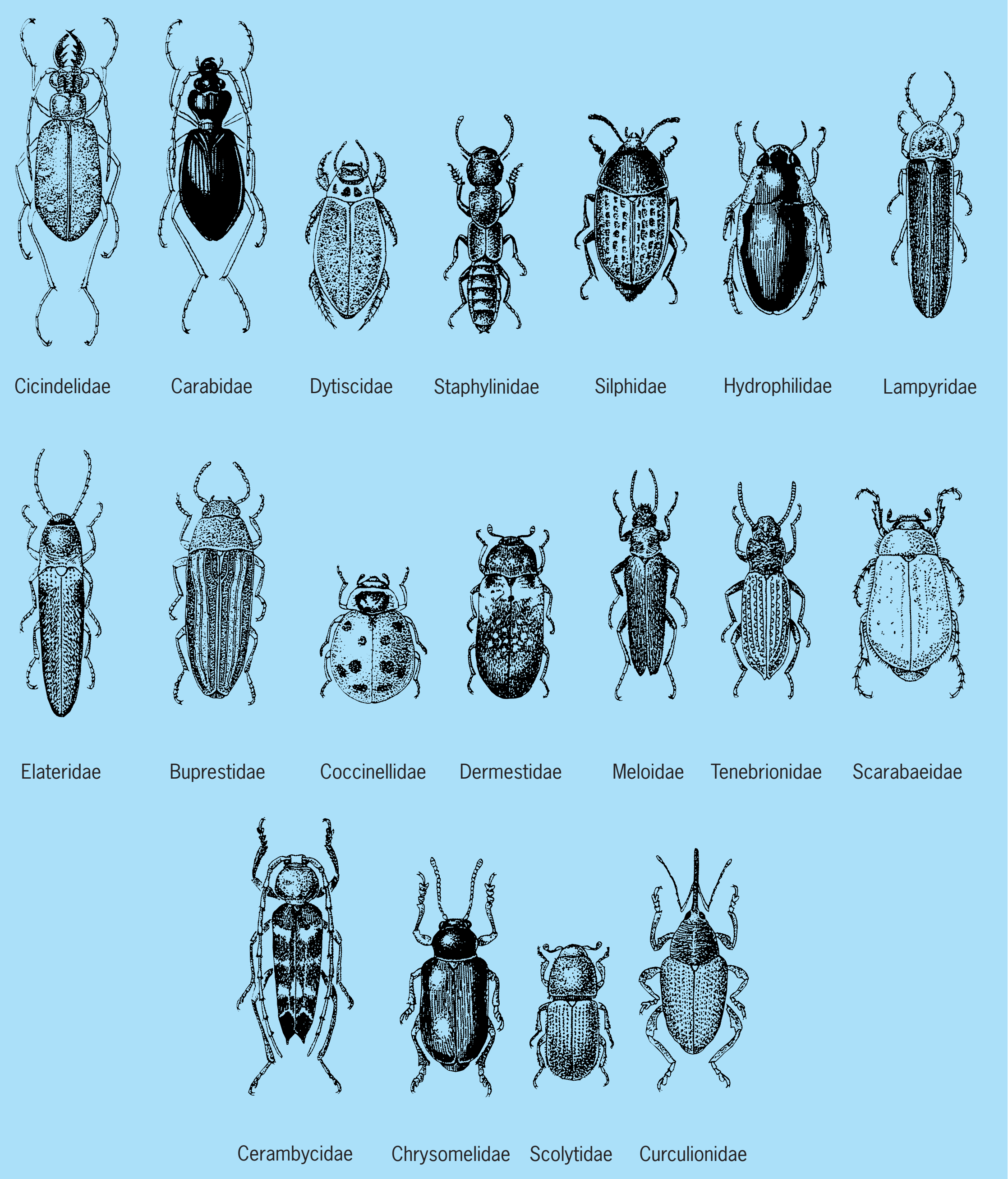

Fig. 2. Representatives of well-known families of Coleoptera. (*After T. I. Storer and R. L. Usinger, General Zoology, 3d ed., McGraw-Hill, 1957*)

A common feature is for the exoskeleton to form an unusually hard and close-fitting suit of armor, correlated with a tendency for the adults to be less mobile but longer-lived than those of other orders of higher insects. It seems to be common in a number of groups for adults to survive and breed in 2 or more successive years, a rare occurrence in other Endopterygota. Most beetles, at least in markedly seasonal climates, have a 1-year life cycle, with developmental stages adapted to specific seasons, but many larger species (particularly when larvae burrow in wood or the soil) may take 2 or more years per generation, and in suitable climates some (usually smaller) species may have more than one generation per year. Another feature unusual in Endopterygota is that many beetles have adults and larvae living in the same habitats and feeding on similar food, though many others have adult foods and habitats quite different from the larval ones. Adult beetles tend to be better runners than most other Endopterygota, and some (such as Cicindelidae) are among the fastest of running insects.

Wings and flight. The flight of most beetles is not very ready or frequent, often requiring prior climbing up onto some eminence, and in many beetles occurs only once or twice in an average life. The elytra may be held in a rigid lateral projection, as in Adephaga, or vibrate through some (usually small) angle in phase with the hindwings, as in many Polyphaga, or be held vertically upward or over the abdomen, almost in the position of repose. In a number of groups, there is evidence that the elytra contribute significantly to lift or to stability in flight. In males of Stylopidae (Strepsiptera) they are reduced to structures resembling (and probably functioning like) the halteres of Diptera. The hindwings have their insertions shifted very far forward, making the pleura of the metathorax very oblique, and their area is expanded in the anal region. Wing loading and wing-beat frequency are usually higher than in most other Pterygota, with the indirect flight muscles of the metathorax of the asynchronous type, contracting several times in response to a single nerve impulse. Wing venation is adapted to the needs of folding as well as of flight. In some groups, the wings unfold automatically if the elytra are lifted (as in Staphylinidae), but folding after flight is a more complex process, involving active participation of the flexible abdomen. In others unfolding requires considerable abdominal activity, but folding is quick and quasi-automatic, resulting from muscle pulls on the axillary sclerites of the wing base. Most beetles seem to be inherently stable (hence not very maneuverable) in flight. In a number of groups (such as Pleocomidae, Cebrionidae, Drilidae, Phengodidae, and Stylopidae), flight may be confined to the males, indicating that its prime function is to promote gene dispersal.

Cuticle. Apart from a tendency for the sclerotized layers to be thicker, the cuticle of beetles differs little from that of other insects in constitution or ultrastructure. The epicuticular wax layer shows diversity, being particularly well developed in some of the desert Tenebrionidae. Macrochaetae on the body surface may develop into scales (a trait of many Curculionidae) but are rarely plumose; in larval Dermestidae, very complex defensive hairs are developed.

The black coloring which is prevalent in many groups of beetles is produced by deposition of melanin in the process of cuticle hardening. In many groups, with adults active by day, the black is masked by a metallic structural color produced by interference in the surface cuticle layers. Pigmentary colors, mainly ommochromes, giving reddish to yellowish colors, occur in the cuticle of many species, whereas some groups, notably the tortoise beetles (Cassidinae), may have more unstable greenish pigments in the hypodermal cells beneath the cuticle. Pigmentary colors are often adapted to produce aposematic or pseudaposematic appearances, or cryptic ones. *See* PROTECTIVE COLORATION.

Defense adaptations. Special defenses against predation are common in species with long-lived adults, particularly the ground-living species of Carabidae, Staphylinidae, and Tenebrionidae. These groups commonly possess defensive glands, with reservoirs opening on or near the tip of the abdomen, secreting quinones, unsaturated acids, and similar toxic substances. In some cases, the secretion merely oozes onto the body surface, but in others may be expelled in a jet. In the bombardier beetles (Brachinini), the jet contains quinones and is expelled forcibly at nearly 212°F (100°C) through the agency of hydrogen peroxide in an explosion chamber. In other groups, toxins may be dispersed in the body, as in species of Coccinellidae, Lycidae, and Meloidae, and warning (aposematic) coloration is frequently developed.

Other common defensive adaptations include cryptic and mimetic appearances. The most frequent behavioral adaptations are the drop-off reflex and appendage retraction. Numerous Chrysomelidae, Curculionidae, and other adults will react to visual or tactile stimuli by dropping off the plant foliage on which they occur, falling to the ground with retracted appendages, and lying there for some time before resuming activity. In death feigning, the appendages are tightly retracted, often into grooves of the cuticle, and held thus for some time. In such conditions, beetles often resemble seeds and are difficult for predators to perforate or grasp.

Stridulation. Sound production (stridulation) is widespread in beetles and may be produced by friction between almost any counterposed movable parts of the cuticle. Stridulatory organs may show sex dimorphism, and in some species (such as among Scolytinae) may play an important role in the interrelations of the sexes. Elsewhere, as in species of *Cychrus, Hygrobia,* and *Necrophorus,* stridulation is a common response to molestation. Specialized sound-detecting organs, other than Johnston's organ in the antennal pedicel, are not well documented in Coleoptera.

Cryptonephrism. Cryptonephrism, in which the apical parts of the malpighian tubules are closely applied to the hindgut in the region of the rectal glands, is characteristic of a large section of Polyphaga, including all the "stored product" pests and the dominant desert beetles. This condition, not known in other adult insects, has been shown in *Tenebrio* to economize water by extracting it from the rectal contents to produce very dry feces. In cryptonephric groups, certain more or less aquatic members seem to have lost the condition secondarily.

Symbioses. Of the many types of symbiotic relations into which beetles enter with other organisms, perhaps the most ecologically important are those with fungi, which can be divided into ecto- and endosymbioses. In ectosymbiosis, the beetles carry spores or propagules of the fungi and introduce them into suitable new habitats, and are themselves nutritionally dependent (at least as larvae) on the presence of the right type of fungus in the habitat. Classic examples are in numerous bark beetles (Scolytinae) and Lymexylidae. In endosymbiosis, fungi (or sometimes bacteria) are maintained in the gut (or in mycetomes attached to it), usually of the larvae, and contribute either essential nutrients (such as steroids) or essential enzymes. Endosymbionts are usually passed externally or internally to the eggs by the ovipositing female. In endosymbiosis, it seems that as a rule the symbionts are specific to the beetles concerned, to a rather greater degree than in ectosymbionts.

Genetics. The large majority of beetles have an X-y type of chromosomal sex-determining system, with the y often small (or lost altogether) and forming a "parachute" figure with the X in meiosis. Sex ratios in natural populations are usually 50:50, and sex dimorphism, usually slight, is sometimes very marked. Thelytokous parthenogenesis, often accompanied by polyploidy, is developed in several groups. A haploid male system, like that of Hymenoptera, has been found in Micromalthidae and a few *Xyleborus* ambrosia beetles. A basic complement of nine pairs of autosomes, plus the sex pair, is maintained in many groups of beetles. *See* GENETICS.

Mating and life cycle. Mating in beetles is often a simple process, the male climbing onto the back of the female after a minimum of courtship, but in some groups (such as many Meloidae, Cerambycidae, and Scarabaeidae) more elaborate courtship is the rule. In long-lived species, individuals may copulate several times, often with different partners. Care for the young is commonly limited to the deposition of the eggs in suitable habitats under some sort of cover, but nest construction and provisioning, after the manner of solitary Aculeata Hymenoptera, develop particularly in the dung-feeding Scarabaeinae and Geotrupidae, and in a few Carabidae. Other beetles showing unusual provisions for their offspring include the ambrosia beetles or Attelabidae, some Staphylinidae-Oxytelinae, and some Lamiinae.

Beetle eggs rarely have heavily sculptured chorions or specialized caps for eclosion. Embryonic development is of typically insect types but shows considerable variation within the order. Eggs are often adapted to absorb moisture during embryonic development.

Larvae are very diverse, but usually have a well-developed head capsule with biting mouthparts, often have thoracic legs but very rarely abdominal prolegs (other than a pygopod developed from segment X), and never have true appendages on segment X. The tergite of segment IX often bears paired (sometimes articulated) posterior outgrowths known as urogomphi. First instars often differ considerably from later ones and may have toothlike egg bursters on parts of the body. The number of larval instars usually lies between 3 and 10. Pupae are usually white and exarate, resting on their backs on dorsal spines in some kind of pupal cell. They are never decticous, nor does the adult become active inside the pupal skin.

Hypermetamorphosis, in which two or more sharply different larval forms succeed during individual development, is known in several parasitic or wood-boring groups of beetles. The most common type has an active long-legged first-instar larva which seeks out a suitable feeding site and molts into a grublike type with reduced legs, as in Stylopidae, Rhipiphoridae, and Micromalthidae. The bee-parasitic Meloidae are notable in having two or even three distinct later larval stages.

Adult Anatomy

The head of beetles rarely has a marked posterior neck, and the antennal insertions are usually lateral, rather than dorsal as in most other Endopterygota, a feature possibly related to an original habit of creeping under bark. In most Curculionoidea and a few other groups, the head may be drawn out in front of the eyes to form a rostrum. Paired ventral gular sutures (sometimes partially confluent) are usually present, giving rise to a fairly normal tentorium; a frontoclypeal suture (representing an internal ridge) is often present. Two pairs of ventral cervical sclerites are found in Polyphaga only. Dorsal ocelli are rarely present, and never more than two; compound eyes range from occupying most of the head surface (as in male Phengodidae) to total absence (as in many cavernicolous or subterranean forms). Antennal forms are very various, with the number of segments often reduced, but rarely increased, from the basic 11. Mandible forms are very diverse and related to types of food.

Thorax. The prothorax commonly has lateral edges which separate the dorsal part (notum) from the ventral part (hypomeron) of the tergum. The propleuron may be fully exposed (Adephaga, Archostemata) or reduced to an internal sclerite attached to the trochantin (Polyphaga). The front coxal cavities may or may not be closed behind by inward processes from the hypomera or pleura to meet the prosternal process.

The mesothorax is the smallest thoracic segment. Dorsally, its tergum is usually exposed as a small triangular sclerite (scutellum) between the elytral bases, and ventrally, its sternite may have a median pit receiving the tip of the prosternum. The elytra of beetles develop in a different way from those of earwigs, cockroaches, and such. The first stage is the modification of wing venation to form a series of parallel longitudinal ridges connected by a latticework of crossveins (as seen in many modern Archostemata). The veins then expand to obliterate the remaining membrane, often leaving 9 or 10 longitudinal grooves or rows of punctures representing the original wing membrane and having internal pillars (trabeculae) connecting the upper and lower cuticle. There are various types of dovetailing along the sutural margins of the elytra, and their outer margins are often inflexed to form epipleura.

The form of the metathorax is affected by far-forward insertions of the hindwings and far-posterior ones of the hindlegs, so that the pleura are extremely oblique and the sternum usually long. Usually, the episterna are exposed ventrally, but the epimera are covered by the elytral edges. The metasternum commonly has a median longitudinal suture (with internal keel), and primitively, there may be a transverse suture near its hind edge. Internally, the endosternite takes diverse and characteristic forms.

Tarsi. The tarsi of beetles show all gradations from the primitive five-segmented condition to total disappearance. The number of segments may differ between the legs of an individual or between the sexes of a species. A very common feature in the order is the development of ventral lobes, set with specialized adhesive setae, on some tarsal segments. Often, strong lobes of this kind occur on the antepenultimate segments, and the penultimate one is very small and more or less fused to the claw joint. Lobed tarsi are particularly characteristic of species frequenting plant foliage.

Abdomen. Most beetles have the entire abdomen covered dorsally by the elytra in repose, and ventrally only five or six sternites (of segments III to VII or VIII) exposed; segment IX is retracted inside VIII in repose. Tergites I–VI are usually soft and flexible, those of VII and VIII more or less sclerotized. In some groups, the elytra may be truncate, leaving parts of the abdomen exposed dorsally, in which case the exposed tergites are sclerotized. Sternite IX is usually a single (internal) sclerite in males, but divided in females to form a pair of valvifers. Male gonapophyses are typically represented by a median basal piece bearing a pair of parameres (lateral lobes), and those of the female by a pair of coxites and styli attached to the valvifers. In females of many groups, an elongate ovipositor is produced by elongation into rods of sclerites of abdominal segment IX.

Elytra. A feature developed in several groups of Coleoptera, but particularly in Staphylinidae, is the abbreviation of the elytra to leave part of the abdomen uncovered in repose, but usually still covering the folded wings. One advantage of this may be to give greater overall flexibility to the body. This is probably of particular advantage to species living in the litter layer in forests, a habitat in which Staphylinidae are strikingly dominant. Perhaps surprisingly, many beetles with short elytra fly readily.

Internal anatomy. Internally, the gut varies greatly in length and detailed structure. The foregut commonly ends in a distended crop whose posterior part usually has some internal setae and may be developed into a complex proventriculus (Adephaga, many Curculionoidea); the midgut may be partly or wholly covered with small papilae (regenerative crypts) and sometimes has anterior ceca. The four or six malpighian tubules open in various ways into the beginning of the hindgut and in many Polyphaga have their apices attached to it (cryptonephric). The central nervous system shows all degrees of concentration of the ventral chain, from having three thoracic and eight abdominal ganglia distinct (as in some Cantharoidea) to having all of these fused into a single mass (as in some higher Scarabaeidae). There are two main types of testes in the males: Adephaga have each testis as a single, long, tightly coiled tube wrapped around in a membrane; Polyphaga have testes usually of several follicles. In the female, Adephaga have polytrophic ovarioles, while Polyphaga have acrotrophic ones, unlike any others known in Endopterygota.

Larval Anatomy

The head capsule in beetle larvae is usually well developed with fairly typical biting mouthparts, with or without a ventral closure behind the labium. Antennae are basically three-segmented, segment II (pedicel) usually bearing a characteristic sensory appendage beside segment III. In several groups, segment I may be divided to give four-segmented antennae (Carabidae, many Staphylinidae, Scarabaeidae), but division of segment III seems to be peculiar to Helodidae. There are up to six ocelli on each side, variously grouped. The frontal sutures (ecdysial lines) often have a characteristic inverted horseshoe form; a median coronal suture may be present. The mandibles have very diverse forms, related to types of food, and the labrum is often replaced by a toothed nasale, particularly in carnivorous types practicing extraoral digestion. The maxillae also vary considerably. In the more specialized predatory types, the cardo tends to be reduced. In some groups, maxillae and labium are more or less fused together to form a complex resembling the gnathochilarium of Millipedes. In some groups with burrowing or internal-feeding larvae, the head capsule may be largely retracted into the prothorax, with corresponding reductions of sclerotization.

Thorax. In the thorax, the prothorax is usually markedly different from the next two segments. The legs are often well developed, particularly in ground-living predatory types, and in Adephaga and Archostemata may have a separate tarsus with two claws. Reduction or loss of legs is characteristic of many burrowing or internal-feeding larvae. The first pair of spiracles is usually situated close to the front border of the mesothorax, lateroventrally; very rarely, a second thoracic spiracle is distinct.

Abdomen. Ten abdominal segments are usually visible, prolegs are rarely developed on any of the first eight segments, but segment X often forms a proleglike pygopod. The tergite of segment IX is often drawn out into posterior processes known as urogomphi, which may become articulated and movable (as in Hydradephaga, Staphylinoidea). In some aquatic larvae, segments IX and X are reduced, and the spiracles of segment VIII become effectively terminal, as in most Diptera larvae. Larval spiracles take diverse forms, which are systematically important.

Body types. The more specialized burrowers among beetle larvae may be divided into two broad types, the straight- and the curved-bodied (**Fig. 3**). Straight burrowing larvae are normal in Archostemata, Carabidae, Elateroidea, various Heteromera, Cerambycidae, and halticine Chrysomelidae, while curved larvae are the norm in Scarabaeoidea, Bostrychoidea, Chrysomelidae-Eumolpinae, and Curculionoidea. The basic difference is probably in the way in which the larva anchors itself in its burrow, using its mandibles to burrow into a resistant medium. In straight larvae, purchase may be secured by short stout legs (as in Elateridae), by terminal abdominal structures, or by protrusible asperate tuberosities (ampullae) on trunk segments (as is the case with Archostemata and Cerambycidae). In both groups, ocelli rarely number more than one and are often lost, and legs are liable to be reduced or lost. The antennae, which are always reduced in straight burrowers, may be quite long in some curved ones, such as Scarabaeoidea.

Physiology

In the basic life functions, such as digestion, respiration, excretion, circulation, muscle contraction,

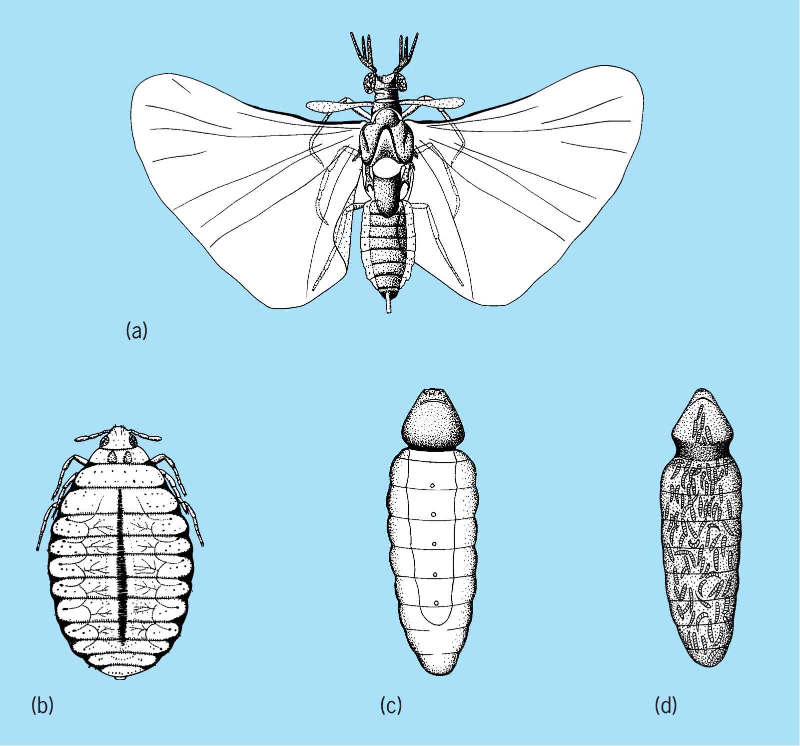

Fig. 3. Stylopidae. (*a*) *Eoxenos laboulbeni*, adult male and (*b*) adult female. (*c*) *Stylops melittae*, adult female (ventral view) and (*d*) gravid female with larvae. (*After C. P. Clausen, Entomophagous Insects, McGraw-Hill, 1940*)

nerve conduction, sense reception, and growth, most beetles show normal insect features, but certain groups are unusual in one or another of these respects. In digestion, some dermestid larvae can digest keratin, a faculty otherwise known only in some tineoid moth larvae. Some wood-boring larvae, notably in Anobiidae and Cerambycidae, have some ability to digest celluloselike substances, apparently through the aid of microorganisms carried in mycetomes associated with the midgut, and some scarabaeid larvae make similar use of microorganisms in a fermentation chamber in the hindgut. Some beetle larvae are able to live and develop normally in fungus-infested decaying wood that is very low in oxygen and high in CO_2. Some aquatic beetles and their larvae may be found living normally in hot springs at temperatures up to 111°F (44°C). In some adult Scolytinae, it has been found that the indirect flight muscles of the metathorax may be greatly reduced and absorbed during gonad development after an initial nuptial flight, yet redeveloped to become functional again with post-reproductive adult feeding. Effective color change in adults, mainly through changes in the hydration of cuticular layers, has been found in certain Scarabaeidae-Dynastinae and Chrysomelidae-Cassidinae. Something approaching homothermy during periods of adult activity has been reported in some of the larger scarabaeoid beetles, utilizing heat generation by muscles in a preliminary warm-up stage, and air-cooling of the thorax by large tracheae during high activity.

Digestion. The digestive organs and capacities of beetles, and their food requirements, are generally like those of other insects, but some groups have unusual features. In many predatory larvae, also in some adults, extraoral digestion occurs, commonly marked in larvae by the development of a rigid toothed nasale in place of the labrum. In some such larvae, particularly when aquatic, the mandibles may become tubular-channeled. In at least some staphylinine larvae, there appear to be "venom" glands developed in the mandibles.

Among herbivores and wood-borers, capacities to digest celluloses and other "difficult" carbohydrates may be developed, usually and perhaps always by the aid of symbiotic microorganisms producing suitable enzymes. Dermestid larvae have developed the ability to digest keratin, breaking its disulfide bonds in an unusually alkaline midgut and producing free hydrogen sulfide as in some tineoid larvae.

Sense organs. The sense organs of beetles, adult or larval, are generally similar in type and function to those of other insects. For vision, the adult compound eyes show great diversity in form and ommatidial structure. Some types, such as *Cicindela*, are adapted for high visual acuity in bright light, others to high sensitivity in poor light, and many show light-dark adaptations of screening pigment. Color vision seems to be restricted to certain groups in the order, notably some of the floricolous Cetoniinae. In certain beetles, specialized infrared sensitivity is evidenced, notably in the region of the vertex of the head in many Curculionidae, and in complex metasternal organs in certain Buprestidae which are attracted to burning trees in coniferous forests. *See* EYE (INVERTEBRATE).

Antennae. Antennae in bettles are mainly receptors for smell and touch, but detection of aerial vibrations (by Johnston's organ in the pedicel) may be important in some. Some of the long hairlike sensilla may detect movements in the air and serve as "wind socks" when beetles are about to fly. Many of the more actively flying groups have the antennal insertions shifted dorsally from their primitive lateral position. The olfactory sensilla, which commonly are thin-walled multiperforate setae, are often concentrated on expanded apical segments, forming a club. This arrangement probably helps in the detection of odor gradients in still air by crawling beetles. Sex dimorphism in the antennae is not uncommon in groups with short-lived adults, the males being specialized to detect female pheromones. Fairly high olfactory acuities for specific substances have been found, especially in some carrion beetles.

Taste. Taste, or contact chemoreception, is usually mediated by sensilla with a single large apical opening. These sensilla are concentrated on the palpi and other mouthparts and are often found on tibiae or tarsi of the front legs (also probably on the ovipositor in many). In water beetles, the smell-taste distinction becomes obscured.

Sound receptors. Specialized sound receptors, other than Johnston's organ, have not been much studied in Coleoptera, though many species produce sounds and in some cases (in various Scolytinae and other Curculionidae, for example) these play a significant part in courtship. The tibial spurs, in at least some species, serve to detect vibrations in the substratum. *See* ANIMAL COMMUNICATION.

Trichobothria. Very long slender hairs arising from deep cuticular pits occur in many blind cave beetles, along the outer edges of the elytra in most Carabidae, and in larvae of Staphylinidae-Paederinae. These organs are believed to register slight movements in the air, resulting from nearby activity of potential prey or predators.

Gravitational sense. A gravitational sense is evident in many burrowing bettles, which are able to sink accurately vertical burrows despite inclinations of the surface started from. Indications are that such a sense is located in the legs rather than in the antennae, though no beetles are known to have subgenual organs, which may serve this function in other insects.

Temperature sense. A temperature sense is clearly present in some beetles and larvae, but little is known of the sensilla concerned. A type of coeloconic sensillum has been shown to serve this function in palpi of Culicidae, and very similar sensilla have been found in Coleoptera (as on the head capsule of elaterid larvae), which may be sensitive to differences in soil temperature.

Biological clock. What might be called a time sense (otherwise known as a biological clock) clearly operates in many beetles that react specifically to changing daylight lengths marking the seasons in nontropical latitudes. It also manifests itself as a circadian rhythm in "wild" beetles maintained artificially in conditions of uniform temperature, illumination, and humidity. *See* INSECT PHYSIOLOGY; PHOTOPERIODISM.

Food Specialization

The biting mouthparts of many adult and larval beetles are adaptable to many types of food, and fairly widely polyphagous habits are not uncommon in the order, though most species can be assigned to one or another of a few main food categories: fungivores, carnivores, herbivores, or detritivores. Included in the last category are species feeding on decaying animal or vegetable matter and on dung. Most parasites could be included with carnivores, but those myrmecophiles and termitophiles which are fed by their hosts, and those Meloidae which develop on the food stores of bees, form special categories.

There are reasons for thinking that ancestral Coleoptera fed on fungi on dead wood, and beetles of many groups today are largely or wholly fungus eaters. Many are specialists of particular types of fungi, among whose hosts most major groups of fungi are represented. It could well be that the habit of producing fruit bodies and spores underground (as in truffles, and *Endogone*) originally coevolved in relation to the activities of burrowing beetles (such as Liodini and some Scarabaeoidea), which may still be important spore-dispersal agents for such fungi. The long-lasting fruit bodies of various Polyporaceae on dead wood are important breeding grounds for beetles of a number of families, but few beetles can complete their larval development fast enough to exploit the short-lived types of toadstool. Beetles of several families (including the Scolytinae) may serve as effective vectors, inoculating new habitats with fungi which are significant for the beetles' nutrition.

Predators. Predation, mainly on other insects, is probably the fundamental mode of life in adult and larval Adephaga, and has developed in a number of different lines of Polyphaga. Many carnivorous beetles (such as Carabidae and Staphylinidae) are fairly widely polyphagous and liable to supplement their diets with nonanimal matter to some extent, but more specialized predation also occurs (for example, among Histeridae and various Cleridae). Predacious larvae may give rise to largely herbivorous adults (such as in many Hydrophilidae and Melyridae); the converse relation, though rarer, also occurs (in some Cerambycidae, for example). Predatory beetles often do not require movement of the prey to stimulate attack and feeding behavior, and may feed extensively on eggs or pupae of other insects which escape many other predators. Predation on pupae by beetle larvae may lead to parasitic-type habits, as in Lebiini and Brachinini among Carabidae, or Aleocharini among Staphylinidae.

Herbivores. Herbivorous beetles may eat green plants of all groups, from algae to angiosperms, may attack any part of the plant, and display a great range in host plant specialization. Some, like the Colorado beetle, will feed and develop only on a few closely related species of a single genus. Others, like many of the short-nosed weevils, are highly polyphagous, and are able to live on angiosperms of many different families. Feeding on roots, or on the enclosed seeds of Angiospermae, are mainly larval habits, whereas adults usually eat stems, leaves, or flowers. Many species are injurious to crops (**Fig. 4**), and a few have been used successfully in the biological control of weeds (such as *Chrysolina* spp. against *Hypericum*). A number of beetles are effective transmitters of viruses of field crops (such as *Phyllotreta* spp. on Cruciferae); some may be useful pollinators (such as *Meligethes* spp. on Cruciferae). Many botanists believe that beetle pollination was a feature of the first

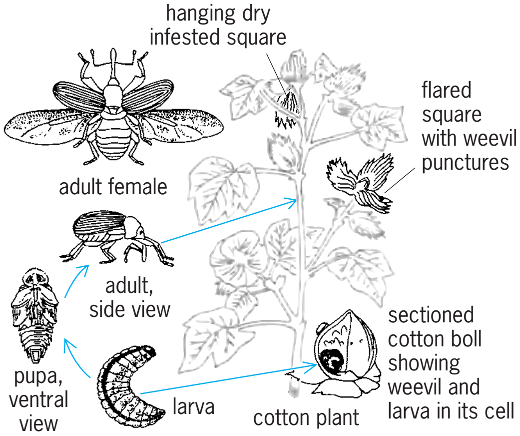

Fig. 4. Cotton boll weevil (*Anthonomus grandis* Boheman). (*After C. H. Metcalf, W. F. Flint, and R. L. Metcalf, Destructive and Useful Insects, 3d ed., McGraw-Hill, 1951*)

Angiospermae and that the enclosed carpels were developed to protect ovules against floricolous beetles.

Adults of a number of families frequent flowers, often eating pollen as well as licking nectar. Botanists distinguish cantharophilous flowers, which depend particularly on beetles for their pollination, and which include what are believed to be some of the most primitive surviving Angiospermae. Characteristic features are white flowers, either large or massed in heads, abundant pollen production, and open shapes, with nectar production often absent.

Larvae developing in flowers or buds are characteristic of Meligethinae and Cateretinae in Nitidulidae. In the latter group, larvae tend to feed on the gynoecium; in the former, on the anthers. Other groups, such as Bruchidae and various weevils, have larvae developing later, in the ripening fruits, and less typically floricolous adults. The tough exines of pollen grains are not easily permeable. For assimilation of the contents, it may be necessary either to crack the outer wall by the mandibles or to cause the grains to begin germination in the crop, as may happen in Oedemeridae and Mordellidae, for example.

Water Beetles

Beetles are unusual among the higher insects in that aquatic habits, where present, usually affect adults as well as larvae. The elytra (like the hemielytra of Heteroptera) may have been preadaptive to the invasion of water. Almost any type of fresh or brackish water body is liable to contain some types of water beetles, though very few species can live permanently in full marine salinities. Almost all aquatic beetles maintain an air reservoir, into which the second thoracic and abdominal spiracles open, under their elytra; and some, mainly small, species may have plastrons or physical gills. Aquatic larvae tend to have a last pair of abdominal spiracles that is large and effectively terminal, or tend to develop tracheal gills. Pupae are terrestrial in the large majority of water beetles, and eggs, when deposited underwater, are commonly laid in contact with airspaces in the stems of water plants, or in an air-filled egg cocoon (Hydrophilidae). Most water beetles are confined to shallow waters, and many of them are ready colonists of temporary pools, through adult flight.

Many of the adults, but fewer of the larvae, are active swimmers by means of the legs, while others rely mainly on crawling for locomotion. The whirligig beetles (Gyrinidae) are exceptional in that the adults swim very fast on the water surface, with only the ventral side submerged, by means of highly modified middle and hind legs, and are able to dive when alarmed, while the larvae are fully aquatic with long tracheal gills. The special modifications of the adults include divided compound eyes, one part for aerial, one for underwater vision; short antennae with a highly developed Johnston's organ, serving to pick up vibrations from potential prey or from the movements of other Gyrinidae in the surface film; long raptorial front legs; and a rudderlike end of the abdomen.

Aquatic larvae and more or less terrestrial adults occur in Psephenidae, some Ptilodactylidae, and the Donaciine leaf beetles; the converse relation is known in at least some Hydraenidae.

The foods of water beetles include algae (Myxophaga, Hydraenidae, many Dryopoidea), higher plants (larval Donaciinae, some Curculionidae, adults of many Hydrophilidae), other small animals (most Hydradephaga, Hydrophilid larvae), and mixed diets.

Special Habitats and Adaptations

More or less unusual adaptations and modes of life are manifest in dung and carrion beetles, ambrosia beetles, cave and subterranean beetles, desert beetles, and luminous beetles. Dung and carrion beetles exploit sporadic and very temporary food resources in which competition (particularly with Diptera larvae) tends to be fierce. Many dung beetles avoid the difficulties by burying dung stores in underground cells where their larvae can develop safely, and some beetles (Necrophorinae) adopt a similar strategy for carrion. They may also develop phoretic and symbiotic relations with specific mites preying on fly eggs.

In ambrosia beetles, the adults usually excavate burrows in wood, carrying with them spores of special fungi, which proceed to develop along the walls of the burrows and are fed on by larvae developing from eggs laid there. This type of relation between beetles, fungi, and trees exists in various forms in a number of families and may be of ecological importance if the fungi concerned are liable to kill trees.

Marginal habitats. More than one family of beetles contains highly adapted types living exclusively in deeper cave systems (cavernicolous) or the deeper layers of the soil (hypogeous). Such species are usually flightless and eyeless, poorly pigmented, and slow-moving, and of very restricted geographical distribution. In the cavernicoles, long trichobothrium-type setae are often developed on the body, and the adults may produce very large eggs singly, with a very abbreviated larval development, approaching the pupiparous condition of some Diptera.

Another marginal habitat in which beetles are the principal insect group represented is the desert, where Tenebrionidae are the dominant group. Here, too, wings are usually lost, but the cuticle tends to be unusually thick, firm, and black. Most desert beetles have burrowing larvae, and the adults also usually take refuge in the soil during the heat of the day. Elaborate adaptations for water economy and dew collection are frequent.

Another marginal habitat in which beetles may be found is hot springs. *Hydroscapha* and certain Hydrophilidae have been found breeding apparently normally in water of temperatures up to 111°F (44°C), which would be lethal for most other animals. A few water beetles are adapted to underground (phreatic) waters, showing parallel features with the cavernicolous and hypogeous terrestrial ones.

Dung and carrion beetles. Dung and carrion provide important but temporary food resources whose insect users are almost exclusively beetles and Diptera. Dung and carrion beetles are almost always good fliers, with strong antennal clubs bearing heavy concentrations of sensilla. Many of the adults are burrowers and, particularly among dung beetles, frequently make and provision underground nests, thereby removing the food supply for their larvae from the twin dangers of Diptera and drying up. Necrophorini among carrion beetles shows similar features, with the added feature of actual feeding of the larvae by adults. Another special feature of *Necrophorus* and some dung beetles is an apparently symbiotic relation with *Poecilochirus* and allied mites, which are carried on the bodies of adult beetles and which specifically attack the eggs of competing Diptera in the breeding habitat. A well-known feature of many Scarabaeine dung beetles is the formation of a ball of dung which is rolled to a nest site some distance from the dung patch.

Wood borers. One mode of life in which beetles are undoubtedly the dominant group among insects is wood boring, mainly pursued by larvae, but also by adults in some Bostrychidae, Scolytinae, and Platypodinae. Rather few beetles bore normally into the wood of healthy living trees, which are liable to drown borers in sap, but moribund, dead, or decaying timber is liable to heavy attack. Some borers can develop only in unseasoned wood, requiring remains of cell contents; others develop in seasoned wood; and many require the presence of some type of fungus for successful development. Hardwoods and softwoods have their beetle specialists, and females of some Cerambycidae restrict their oviposition to branches or trunks of some particular girth.

Parasites. More or less parasitic relations to animals of other groups have developed in a number of lines of Coleoptera. The closest parallels to Hymenoptera-Parasitica are to be seen in the families Stylopidae (Strepsiptera of many authors; Fig. 3) and Rhipiphoridae. Stylopid larvae are exclusively endoparasites of other insects, while the adult females are apterous, often legless, and remain in the host's body, while males have large fanlike hindwings and the elytra reduced to haltere-like structures. Adult mouthparts are vestigial in both sexes. The more modified of Rhipiphoridae, parasitizing cockroaches, show close parallels with the more primitive Stylopidae, while more primitive ones, probably parasitizing wood-boring beetles, resemble the allied nonparasitic Mordellidae. Larvae ectoparasitic on lignicolous beetle larvae or pupae are found in Passandridae and some Colydiidae.

A considerable variety of Coleoptera develop normally in the nests of termites and social or solitary Hymenoptera-Aculeata, some being essentially detritivores or scavengers, but most feed either on the young or the food stores of their hosts. Many of the myrmecophiles and termitophiles are highly modified structurally and behaviorally and highly host-specific. Some of these beetles appear to have successfully "broken" the chemical or tactile communication codes of their hosts.

Ectoparasitism on birds or mammals is a rare development in beetles, the best-known examples being in Liodidae-Leptininae, with adults and sometimes larvae living on the bodies of small mammals, and Staphylinidae-Amblyopinini, with apparently similar habits. A few Cryptophagidae and Languiriidae-Loberinae have been recorded as adults on bodies of rodents. In the little-known Cavognathidae of the Southern Hemisphere, in at least some species and probably in all of them, the breeding habitat is birds' nests and the larvae feed on nestling birds. *See* POPULATION ECOLOGY.

Luminescence. The beetles are notable in that some of them manifest the highest developments of bioluminescence known in nonmarine animals, the main groups concerned being Phengodidae, Lampyridae, and Elateridae-Pyrophorini, the glowworms and fireflies. In luminescent beetles, the phenomenon always seems to be manifest in the larvae and often in the pupae, but not always in the adults. *See* BIOLUMINESCENCE.

In luminous adult beetles, there is often marked sex dimorphism, and a major function of the lights seems to be the mutual recognition of the sexes of a species. In such cases, there is often a rapid nervous control of the luminescence, and a development of species-specific flash codes. In some cases, notably in adult Pyrophorini and some larval Phengodidae, an individual may carry lights of two different colors.

Another possible function of adult luminosity, and the only one seriously suggested for larvae, is as an aposematic signal. There is definite evidence that some adult fireflies are distasteful to some predators, and the luminous larvae of Phengodidae have dorsal glandular openings on the trunk segments that probably have a defensive function.

Phylogenetic History

Coleoptera are older than the other major endopterygote orders. The earliest fossils showing distinctively beetle features were found rather before the middle of the Permian Period and generally resemble modern Archostemata. By the later Permian, fossils indicate that beetles had become numerous and diverse, and during the Mesozoic Era they appear as a dominant group among insect fossils. Fossils in Triassic deposits have shown features indicative of all four modern suborders, and the Jurassic probably saw the establishment of all modern superfamilies. By early Cretaceous times, it is likely that all "good" modern families had been established as separate lines. In the Baltic Amber fauna, of later Paleogene age (about 40,000,000 years ago), about half the fossil beetle genera appear to be extinct, and the other half still-living representatives (often in remote parts of the world). Beetle fossils in Quaternary (Pleistocene) deposits are very largely of still-living species.

Beetles appear to have been the first insect wood borers, with insect borings in fossil wood of Triassic age (for example, in the Petrified Forest of Arizona) being probably the work of larval

Archostemata. Some fossil woods of slightly younger age have shown the oldest indications of a resin-secreting system, probably a defensive reaction against the attacks of wood-boring beetles. Later still, it seems that beetles may have played a major part in the evolution of the angiosperm-type of flower. The Adephaga probably evolved as ground-living predators, and their pygidial defensive glands may well have been a response to amphibian predation, much like the metathoracic glands of the roughly coeval Hemiptera-Heteroptera. Fossils clearly of adephagan water beetles are known from Lower Jurassic deposits, making a further parallel with Heteroptera-Cryptocerata.

Classification

A modern classification of beetles is given below. This system is adapted from that of Crowson (1955) and is intended to be phylogenetic in the sense of Hennig. An asterisk indicates that the family is not known in the fauna of the United States; a dagger, that the family is not known from the New World.

- Suborder Archostemata
  - Superfamily Cupedoidea
    - Family: Ommadidae†
    - Tetraphaleridae*
    - Cupedidae
    - Micromalthidae
- Suborder Adephaga
  - Superfamily Caraboidea
    - Family: Paussidae (including Ozaeninae, Metriinae, Sicindisinae)
    - Cicindelidae
    - Carabidae (including Omophroninae, Rhysodinae)
    - Trachypachidae
    - Amphizoidae
    - Haliplidae
    - Hygrobiidae†
    - Noteridae
    - Dytiscidae
    - Gyrinidae
- Suborder Myxophaga
  - Superfamily Sphaeroidea
    - Family: Lepiceridae (Cyathoceridae)*
    - Torridincolidae*
    - Hydroscaphidae
    - Sphaeridae (Sphaeriidae)
- Suborder Polyphaga
  - Series Staphyliniformia
    - Superfamily Hydrophiloidea
      - Family: Hydraenidae
      - Spercheidae
      - Hydrochidae
      - Georyssidae
      - Hydrophilidae
    - Superfamily Histeroidea
      - Family: Sphaeritidae
      - Synteliidae*
      - Histeridae (including Niponiidae)
    - Superfamily Staphylinoidea
      - Family: Ptiliidae (including Limulodidae)
      - Empelidae
      - Liodidae (including Leptininae, Catopinae, Coloninae, Catopocerinae)
      - Scydmaenidae
      - Silphidae
      - Dasyceridae
      - Micropeplidae
      - Staphylinidae (including Scaphidiinae)
      - Pselaphidae
  - Series Eucinetiformia
    - Superfamily Eucinetoidea
      - Family: Clambidae
      - Eucinetidae
      - Helodidae
  - Series Scarabaeiformia
    - Superfamily Scarabaeoidea
      - Family: Pleocomidae
      - Geotrupidae
      - Passalidae
      - Lucanidae
      - Trogidae
      - Acanthoceridae
      - Hybosoridae
      - Glaphyridae
      - Scarabaeidae
    - Superfamily Dascilloidea
      - Family: Dascillidae
      - Karumiidae*
      - Rhipiceridae (Sandalidae)
  - Series Elateriformia
    - Superfamily Byrrhoidea
      - Family Byrrhidae
    - Superfamily Dryopoidea
      - Family: Eulichadidae
      - Ptilodactylidae
      - Chelonariidae
      - Psephenidae
      - Elmidae (Elminthidae)
      - Lutrochidae
      - Dryopidae
      - Limnichidae
      - Heteroceridae
    - Superfamily Buprestoidea
      - Family Buprestidae (including Schizopidae)
    - Superfamily Artematopoidea
      - Family: Artematopidae
      - Callirhipidae
    - Superfamily Elateroidea
      - Family: Cebrionidae
      - Elateridae
      - Throscidae
      - Cerophytidae
      - Perothopidae
      - Phylloceridae†
      - Eucnemidae
    - Superfamily Cantharoidea
      - Family: Brachypsectridae
      - Cneoglossidae*

Family: Plastoceridae†
Homalisidae†
Lycidae
Drilidae†
Phengodidae
Telegeusidae
Lampyridae
Omethidae
Cantharidae
Series Bostrychiformia
Superfamily Dermestoidea
Family: Derodontidae
Nosodendridae
Dermestidae
Thorictidae†
Jacobsoniidae (Sarothriidae)*
Superfamily Bostrychoidea
Family: Bostrychidae (including Lyctinae)
Anobiidae
Ptinidae (including Ectrephini, Gnostini)
Series Cucujiformia
Superfamily Cleroidea
Family: Phloiophilidae†
Series: Peltidae
Family: Lophocateridae
Trogossitidae
Chaetosomatidae†
Cleridae
Acanthocnemidae
Phycosecidae†
Melyridae (including Malachiinae)
Superfamily Lymexyloidea
Family: Lymexylidae
Stylopidae (Strepsiptera, Stylopoidea)
Superfamily Cucujoidea
Family: Nitidulidae
Rhizophagidae (including Monotominae)
Protocucujidae*
Sphindidae
Boganiidae†
Cucujidae
Laemophloeidae
Passandridae
Phalacridae
Phloeostichidae*
Silvanidae
Cavognathidae*
Cryptophagidae (including Hypocoprinae)
Lamingtoniidae†
Helotidae†
Languriidae
Erotylidae (including Pharaxonothinae)
Biphyllidae
Cryptophilidae (including Propalticinae)†
Cerylonidae
Corylophidae
Alexiidae (Sphaerosomatidae)†
Endomychidae
Coccinellidae
Discolomidae
Merophysiidae
Lathridiidae
Byturidae
Mycetophagidae
Cisidae
Pterogeniidae†
Tetratomidae
Melandryidae
Mordellidae
Rhipiphoridae
Merycidae†
Colydiidae
Synchroidae
Cephaloidae
Pythidae
Pyrochroidae
Anthicidae
Meloidae
Aderidae
Scraptiidae (including Anaspidinae)
Oedemeridae
Cononotidae
Othniidae
Salpingidae
Inopeplidae
Mycteridae (including Hemipeplinae)
Monommidae
Zopheridae
Tenebrionidae (including Lagriinae, Nilioninae, Alleculinae)
Superfamily Chrysomeloidea
Family: Disteniidae (including Oxypeltinae, Philinae,† Vesperinae)
Cerambycidae
Megalopodidae (including Zeugophorinae)
Bruchidae (including Sagrinae)
Chrysomelidae
Superfamily Curculionoidea
Family: Nemonychidae
Anthribidae (including Bruchelinae)
Belidae*
Oxypeltidae*
Aglycyderidae (Proterhinidae)†
Allocorynidae
Attelabidae
Apionidae (including Antliarrhininae,† Ithycerinae, Nanophyinae)
Brenthidae
Curculionidae (including Scolytinae and Platypodinae)

This classification is based on a great variety of characteristics, including internal ones and those of immature stages, and takes account of the fossil evidence. Important characteristics include the structure of the propleura, the cervical sclerites, the ovarioles, larval leg segments, form of testes, wing venation and folding, number and arrangement of malpighian tubules, forms of the female and male external genitalia, presence or absence of a free larval labrum, larval spiracular structures, mode of formation of adult midgut in the pupa, form of the metendosternite, number of female accessory glands, form of adult antennae, tarsal segmentation, presence of pupal "gin traps," number of pupal spiracles, number of adult abdominal spiracles, presence of defensive glands in adults or larvae, egg bursters of the first-instar larva, form of adult tentorium and gular sutures, forms of adult coxal cavities, and internal structure of adult ommatidia.

Geographical Distribution

Almost every type of continuous or discontinuous distribution pattern which is known in any animal group could be matched in some taxon of Coleoptera, and every significant zoogeographical region or area could be characterized by endemic taxa of beetles. In flightless taxa, distributional areas are generally more limited than those of comparable winged taxa. Distinct distributional categories can be seen in those small, readily flying groups (in Staphylinidae and Nitidulidae, for example) which are liable to form part of "aerial plankton," and in those wood borers which may survive for extended periods in sea-drifted logs, both of which are liable to occur in oceanic islands beyond the ranges of most other beetle taxa. Climatic factors often seem to impose limits on the spread of beetle species (and sometimes of genera or families), and beetle remains in peats have been found to be sensitive indicators of climatic changes in glacial and postglacial times. *See* INSECTA; SOCIAL INSECTS. Roy A. Crowson

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Coliiformes

A small order of birds containing only the family Coliidae with six species (the mousebirds) restricted to Africa. Mousebirds, or colies, are small, grayish to brownish, with a crest on the head and long tail (see **illustration**). The legs are short and the feet strong, with the four toes movable into many positions, from all four pointing forward to two reversed backward. Mousebirds perch, climb, crawl, and scramble agilely in bushes and trees. They are largely vegetarian but eat some insects. They are nonmigratory and gregarious, living in flocks and sleeping in clusters, but they are monogamous in loose colonies as breeders. The nest is an open cup in a tree or bush, and the two to four young remain in the nest, cared for by both adults until they can fly.

White-headed mousebirds (*Colius leucocephalus*). (© *2004 DonGettyPhoto.com*)

The relationships of the mousebirds to other birds are obscure. Mousebirds have a surprisingly good fossil record from the Miocene of France and Germany, suggesting a wider distribution of this group. *See* AVES. Walter J. Bock

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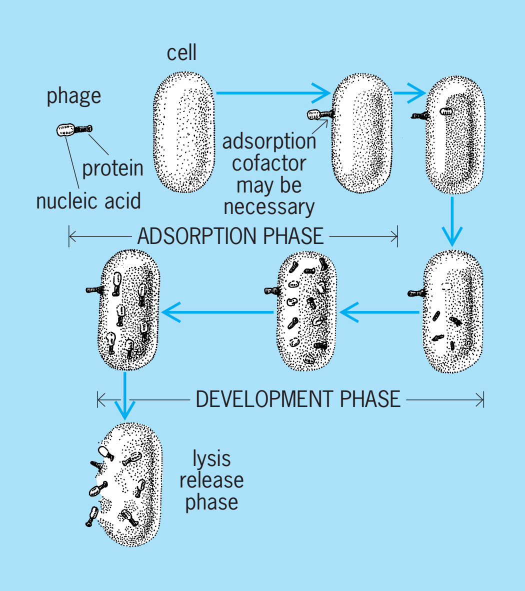
Coliphage

Any bacteriophage able to infect the bacterium *Escherichia coli*. Many are phages able to attack more than one strain of this organism. The T series of phage (T1–T7), propagated on a special culture of *E. coli*, strain B, have been used in extensive studies from which most of the knowledge of phages is derived.

A typical phage particle is shaped something like a spermatozoon. The outer skin, or shell, consists of protein and encloses contents of deoxyribonucleic acid (DNA). This DNA can be separated from the protein by osmotic shock, and it is then found that the protein shell alone can cause death of a bacterium when adsorbed to the cell surface. This does not constitute a true infection, however, since no new phage is formed.

The usual lytic infection of a *coli* B cell by a T phage proceeds as follows (see **illus.**). The phage is adsorbed, by its tail, to the cell surface. Following this adsorption, the phage DNA gains access to the cell. The protein skin has now served its purpose and, if desired, can be removed from the cell surface without affecting subsequent events. Phage in



Steps in the two phases of a lytic infection by phage. (*After E. L. Oginsky and W. W. Umbreit, An Introduction to Bacterial Physiology, Freeman, 1954*).

an infectious state no longer exists; it is now spoken of as vegetative phage and will remain in this state during its life cycle until the production of new infective particles occurs. Immediately following the injection of the DNA, the metabolic activities of the cell are profoundly altered. Normal growth ceases abruptly, although respiration continues at a steady rate. Cell enzymes still function, but their activity is now redirected and controlled by "information" supplied by the phage DNA. New protein synthesis can be detected at once; this is not bacterial protein, however, but phage protein which is to serve later as part of the new phage particles. Synthesis of bacterial ribonucleic acid (RNA) ceases. Bacterial DNA breaks down, and after about 10 min, phage DNA begins to make its appearance, formed in part from the bacterial DNA and in part from new synthesis. This new DNA is incorporated with the phage protein to make a new phage which can now be detected as an infectious unit. In another 10 min or so, lysis occurs after more phage has accumulated within the cell. The time will vary with different phages. The infectious phage, released in numbers of 100 or more particles, is able to infect susceptible bacteria. *See* BACTERIOPHAGE; LYSOGENY; LYTIC INFECTION; VIRUS.

Philip B. Cowles

Collagen

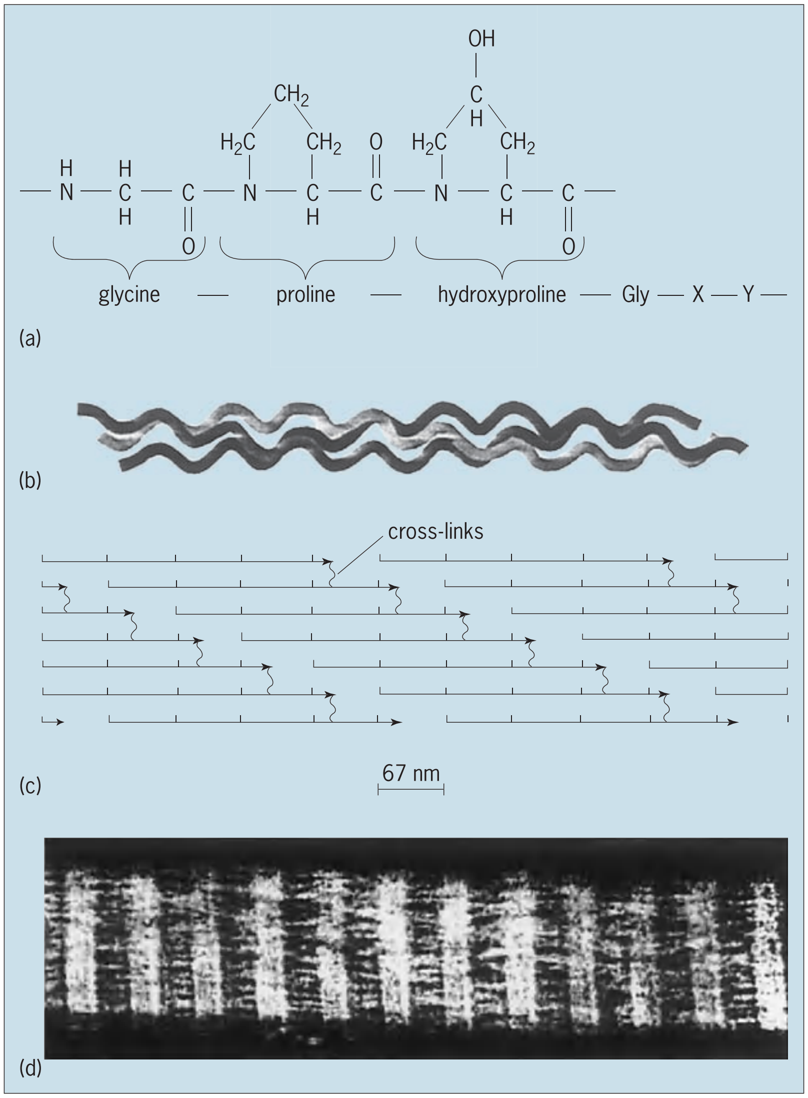
The major fibrous protein in animals. Collagen is present in all types of multicellular animals and is probably the most abundant animal protein in nature. It is estimated that collagen accounts for about 30% of the total human body protein. Collagen is located in the extracellular matrix of connective tissues. It is part of the interacting network of proteoglycans and proteins that provides a structural framework for both soft and calcified connective tissues. By self-associating into fibrils and by binding to proteoglycans and other matrix components, collagen contributes to tissue integrity and mechanical properties. Collagen interacts with cells through the integrin cell receptors and mediates cellular adhesion and migration. Important roles for collagen have been identified in development, wound healing, platelet aggregation, and aging. Its commercial importance in leather and the production of gelatin and glue have long been recognized. More recently, it is being used as a basis for biomaterials. Examples of its biomedical applications include injectable collagen to lessen facial wrinkles and defects; surgical collagen sponges to increase blood clotting; and artificial skin for the treatment of burns. *See* GELATIN; LEATHER AND FUR PROCESSING.

Structure and properties. The classification of an extracellular matrix protein as a collagen is based on the presence of a domain with the distinctive triple-helical conformation. The collagen triple helix consists of three polypeptide chains, each of which adopts an extended polyproline II–like helix. The three chains are supercoiled about a common axis and linked by hydrogen bonds. Only recently were the detailed features of this conformation determined by x-ray crystallography, confirming the general structure and showing an extensive network of ordered water hydrogen bonded to the triple helix.

The triple-helical conformation requires unique amino acid sequence features. Glycine, which is the smallest amino acid, must be present as every third residue. A high content of the sterically restricted imino acids, proline and hydroxyproline, is also necessary to stabilize the extended helix. Hydroxyproline provides additional stability through water-mediated hydrogen bonds. Collagen is the only animal protein, other than elastin, with significant amounts of hydroxyproline and hydroxylysine residues. It is easy to identify a collagen triple helix from its amino acid sequence pattern of repeating glycine-X-Y sequences, and glycine-proline-hydroxyproline is the most frequent tripeptide sequence (see **illus.**).

Types. At least 19 distinct molecules have been classified as collagens, and specific types are associated with particular tissues. The most prevalent and well-studied collagens belong to the fibril-forming or interstitial collagen family. These collagens form the characteristic fibrils seen by electron microscopy with a 67-nanometer repeating banding pattern. The banding pattern arises from the axial staggering of the collagen molecules. The molecules in a fibril are covalently cross-linked by an enzymatic mechanism to strengthen and stabilize them. Inhibition of the enzyme involved in cross-linking results in a dramatic decrease in the tensile strength of tissues, a condition known as lathyrism.

Type I is the most common fibril-forming collagen. Its fibrils make up the mineralized matrix in bone, the strong parallel bundles of fibers in tendon, and the plywoodlike alternating layers in the transparent cornea. Type II is the major fibril-forming collagen



Levels of collagen structure. (*a*) Typical amino acid repeating sequence. (*b*) Triple-helical molecular structure. (*c*) Staggered arrangement of molecules which generates the 67-nm periodic fibrils. (*d*) Electron micrograph of collagen fibril.

in cartilage, while type III is found in blood vessels and skin, together with type I. The family known as fibril-associated collagens with interrupted triple helices, or FACIT collagens, decorates the outside of the 67-nm periodic fibrils. The FACIT collagens appear to link fibrils and bind to other matrix components.

Basement membranes, which serve to separate cell layers and act as filtration barriers, contain a distinctive group of collagens, denoted as type IV collagens. Type IV collagens have many breaks in the repeating glycine-X-Y pattern of their triple helix. These collagens are organized into a network or meshlike sheet structure. In the kidney glomerulus, the network based on type IV collagen acts as a filter to determine which molecules will pass from the blood into the urine.

A number of proteins involved in host defense functions also contain collagenous amino acid sequences that adopt a triple-helical conformation. These include the complement protein C1q and mannose-binding protein. The collagenous domains of these proteins associate into hexamers or other oligomers to form the functional molecule, and are also involved in receptor and enzyme binding. *See* BONE; CONNECTIVE TISSUE; FIBROUS PROTEIN.

Biosynthesis and degradation. The genes coding for different collagen types have many exons, and the biosynthesis of collagen is a complex multistage process. The synthesis of collagen takes place in the endoplasmic reticulum. Hydroxyproline and hydroxylysine are formed by enzymes after proline and lysine are incorporated into polypeptide chains, but before the chains are folded into a triple helix. Vitamin C (ascorbic acid) is required for the hydroxylating enzymes; the failure to make hydroxyproline residues and stable collagen leads to the fragile blood vessels and skin lesions found in scurvy. After three chains associate to form the triple helix, the molecule is secreted by the cell and, following cleavage of precursor regions, fibril formation or other molecular association occurs in the matrix. Enzymes required for the posttranslational modifications of collagen include hydroxylases, enzymes involved in the attachment of sugars, proteases which cleave precursor regions, and lysyl oxidase for cross-linking.

An orderly breakdown of collagen is necessary during development and tissue remodeling. For instance, following childbirth, the uterus reduces in size, which involves a massive degradation of collagen. Collagen is resistant to degradation by most vertebrate proteases, but it is cleaved by several specific matrix metalloproteinases (collagenases). These zinc-requiring enzymes cleave fibril-forming collagens at one specific site. An abnormal increase in the degradation of cartilage collagen is seen in osteoarthritis. Collagen breakdown also appears to be essential for tumor metastases. With the recent determination of the three-dimensional structures of several matrix metalloproteinases, there are active attempts by pharmaceutical companies to develop enzyme inhibitors for use in arthritis and cancer therapies.

Diseases. Collagen is impaired in both inherited and acquired diseases involving connective tissues. A number of hereditary diseases have been shown to be due to mutations in specific collagen genes. Osteogenesis imperfecta (brittle bone) disease is characterized by fragile bones and is due to mutations in type I collagen, the major collagen in bone. Some cartilage disorders are caused by mutations in type II collagen. Ruptured arteries are found in Ehlers-Danlos syndrome type IV, which arises from mutations in type III collagen, important in blood vessels. The most common type of mutations in collagen are single-base substitutions that result in a substitution of glycine by another amino acid. Such a substitution breaks the repeating glycine-X-Y triplet pattern which is essential to form a good triple helix. Transgenic mice are being used as models for human collagen diseases.

Barbara Brodsky

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Collard

A cool-season biennial crucifer, *Brassica oleracea* var. *acephala*, similar to nonheading cabbage. Collard is of Mediterranean origin and is grown for its rosette of leaves which are cooked fresh as a vegetable (see **illus.**). Kale and collard differ only in the form of their leaves; both have been referred to as coleworts, a name taken from the Anglo-Saxon term meaning cabbage plants.

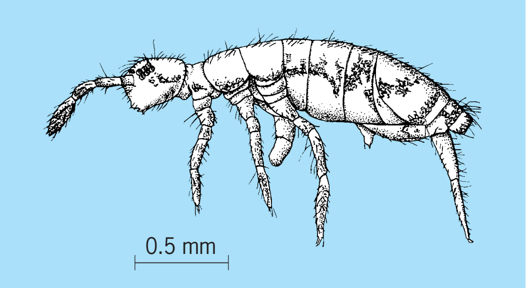
Collard (*Brassica oleracea* var. *acephala*).

Propagation is by seed. Cultural practices are similar to those used for cabbage; however, collards are more tolerant of high temperatures. Georgia and Vates are popular varieties (cultivars). Collard is moderately tolerant of acid soils. Harvesting is usually 75 days after planting. Important production centers are in the southern United States, where collards are an important nutritious green, especially during winter months. *See* CABBAGE; CAPPARALES; KALE.

H. John Carew

Collembola

An order of primitive insects, commonly called springtails, belonging to the subclass Apterygota. These tiny insects do not undergo a metamorphosis. They have six abdominal segments, some of which may be ankylosed to give an apparently smaller number (see **illus.**).



A collembolan, *Entomobrya cubensis*. (*After J. W. Folsom, Proc. U.S. Nat. Mus., 72*(6), *plate 6, 1927*).

The tarsi are united with the tibiae, and a pretarsus is present, which bears a dorsal median claw and usually a ventral clawlike appendage. The ventral tube always occurs on the first abdominal segment and connects with the mouthparts through a ventral canal consisting of two integumentary folds which overlap. Appended to the fourth abdominal segment in most of the species is a spring, or furcula. This consists of a basal piece and two apical parallel structures which end in hooks. Another pair of structures, united at the base, occur ventrally on the third abdominal segment. These bear teeth which engage with the furcula and hold it beneath the body. When released, the spring flies backward, catapulting the insect. Two families, Sminthuridae and Actaletidae, have simple tracheal systems, while the others breathe through the integument. Collembola live in humid places, often in leaf mold. Some species are active at cool temperatures, hence another common name, snowflea, is used. The earliest known insect fossil, *Rhyniella praecursor*, is thought to belong to this order.

Harlow B. Mills

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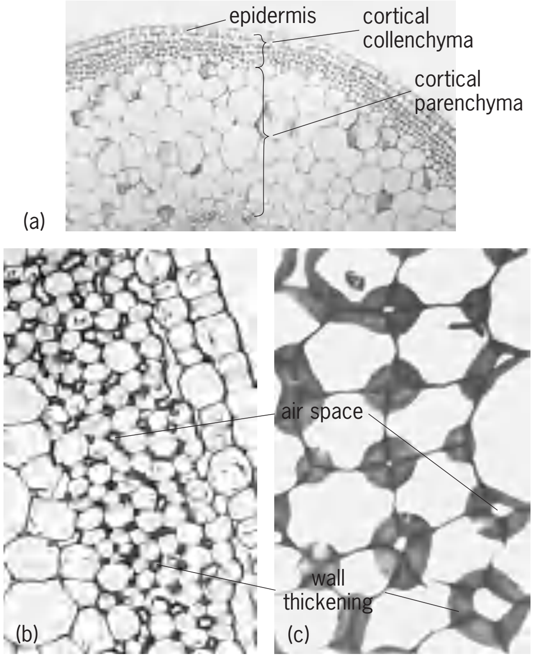
Collenchyma

A primary, or early differentiated, supporting tissue of young shoot parts appearing while these parts are still elongating. It is located near the surface, usually just under the epidermis (**illus.** *a*). When observed in transverse sections, it is characterized structurally by cell walls that are intermittently thickened, generally in the corners or places of juncture of three or more cells (illus. *b* and *c*). Collenchyma is typically formed in the petioles and vein ribs of leaves, the elongating zone of young stems, and the pedicels of flowers. *See* CELL WALLS (PLANT).

As in parenchyma, the cells in collenchyma are living and may contain chloroplasts and starch grains. The cell wall of a collenchyma cell is its most striking feature structurally and functionally. It is composed of cellulose and pectic compounds plus a very high proportion of water. In some studies collenchyma cell walls were found to contain 50–60% water by fresh weight in a variety of species examined. The cellulose and pectic compounds are present in alternating layers. A striking feature of collenchyma cell walls is their plasticity. They are capable of great



Transverse sections of Jimsonweed (*Datura stramonium*), progressively magnified. (*a*) Stem section. (*b*) Stem section, showing the corner thickenings of collenchyma cell walls and air spaces surrounded by wall thickenings. (*c*) Collenchyma section, showing lamellation of the cell wall forming the corner thickenings. (*Courtesy of W. S. Walker*)

elongation during the period of growth in length of the plant. Despite this elongation, the characteristic thickening of the wall continues to increase because new wall material is added during growth. The plasticity of collenchyma is associated with a tensile strength comparable to that shown by fibers of sclerenchyma. The combination of strength and plasticity makes the collenchyma effective as a strengthening tissue in developing stems and leaves having no other supporting tissue at that time. *See* CELLULOSE; CHLOROPHYLL; EPIDERMIS (PLANT); FLOWER; LEAF; PARENCHYMA; PECTIN; STEM. Robert L. Hulbary

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Collision (physics)

Any interaction between particles, aggregates of particles, or rigid bodies in which they come near enough to exert a mutual influence, generally with exchange of energy. The term collision, as used in physics, does not necessarily imply actual contact.

In classical mechanics, collision problems are concerned with the relation of the magnitudes and direction of the velocities of colliding bodies after collision to the velocity vectors of the bodies before collision. When the only forces on the colliding bodies are those exerted by the bodies themselves, the principle of conservation of momentum states that the total momentum of the system is unchanged in the collision process. This result is particularly useful when the forces between the colliding bodies act only during the instant of collision. The velocities can then change only during the collision process, which takes place in a short time interval. Under these conditions the forces can be treated as impulsive forces, the effects of which can be expressed in terms of an experimental parameter known as the coefficient of restitution, which is discussed later. *See* CONSERVATION OF MOMENTUM; IMPACT.

The study of collisions of molecules, atoms, and nuclear particles is an important field of physics. Here the object is usually to obtain information about the forces acting between the particles. The velocities of the particles are measured before and after collision. Although quantum mechanics instead of classical mechanics should be used to describe the motion of the particles, many of the conclusions of classical collision theory are valid. *See* SCATTERING EXPERIMENTS (ATOMS AND MOLECULES); SCATTERING EXPERIMENTS (NUCLEI).

Classification. Collisions can be classed as elastic and inelastic. In an elastic collision, mechanical energy is conserved; that is, the total kinetic energy of the system of particles after collision equals the total kinetic energy before collision. For inelastic collisions, however, the total kinetic energy after collision is different from the initial total kinetic energy.

In classical mechanics the total mechanical energy after an inelastic collision is ordinarily less than the initial total mechanical energy, and the mechanical energy which is lost is converted into heat. However, an inelastic collision in which the total energy after collision is greater than the initial total energy sometimes can occur in classical mechanics. For example, a collision can cause an explosion which converts chemical energy into mechanical energy. In molecular, atomic, and nuclear systems, which are governed by quantum mechanics, the energy levels of the particles can be changed during collisions. Thus these inelastic collisions can involve either a gain or loss in mechanical energy.

Consider a one-dimensional collision of two particles in which the particles have masses m_1 and m_2 and initial velocities u_1 and u_2. If they interact only during the collision, an application of the principle of conservation of momentum yields Eq. (1), where

$$m_1u_1 + m_2u_2 = m_1v_1 + m_2v_2 \qquad (1)$$

v_1 and v_2 are the velocities of m_1 and m_2, respectively, after collision.

Coefficient of restitution. It has been found experimentally that in collision processes Eq. (2) holds,

$$e = \frac{v_2 - v_1}{u_1 - u_2} \qquad (2)$$

where e is a constant known as the coefficient of restitution, the value of which depends on the properties of the colliding bodies. The magnitude of e varies from 0 to 1. A coefficient of restitution equal to 1 can be shown to be equivalent to an elastic collision, while a coefficient of restitution of zero is equivalent to what is sometimes called a perfectly inelastic collision. From the definition of e one can show that in a perfectly inelastic collision the colliding bodies stick together after collision, as two colliding balls of putty or a bullet fired into a wooden block would do. Equations (1) and (2) can be solved for the unknown velocities υ_2 and υ_1 in the one-dimensional collision of two particles.

The concept of coefficient of restitution can be generalized to treat collisions involving the plane motion of smooth bodies—both of particles and larger bodies for which rotation effects must be considered. For these collisions, experiments show that the velocity components to be used in Eq. (2) for *e* are the components along the common normal to the surfaces of the bodies at the point where they make contact in the collision. For smooth bodies the velocity components perpendicular to this direction are unchanged. Use of this result and the principle of conservation of momentum is sufficient to solve two-dimensional collision problems of smooth bodies. For collisions of smooth spheres the velocity components to be used in Eq. (2) for *e* are those on the line joining the centers of the spheres. Velocity components perpendicular to this direction are unchanged.

Center-of-mass coordinates. A simplification of the description of both classical and quantum mechanical collisions can be obtained by using a coordinate system which moves with the velocity of the center of mass before collision. (Since for an isolated system the center of mass of the system can be shown to be unaccelerated at all times, the velocity of the center of mass of the system of particles does not change during collision.) The coordinate system which moves with the center of mass is called the center-of-mass system, while the stationary system is the laboratory system.

The description of a collision in the center-of-mass system is simplified because in this coordinate system the total momentum is equal to zero, both before and after collision. In the case of a two-particle collision the particles therefore must be oppositely directed after collision, and the magnitude of one of the velocities in the center-of-mass system can be determined if the other magnitude is known. *See* CENTER OF MASS.

Paul W. Schmidt

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Colloid

A state of matter characterized by large specific surface areas, that is, large surfaces per unit volume or unit mass. The term colloid refers to any matter, regardless of chemical composition, structure (crystalline or amorphous), geometric form, or degree of condensation (solid, liquid, or gas), as long as at least one of the dimensions is less than approximately 1 micrometer but larger than about 1 nanometer. Thus, it is possible to distinguish films (for example, oil slick), fibers (spider web), or colloidal particles (fog) if one, two, or three dimensions, respectively, are within the submicrometer range.

Types of colloid dispersions

Medium	Dispersed matter	Technical name	Examples
Gas	Liquid	Aerosol	Fog, sprays
	Solid	Aerosol	Smoke, atmospheric or interstellar dust
Liquid	Gas	Foam	Head on beer, lather
	Liquid	Emulsion	Milk, cosmetic lotions
	Solid	Sol	Paints, muddy water
Solid	Gas	Solid foam	Foam rubber
	Liquid	Solid emulsion	Opal
	Solid	Solid sol	Steel

A colloid consists of dispersed matter in a given medium. In the case of finely subdivided particles, classification of a number of systems is possible, as given in the **table**. In addition to the colloids in the table, there are systems that do not fit into any of the listed categories. Among these are gels, which consist of a network-type internal structure loaded with larger or smaller amounts of fluid. Some gels may have the consistency of a solid, while others are truly elastic bodies that can reversibly deform. Another colloid system that may occur is termed coacervate, and is identified as a liquid phase separated on coagulation of hydrophilic colloids, such as proteins. *See* GEL.

It is customary to distinguish between hydrophobic and hydrophilic colloids. The former are assumed to be solvent-repellent, while the latter are solvent-attractant (dispersed matter is said to be solvated). In reality there are various degrees of hydrophilicity for which the degree of solvation cannot be determined quantitatively.

Properties. Certain properties of matter are greatly enhanced in the colloidal state due to the large specific surface area. Thus, finely dispersed particles are excellent adsorbents; that is, they can bind various molecules or ions on their surfaces. This property may be used for removal of toxic gases from the atmosphere (in gas masks), for elimination of soluble contaminants in purification of water, or decolorization of sugar, to give just a few examples. *See* ADSORPTION.

Colloids are too small to be seen by the naked eye or in optical microscopes. However, they can be observed and photographed in transmission or scanning electron microscopes. Owing to their small size, they cannot be separated from the medium (liquid or gas) by simple filtration or normal centrifugation. Special membranes with exceedingly small pores, known as ultrafilters, can be used for collection of such finely dispersed particles. The ultracentrifuge, which spins at very high velocities, can also be employed to promote colloid settling. *See* ELECTRON MICROSCOPE; SCANNING ELECTRON MICROSCOPE; ULTRACENTRIFUGE; ULTRAFILTRATION.

Colloids show characteristic optical properties. They strongly scatter light, causing turbidity such as in fog, milk, or muddy water. Scattering of light (recognized by the Tyndall beam) can be used for the observation of tiny particles in the ultramicroscope. Colloidal state of silica is also responsible for iridescence, the beautiful effect observed with opals. *See* SCATTERING OF ELECTROMAGNETIC RADIATION; TYNDALL EFFECT.

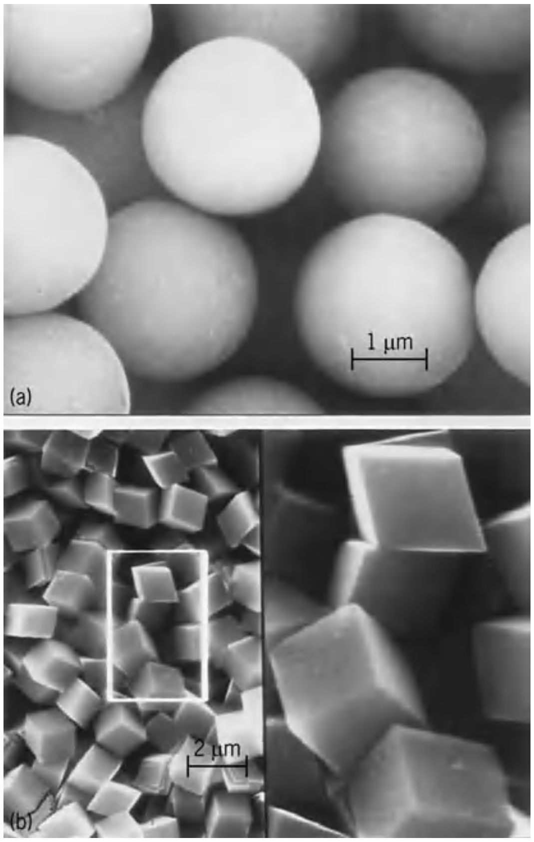
Preparation. Since the characteristic dimensions of colloids fall between those of simple ions or molecules and those of coarse systems, there are in principle two sets of techniques available for their preparation: dispersion and condensation. In dispersion methods the starting materials consist of coarse units which are broken down into finely dispersed particles, drawn into fibers, or flattened into films. For example, colloid mills grind solids to colloid sizes, nebulizers can produce finely dispersed droplets from bulk liquids, and blenders are used to prepare emulsions from two immiscible liquids (such as oil and water). *See* EMULSION.

In condensation methods, ions or molecules are aggregated to give colloidal particles, fibers, or films. Thus, insoluble monolayer films can be developed by spreading onto the surface of water a long-chain fatty acid (for example, stearic acid) from a solution in an organic liquid (such as benzene or ethyl ether). Colloidal aggregates of detergents (micelles) form by dissolving the surface-active material in an aqueous solution in amounts that exceed the critical micelle concentration. *See* MICELLE; MONOMOLECULAR FILM.

The most common procedure to prepare sols is by homogeneous precipitation of electrolytes. Thus, if aqueous silver nitrate and potassium bromide solutions are mixed in proper concentrations, colloidal dispersions of silver bromide will form, which may remain stable for a long time. Major efforts have focused on preparation of monodispersed sols, which consist of colloidal particles that are uniform in size, shape, and composition (see **illus.**). *See* PRECIPITATION (CHEMISTRY).

Dispersion stability. Dispersions of colloids (sols) are inherently unstable because they represent systems of high free energy. Particles may remain in suspended state as long as they are small enough for gravity to be compensated by the kinetic energy (brownian movement). Consequently, particle aggregation on collision must be prevented, which can be achieved by various means. *See* BROWNIAN MOVEMENT.

The most common cause for sol stability is electrostatic repulsion, which results from the charge on colloidal particles. The latter can be due to adsorption of excess ions (such as of bromide ions on silver bromide particles), surface acid or base reactions (for example, removal or addition of protons on the surface of metal hydroxides), or other interfacial chemical reactions. Alternately, sol stability can be induced by adsorption of polymers or by solvation. Stability of colloid dispersions that occur naturally may represent an undesirable state, as is the case with muddy waters whose turbidity is due to the presence of tiny particles (clays, iron oxides, and so forth). When needed, stability can be artificially induced, as in the production of paints. *See* SOLVATION.



Examples of colloid particles. (*a*) Zinc sulfide (sphalerite). (*b*) Cadmium carbonate, with an enlargement of the boxed section (*courtesy of Egon Matijević*).

Coagulation or flocculation. Processes by which a large number of finely dispersed particles is aggregated into larger units, known as coagula or flocs, are known as coagulation or flocculation; the distinction between the two is rather subtle. The concepts most commonly refer to colloidal solids in liquids (sols), although analogous principles can be employed in explaining aggregation of solid particles or liquid droplets in gases (aerosols).

Coagulation of stable sols can be accomplished by various additives (electrolytes, surfactants, polyelectrolytes, or other colloids) whose efficiency depends on their charge and adsorptivity, as well as on the nature of suspended particles to be treated. A common example of applications of coagulation is in water purification in which particulate colloid contaminants must be aggregated in order to be removed. Coagulation is also used to describe solidification of polymers (for example, proteins), which can be achieved by heating, as exemplified by boiling an egg. *See* EMULSION; FOAM; FOG; POLYMER; SMOKE. Egon Matijević

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Colloidal crystals

Periodic arrays of suspended colloidal particles. Common colloidal suspensions (colloids) such as milk, blood, or latex are polydisperse; that is, the suspended particles have a distribution of sizes and shapes. However, suspensions of particles of identical size, shape, and interaction, the so-called monodisperse colloids, do occur. In such suspensions, a new phenomenon that is not found in polydisperse systems, colloidal crystallization, appears: under appropriate conditions, the particles can spontaneously arrange themselves into spatially periodic structures. This ordering is analogous to that of identical atoms or molecules into periodic arrays to form atomic or molecular crystals. However, colloidal crystals are distinguished from molecular crystals, such as those formed by very large protein molecules, in that the individual particles do not have precisely identical internal atomic or molecular arrangements. On the other hand, they are distinguished from periodic stackings of macroscopic objects like cannonballs in that the periodic ordering is spontaneously adopted by the system through the thermal agitation (brownian motion) of the particles. These conditions limit the sizes of particles which can form colloidal crystals to the range from about 0.01 to about 5 micrometers. *See* BROWNIAN MOVEMENT; KINETIC THEORY OF MATTER.

The most spectacular evidence for colloidal crystallization is the existence of naturally occurring opals. The ideal opal structure is a periodic close-packed three-dimensional array of silica microspheres with hydrated silica filling the spaces not occupied by particles. Opals are the fossilized remains of an earlier colloidal crystal suspension. Synthetic opals can be made by allowing suspensions of silica spheres to sediment and then letting the suspending medium evaporate. Colloidal crystals can also be made from suspensions of synthetic plastic (organic polymer) microspheres, formed by emulsion polymerization. Such suspensions have become important systems for the study of colloidal crystals, by virtue of the controllability of the particle size and interaction. Colloidal crystals have also been found in aqueous emulsions of oil drops in water, in which all the drops are made the same size by fractionation. Another important class of naturally occurring colloidal crystals are found in concentrated suspensions of nearly spherical virus particles, such as *Tipula* iridescent virus and tomato bushy stunt virus. *See* OPAL; VIRUS.

Crystal structure and properties. In order for colloidal crystals to form, the forces between the particles must be repulsive, since if the forces are attractive the particles will aggregate into noncrystalline clusters. The repulsion can be electrostatic, if the particles are charged (charge-stabilized), or can come from interparticle collisions (steric-stabilized). In the latter case the particle surface must be treated with an amphiphilic or polymer layer to prevent the particles from sticking together.

Similarities to atomic crystals. In colloidal crystals of spherical or nearly spherical particles, the crystal structures adopted are identical to those found in crystals formed by spherical atoms, such as the noble gases and alkali metals. The phase behavior is also quite similar.

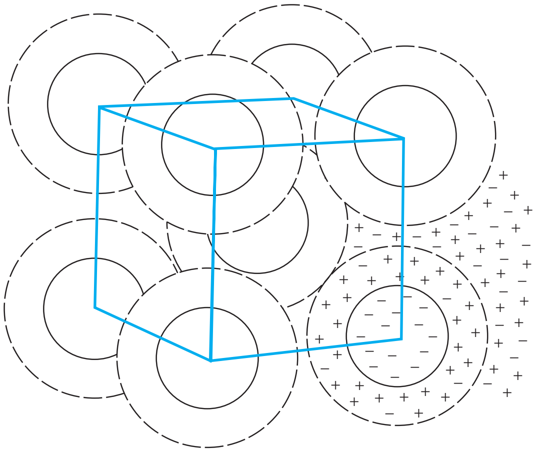

Fig. 1. Arrangement of particles and distribution of electrical charges in a charged stabilized body-centered-cubic colloidal crystal. Spheres indicated by broken lines show extent of positive counterion clouds.

For example, in suspensions of polymer spheres in organic solvents the interaction between the spheres is short-ranged, consisting only of repulsion on contact (the hard sphere limit). As with the noble gas crystals where the interatomic repulsion is short-ranged, the crystals formed are close-packed, either hexagonal or face-centered cubic, first appearing when the spheres' volume fraction is about 55%.

In aqueous suspension the particles can interact electrically, without ever actually touching. Polymer particles are readily prepared with acid surface groups which dissociate in water, leaving the particle with a large negative charge (as large as several thousand electron charges). This charge attracts positively charged small ions, which form clouds around the particles (**Fig. 1**). The spheres will repel each other if they come close enough so that their ion clouds overlap. At low concentration, the particles rarely encounter one another, executing independent brownian motion and forming the colloidal gas phase. As the concentration is increased to where the average interparticle separation is comparable to the overlap separation, the particles become strongly confined by their neighbors and form the colloidal liquid phase. If the concentration is further increased, an abrupt freezing transition to the ordered colloidal crystal phase will occur. The colloidal crystal structure found near the freezing transition is the body-centered cubic, as is found in the alkali metals, where the atomic repulsion is more long-ranged. *See* GAS; LIQUID.

Differences from atomic crystals. Despite these structural similarities, atomic and colloidal crystals are characterized by vastly different length, stiffness, and time scales.

First, particles in atomic crystals are separated by less than a nanometer compared to micrometers in colloidal crystals. This means that colloidal crystal structure can be determined by visible-light

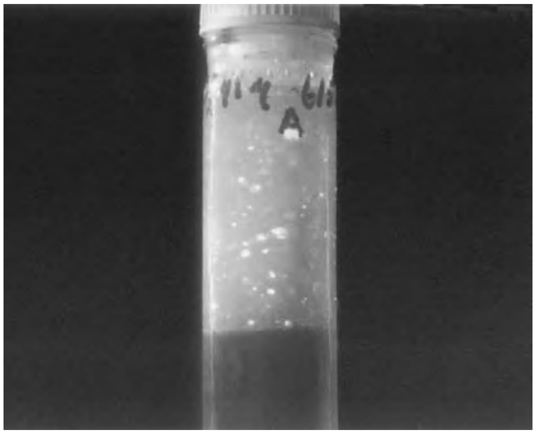

Fig. 2. Reflection of white light from a polycrystalline colloidal crystal suspension. The crystals are body-centered cubic, with a particle diameter of 0.1 μm and interparticle spacing of 1.5 μm.

techniques, as opposed to x-rays, which are required in the atomic crystal case. The spectacular iridescent appearance of opal and other colloidal crystals (**Fig. 2**) is a direct result of constructive interference in the reflection of light by the particles' periodic lattice structure; that is, the colloidal crystals Bragg-reflect visible light in the same way as atomic crystals Bragg-reflect x-rays. *See* OPALESCENCE; X-RAY CRYSTALLOGRAPHY; X-RAY DIFFRACTION.

This optical property is being developed for photonic bandgap applications, in which light of frequency in a particular range is reflected for all possible propagation directions. The search for useful photonic crystals has led to the development of inverse colloidal crystals and opals, in which a hard-sphere colloidal crystal is made (of silica particles, for example), the void space (74% of the volume for a close-packed structure) is filled with another material (a polymer, for example), and then the original particles are chemically removed (by dipping in hydrofluoric acid in the case of silica). The result is a crystal structure in which the solid material occupies only about 25% of the volume (**Fig. 3**).

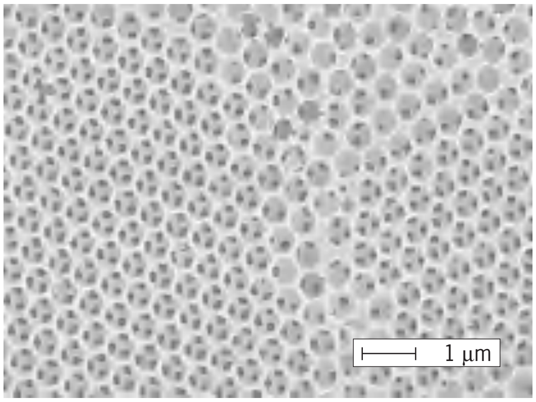

Fig. 3. Inverse opal structure formed by filling the void space of a face-centered cubic colloidal crystal emulsion of oil drops in water and then condensing silica in the aqueous void spaces. (*D.J. Pine, University of California at Santa Barbara*)

Second, colloidal crystals are about 10^8 times weaker than atomic crystals; that is, their elastic constants are 10^8 times smaller. Consequently, colloidal crystals can be melted very easily, even by a gentle shearing of the suspension.

Finally, significant atomic motions, such as the relative vibration of adjacent particles, occur in 10^{-12} s, whereas the equivalent time in a colloidal system is 10^{-2} s. Hence, it is possible to watch in detail through a microscope the motions of particles in a colloidal lattice. The distinctive properties of colloidal crystals thus provide a new avenue to the understanding of many phenomena found in atomic systems, such as lattice vibrations (sound waves), crystal dislocation and other defects, the response of crystals to large stresses (plastic flow), and crystallization itself. *See* CRYSTAL DEFECTS; CRYSTAL GROWTH; LATTICE VIBRATIONS; PLASTICITY.

Colloidal crystallization has been studied in space, taking advantage of the microgravity environment to avoid the sedimentation arising from the density mismatch between particles and suspending medium. Crystals form in space under conditions where the suspensions remain liquid on Earth.

Complex systems. In addition to the simple colloidal crystals found in bulk (three-dimensional) suspensions of spherical particles, there are a number of more exotic colloidal systems. Colloidal alloys can be formed in suspensions containing particles of several different sizes. Binary mixtures form mixed crystals, sometimes with approximately 100 particles per unit cell, analogous to the alloy structures found in binary atomic metal mixtures. Other systems include colloidal glasses, which are binary or multicomponent suspensions that exhibit shear rigidity without periodic structure; two-dimensional colloidal crystals, which are obtained by trapping a monolayer or several layers of particles; and colloidal liquid crystals, which are found in suspensions of interacting non-spherical (rod- or disk-shaped) particles such as tobacco mosaic virus. *See* ALLOY STRUCTURES; AMORPHOUS SOLID; COLLOID; CRYSTAL STRUCTURE; LIQUID CRYSTALS.

Noel A. Clark

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Colon

The portion of the intestine that runs from the cecum to the rectum; in some mammals, it may be separated from the small intestine by an ileocecal valve. It is also known as the large intestine. The colon is usually divided into ascending, transverse, and descending portions. In the humans a fourth section, the sigmoid, is found. The colon is longer in herbivores and shorter in carnivores, and is about 4 to 6 ft (1 to 2 m) long in humans. Although no digestive enzymes are secreted in the colon, digestion is assisted by an alkaline fluid. Much digestion (for example, all breakdown of cellulose) occurs by bacteria, of which *Escherichia coli is* the most common. Most of the fluid added to the food during digestion is reabsorbed into the body in the colon. All digestive action, water absorption, and so on, is completed before the food materials pass out of the colon into the rectum. *See* DIGESTIVE SYSTEM. Walter J. Bock

Color

That aspect of visual sensation enabling a human observer to distinguish differences between two structure-free fields of light having the same size, shape, and duration. Although luminance differences alone permit such discriminations to be made, the term color is usually restricted to a class of differences still perceived at equal luminance. These depend upon physical differences in the spectral compositions of the two fields, usually revealed to the observer as differences of hue or saturation.

Photoreceptors. Color discriminations are possible because the human eye contains three classes of cone photoreceptors that differ in the photopigments they contain and in their neural connections. Two of these, the L and M cones, are sensitive to all wavelengths of the visible spectrum from 380 to 700 nanometers. (Even longer or shorter wavelengths may be effective if sufficient energy is available.) L cones are maximally sensitive at about 570 nm, M cones at about 540 nm. The ratio L/M of cone sensitivities is minimal at 465 nm and increases monotonically for wavelengths both shorter and longer than this. This ratio is independent of intensity, and the red-green dimension of color variation is encoded in terms of it. The S cones, whose sensitivity peaks at about 440 nm, are not appreciably excited by wavelengths longer than 540 nm. The perception of blueness and yellowness depends upon the level of excitation of S cones in relation to that of L and M cones. No two wavelengths of light can produce equal excitations in all three kinds of cones. It follows that, provided they are sufficiently different to be discriminable, no two wavelengths can give rise to identical sensations.

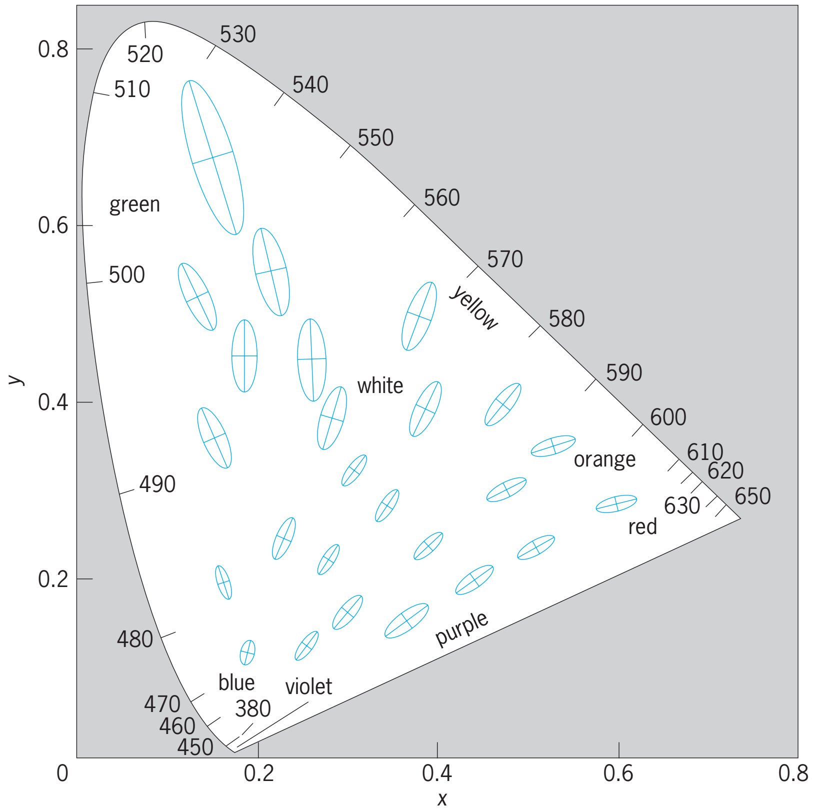
The foregoing is not true for the comparison of two different complex spectral distributions. These usually, but not always, look different. Suitable amounts of short-, middle-, and long-wavelength lights, if additively mixed, can for example excite the L, M, and S cones exactly as does a light containing equal energy at all wavelengths. As a result, both stimuli look the same. This is an extreme example of the subjective identity of physically different stimuli known as chromatic metamerism. Additive mixture is achievable by optical superposition, rapid alternation at frequencies too high for the visual system to follow, or (as in color television) by the juxtaposition of very small elements which make up a field structure so fine as to exceed the limits of visual acuity. The integration of light takes place within each receptor, where photons are individually absorbed by single photopigment molecules, leading to receptor potentials that carry no information about the wavelength of the absorbed photons. *See* EYE (VERTEBRATE); LIGHT.

Colorimetry. Although colors are often defined by appeal to standard samples, the trivariant nature of color vision permits their specification in terms of three values. Ideally these might be the relative excitations of the L, M, and B cones. Because too little was known about cone action spectra in 1931, the International Commission on Illumination (CIE) adopted at that time a different but related system for the prediction of metamers (the CIE system of colorimetry). This widely used system permits the specification of tristimulus values X, Y, and Z, which make almost the same predictions about color matches as do calculations based upon cone action spectra. If, for fields 1 and 2, $X_1 = X_2$, $Y_1 = Y_2$, and $Z_1 = Z_2$, then the two stimuli are said to match (and therefore have the same color) whether they are physically the same (isometric) or different (metameric).

The use of the CIE system may be illustrated by a sample problem. Suppose it is necessary to describe quantitatively the color of a certain paint when viewed under illumination by a tungsten lamp of known color temperature. The first step is to measure the reflectance of the paint continuously across the visible spectrum with a spectrophotometer. The reflectance at a given wavelength is symbolized as R_λ. The next step is to multiply R_λ by the relative amount of light E_λ emitted by the lamp at the same wavelength. The product $E_\lambda R_\lambda$ describes the amount of light reflected from the paint at wavelength λ. Next, $E_\lambda R_\lambda$ is multiplied by a value $\bar{x}_\lambda$, which is taken from a table of X tristimulus values for an equal-energy spectrum. The integral $\int E_\lambda R_\lambda \bar{x}_\lambda d_\lambda$ gives the tristimulus value X for all of the light reflected from the paint. Similar computations using $\bar{y}_\lambda$ and $\bar{z}_\lambda$ yield tristimulus values Y and Z.

Tables of $\bar{x}_\lambda$, $\bar{y}_\lambda$, and $\bar{z}_\lambda$ are by convention carried to more decimal places than are warranted by the precision of the color matching data upon which they are based. As a result, colorimetric calculations of the type just described will almost never yield identical values, even for two physically different fields that are identical in appearance. For this and other reasons it is necessary to specify tolerances for color differences. Such differential colorimetry is primarily based upon experiments in which observers attempted color matches repeatedly, with the standard deviations of many matches being taken as the discrimination unit.

Chromaticity diagram. Colors are often specified in a two-dimensional chart known as the CIE chromaticity diagram, which shows the relations among tristimulus values independently of luminance. In this plane, y is by convention plotted as a function of



The 1931 CIE chromaticity diagram showing MacAdam's ellipses 10 times enlarged. (*After G. W. Wyszecki and W. S. Stiles, Color Science, Wiley, 1967*)

x, where $y = Y/(X + Y + Z)$ and $x = x/(x + Y + Z)$. [The value $z = Z/(X + Y + Z)$ also equals $1 - (x + y)$ and therefore carries no additional information.] Such a diagram is shown in the **illustration**, in which the continuous locus of spectrum colors is represented by the outermost contour. All nonspectral colors are contained within an area defined by this boundary and a straight line running from red to violet. The diagram also shows discrimination data for 25 regions, which plot as ellipses represented at 10 times their actual size. A discrimination unit is one-tenth the distance from the ellipse's center to its perimeter. Predictive schemes for interpolation to other regions of the CIE diagram have been worked out.

If discrimination ellipses were all circles of equal size, then a discrimination unit would be represented by the same distance in any direction anywhere in the chart. Because this is dramatically untrue, other chromaticity diagrams have been developed as linear projections of the CIE chart. These represent discrimination units in a relatively more uniform way, but never perfectly so.

A chromaticity diagram has some very convenient properties. Chief among them is the fact that additive mixtures of colors plot along straight lines connecting the chromaticities of the colors being mixed. Although it is sometimes convenient to visualize colors in terms of the chromaticity chart, it is important to realize that this is not a psychological color diagram. Rather, the chromaticity diagram makes a statement about the results of metameric color matches, in the sense that a given point on the diagram represents the locus of all possible metamers plotting at chromaticity coordinates x, y. However, this does not specify the appearance of the color, which can be dramatically altered by preexposing the eye to colored lights (chromatic adaptation) or, in the complex scenes of real life, by other colors present in nearby or remote areas (color contrast and assimilation). Nevertheless, within limits, metamers whose color appearance is thereby changed continue to match.

For simple, directly fixated, and unstructured fields presented in an otherwise dark environment, there are consistent relations between the chromaticity coordinates of a color and the color sensations that are elicited. Therefore, regions of the chromaticity diagram are often denoted by color names, as shown in the illustration.

Although the CIE system works rather well in practice, there are important limitations. Normal human observers do not agree exactly about their color matches, chiefly because of the differential absorption of light by inert pigments in front of the photoreceptors. Much larger individual differences exist for differential colorimetry, and the system is overall inappropriate for the 8% of the population (mostly males) whose color vision is abnormal. The system works only for an intermediate range of luminances, below which rods (the receptors of night vision) intrude, and above which the bleaching of visual photopigments significantly alters the absorption spectra of the cones. *See* COLOR VISION.

Robert M. Boynton

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Color (quantum mechanics)

A term used to describe a quantum number carried by the quarks which make up the strongly interacting elementary particles, such as the proton and neutron of the atomic nucleus. It has nothing to do with the ordinary, visual use of the word color.

The quarks which are thought to make up the strongly interacting particles have a spin angular momentum of one-half unit of $\hbar$ (Planck's constant). According to a fundamental theorem of relativity combined with quantum mechanics, they must therefore obey Fermi-Dirac statistics and be subject to the Pauli exclusion principle. No two quarks within a particular system can have exactly the same quantum numbers. *See* EXCLUSION PRINCIPLE; FERMI-DIRAC STATISTICS.

In making up a baryon, however, it often seemed necessary to violate this principle. The omega particle, for example, is made of three strange quarks, and all three had to be in exactly the same state. O. W. Greenberg was responsible for the essential idea for the solution to this paradox. In 1964 he suggested that each quark type (*u, d,* and *s*) comes in three varieties identical in all measurable qualities but different in an additional property, which has come to be known as color. The exclusion principle could then be satisfied and quarks could remain fermions, because the quarks in the baryon would not all have the same quantum numbers. They would differ in color even if they were the same in all other respects.

The color hypothesis triples the number of quarks but does not increase the number of baryons and mesons. The rules for assembling them ensures this. Tripling the number of quarks does, however, have at least two experimental consequences. It triples the rate at which the neutral π meson decays into two photons and brings the predicted rate into agreement with the observed rate.

The total production cross section for baryons and mesons in electron-positron annihilation is also tripled. The experimental results at energies up to 60 GeV are in good agreement with the color hypothesis and completely incompatible with the simple quark model without color. *See* BARYON; ELEMENTARY PARTICLE; GLUONS; MESON; QUARKS.

Thomas Appelquist

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Color centers

Atomic and electronic defects of various types in solids which produce optical absorption bands in otherwise transparent crystals such as the alkali halides, alkaline earth fluorides, or metal oxides. They are general phenomena found in a wide range of materials. Color centers are produced by gamma radiation or x-radiation, by addition of impurities or excess constituents, and sometimes through electrolysis. A well-known example is that of the *F*-center in alkali halides such as sodium chloride (NaCl). The designation *F*-center comes from the German word *Farbe*, which means color. *F*-centers in sodium chloride produce a band of optical absorption toward the blue end of the visible spectrum; thus the colored crystal appears yellow under transmitted light. On the other hand, potassium chloride (KCl) with *F*-centers appears magenta, and potassium bromide (KBr) appears blue. *See* CRYSTAL DEFECTS.

Theoretical studies guided by detailed experimental work have yielded a deep understanding of specific color centers. The crystals in which color centers appear tend to be transparent to light and to other forms of electromagnetic radiation, such as microwaves. Consequently, experiments which can be carried out include optical spectroscopy, luminescence and Raman scattering, magnetic circular dichroism, magnetic resonance, and electromodulation. Color centers find practical application in radiation dosimeters, x-ray image storage phosphors, and tunable lasers. *See* ABSORPTION OF ELECTROMAGNETIC RADIATION.

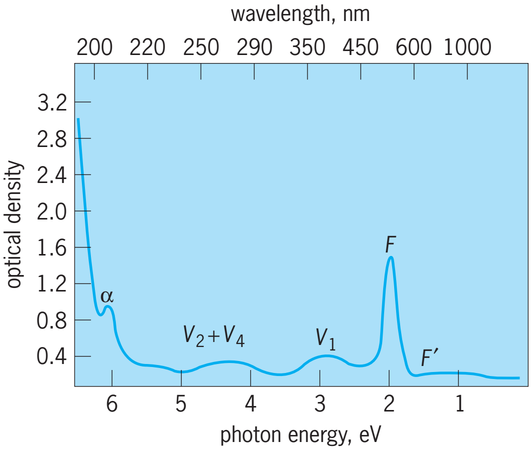

Fig. 1. Absorption bands produced in KBr crystal by exposure to x-rays at 81 K. Optical density is equal to $\log_{10}(I_0/I)$, where I_0 is the intensity of incident light and *I* the intensity of transmitted light. Steep rise in optical density at far left is due to intrinsic absorption in crystal (modified slightly by existence of *F*-centers).

Origin. **Figure 1** shows the absorption bands due to color centers produced in potassium bromide by exposure of the crystal at the temperature of liquid nitrogen (81 K) to intense penetrating x-rays. Several prominent bands appear as a result of the irradiation. The *F*-band appears at 600 nanometers and the so-called *V*-bands appear in the ultraviolet. Uncolored alkali halide crystals may be grown readily from a melt with as few imperfections as one part in 10^5. In the unirradiated and therefore uncolored state, they show no appreciable absorption from the far-infrared through the visible, to the region of characteristic absorption in the far-ultraviolet (beginning at about 200 nm in Fig. 1).

Color bands such as the *F*-band and the *V*-band arise because of light absorption at defects dispersed throughout the lattice. This absorption is caused by electronic transitions at the centers. On the other hand, colloidal particles, each consisting of many atoms, dispersed through an optical medium also produce color bands. In this case, if the particles are large enough, the extinction of light is due to both light scattering and light absorption. Colloidal gold is responsible for the color of some types of ruby glass. Colloids may also form in alkali halide crystals—for example, during heat treatment of an additively colored crystal which contains an excess of alkali metal.

Atomically dispersed centers such as *F*-centers are part of the general phenomena of trapped electrons and holes in solids. The accepted model of the *F*-center is an electron trapped at a negative ion vacancy. Many other combinations of electrons, holes,

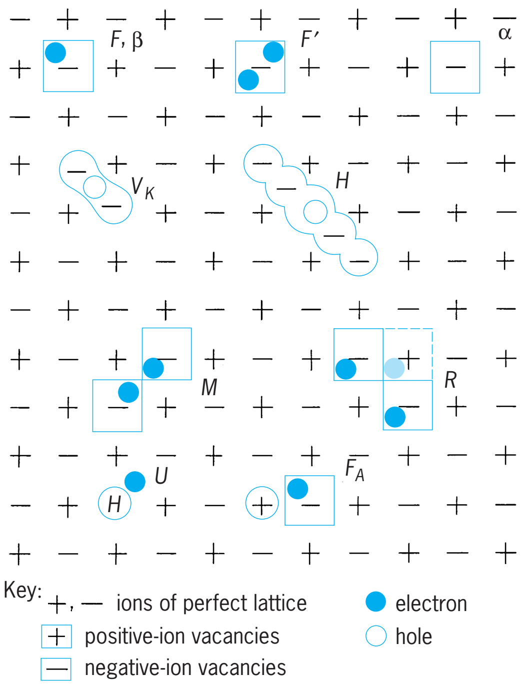

Fig. 2. Well-established models for several color centers in ionic crystal of NaCl structure. Designation β for *F*-center signifies disturbing influence of *F*-centers on tail of fundamental absorption band; characteristic absorption is also influenced by presence of vacancies, or α-centers (see Fig. 1). The V_K-center can be described as a self-trapped hole forming a Cl_2-molecule-ion, and the *H*-center can be described as a hole trapped at an interstitial halide ion. Both are stable at low temperature only. The *R*-center contains three negative-ion vacancies, one of which is in an adjacent lattice plane. *H* in circle at lower left represents hydrogen impurity, which, together with an electron, forms a *U*-center. The F_a-center is an *F*-center adjacent to a monovalent positive-ion impurity.

and clusters of lattice vacancies have been used to explain the various absorption bands observed in ionic crystals. The centers and models shown in **Fig. 2** have been positively identified either by electron spin resonance or by a combination of other types of experimental evidence. *See* HOLE STATES IN SOLIDS.

Impurities can play an important role in color-center phenomena. Certain impurities in ionic crystals produce color bands characteristic of the foreign ion. For example, hydrogen can be incorporated into the alkali halides as H^- ions substituting for halogen ions with resultant appearance of an absorption band (the *U*-band) in the ultraviolet (Fig. 2). The rate at which *F*-centers are produced by x-irradiation is greatly increased by the incorporation of hydrogen, the *U*-centers being converted into *F*-centers with high efficiency.

F-centers. *F*-centers may be produced in uncolored crystals by irradiation with ultraviolet, x-rays, gamma rays, and high-speed particles, and also by electrolysis. However, one of the most convenient methods is that of additive coloration. Alkali halide crystals may be additively colored by heating to several hundred degrees Celsius in the presence of the alkali metal vapor, then cooling rapidly to room temperature. The *F*-band that results is the same as that produced by irradiation and is dependent upon the particular alkali halide used, not upon the alkali metal vapor. For example, the coloration produced in potassium chloride is the same whether the crystal is heated in potassium or in sodium vapor. This and other evidence indicate that excess alkali atoms enter the crystal as normal lattice ions by donating an electron to accompanying negative-ion vacancies to form *F*-centers. **Figure 3** shows the position of the *F*-band in several alkali halides.

Both the width and the exact position of the *F*-band change with temperature in the manner shown in **Fig. 4**. This behavior can be explained in terms of the thermal motion of the ions surrounding the center. Thermal motion is most important at high temperatures, whereas at low temperatures the width of the absorption band becomes less and approaches a constant value which prevails down to the very lowest temperatures.

Concentration of centers. The height of the absorption maximum and the width at half maximum may be used to calculate the concentration N of absorbing centers. For potassium chloride, classical theory gives the concentration as $N = 1.3 \times 10^{16}\, AH\ \mathrm{cm}^{-3}$,

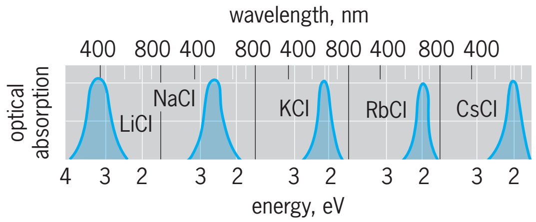

Fig. 3. *F*-bands in different alkali halide crystals.

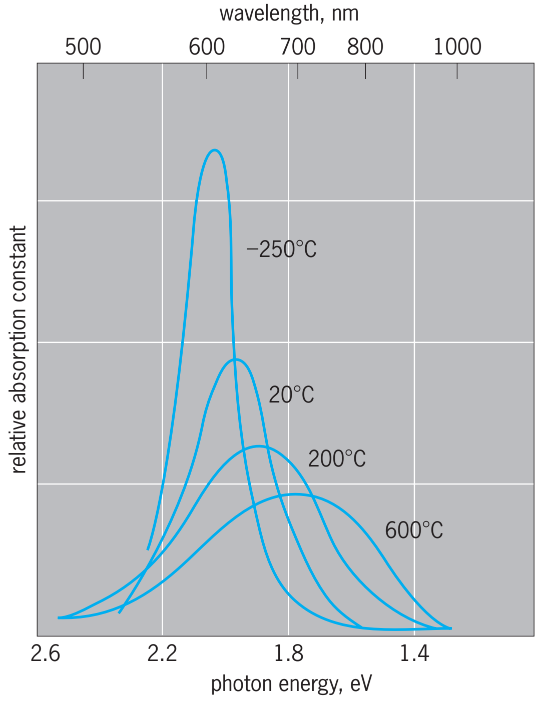

Fig. 4. Variation with temperature of the width of the *F*-band in a crystal of potassium bromide. °F = (°C × 1.8) + 32°.

where A is the maximum absorption in cm^{-1}, and H is the half width of the absorption band in electronvolts. The numerical factor in this equation depends upon the material under consideration and is given here for potassium chloride. The general relation between absorption characteristics and defect concentration is slightly more complicated but is nevertheless useful to determine concentrations below the limit of detection by chemical means.

Shape of F-band. Refined measurements of the *F*-band at low temperatures show that it is not a simple bell-shaped curve indicated in Figs. 3 and 4. In fact, it is found to contain a shoulder on the short-wavelength side, which is referred to as the *K*-band. It has been proposed that the *K*-band is in agreement with a model for the *F*-center in which an electron is trapped in a vacancy surrounded by point ions which produce the cubic crystal field of the lattice. An electron in the vicinity of a negative-ion vacancy should have a ground state and one or more excited states below the bottom of the conduction band. The main absorption peak corresponds to excitation of the electron from the 1*s*-like ground state to an excited 2*p*-like state. The *K*-band is thought to be due to transitions to the 3*p* and higher states which finally merge with the conduction band itself. *F*-center photoconductivity measurements tend to confirm the idea of discrete excited states, such as the 2*p*, which lie below the conduction band or continuum. *See* PHOTOCONDUCTIVITY.

Magnetic experiments. Some of the most detailed information on *F*-centers comes from electron spin resonance and from electron-nuclear double resonance. From these experiments the extent and character of the wave function of the electron trapped at the halogen-ion vacancy can be obtained. The electron even in the ground state is not highly localized but is spread out over the six neighboring alkali ions and to some extent over more distant neighbors. Faraday rotation studies indicated fine structure in the excited state of the *F*-center due to spin-orbit interaction. *See* MAGNETIC RESONANCE.

Lifetime of excited F-center. At low temperature an excited *F*-center decays spontaneously to the ground state with the emission of an infrared luminescent quantum. The radiative lifetime has been measured and found to be unexpectedly long, 0.57 microsecond in potassium chloride and as long as 2.0 μs in potassium iodide (KI). There are indications that this is due to a drastic change in the wave function following excitation and lattice relaxation. Lattice polarization must be taken into account in order to calculate the effect. The relaxed excited state is very spread out in the lattice, whereas the ground state is somewhat more localized.

F′-centers. When a crystal containing *F*-centers is irradiated at low temperature with light in the *F*-band itself, the *F*-absorption decreases and a new band, known as the *F′* band, appears (**Fig. 5**). Experiments have shown that for every *F′*-center created, two *F*-centers are destroyed. The *F′*-center consists of an *F*-center which has captured an extra electron. Important photoelectric effects occur during conversion of *F*- to *F′*-centers and during irradiation of alkali halides with *F*-band light.

V-centers. As Fig. 1 shows, absorption bands arise in the ultraviolet as well as in the visible portion of the spectrum when potassium bromide is irradiated while cold. These *V*-bands are apparently not present in crystals additively colored by the alkali metal vapor. Irradiation of a crystal produces both electrons and holes so that bands associated with trapped positive charges are to be expected in addition to electrons trapped at negative-ion vacancies (*F*-centers). *V*-bands can also be produced, at least in the case of potassium bromide and potassium iodide, by introduction of an excess of halogen into the crystal.

Crystals containing *V*-centers have been studied by spin resonance techniques with the result that a center not previously observed optically has been identified. This center, sometimes referred to as the V_K-center (Fig. 2), is due to a hole trapped in the vicinity of two halogen ions which have become displaced from their normal lattice position to form a Cl_2-molecule-ion (in the case of potassium chloride). It has been found in several different alkali halides, and its optical absorption and energy level structure have been correlated. The V_K-center is known to play an important role in the intrinsic luminescence of ionic crystals.

Mechanism of radiation damage. When an alkali halide crystal is exposed to ionizing radiation, such as ultraviolet light, x-rays, or beta particles, radiation damage occurs in the form of point defects. *F*-centers and *H*-centers are now known to be the primary defects formed. They are produced mainly by recombination of electron-hole pairs associated with ionizing radiation. Luminescence may also occur, depending upon temperature and upon the presence of impurities. Practical applications of these phenomena include dosimeters for detecting ionizing radiation and image plate detectors for x-rays. Analogous

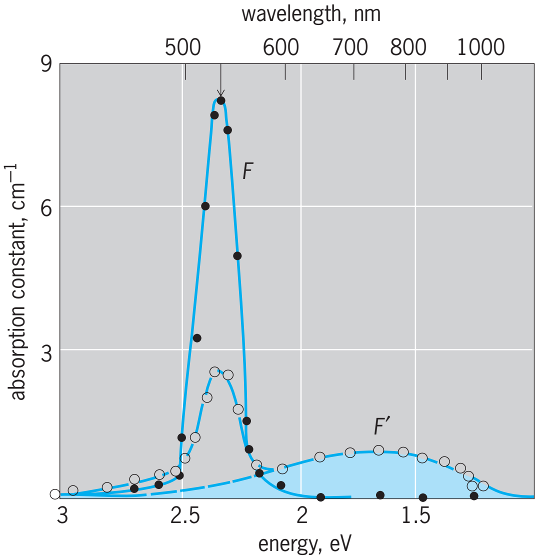

Fig. 5. ***F*- and *F′*-bands in KCl at −235°C (−391°F). *F′*-band was produced by irradiating crystal with light of wavelength shown by arrow at center of *F*-band. Such light causes the *F*-band to bleach as *F′*-band grows.**

phenomena occur in the case of crystals of the fluorite structure (CaF_2) and also in oxides such as calcium oxide (CaO) and magnesium oxide (MgO). In these cases the photolytic processes are somewhat different and apparently not as efficient as in the alkali halides. *See* DOSIMETER; ELECTRON-HOLE RECOMBINATION; PHOTOLYSIS; RADIATION DAMAGE TO MATERIALS.

Frederick C. Brown

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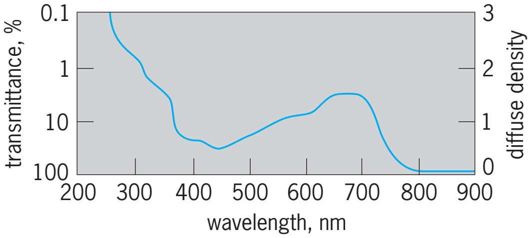
Color filter

An optical element that partially absorbs incident radiation, often called an absorption filter. The absorption is selective with respect to wavelength, or color, limiting the colors that are transmitted by limiting those that are absorbed. Color filters absorb all the colors not transmitted. They are used in photography, optical instruments, and illuminating devices to control the amount and spectral composition of the light.

Color filters are made of glass for maximum permanence, of liquid solutions in cells with transparent faces for flexibility of control, and of dyed gelatin or plastic (usually cellulose acetate) for economy, convenience, and flexibility. The plastic filters are often of satisfactory permanence, but they are sometimes cemented between glass plates for greater toughness and scratch resistance. They do not have as good quality as gelatin filters.

Color filters are sometimes classified according to their type of spectral absorption: short-wavelength pass, long-wavelength pass or band-pass; diffuse or sharp-cutting; monochromatic or conversion. The short-wavelength pass transmits all wavelengths up to the specified one and then absorbs. The long-wavelength pass is the opposite. Every filter is a band-pass filter when considered generally. Even an ordinary piece of glass does not transmit in the ultraviolet or infrared parts of the spectrum. Color filters, however, are usually discussed in terms of the portion of the visible part of the spectrum. Sharp and diffuse denote the sharpness of the edges of the filter band pass. Monochromatic filters are very narrow band-pass filters. Conversion filters alter the spectral response or distribution of one selective detector or source to that of another, for example, from that of a light bulb to that of the Sun (see **illus.**).

Neutral-density filters transmit a constant fraction of the light across the spectrum considered. They are made either by including an appropriate absorbent like carbon that is spectrally nonselective, or by a thin, partially transparent reflective layer, often of aluminum.



Transmission of a conversion filter, used to convert the spectral distribution of a light bulb (color temperature of 2360 K or 3790°F) to that of the Sun (color temperature of 5500 K or 9440°F). (*After Eastman Kodak Co., Kodak Filters for Scientific and Technical Uses, 1972*)

The transmittance of a filter is the ratio of the transmitted flux to the incident flux, expressed as either a ratio or a percentage. The density of a filter is the logarithm to base 10 of the reciprocal of the transmittance. For example, a filter with a 1% transmittance has a density of 2.

Other, closely related filters are the Christiansen, Lyot or birefringent, residual-ray, and interference filters. They use the phenomena of refraction, polarization, reflection, and interference. *See* ABSORPTION OF ELECTROMAGNETIC RADIATION; COLOR; INTERFERENCE FILTER; REFLECTION OF ELECTROMAGNETIC RADIATION; SUN.

William L. Wolfe

Color index

A quantitative measure of a star's color. Even a casual look at the night sky reveals the stars to be colored. From spectral analysis and the laws of radiation, it has been known since the 1920s that such color is closely related to temperature. Stars are reddish at about 3000 K (4940°F), orange at about 4500 K (7640°F), yellowish-white at about 6000 K (10,340°F), white at about 10,000 K (17,540°F), and bluish-white above 10,000 K. With proper calibration, color provides a means by which the temperature and spectral class can be evaluated. Visual examination is too crude, however. Instead, color must be properly defined and quantified. *See* SPECTRAL TYPE; STAR.

Color is defined through a star's various magnitude measures (m), which indicate brightness at different wavelengths. The unaided-eye stars are historically grouped into six magnitude classes, 1st magnitude being the brightest and 6th magnitude the faintest. The system was quantified in the nineteenth century so that five magnitude divisions were made to correspond to a factor of 100 in brightness. One magnitude division is then a factor of 2.512 . . . . The star Vega, with $m = 0.03$, now provides a fundamental calibration point. Telescopes extend the range to magnitude 30. *See* MAGNITUDE (ASTRONOMY).

The original magnitudes were visual, m being estimated by eye, and depended on the eye's response, which is maximized for yellow light. Photography provided a way of permanently recording starlight and of measuring magnitudes. Early photographic emulsions, however, were sensitive primarily to blue

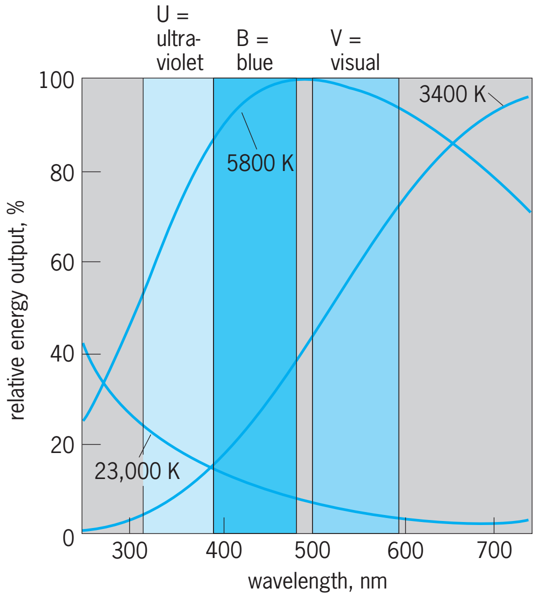


Fig. 1. Responses of the U, B (close to photographic), and V (close to visual) filters are superimposed onto blackbody curves for 3400, 5800, and 23,000 K (5660, 9980, and 40,940°F). The higher-temperature body is brighter in the blue and has a lower magnitude. (*After S. P. Wyatt and J. B. Kaler, Principles of Astronomy: A Short Version, Allyn and Bacon, 1981*)

light. As a result, blue stars look relatively brighter to the photographic plate than they do the eye, and red stars considerably fainter (**Fig. 1**). It was then necessary to establish a separate magnitude system for photography, called m_{ptg}. The original visual magnitudes were distinguished by calling them m_{vis}. The two magnitudes were set equal for white class A0-A1 stars with temperatures of 9600 K (16,820°F). Color can then be quantified by taking the difference between the two magnitudes, the color index becoming m_{ptg}-m_{vis}. Blue stars have slightly negative color indices, red stars positive ones (**Fig. 2**). *See* ASTRONOMICAL IMAGING.

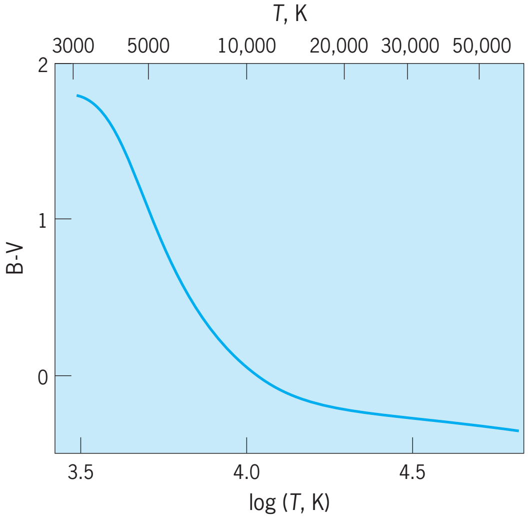


Fig. 2. Graph of the color index B-V versus the logarithm of the temperature *T* (in kelvins). As temperature climbs, the B-V color index decreases. (*After P. J. Flower, Transformations from theoretical Hertzsprung-Russell diagrams to color-magnitude diagrams: Effective temperatures, B-V colors, and bolometric corrections, Astrophys. J., 469:355–365, 1996*)

Photoelectric photometry allowed the establishment of the more precise UBV system, wherein V (yellow) and B (blue) filters respectively mimic the response of the human eye and the untreated photographic plate, and a U filter is added in the ultraviolet (Fig. 1). The traditional color index is then replaced by B-V, and the addition of U allows a second color index, U-B. Main-sequence stars trace a locus on the color-color diagram in which U-B is plotted against B-V. Deviations from the plot allow the evaluation of the degree of interstellar extinction. *See* HERTZSPRUNG-RUSSELL DIAGRAM; INTERSTELLAR EXTINCTION.

The standard system has been expanded into the red with an R filter, into the near-infrared with an I filter, and even deeper into the infrared with J, K, H, L, and M filters that go all the way to $4.75\ \mu$m. Numerous color indices are then available to examine stars that radiate primarily in the infrared. Other photometric schemes, such as the Strömgren four-color system (uvby, for ultraviolet, violet, blue, and yellow) and that used by the Sloan Survey (u′g′r′i′z′, which run from the ultraviolet to the near-infrared), allow more sophisticated color indices (for example g′-r′ instead of B-V) that are responsive not only to temperature but also to a variety of other parameters. *See* INFRARED ASTRONOMY; SLOAN DIGITAL SKY SURVEY.

James B. Kaler

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Color vision

The ability to discriminate light on the basis of wavelength composition. It is found in humans, in other primates, and in certain species of birds, fishes, reptiles, and insects. These animals have visual receptors that respond differentially to the various wavelengths of visible light. Each type of receptor is especially sensitive to light of a particular wavelength composition. Evidence indicates that primates, including humans, possess three types of cone receptor, and that the cones of each type possess a pigment that selectively absorbs light from a particular region of the visible spectrum.

If the wavelength composition of the light is known, its color can be specified. However, the reverse statement cannot be made. A given color may usually be produced by any one of an infinite number of combinations of wavelength. This supports the conclusion that there are not many different types of color receptor. Each type is capable of being stimulated by light from a considerable region of the spectrum, rather than being narrowly tuned to a single wavelength of light. The trichromatic system of colorimetry, using only three primary colors, is based

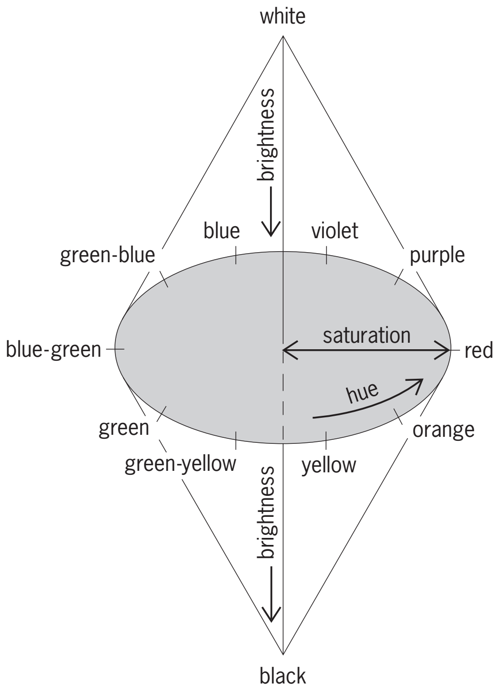

Fig. 1. **Diagram of a color solid for illustrating the appearance of surface colors. (*After N. L. Munn, Psychology, 2d ed., Houghton Mifflin, 1951*)**

on the concept of cone receptors with sensitivities having their peaks, respectively, in the long, middle, and short wavelengths of the spectrum. The number of such curves and their possible shapes have long been subjects for study, but not until the 1960s were direct measurements made of the spectral sensitivities of individual cone receptors in humans and various animals. *See* COLOR.

Color recognition. Color is usually presented to the individual by the surfaces of objects on which a more or less white light is falling. A red surface, for example, is one that absorbs most of the short-wave light and reflects the long-wave light to the eye. The surface colors are easily described by reference to the color solid shown in **Fig. 1**. The central axis defines the lightness or darkness of the surface as determined by its overall reflectance of white light, the lowest reflectance being called black and the highest, white. The circumference denotes hue, related primarily to the selective reflectance of the surface for particular wavelengths of light. The color solid is pointed at its top and bottom to represent the fact that as colors become whiter or blacker they lose hue. The distance from central axis to periphery indicates saturation, a characteristic that depends chiefly on the narrowness, or purity, of the band of wavelengths reflected by the surface. At the center of the figure is a medium-gray surface, one which exhibits a moderate amount of reflectance for all wavelengths of light. Colors that are opposite one another are called complementaries, for example, yellow and blue, red and blue-green, purple and green, and white and black.

Color mixture and contrast. Two complementaries, when added together in the proper proportions, can oppose or neutralize one another to produce a colorless white or gray. Various contrast effects also attest to the opposition of the complementaries. Staring at a bright-red surface against a gray background results in the appearance of a blue-green border around the red; this is an example of simultaneous contrast. Similarly, when a red light is turned off, there is frequently a negative afterimage that appears to have the opposite color, blue-green.

A set of primary colors can be chosen so that any other color can be produced from additive mixtures of the primaries in the proper proportions. Thus, red, green, and blue lights can be added together in various proportions to produce white, purple, yellow, or any of the various intermediate colors. Three-color printing, color photography, and color television are examples of the use of primaries to produce plausible imitations of colors of the original objects. *See* PHOTOGRAPHY; PRINTING.

Achromatic colors. Colors lying along a continuum from white to black are known as the gray, or achromatic, colors. They have no particular hue, and are therefore represented by the central axis of the color diagram in Fig. 1. White is shown at the top of the diagram since it represents the high-brightness extreme of the series of achromatic colors. With respect to the surface of an object, the diffuse, uniform reflectance of all wavelengths characterizes this series from black through the grays to white in order of increasing reflectance. Whiteness is a relative term; white paper, paint, and snow reflect some 80% or more of the light of all visible wavelengths, while black surfaces typically reflect less than 10% of the light. The term white is also applied to a luminous object, such as a gas or solid, at a temperature high enough to emit fairly uniformly light of all visible wavelengths. In the same connotation, a sound is described as white noise if its energy is nearly the same at all audible frequencies.

Gray. Gray is the term applied to all the intermediate colors in the series of achromatic colors. Gray may result from a mixture of two complementary colors, from a mixture of all primary colors, or from a fairly uniform mixture of lights of all wavelengths throughout the visible spectrum. Grayness is relative; a light gray is an achromatic color that is lighter than its surroundings, while a dark gray is so called because it is darker than its surroundings. Thus, the same surface may be called light or dark gray when carried from one situation to another. A gray color is one of minimum saturation; it corresponds to zero on a scale of excitation purity. At the other extreme on this scale is the color evoked by pure monochromatic light.

Black. The opposite extreme from white in the series of achromatic colors is black. Blackness is a relative term applied to surfaces that uniformly absorb large percentages of light of all visible wavelengths. A black object in sunlight absorbs a large percentage of the light, but it may reflect a larger absolute quantity of light to the eye than does a white object in the shade. Black may also be used to refer to invisible light; ultraviolet rays, for example, may be called black light if they fall on fluorescent materials that thereby emit visible light.

Color blindness. Color blindness is a condition of faulty color vision. It appears to be the normal state of animals that are active only at night. It is also characteristic of human vision when the level of illumination is quite low or when objects are seen only at the periphery of the retina. Under these conditions, vision is mediated not by cone receptors but by rods, which respond to low intensities of light. In rare individuals, known as monochromats, there is total color blindness even at high light levels. Such persons are typically deficient or lacking in cone receptors, so that their form vision is also poor.

Dichromats are partially color-blind individuals whose vision appears to be based on two primaries rather than the normal three. Dichromatism occurs more often in men than in women because it is a sex-linked, recessive hereditary condition. One form of dichromatism is protanopia, in which there appears to be a lack of normal red-sensitive receptors. Red lights appear dim to protanopes and cannot be distinguished from dim yellow or green lights. A second form is deuteranopia, in which there is no marked reduction in the brightness of any color, but again there is a confusion of the colors normally described as red, yellow, and green. A third and much rarer form is tritanopia, which involves a confusion among the greens and blues. *See* HUMAN GENETICS.

Many so-called color-blind individuals might better be called color-weak. They are classified as anomalous trichromats because they have trichromatic vision of a sort, but fail to agree with normal subjects with respect to color matching or discrimination tests. Protanomaly is a case of this type, in which there is subnormal discrimination of red from green, with some darkening of the red end of the spectrum. Deuteranomaly is a mild form of red-green confusion with no marked brightness loss. Nearly 8% of human males have some degree of either anomalous trichromatism or dichromatism as a result of hereditary factors; less than 1% of females are color-defective. A few forms of color defect result from abnormal conditions of the visual system brought on by poisoning, drugs, or disease.

Color blindness is most commonly tested by the use of color plates in which various dots of color define a figure against a background of other dots. The normal eye readily distinguishes the figure, but the colors are so chosen that even the milder forms of color anomaly cause the figure to be indistinguishable from its background. Other tests involve the ability to mix or distinguish colored lights, or the ability to sort colored objects according to hue.

Theories. Theories of color vision are faced with the task of accounting for the facts of color mixture, contrast, and color blindness. The schema shown in **Fig. 2** may be useful in considering the various theories of color vision. It has no necessary resemblance to the structures or functions that are actually present in the visual system.

Young-Helmholtz theory. Thomas Young, early in the nineteenth century, realized that color is not merely a property of objects or surfaces. Rather, it involves a sensory experience, the characteristics of which are determined by the nature of the visual receptors and the way in which the signals that they generate are processed within the nervous system. Young was thus led to a trichromatic theory of color vision, because he found that only three types of excitation were needed to account for the range of perceived colors. Hermann von Helmholtz clarified the theory and provided it with the idea of differential absorption of light of various wavelengths by each of three types of receptor. Hence, the theory, commonly known as the Young-Helmholtz theory, is concerned with the reception phase in the color vision schema shown. This theory assumes the existence of three primary types of color receptor that respond to short, medium, and long waves of visible light, respectively. Primary colors are those that stimulate most successfully the three types of receptor; a mixture of all three primaries is seen as white or gray. A mixture of two complementary colors also stimulates all three. Blue light, for example, stimulates the blue-sensitive receptors; hence, its complementary color is yellow, which stimulates both the red receptors and the green. Similarly, the complement of red is blue-green and the complement of green is purple (blue and red). Protanopia is explained as a condition in which no long-wave sensitive receptors are present. Deuteranopia results from loss of the green receptor.

Hering theory. The theory formulated by Ewald Hering is an opponent-colors theory. In its simplest form, it states that three qualitatively different processes are present in the visual system, and that each of the three is capable of responding in two opposite ways. Thus, this theory is concerned with the processing phase (Fig. 2), in which there is a yellow-blue process, a red-green process, and a black-white process. The theory obviously was inspired by the opposition of colors that is exhibited during simultaneous contrast, afterimages, and complementary colors. It is a theory best related to the phenomenal

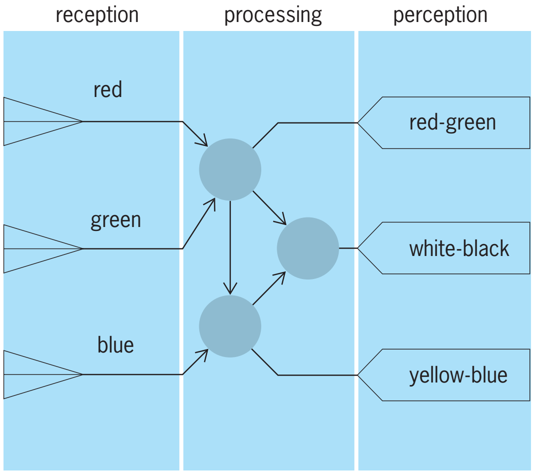

Fig. 2. **Schematic representation of the three phases of color vision which can be generally used to describe the various theories of color vision.**

and the neural-processing aspects of color rather than to the action of light on photopigments. This theory gains credibility when it is realized that opponent responses are common enough in the central nervous system. Well-known examples are polarization and depolarization of cell membranes, excitation and inhibition of nerve impulses, and reciprocal innervation of antagonistic response mechanism. The theory also maintains that there are four primary colors, since yellow appears to be just as unique perceptually, as red, green, or blue. However, it does not necessarily assume the existence of a separate yellow receptor.

Other theories. Various forms of stage theory or zone theory of color vision have been proposed. One form combines the principles of the Young-Helmholtz and Hering theories. It proposes that (1) there are three types of cone receptor; (2) the responses of red-sensitive, green-sensitive, and blue-sensitive receptors (and possibly others) are conducted to the higher visual centers; (3) at the same time, interactions are occurring at some stage along these separate conducting paths so that strong activity in a red response path inhibits, for example, the activity of the other response paths; and (4) this inhibiting effect is specific to the time and place of the strong red activity. The last point means that in neighboring regions and at subsequent times the blue and green mechanisms are less inhibited, so that blue-green afterimages and borders are commonly experienced as an opponent reaction to strong red stimulation.

Experimental evidence. Techniques of microspectrophotometry have been used to measure the absorption of light by single cone receptors from the eyes of primates, including humans. The results confirm the major assumption of the Young-Helmholtz theory, namely, that three types of visual receptor are specialized to absorb light over characteristic ranges of wavelength, with a maximum absorption at particular regions of the spectrum. Wide differences are found, from one receptor to another, in the wavelength at which this maximum absorption of light occurs. The three types of human cone receptors absorb maximally at about 420, 530, and 560 nanometers. In addition there are rod receptors sensitive to low intensities of light over a broad range of wavelengths peaking at about 500 nm. In each of the four types of receptor there is a photosensitive pigment that is distinguished by a particular protein molecule. This determines the range and spectral location of the light which it absorbs.

In other experiments, a microelectrode has been used to penetrate individual cone receptors in living retinal tissue of certain species of fish. Electrical responses are thus recorded as the receptor cell is stimulated by a beam of light. The wavelength of this test beam is varied from one end of the spectrum to the other. The result is that each cone shows an electrical response to light which presumably initiates impulses in the nerve cells of the visual system and is qualitatively the same regardless of the wavelength of the stimulating light. Quantitatively, however, the cones are found to differ widely in the size of response potential that they generate at each wavelength. In fact, they fall into three classes, responding maximally at about 460, 530, and 610 nm. This confirms, at least in the case of certain species of fish, the trichromatic aspect of the Young-Helmholtz theory.

The Hering theory has also received powerful support from electrophysiological experiments. A microelectrode may be used to record from retinal nerve cells that are close to the cone receptors described above in the fish. Electrical responses from some of these cells are again found to depend on the wavelength of the stimulating light. But, unlike the receptors themselves, these cells often have qualitatively different responses depending on wavelength of stimulation. Thus, a given cell may exhibit a positive response potential over one region of the spectrum and a negative one over another region. A retinal basis thus exists in these cells for the opponent process aspect of the Hering theory.

In monkeys having visual systems similar to that of humans, experiments have also shown opponent-color modes of responding. Cells in certain lower brain centers, for example, exhibit nerve impulses more or less continuously. Some of these cells are found to increase their activity in response to red light, for example, but decrease it in response to green. Other cells have the opposite reaction, and still others show blue-yellow opposition of the sort that is also demanded by the Hering theory.

Central nervous system factors are evident from the fact that a red light in one eye and a green light in the other can sometimes be fused to produce an appearance of yellow. Further evidence of central effects is found in the phenomenon of color constancy. The greenness of trees or the redness of bricks is only slightly less vivid when both are viewed through dark or yellow goggles; a black cat in the sunshine reflects more light to the eye than a white cat seen by indoor illumination. Color vision, like other forms of perception, is highly dependent on the experience of the observer and on the context in which the object is perceived. *See* EYE (INVERTEBRATE); EYE (VERTEBRATE); NERVOUS SYSTEM (VERTEBRATE); PERCEPTION; PHOTORECEPTION; VISION. Lorrin A. Riggs

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Columbiformes

An order of birds containing the family Columbidae (worldwide; true pigeons and doves) and two smaller related families. The members of this order are characterized by an ability to drink water by "sucking" (actually lapping using the tongue) instead of the sip-and-tilt method of most birds. However, some other groups of birds are able to "suck" water by various methods. *See* CHARADRIIFORMES.

Classification. Columbiformes is here divided into the suborder Pterocletes, with the single family Pteroclidae (sandgrouse; 16 species; Old World except Australasia), and the suborder Columbae with the families Raphidae (dodos; 3 species; Mascarene Islands, western Indian Ocean) and Columbidae (pigeons and doves; 303 species; worldwide, with most groups found in Australasia to Southeast Asia). However, the relationships of the sandgrouse (Pteroclidae) are disputed; many workers argue that these birds are members of the Charadriiformes. The pigeons are divided into several subfamilies: the worldwide true pigeons (Columbinae), the pheasant-pigeon of New Guinea (Otidiphapinae), the large, crowned pigeons of New Guinea (Gourinae), the tooth-billed pigeon of Samoa (Didunculinae), and the fruit pigeons of the Old World tropics (Treroninae). Relationships of Columbiformes appear to be to the Charadriiformes in one direction and to the Psittaciformes in another. Possibly, the Columbiformes are a central stock in the evolution of birds. *See* PSITTACIFORMES.

Fossil record. The fossil record of the Columbiformes is meager, as would be expected for these terrestrial, mainly woodland and grassland birds. The extinct dodos (Raphidae), from the Mascarene Islands, are known mainly from subfossil remains.

Columbidae. Pigeons are found mainly in the tropics, but a number of species are common in temperate regions. They have a sleek plumage ranging from browns and grays to the brilliant greens, yellows, and reds of the tropical fruit pigeons (see **illustration**). They feed on seeds, fruit, and other vegetarian food. Most pigeons live in flocks but breed solitarily. Almost all are nonmigratory. The one or two young remain in the nest where they are fed by both parents, first on milk produced in the crop and then on seeds mixed with this milk. The extinct North American passenger pigeon (*Ectopistes migratorius*) lived and bred obligatorily in vast flocks, feeding largely on acorns and other mast. Although the passenger pigeon was once an abundant bird, its numbers dwindled because of overhunting and the reduction of extensive eastern forests on which it depended for food and breeding; the last individual died in captivity in 1914.

Pigeons are important game birds throughout the world. Two species of Old World origin, the rock dove (*Columba livia*) and the ring dove (*Streptopelia risoria*), have been domesticated; both have escaped and exist as feral birds throughout the world. Numerous breeds of the rock dove have been developed, which served as the primary example used by Charles Darwin in introducing his idea of evolution by natural selection. One breed of rock doves, the carrier pigeons, have served for centuries to transport messages back to their home loft. Most species of pigeons are kept and bred by aviculturists. Both domesticated species have important roles in biological research, such as studies of orientation and navigation, including work on the "magnetic compass" possessed by birds. In spite of hunting pressures, most species of pigeons are still in good numbers. A few, however, are endangered. *See* MIGRATORY BEHAVIOR.

Triangular-spotted pigeon (*Columba guinea guinea*), Fresno Zoo, California. (*Photo by Dr. Lloyd Glenn Ingles, © 2001 California Academy of Sciences*)

Raphidae. The three species of dodos and solitaires were found only in the several Mascarene Islands and were completely exterminated by the seventeenth century by sailors and released pigs. They are the symbol of extinction, with the slogan "dead as a dodo." One of the common forest trees of these islands has almost become extinct as a result; its fruits were eaten by dodos, and the hard seeds were adapted to the grinding action of the bird's stomach. The hard seed coat had to be cracked in this way so that water could reach the ovary of the excreted seed and start germination. Seeds can now be planted after cracking the seed coat artificially.

Pteroclidae. The dull-colored, ground-dwelling sandgrouse live in flocks in dry grasslands and deserts of the Old World, but depend on ponds of water to which flocks come in large numbers. The nest is generally a long distance from water, which is transported to the young by the adults by soaking their specialized belly feathers. The young drink only from these moistened feathers, and will refuse water in pans placed before them. *See* AVES. Walter J. Bock

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Column

A structural member that carries its load in compression along its length. Most frequently, as in a building, the column is in a vertical position transmitting gravity loads from its top down to its base. Columns are present in other structures as well, such as in bridges, towers, cranes, airplanes, machinery, and furniture. Other terms used by both engineers and lay persons to identify a column are pillar, post, and strut. Columns of timber, stone, and masonry have been constructed since the dawn of civilization; modern materials also include steel, aluminum, concrete, plastic, and composite material. *See* COMPOSITE MATERIAL; LOADS, TRANSVERSE; STRUCTURAL MATERIALS; STRUCTURAL STEEL.

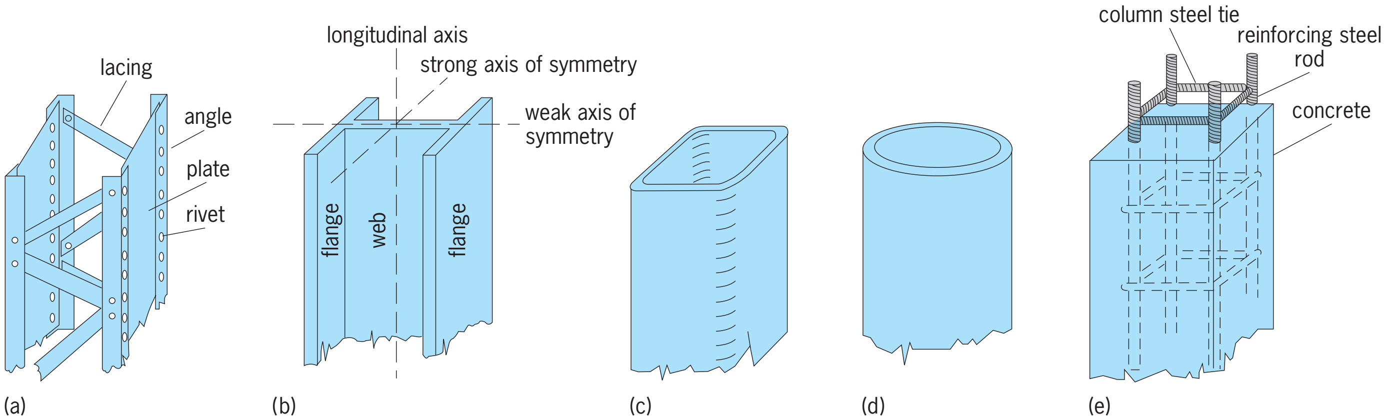
Fabrication. In the past, steel columns were built up of angle and plate elements welded or riveted together to form the desired cross-sectional shape (**illus**. *a*). Modern steel columns are made by rolling, extruding, or forming hot steel into predetermined cross-sectional shapes in the manufacturing facility (illus. *b*–*d*). Reinforced concrete columns are fabricated either in their final locations (cast-in-place concrete) or in a precast plant (precast concrete) with steel reinforcing rods embedded in the concrete (illus. *e*). Masonry columns are usually built in their final locations; they are made of brick or concrete masonry blocks; sometimes steel reinforcing rods are embedded within the masonry. *See* BRICK; CONCRETE; MASONRY; PRECAST CONCRETE; REINFORCED CONCRETE.

Classification. According to their behavior under load, columns are classified as short, slender, or intermediate. Definitions of these ranges are qualitative rather than quantitative.

A short column is one whose length is relatively short in comparison to its cross-sectional dimensions and, when loaded to its extreme, fails by reaching the compressive strength of its material. This is called failure in axial compression. A slender column is one whose length is large in comparison to its cross-sectional dimensions and, when loaded to its extreme, fails by buckling (abruptly bending) out of its straight-line shape and suddenly collapsing before reaching the compressive strength of its material. This is called a condition of instability, and it is reached at a load that depends not on the compressive strength of the material but on the stiffness of the material and the geometric properties of the column. (Stiffness is a property of materials expressed in terms of the magnitude of the load that produces a unit deformation. The greater the load required to produce a unit deformation, the stiffer the material. The geometric properties that influence the buckling of a column are the area and shape of the cross section, and the length of the column). An intermediate column falls between the classifications of short and slender. When loaded to its extreme, the intermediate column fails by a combination of compression and instability.

In addition to its length and cross section, the methods of support or fixity at the two ends of the column also influence its strength: the more effective the fixity of support, the more stable the column. (End fixity is the amount of restraint against displacement and rotation of the end of a column.)

Equilibrium, instability, and loads. As the axial load on a perfectly straight slender column with elastic material properties is increased in magnitude, this ideal column passes through three states: stable equilibrium, neutral equilibrium, and instability. The straight column under load is in stable equilibrium if a lateral force, applied between the two ends of the column, produces a small lateral deflection which disappears and the column returns to its straight form when the lateral force is removed. If the column load is gradually increased, a condition is reached in which the straight form of equilibrium becomes so-called neutral equilibrium, and a small lateral force will produce a deflection that does not disappear and the column remains in this slightly bent form when the lateral force is removed. The load at which neutral equilibrium of a column is reached is called the critical or buckling load. The state of instability is reached when a slight increase of the column load causes uncontrollably growing lateral deflections leading to complete collapse. *See* STRESS AND STRAIN; STRUCTURAL DEFLECTIONS.



Typical column configurations. (*a*) Built-up steel column. (*b*) Wide-flange steel column. (*c*) Tubular steel column. (*d*) Pipe column. (e) Reinforced concrete column.

For an axially loaded straight column with any end support conditions, the equation of static equilibrium, in the form of a differential equation, can be solved for the deflected shape and critical load of the column. With hinged, fixed or free end support conditions the deflected shape in neutral equilibrium of an initially straight column with uniform cross section throughout its length always follows a partial or composite sinusoidal curve shape, and the critical load is given by Eq. (1), where E = modulus of elasticity of the material, I = moment of inertia of the cross section, and l = length of the longest half sine wave along the deflected shape. A variant of (1) is given by Eq. (2), where L = actual length of the column between its two end supports, K = ratio of the longest half sine wave to the actual column length, and KL = effective length (length of an equivalent hinged-hinged column). From Eq. (2) it can be noted that the buckling strength of a column is inversely proportional to the square of its length.

$$P_{\text{cr}} = \frac{\pi^2 EI}{l^2} \qquad (1)$$

$$P_{\text{cr}} = \frac{\pi^2 EI}{(KL)^2} \qquad (2)$$

When the critical stress, F_{cr} ($F_{\text{cr}} = P_{\text{cr}}/A$, where A = cross-sectional area of the column), is greater than the proportional limit of the material, the column is experiencing inelastic buckling. Since at this stress the slope of the material's stress-strain curve, E_t (called the tangent modulus), is smaller than that below the proportional limit, the critical load at inelastic buckling is reduced. More complex formulas and procedures apply for such cases, but in its simplest form the critical buckling load formula is given as Eq. (3), where E_t = tangent modulus at the stress F_{cr}.

$$P_{\text{cr}} = \frac{\pi^2 E_t I}{(KL)^2} \qquad (3)$$

A column with a cross section that lacks symmetry may suffer torsional buckling (sudden twisting) before, or in combination with, lateral buckling. The presence of the twisting deformations renders both theoretical analyses and practical designs rather complex. *See* TORSION.

Eccentricity of the load, or imperfections such as initial crookedness, decreases column strength. If the axial load on the column is not concentric, that is, its line of action is not precisely coincident with the centroidal axis of the column, the column is characterized as eccentrically loaded. The eccentricity of the load, or an initial curvature, subjects the column to immediate bending. The increased stresses due to the combined axial-plus-flexural stresses result in a reduced load-carrying ability. *See* BEAM COLUMN.

Design standards. Since it is difficult, if not impossible, to construct a perfectly frictionless pin and an infinitely rigid fixity as practical column support, the theoretical formulas are only approximations for real structures. The various structural design codes and standards recognize this, and they specify adjustment factors in the form of modified effective lengths or load eccentricities. In addition, because the geometries of actual columns and the materials of which they are constructed are not perfect and since actual loadings cannot be predicted precisely, factors of safety are prescribed by design codes and standards. These are applied to the calculated capacities of ideal columns to provide margins of safety against failure.

A column that contains relatively thin plate elements, such as columns of steel, aluminum, and other metals, may fail at a load less than the critical load for the column as a whole, because one or more of the plate elements buckle locally into one or a series of short waves or wrinkles. Outstanding legs of thin angles, flanges of channels, and other such plates are elements that are susceptible to local buckling, thereby reducing the stiffness, and hence the stability, of the entire column. The likelihood of local buckling can be predicted by the mathematical theory of flat plates, and its strength reduction influence is addressed by the design codes and standards for steel, aluminum, and other metals. *See* PLATE GIRDER.

Extensions. When a column is too long to be built or transported in one piece, it has to be extended or spliced at the construction site. A reinforced concrete column is extended by having the steel reinforcing bars protrude a few inches or feet above the top of the concrete, then placing the next level of reinforcing bars to overlap, and pouring the concrete of the next level. A steel column is extended by welding or bolting splice plates on the flanges and webs or walls of the columns to provide a few inches or feet of load transfer from the upper to the lower column section. A timber column is usually extended by the use of a steel tube or wrapped-around sheet-metal plate bolted onto the two connecting timber sections.

Foundations. A column that carries the load down to a foundation must have means to transfer the load without overstressing the foundation material. Reinforced concrete and masonry columns are generally built directly on top of concrete foundations. A steel column, when seated on a concrete foundation, must have a base plate to spread the load over a larger area and thereby reduce the bearing pressure. The base plate is a thick rectangular steel plate usually welded to the bottom end of the column. *See* BUILDINGS; FOUNDATIONS. Robert T. Ratay

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Combinatorial chemistry

A method in which very large numbers of chemical entities are synthesized by condensing a small number of reagents togther in all combinations defined by a small set of reactions. The main objective of combinatorial chemistry is synthesis of arrays of chemical or biological compounds called libraries. These libraries are screened to identify useful components, such as drug candidates. Synthesis and screening are often treated as separate tasks because they require different conditions, instrumentation, and scientific expertise. Synthesis involves the development of new chemical reactions to produce the compounds, while screening aims to identify the biological effect of these compounds, such as strong binding to proteins and other biomolecular targets.

Chemical Libraries

Combinatorial chemistry is sometimes referred to as matrix chemistry. If a chemical synthesis consists of three steps, each employing one class of reagent to accomplish the conversion, then employing one type of each reagent class will yield $1 \times 1 \times 1 = 1$ product as the result of $1 + 1 + 1 = 3$ total reactions. Combining 10 types of each reagent class will yield $10 \times 10 \times 10 = 1000$ products as the result of as few as $10 + 10 + 10 = 30$ total reactions; 100 types of each reagent will yield 1,000,000 products as the result of as few as 300 total reactions. While the concept is simple, considerable strategy is required to identify 1,000,000 products worth making and to carry out their synthesis in a manner that minimizes labor and maximizes the value of the resulting organized collection, called a chemical library. *See* MATRIX THEORY.

The earliest work was motivated by a desire to discover novel ligands (that is, compounds that associate without the formation of covalent bonds) for biological macromolecules, such as proteins. Such ligands can be useful tools in understanding the structure and function of proteins; and if the ligand meets certain physiochemical constraints, it may be useful as a drug. For this reason, pharmaceutical applications provided early and strong motivation for the development of combinatorial chemistry. *See* LIGAND.

Peptide libraries. In 1984 H. M. Geysen reported on the synthesis of a library of peptides and the screening of that library to probe how changes in a single amino acid in a peptide would change its association strength with an antibody. Biochemists assume that the detailed chemical structure of any ligand will affect that ligand's binding strength to a macromolecular receptor, but even with powerful modern computer modeling methods it is normally not possible to predict either the magnitude or even the direction of the effect. By synthesizing a large number of peptides, each varying from another by only one amino acid, it was possible to determine empirically which amino acid substitutions made binding stronger and which made it weaker. The synthesis of this library benefited from the fact that chemical methods for linking amino acids together to make peptides had been optimized such that little optimization of the reaction conditions was required. Instead, the challenge was how to conveniently make thousands of peptides in a format that facilitated their use in the subsequent binding studies. The solution was to synthesize the peptides on a rack of plastic pins and to test their binding ability while the peptides remained chemically attached to the pin. While solving technical challenges, perhaps more importantly this approach highlighted a philosophy in studying ligand-receptor binding problems: start with a source of molecular diversity (that is, lots of compounds) organized in a way that makes their empirical testing straightforward; then test them all and analyze the results at the end.

Because there are 20 naturally occurring amino acids, the synthesis of a linear peptide that is n amino acids long can be done in $20n$ different ways. Thus, there are 64,000,000 possible hexapeptides ($n = 6$). It would not be convenient, perhaps not even possible, to synthesize that many peptides on individual pins. In 1985 a synthesis method was reported in which the plastic used for synthesis was encased in an inert mesh resembling a tea bag. Collections of such tea-bag reactors were subjected to the chemical addition of an amino acid at the same time. After the addition, the bags were washed thoroughly and the bags (not the bag contents) mixed. The bags were redistributed to new beakers, and another amino acid was chemically added. In this method, each bag contains only one peptide. By chemically cleaving the peptide from the polymeric support, the peptide itself can be obtained. In a variant of this procedure, a mixture of reagents can be used in any given beaker such that each bag contains a mixture of peptides bound to the polymer. While the production of such mixtures complicates the subsequent assay step, it does provide for a much greater number of assays to be accomplished. Still unresolved is the question of whether the time economy afforded by using mixtures compensates for the pitfalls inherent in their testing for binding activity.

To make very large numbers of individual peptides would require very small bags for purely practical reasons. In 1988 work involving the use of polymer resin beads was reported; approximately one-tenth the width of a pinhead, these beads served as a kind of bag. By utilizing the "split-pool" approach, it was possible to synthesize extremely large peptide libraries in which each bead possessed a single peptide. The amount of peptide on one bead is only around 200 picomoles; however, this is enough both for a simple ligand-receptor binding assay and for the analytical techniques required to establish the exact chemical structure of that peptide. *See* PEPTIDE.

Organic libraries. Because much of the practical application in discovering tightly binding ligands derives from the pharmaceutical industry, the combinatorial synthesis of druglike compound libraries is of great interest. Two practical considerations make this a greater experimental challenge than the synthesis of peptide libraries.

The synthetic methods required to make druglike molecules (that is, low-molecular-weight, organic molecules) on a polymer support have not been optimized. While solid-supported peptide synthesis originated in the early 1960s and has been extensively developed since, initial experiments with organic solid-phase synthesis in the early 1970s were not followed up widely. In addition, while there are only 20 naturally occurring amino acids and therefore a finite number of reactions required to use them efficiently, an almost infinite number of organic chemical reagents exists and a very large number of reaction types. However, by the early 1990s several groups had reported the synthesis of moderately sized organic libraries by the solid-phase synthesis method. Each approach utilized a strategy like that of the Geysen pin method and thus was amenable to the parallel synthesis of hundreds to thousands of compounds.

The synthesis of much larger-membered libraries using the polymer-resin-bead approach was inhibited by the second practical issue: while 200 picomoles of an organic compound is enough for the ligand-receptor study, it is not enough to identify the structure of the ligand. The reason is that analytical methods for structure determination are both easier and more advanced for use with biological macromolecules such as polypeptides and polynucleotides. Beginning in the mid-1990s, the solution of bead tagging, or encoding, solved this issue. The strategy is simple: if the result of a chemical synthesis step cannot be easily read at low concentration, something should be added to the bead that conveniently encodes the reaction history of that bead for later analysis. The first reported methods of bead encoding involved the use of biological macromolecules themselves. After each step in the organic synthesis, either an amino acid or a nucleotide was added to a growing oligopeptide or oligonucleotide on the same bead so that the specific sequence could be read later, and from that sequence the reaction history could be elucidated. However, neither oligopeptides nor oligonucleotides are chemically inert enough to survive the conditions required for organic synthesis. Later, tags were introduced that were much more inert chemically. *See* ORGANIC SYNTHESIS.

More recent methods of encoding include the use of radio-frequency memory microchips and optical bar-coding strategies. **Figure 1** shows a scheme that uses optical-pattern encoding for the synthesis of a combinatorial library. Each of the nine chips has a different pattern written on it with a laser (a 3 × 3 matrix pattern as shown could encode for 2^9, or 512, unique chips). With the use of pattern-recognition software, the chips are sorted into appropriate reaction vessels so that chemical groups A, B, and C can be covalently added to the core organic molecule on them. After pooling the chips, optical scanning again permits sorting into appropriate reaction vessels so that a new set of three chemical groups can be added. At the end of this combinatorial synthesis involving two steps with three reagents at each, a total of 3^2, or 9, different products is obtained. Larger libraries are obtained by employing additional reaction steps, additional reagents per step, and an appropriately larger matrix pattern to enable the unique encoding of each product in the library. *See* OPTICAL INFORMATION SYSTEMS.

Major challenges in combinatorial chemistry focus on both the characterization of compounds and the screening of very large compound libraries. In addition, the use of combinatorial chemistry methods is under active study for the discovery of new catalysts, chemosensors, and other chemical substances in which prior binding of the cognate ligand (the molecule that fits into another, usually larger molecule) is necessary. *See* MOLECULAR RECOGNITION. Anthony W. Czarnik

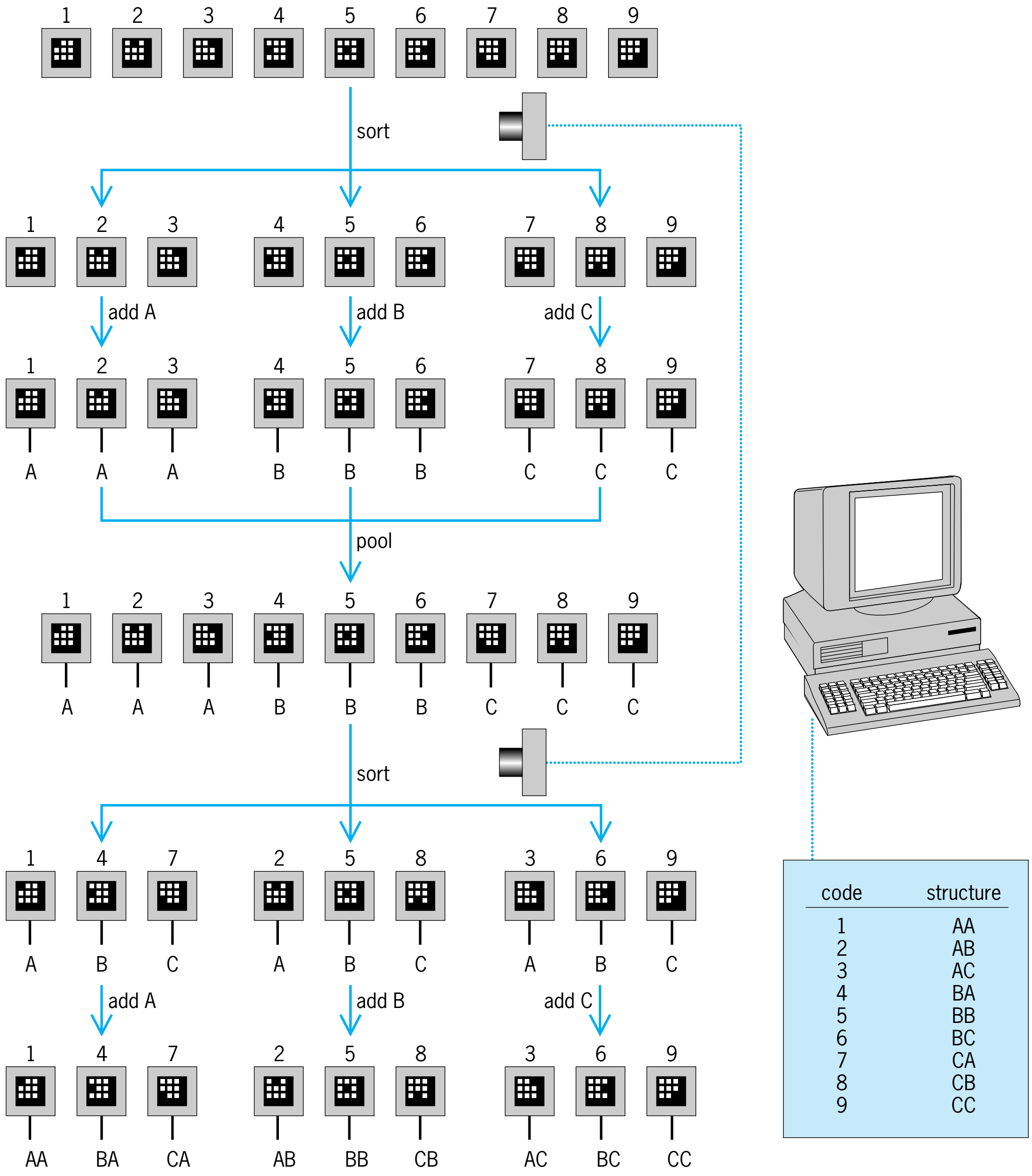
Assaying Problems

In combinatorial chemistry, attention has been focused on the problem of how to identify the set of molecules that possess the desired combination of properties. In a drug-discovery effort, the library members that strongly bind to a particular biological receptor are of interest. In a search for new materials that behave as superconductors at relatively high temperatures, the special combination of elements yielding the best electrical properties is a goal. In each case, the library might consist of up to a million members, while the subset of target molecules might consist of several thousand contenders or just a single highly selective binder. This subset could then be studied in more detail by conventional means.

To take advantage of the parallel nature of the combinatorial chemistry strategy, rapid screening and assaying protocols are necessary. For example, gas chromatography/mass spectrometry of bead-encoded libraries is currently limited to several analyses per hour, a difficult proposition when the researcher is faced with analyzing several thousand samples. The problem is to find ways of keeping track of each library member so that parallel screening can be coupled with parallel assaying.

Spatial array. Several emerging strategies promise to address this problem. In the first case, a library is constructed in a spatial array such that the chemical composition of each location in the array is noted during the construction. The binding molecules, usually labeled with a fluorescent tag, are exposed to the entire assay. The locations that light up can then be immediately identified from their spatial location. This approach is being actively developed for libraries of proteins and nucleotides. A problem is that the chemistry required to attach various molecules to the solid surface, usually silicon, is quite tricky and difficult to generalize. The assaying strategy is intertwined with the available procedures for synthesizing the libraries themselves.

Polystyrene-bead support. A conceptually straightforward approach is to first synthesize the library by using polystyrene beads as the solid support. The product molecules are then stripped from the support and pooled together into a master solution. This complex mixture consisting of a potentially large selection of ligand molecules could then be exposed to an excess of a target receptor. The next step is to devise a method for identifying the ligand-receptor pairs that point to molecularly specific binding. One approach is to examine a part of the mixture en masse by using affinity capillary electrophoresis. With this technique, the migration times of the ligand-receptor pair are significantly longer than the



code	structure
1	AA
2	AB
3	AC
4	BA
5	BB
6	BC
7	CA
8	CB
9	CC

Fig. 1. Scheme for using optical pattern encoding for the synthesis of a combinatorial library. (*Courtesy of X. Xiao*)

unreactive ligands, and can be interrogated by electrospray mass spectrometry.

Mass spectrometry. The mass spectrometric method often provides a direct structural identification of the ligand, either by determination of its molecular weight or by collision-induced dissociation experiments. In the latter case, the molecular ion is selected by a primary mass spectrometer and is driven into a region of high-pressure inert gas for fragmentation. The fragment ions are then used to reconstruct the original molecular structure. This direct approach to screening and assaying has the advantage that the screening is carried out in solution rather than on a solid support, and it avoids steric problems associated with resin-bound molecules. At present the approach seems limited to libraries of about 1000 compounds because of interference from unbound ligands, and limited by sensitivity issues. New strategies using mass spectrometry may eliminate this limit.

A different tack involves assaying the polystyrene beads one by one after the resin-bound molecules are exposed to a receptor. With this approach, active beads may be identified by color or by fluorescence associated with the receptor, and are subsequently indexed in standard 96-well titer plates. Identification is then possible by using a variety of spectroscopic techniques; at present, the most popular methods are electrospray mass spectrometry and matrix-assisted laser desorption ionization mass spectrometry.

Successful structure determination using mass spectrometry is often routine, particularly for protein libraries where sequencing strategies have been worked out; however, ambiguities often arise for nonpeptide libraries. Encoding strategies promise to resolve this issue. For example, it is now possible to construct the library such that the first molecule attached to the resin can be identified by its ratio of carbon-13 to carbon-12. By using isotope enrichment protocols, a particular isotope ratio can be associated with a specific molecule. Then, for a library synthesized with three steps, the molecule in the first step can be identified from its isotope ratio, the molecule in the third step is known from the synthesis, and the molecular weight is measured by mass spectrometry. Hence, the molecular weight of the molecule used in the second step can be determined by the difference. This approach has been successfully employed to assay a 1000-member library. There are many ways that this approach could be extended to larger systems.

Another advantage of the isotope-encoding strategy is that the code is actually carried with the molecule after it is cleaved from the bead. This property may have important implications when performing bioassays. This scheme appears to be functional in a practical sense. The mass spectrometry methods are generally sensitive enough ($\approx$100 femtomole) to provide a reliable assay, and robotic techniques can be developed to increase the number of assays to perhaps a few dozen per hour.

Another level of sophistication involves the assay of a single polystyrene bead by using a method such as infrared spectroscopy. The advantages of optical techniques are that they are nondestructive and can be employed without removing the target molecules from the linker. There are, however, several obvious drawbacks, including lack of specificity and sensitivity for single-bead studies. Recently, however, experiments using infrared microspectroscopy have partially overcome the sensitivity limitations. The selectivity issue has been addressed by using a carbon-deuterium stretching frequency to determine the deuterium content of a given compound. This signature can lead to identification under suitable circumstances. *See* MASS SPECTROMETRY.

Improving assaying power. It would be desirable to speed up the whole process. To fully capitalize on the elegant concept implicit in combinatorial chemistry, parallel screening methods capable of identifying large numbers of library members need to be developed. When the libraries are synthesized on beads, it would also be preferable to assay the compound without cleaving it from the polymeric resin support. This process inherently destroys the library and opens the possibility of incomplete cleaving reactions. One approach is to take advantage of a special type of mass spectrometry where it is possible to record spectra from very small areas of a solid surface. With this technique, the sample is bombarded by a focused energetic ion beam having a kinetic energy of several thousand electronvolts. The energetic particle loses some of its momentum in the top layers of the solid, causing desorption of molecular ions near the point of impact. If the energetic ion beam is formed in a short (nanosecond) pulse, the secondary ions may be measured by using time-of-flight detection. The resulting mass spectra can be recorded from an area that is much less than 1 square micrometer. Hence, it is feasible to spatially resolve the chemical components on a single resin particle that is typically in the 20–300-μm size range.

Experiments using this idea were attempted in the late 1990s. The first attempts were successful only if the covalent bonds attaching the molecules to the resin were first clipped. This was accomplished by exposing the bead to a vapor of trifluoracetic acid, a standard release agent for acid-sensitive linking moieties. After clipping, the molecules were found to remain on their respective beads, even if prior to their treatment they were essentially touching. For example, in this method, two distinct types of coated beads can be used—one with phenylalanine and one with leucine. It might be possible to extend this method to a collection of thousands of beads arrayed onto a plate.

None of the above approaches provides assaying power that satisfies the need to characterize massive combinatorial libraries. Many schemes appear to have enough sensitivity or selectivity to perform the job, but whether any will be truly practical remains to be seen. It is likely, given the high level of activity in this field, that one of the above methods (or perhaps a completely new one) will become practical. *See* ANALYTICAL CHEMISTRY; ELECTROPHORESIS.

Nicholas Winograd

Dynamic Combinatorial Chemistry

Dynamic combinatorial chemistry is in its early developmental stage. It integrates library synthesis and screening in one process, potentially accelerating the discovery of useful compounds. In the dynamic approach the libraries are not created as arrays of individual compounds, but are generated as mixtures of components, similar to natural pools of antibodies. One important requirement is that the mixture components (**Fig. 2**) exist in dynamic equilibrium with each other. According to basic laws of thermodynamics (Le Chatelier's principle), if one of the

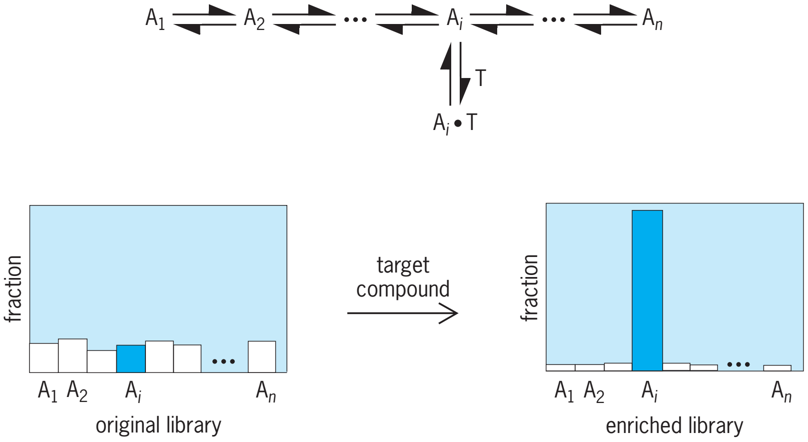


Fig. 2. Dynamic equilibrium for mixture components ($A_1 \ldots A_n$), following Le Chatelier's principle. T indicates the target.

components (A_i) is removed from the equilibrated mixture, the system will respond by producing more of the removed component to maintain the equilibrium balance in the mixture. *See* CHEMICAL EQUILIBRIUM; LE CHATELIER'S PRINCIPLE.

The dynamic mixture, as any other combinatorial library, is so designed that some of the components have potentially high affinity to a biomolecular target. These high-affinity (effective) components can form strong complexes with the target. If the target is added to the equilibrated mixture, when the effective components form complexes with the target they are removed from the equilibrium. This forces the system to make more of these components at the expense of other ones that bind to the target with less strength. As a result of such an equilibrium shift, the combinatorial library reorganizes to increase the amount of strong binders and decrease the amount of the weaker ones (Fig. 2). This reorganization leads to enrichment of the library with the effective components and simplifies their identification.

The general idea of the equilibrium shift is not new, and its combinatorial application was eventually demonstrated by several groups. As an example, researchers described a dynamic library that produced inhibitors for the enzyme carbonic anhydrase. The components of this library were formed by a reversible reaction between two series of compounds: amines and aldehydes (**Fig. 3***a*). The products of this reaction, Schiff bases, existed in the dynamic equilibrium with the starting amines and aldehydes (building blocks) and with each other. Functional groups in the building blocks (R^x and R^y) could recognize binding pockets of the target enzyme, and the best combination of those groups could make a particularly strong binder. To render the library components stable to hydrolysis, they were converted to similar amines (Fig. 3*a*) with retention of their basic target-binding properties. The researchers showed that the addition of carbonic anhydrase to the library led to the preferred formation of a sulfonamide compound (Fig. 3*b*), as compared to other library components. Structures similar to the sulfonamide compound are known to inhibit carbonic anhydrase via strong binding to its active site.

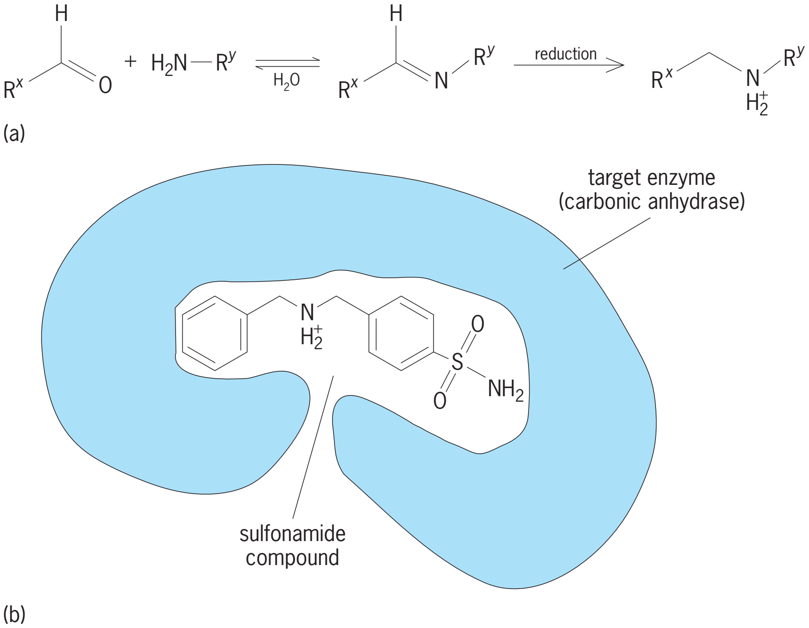


Fig. 3. Equilibrium shift utilized to produce a dynamic library. (*a*) Reversible reaction between amines and aldehydes produces a Schiff base. (*b*) Addition of the enzyme carbonic anhydrase leads to the formation of the preferred sulfonamide compound.

This example shows that the dynamic combinatorial approach requires a reversible reaction that can keep multiple components in equilibrium. A number of such reactions have been used, leading to various types of dynamic libraries. These reactions include peptide bond formation and cleavage to form libraries of peptides that bind to an antibody, photoisomerization of alkenes that changes their shape to fit a target amino acid, transesterification resulting in dynamic libraries of macrocycles that can selectively recognize metal ions, thiol-disulfide exchange that organizes a library of artificial peptide receptors, and scrambling of ligands in zinc complexes to find an effective deoxyribonucleic acid (DNA) binder.

All the above examples, dealing with relatively small libraries, were designed to prove the concept of the dynamic approach. Remarkably, however, all the systems described so far use different base reactions, target compounds, reaction media, and instrumentation. This fact indicates that numerous variations of the dynamic approach can be expected to develop in the future.

Problems. The dynamic combinatorial approach has some inherent problems. One is that it combines two intrinsically different processes: equilibrium between the library components and molecular recognition (selective binding) of the target, which generally require different conditions. One way to overcome this problem is to physically separate the equilibration and binding sites. Such separation has been accomplished by a stepwise approach to the organization of the dynamic libraries (chemical evolution). The target compound is immobilized by attachment to solid beads placed in a continuous-flow column, similar to a chromatography column (selection site). The immobilization does not allow the target to leave the column, and retains the target's properties. When the combinatorial mixture passes through the selection site, the effective components remain, bound to the target. Next, the depleted mixture enters another column (equilibration site), where special conditions, such as heating, catalysis, and irradiation, restore the equilibrium in the combinatorial mixture (**Fig. 4**). During this restoration, part of the mixture converts back into the effective components. The combinatorial mixture then returns to the selection site. After a number of such cycles, the original mixture evolves into a high-affinity subset accumulated on the target-containing beads. Later, this subset can be washed off the target and analyzed to identify the effective components.

Dynamic combinatorial chemistry is an emerging method that can potentially grow into a powerful tool for the discovery of new and useful compounds

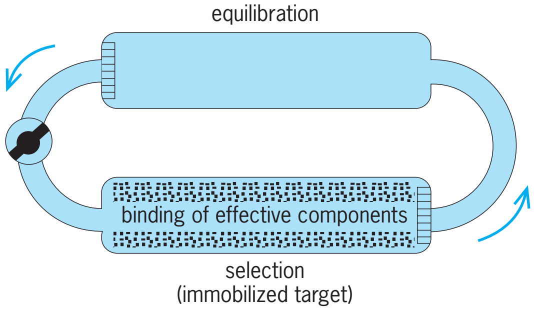


Fig. 4. Separation of equilibration and binding sites in a dynamic combinatorial experiment.

in molecular libraries. This approach may find its niche, for example, in the drug discovery process. The success of this method will depend upon the development of new reversible reactions that can be used to generate the dynamic libraries, and of analytical methods that help identify the structure of components in complex mixtures. **Alexey V. Eliseev**

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Combinatorial synthesis

A method for preparing a large number of chemical compounds, commonly known as a combinatorial library, which are then screened to identify compounds having a desired function, such as a particular biological or catalytic activity. Combinatorial synthesis is an aspect of combinatorial chemistry, which allows for the simultaneous generation and rapid testing for a desired property of large numbers of chemically related compounds. One could regard combinatorial chemistry as the scientist's attempt to mimic the natural principles of random mutation and selection of the fittest. Combinatorial chemistry has already become an invaluable tool in the areas of molecular recognition, materials science, drug discovery and optimization, and catalyst development. *See* COMBINATORIAL CHEMISTRY; ORGANIC SYNTHESIS.

Combinatorial synthesis was developed to prepare libraries of organic compounds containing from a few dozen to several million members simultaneously, in contrast to traditional organic synthesis where one target compound is prepared at a time in one reaction (**Fig. 1**). Thus, a target compound AB, for example, would be prepared by coupling of the substrates A and B in a traditional (orthodox) synthesis and would be isolated after reaction processing (workup) and purification (such as crystallization, chromatography, or distillation). Combinatorial synthesis offers the potential to prepare every combination of substrates, type A_{1-m} and type B_{1-n}, providing a set of compounds, $A_{(1-m)}B_{(1-n)}$. There are two main approaches to combinatorial synthesis: parallel synthesis and split synthesis (also known as split-and-pool or mix-and-split).

Parallel synthesis. In parallel synthesis, each compound is prepared separately in an individual reaction vessel. In order to accomplish parallel combinatorial synthesis, large numbers of reactions must be carried out simultaneously and the resulting products must be isolated and purified very quickly. Recently, various automated devices, such as weighing, reaction, filtration, and chromatography machines, were developed for high-throughput parallel combinatorial synthesis. Another approach employs insoluble reagents that can be removed by filtration from a solution-phase reaction mixture. Acids, bases, reducing reagents, oxidation reagents, or various catalysts are attached to insoluble supports (such as

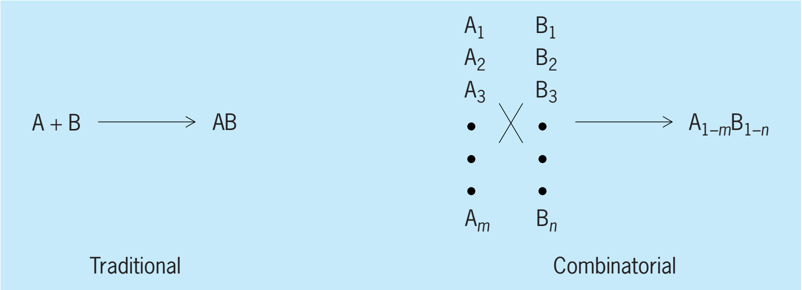

Fig. 1. Traditional synthesis versus combinatorial synthesis.

silica-gel or polymers) in this approach. Functional groups bound to insoluble supports are also applied to scavenge unreacted starting materials in solution.

Transformation of a substrate anchored to an insoluble support by treatment with a solution of reagents, generally called solid-phase synthesis, is a frequently used protocol for combinatorial synthesis. A starting substrate is first attached to a solid support by an appropriate linker group and undergoes various synthetic transformations to furnish a product on the solid support which is readily separated from the unreacted reagents and coproducts in the solution by filtration. The resulting solid-supported product can then be used in subsequent transformation steps. Solid-phase peptide synthesis is a typical example. The final products, as well as the synthetic intermediates, are detached from the solid support on demand. An example of the solid-phase parallel synthesis giving a 3 × 3 = 9-membered library is shown in **Fig. 2**. This library can be screened for optimum "hit" candidates before or after release of the supported products; however, the preferred method for biological screening is to test the compounds in solution after cleavage from the solid support. A_{1-3} and B_{1-3} could be amino acids to give dipeptides, nucleotides to give dinucleotides, or sugars to give disaccharides. *See* NUCLEOTIDE; PEPTIDE.

In both protocols—solution-phase synthesis with solid-supported reagents and solid-phase synthesis with solution-phase reagents—various polymers, glass surfaces, and silica gel are typical solid supports; cross-linked polystyrene beads having appropriate functional groups (such as NH_2, Cl, OH, and COOH) are the most frequently used.

Split synthesis. Polystyrene beads bearing a reactive functional group are also used as a starting support in split synthesis. The beads range from 10 to 200 micrometers in diameter. For example, 1 g of beads having a 100-μm diameter contains about 1 million beads. The split synthesis is illustrated in **Fig. 3** for a library of 3 × 3 × 3 = 27 possible combinations of trimeric products. Three steps of solid-phase synthesis to attach A, B, and C to the starting beads (step 1) are carried out individually to give the supported A, B, and C. The resulting three kinds of beads are suspended in a solvent, mixed by shaking, and filtered to give one portion of a mixture. The pooled mixture of beads is partitioned to three portions where each portion of beads contains A, B, and C in a statistical ratio (1:1:1). Similar manipulations (step 2) afford three portions of beads where each portion contains every combination of nine compounds (from AA to CC) in a statistical ratio. The three portions of a mixture consisting of nine compounds are subjected to coupling with X, Y, and Z (step 3) to give a nine-membered mixture having a terminal group X, a nine-membered mixture having a terminal group Y, and a nine-membered mixture having a terminal group Z, respectively. Finally, the resulting beads are all mixed together to

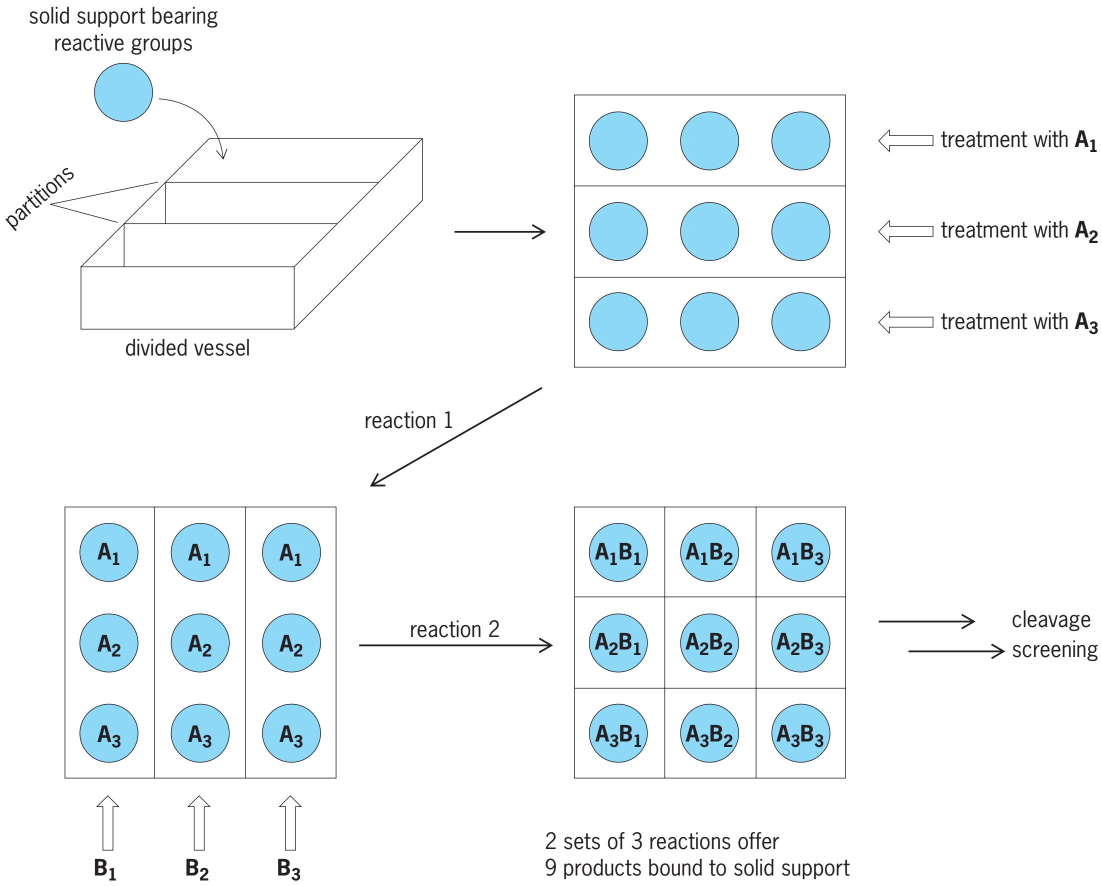

Fig. 2. Solid-phase parallel synthesis of a nine-membered library.

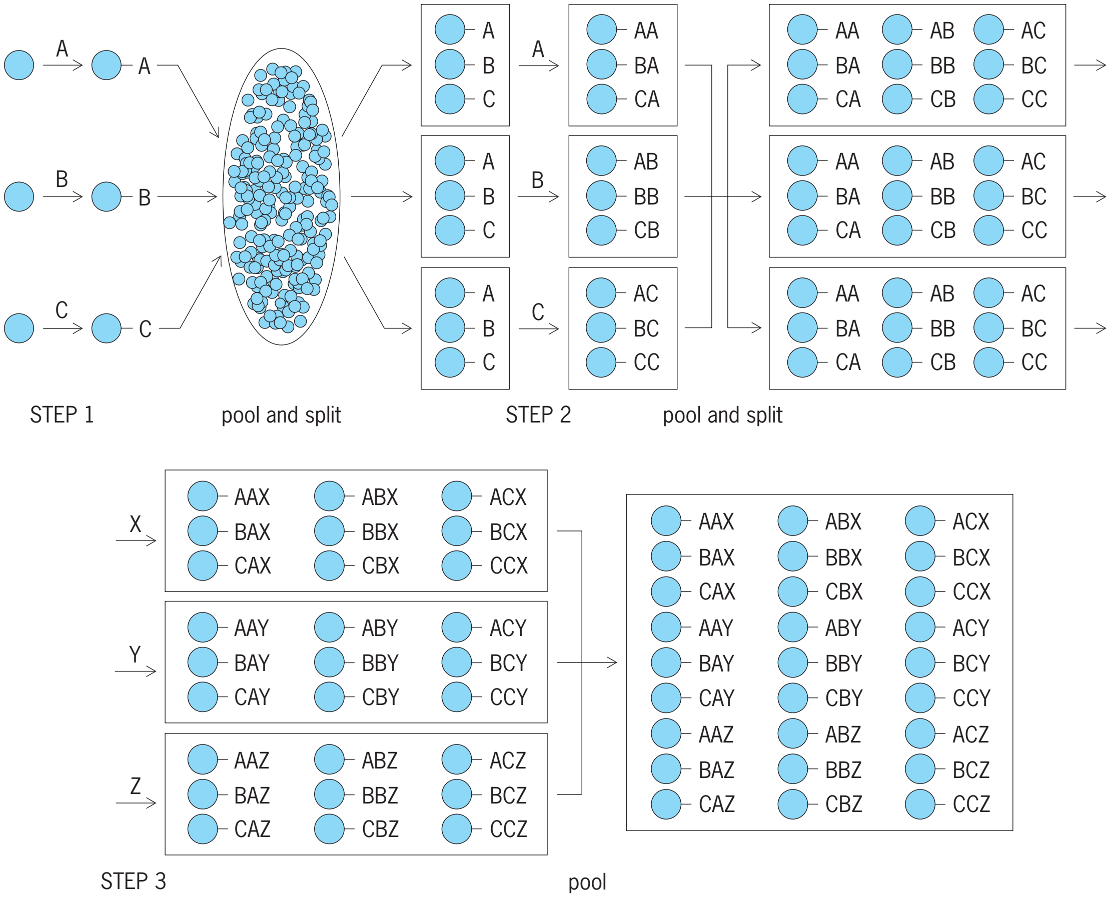

Fig. 3. Solid-phase split synthesis of a library consisting of 27 compounds.

give a library consisting of 27 compounds bound to the solid support, where three sets of three coupling reactions (3 × 3 = 9 manipulations) afford the cube of three ($3^3 = 27$) compounds. In this manner, split synthesis can offer an enormous number of combinatorial products. For example, linear coupling of 10 amino acids five times (10 × 5 = 50 manipulations) can furnish 10^5 pentapeptides. Since one bead of a library prepared by split synthesis must have one compound, the library is also referred to as the one-bead-one-compound library. Identification of the most active compound from the one-bead-one-compound library has gained in popularity with the advent of more efficient methods for one-bead spectroscopic analysis. Yasuhiro Uozumi

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Combinatorial theory

The branch of mathematics which studies arrangements of elements (usually a finite number) into sets under certain prescribed constraints. Problems combinatorialists attempt to solve include the enumeration problem (how many such arrangements are there?), the structure problem (what are the properties of these arrangements and how efficiently can associated calculations be made?), and, when the constraints become more subtle, the existence problem (is there such an arrangement?).

Other names for the field include combinatorial mathematics, combinatorics, and combinatorial analysis, the last term having been coined by G. W. Leibniz in his *Dissertatio de arte combinatoria* (1666) wherein he hoped for application of this field "in the entire sphere of science." Indeed, the availability today of high-speed computers which can deal with large but finite configurations seems to be bringing his prophecy near fulfillment. On the other hand, the study of combinatorial phenomena dates back to the very beginnings of mathematics. According to a Chinese legend recorded in a divinatory book of the lesser Taoists (about 2200 B.C.), the magic square

$$\begin{array}{ccc} 4 & 9 & 2 \\ 3 & 5 & 7 \\ 8 & 1 & 6 \end{array}$$

was observed on the back of a divine tortoise. Apparently, permutations were considered as early as 1100 B.C., and Rabbi Ben Ezra, in the twelfth century, probably knew the formula for the number of k-element subsets of an n-element set.

Enumeration

From the seventeenth well into the twentieth century, combinatorial theory was used primarily to solve certain problems in probability. For example, to compute the probability that exactly three heads appear in five flips of a coin, one need only count the total number of sequences of heads and tails which may occur (32) and divide this number into the number of sequences which result in three heads and two tails (10). *See* PROBABILITY.

Permutations and combinations. In enumeration of arrangements it is always essential to know which arrangements are considered the same and which different. When k objects are to be selected from a set S and different orderings on the selected objects are to be counted separately, the arrangements are called permutations or relabelings of the set of k objects. But if order is to be disregarded, so that attention is focused only on the subset consisting of the k selected elements, then the choice is termed a combination. If elements of S are allowed to be selected more than once, then the arrangements are called permutations with repetition or combinations with repetition. If S has n different elements, Eqs. (1)–(4) enumerate these

$$P(n,k) = n(n-1)(n-2)\cdots(n-k+1) = \frac{n!}{(n-k)!} \tag{1}$$

$$C(n,k) = \binom{n}{k} = \frac{P(n,k)}{k!} = C(n,n-k) \tag{2}$$

$$\overline{P}(n,k) = n^k \tag{3}$$

$$\overline{C}(n,k) = \binom{n+k-1}{k} \tag{4}$$

four basic cases. The number of k-permutations is shown in Eq. (1). In particular, $P(n, n) = n! = n(n-1)\cdots(2)\,2\cdot 1(1)$ is the number of ways to order S. The number of k-combinations (or k-element subsets of S) is shown in Eq. (2). When repetition is allowed, Eq. (3) gives the number of permutations with repetition (or k-tuples) and Eq. (4) gives the number of combinations with repetition. Formula (4), although not as widely known as formula (2), recurs throughout mathematics: for instance, it gives the number of mixed partial derivatives of order k with n variables, or the number of solutions in nonnegative integers of the equation $x_1 + \cdots + x_n = k$. *See* CALCULUS.

Generating functions. The symbol

$$\binom{n}{k}$$

in Eq. (2) is sometimes called a binomial coefficient, because it is the coefficient of x^k in the expansion of $(1+x)^n$ given in Eq. (5). When a finite or infinite

$$C(n,x) = (1+x)^n = \sum_{k=0}^{n} \binom{n}{k} x^k \tag{5}$$

sequence $(a_0, a_1, \ldots)$ is exhibited in this way as the coefficients of a polynomial or series $p(x) = \Sigma a_i x^i$, then $p(x)$ is called a generating function for the sequence. The general method of generating functions was developed by P. S. Laplace in 1812 but had already been used extensively in the eighteenth century by L. Euler. For example, substituting $x = -1$ in Eq. (5) shows that there are exactly as many even subsets of a set as odd subsets (and thus the probability of an even number of heads in n flips of a coin is $^1/_2$). *See* BINOMIAL THEOREM; SERIES.

Recursions. Algebraic identities involving generating functions are often proved from recursions (or difference equations) satisfied by the enumerating sequence. Thus the numbers $C(n,k)$ are uniquely determined by the boundary conditions $C(n,0)=1$ for all n and $C(0,k) = 0$ for all $k > 0$, and by recursion (6). The generating function defined by Eq. (5) satisfies the algebraic identity $C(n,x) = (1+x)C(n-1,x)$.

$$C(n,k) = C(n-1,\ k-1) + C(n-1,\ k) \tag{6}$$

Catalan numbers. The Catalan numbers are given in Eq. (7). They count the ways to insert parentheses in a string of n terms so that their product may be unambiguously carried out by multiplying two quantities at a time. Thus $c_4 = 5$, since *abcde* may be computed by $(ab)(cd)$, $((ab)c)d$, $(a(bc))d$, $a((bc)d)$, or $a(b(cd))$. The Catalan numbers also enumerate the ways to place nonintersecting diameters in a convex polygon with $n + 1$ vertices so that only triangular regions result. Further, c_n gives the number of ways to draw in succession all the balls from a container which originally contains $n - 1$ white balls and $n - 1$ black balls, so that at every stage there are at least as many black balls as white balls remaining in the container. Catalan numbers also appear in the theoretical measurement of preferences. Let A be a finite set, and let f be a function which assigns a real number to each element of A. Then x is said to be preferred to y if $fx \geq f(y) + 1$, and this induces a partial order on the elements of A. Thus, if $A=\{x, y, z\}$ and $f(x) = 0, f(y) = {}^1/_2$, and $f(z) = 1$, the only preference is z to x. Assignments $\{1,2,3\}$, $\{0,1,1\}$, $\{0,0,1\}$, and $\{0,0,0\}$ give the four other essentially distinct preferential orders on A, and, in general, there are $c_n + 1$ such orders on an n-element set.

$$c_n = \frac{1}{n}\binom{2n-2}{n-1} \tag{7}$$

Catalan numbers obey the recursion $c_n = c_1 c_{n-1} + c_{n-2} + \cdots + c_{n-1} c_1$ and have the generating function $c(x) = {}^1/_2\,(1 - \sqrt{1-4x})$, where the root is to be expanded by means of the series form of the binomial expansion.

Stirling numbers. If instead of selecting elements from the set S, it is desired to distribute the elements of S into r indistinguishable cells so that no cell remains empty, there results a set-partition or partition of S into r blocks, and these are counted by the Stirling number of the second kind $S(n, r)$. The Stirling numbers satisfy the boundary conditions $S(n, 1) = S(n, n) = 1$, and the recursion $S(n, r) = S(n-1, r-1) + rS(n-1, r)$ [which may be established by distinguishing within the family of partitions between the distributions for which the first $n-1$ elements of S leave a cell unoccupied which must be filled by the last element and those for which the first $n-1$ elements occupy every cell]. In addition, they satisfy formula (8), where $(x)_r$ stands for falling factorial

$$x^n = \sum_{r=1}^{n} S(n, r)(x)_r \tag{8}$$

$x(x-1)(x-2)\cdots(x-r+1)$. The Bell number, given by Eq. (9), is the total number of partitions

$$B(n) = \sum_{r=1}^{n} S(n, r) \tag{9}$$

of an n-element set. These numbers also give the number of rhyme schemes for a poem of n lines. There are $B(4) = 15$ ways to rhyme a quatrain: *abcd*, *aabc*, *abac*, . . . , *aabb*, . . . , *abbb*, *aaaa*. The Stirling numbers of the first kind, $s(n, r)$, are defined as the coefficients of the generating function of $(x)_n$.

Fibonacci numbers. The Fibonacci numbers are defined by the elementary recursion $f_{n+2} = f_n + f_{n+1}$; $f_0 = 0, f_1 = 1$. Each f_n counts, for example, the number of sequences of $n-2$ zeros and ones with no consecutive zeros. The generating function $f(x)$ of the Fibonacci numbers satisfies the identity $(1 - x - x^2)f(x) = x$, from which the closed form $f_n = (\tau^n - (1-\tau)^n)/\sqrt{5}$; where $\tau = (1+\sqrt{5})/2$, may readily be deduced.

Asymptotic formulas. Occasionally, only a rough estimate of the number of arrangements of a certain kind is desired (for example, to estimate how long a computer will take to list all such arrangements), and then an asymptotic enumeration formula is sought. Thus, $n!$, which is the number of (complete) permutations $P(n,n)$, obeys for large n Stirling's formula (10), where $e = 2.71828\ldots$ [here $f(n) \approx$

$$n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n \tag{10}$$

$g(n)$ means that as n grows without bound the ratio $f(n)/g(n)$ approaches 1]. *See* E (MATHEMATICS).

Integer partitions. An integer partition of n is a nonincreasing sequence of positive integers whose sum is n; the number of these partitions is denoted by $p(n)$. Thus $p(4) = 5$, since 4, $3+1$, $2+2$, $2+1+1$, and $1+1+1+1$ all partition 4. No usable formula for $p(n)$ is known, but Euler discovered an elegant expression for the generating function: $p(x) = (1-x)^{-1}(1-x^2)^{-1}\cdots(1-x^{m)})^{-1}\ldots$. Asymptotically, $p(n)$ obeys formula (11), where e^x is the exponential

$$p(n) \approx \left(\frac{1}{4n\sqrt{3}}\right) e^{\pi\sqrt{2n/3}} \tag{11}$$

function which uses the base e. Thus $p(n)$ is eventually greater than any polynomial function of n but is eventually less than a^n for any $a > 1$.

If the requirement that the sequence be nondecreasing is removed, so that, for example, the partition $1+3$ is considered distinct from the partition $3+1$, then the number of such partitions of n is much easier to count and is 2^{n-1}. If $\overline{p}(n)$ denotes the number of partitions of n into distinct parts, then $\overline{p}(x) = (1+x)(1+x^2)(1+x^3)\cdots$, and if $\overline{p}_k(n)$ is the number of partitions of n into distinct parts whose largest part is at most k, then $\overline{p}_k(x) = (1+x)(1+x^2)\cdots(1+x^k)$.

Partially ordered sets. Results in asymptotic enumeration include a formula for the number of partially ordered sets with n elements. The asymptotic estimate of approximately $2^{n^2/4}$ for the number of partially ordered sets with n elements results from the observation that as n becomes large the partially ordered sets which contain four elements w, x, y, z such that $w < x < y < z$ become asymptotically inconsequential (in the sense that the probability that a random partially ordered set contains a four-element chain approaches zero). *See* LATTICE (MATHEMATICS).

Probabilistic method. A nonconstructive proof technique termed the probabilistic method guarantees the existence of certain configurations by showing that the probability of their occurrence is positive. For any i and j, the existence of a graph all of whose circuits have at least i edges but whose chromatic number is at least j can be demonstrated by this technique. *See* GRAPH THEORY.

Ferrer's diagrams. Associated with an integer partition $n = a_1 + \cdots + a_k$ is an array of dots called its Ferrer's diagram, whose ith row contains a_i dots. Thus $4 = 3 + 1$ gives rise to the diagram $\begin{smallmatrix}\bullet&\bullet&\bullet\\ \bullet&&\end{smallmatrix}$.

A reflection of the diagram through its main diagonal interchanges rows and columns, converting $4 = 3 + 1$ into its dual partition $4 = 2 + 1 + 1$. This correspondence proves a number of identities, such as the number of partitions of n into k parts equals the number of partitions of n which have greatest part k.

Möbius inversion. Another useful counting technique exploits the relationship between a pair of functions f and g defined on a lattice L. Suppose that g satisfies Eq. (12), and that the values of g are known;

$$g(s) = \sum_{s \le t} f(t) \tag{12}$$

then the values of f can be found if the calculation in Eq. (12) can be "inverted" to define f in terms of g. The principle of Möbius inversion states that there is a function $\mu(s, t)$, called the Möbius function of the lattice, defined for pairs of elements (s,t) in L and which depends only on the lattice, such that Eq. (13) holds.

$$f(s) = \sum_{s \le t} \mu(s,t)g(t) \tag{13}$$

For example, assume that the lattice in question is the boolean algebra on the two points H and P. Let the subset $\{H\}$ stand for the property that a specific card in a deck is a heart, $\{P\}$ for the property that it is a picture card, $\{P,H\}$ for the property that it is both a heart and a picture card, and ϕ, the zero of the lattice, for the property that it is neither. As t varies over these four subsets, let $f(t)$ denote the number of cards in the deck which have precisely the property (or properties) t (and no others), and let $g(t)$ denote the number which have at least the property (or properties) t. Then clearly $g(\phi) = 52$, $g(\{H\}) = 13$, $g(\{P\}) = 12$, and $g(\{P,H\}) = 3$, and g and f stand in the relation given by Eq. (12). For boolean algebras the Möbius function is given as follows: $\mu(s,t) = 0$ if s is not a subset of t, and $\mu(s,t) = (-1)^p$ otherwise, where p is the number of elements in t but not in s. [Thus, for all $s \subseteq t$, $\mu(s,t) = 1$ if the difference in sizes of s and t is even and $\mu(s,t) = -4$ if it is odd.] In our example, $f(\phi) = g(\phi) - g(\{H\}) - g(\{P\}) + g(\{P,H\}) = 30$ cards which are neither hearts nor picture cards. *See* BOOLEAN ALGEBRA.

For a general boolean algebra, the Möbius inversion formula for $f(\phi)$ is more often called the principle of inclusion-exclusion, or sieve formula, because at various stages of the summation the correct number is alternately overcounted and then undercounted. Assume S has $n = g(0)$ elements each of which may have some of the properties $P_1, \ldots, P_r$. Further, let $g(i_1, i_2, \ldots, i_k)$ be the number of elements with (at least) properties $P_{i1}, P_{i2}, \ldots, P_{ik}$. Again Eq. (12) is satisfied, so by Eq. (13), one arrives at formula (14) for $f(0) = f(\phi)$.

$$\begin{aligned} f(0) = n - \sum_{1 \le i_1 \le n} g(i_1) + \cdots \\ + (-1)^p \sum_{1 \le i_1 < \cdots < i_p \le n} g(i_1, \ldots, i_p) + \cdots \end{aligned} \qquad (14)$$

Derangements. The derangement numbers D_n count complete permutations (without repetition) subject to the additional constraint that every element be "wrongly labeled." That is, if $S = \{1, \ldots, n\}$, then D_n is the number of ways to order S into sequences $a_1, \ldots, a_n$ such that $a_i \ne i$ for $i = 1, \ldots, n$. If the property P_i of a permutation is that $a_i = i$, then the sieve formula may be applied to prove Eq. (15). In probabilistic terms, Eq. (15) implies that no matter what the size of the decks is, the probability is approximately $1/e$ that two identical and randomly shuffled decks of cards will never have the same card in the same place.

$$\begin{aligned} D_n &= P(n,n) - C(n,1)P(n-1,n-1) \\ &\quad + C(n,2)P(n-2,n-2) - \cdots \\ &= n!\left(1 - 1 + \frac{1}{2!} - \frac{1}{3!} + \cdots \right. \\ &\quad \left. + \frac{(-1)^n}{n}\right) \approx \frac{n!}{e} \end{aligned} \qquad (15)$$

Gaussian coefficients. The Möbius function has been computed for other lattices which arise in enumeration, such as the lattice of all positive divisors of a given integer n (with elements ordered by divisibility), a lattice of integer partitions, the lattice of partitions of an n-element set (ordered by refinement: $s \le t$ if every block of s is contained in a block of t), and the lattice of all subspaces of a vector space of dimension n over a finite field with q elements. The number of subspaces of dimension k in such a vector space is expressed in formula (16) for gaussian coefficients. This apparent rational function of q is, in fact, a polynomial which is the generating function for the numbers $p_{m,k}(n)$ of integer partitions of n into at most m parts whose largest part is at most k, Eq. (17). An easy fact, established from the Ferrer's diagram, is that $p_{m,k}(N) = p_{m,k}(mk - n)$. A much harder result is that the sequence of coefficients is unimodal: $p_{m,k}(n+1) \ge p_{m,k}(n)$ for all $n < mk/2$. *See* LINEAR ALGEBRA.

$$\begin{bmatrix} n \\ k \end{bmatrix}_q = \frac{(q^n - 1)(q^{n-1} - 1)\cdots(q^{n-k+1} - 1)}{(q^k - 1)(q^{k-1} - 1)\cdots(q - 1)} \qquad (16)$$

$$\begin{bmatrix} m+k \\ k \end{bmatrix}_q = \sum_{q=0}^{mk} p_{m,k}(n) q^n \qquad (17)$$

The lattices for boolean algebras, subspaces, and set-partitions show striking similarities [such as the similarity between Eqs. (2) and (16)], which are studied in the general theory of geometric lattices or combinatorial geometries. For example, the methods applied to set partitions to study the four-color theorem of graph theory, when applied to the lattice of subspaces, provide a way to attack the problem of finding efficient error-correcting codes. *See* INFORMATION THEORY.

Magic squares. A (generalized) magic square is an n by n matrix of (not necessarily distinct) nonnegative integers all of whose row and column sums are equal to a prescribed number x. Thus $x = 15$ in the 3×3 magic square given earlier. The number of such magic squares is 1 when $n = 1$, $x + 1$ when $n = 2$, and in general is a polynomial of the form $a_m x^m + a_{m-1}x^{m-1} + \cdots + a_1 x + 1$, where $m = (n-1)^2$. Although the coefficients a_i are not given explicitly in this formula, for each n they may be computed by the method of undetermined coefficients, so that a computer search of magic squares for small values of x will also determine the number of such squares for all values of x. *See* MATRIX THEORY.

Pólya counting formula. If the number of ways to paint the faces of a cube with red and blue is to be computed, formula (3) would seem to give $2^6 = 64$; however, it is reasonable to assume that all six arrangements in which exactly one face is blue are identical, since for all such arrangements a rotation of the cube will make the top face blue. Under the condition that two coloring patterns are to be assumed equivalent if one can be transformed into the other by a rotation, the number of configurations is 10. This number can be derived by exhausting all cases or by the Pólya counting formula. The Pólya formula counts the number of functions from a set D (in the example, the faces of the cube) to a set R (the colors red and blue), with two functions f and g assumed to be the same if some element of a fixed group G of (complete) permutations of D (in this case, the 24 rotations of a cube) takes f into g. Actually, the

Pólya formula provides a way to compute the generating function, with variables $x_1,\ldots,x_k$ corresponding to the elements of R, for which the coefficient of $x_1^{a1} \cdots x_k^{ak}$ is the number of functions which use each x_i value exactly a_i times. (For the painted cube, if x_i = red and x_2 = blue, then the generating function is given by $x_1^6 + x_1^5x_2 + 2x_1^4x_2^2 + 2x_1^3x_2^3 + 2x_1^2x_2^4 + x_1x_2^5 + x_2^6$.) The proof of the Pólya theorem depends on a special case proved earlier by W. Burnside: if G is a group consisting of m (complete) permutations of S, then the number of inequivalent permutations of S is

$$\frac{1}{m}\sum_{\sigma\in G} f(\sigma)$$

Here two permutations π_1 and π_2 are regarded as equivalent if there is some σ in G such that the relabeling that σ effects on the sequence π_1 gives the sequence π_2; and for each σ in G, $f(\sigma)$ denotes the number of permutations of S which do not change when relabeled by σ. *See* GROUP THEORY.

Application of Lefschetz theorem. A wide range of techniques is employed in enumeration theory. For example, the hard Lefschetz theorem from algebraic geometry was used to show that if A is any set of n distinct positive real numbers, and if for any subset B of A, $s(B)$ is the sum of its members, then $s(B)$ is constant on at most $g(n)$ subsets B, where $g(n) = \bar{p}_n([(n + 1)(n)/4])$, the number of partitions of $[(n + 1)(n)/4]$ into distinct parts whose largest part is at most n. Thus $g(n)$ is the middle coefficient of the polynomial $(1 + x)(1 + x^2)(1 + x^3) \cdots (1 + x^n)$ and $g(n)$ is achieved by letting A be the arithmetic progression $\{1,2,\ldots, n\}$ and setting the sum equal to $[(n + 1)(n)/4]$.

Properties of Arrangements

An arrangement is primarily a family of subsets of a set S. An alternate way of formulating this concept is as an incidence system, also called a relation, which specifies when a particular element s of S is in a subset S_i of the family, for example, by means of the incidence matrix $M = [m_{ij}]$ of the family: the rows of the incidence matrix are indexed by the elements $s_1,\ldots, s_n$ of the set S, the columns of the matrix are indexed by the subsets $S_1,\ldots,S_m$ in the family, $m_{ij} = 1$ if s_i is in S_j, and $m_{ij} = 0$ otherwise. For example, if $S = \{s_1,s_2,s_3,s_4\}$, $S_1 = \{s_1, s_2\}$, $S_2 = S_4 = \{s_1,s_3,s_4\}$, and $S_3 = \{s_2\}$, the incidence of matrix of this arrangement is

$$\begin{bmatrix} 1 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 \end{bmatrix}$$

Systems of distinct representatives. If $n = m$ in an incidence system, a system of distinct representatives for the sets is a permutation $a_1,\ldots, a_n$ of S such that a_i is in S_i for $i = 1, 2, \ldots,n$. (In a congressional committee S, where each S_j might denote a particular cause or coalition, it might be desirable to find a system of distinct representatives so that each cause or coalition would have a different proponent.) In the above example, s_1,s_2,s_3,s_4 is such a system.

Marriage theorem. A system of distinct representatives certainly cannot exist unless any k of the subsets S_i together contain at least k distinct elements, and in fact it can be shown that this condition is also sufficient. This theorem is whimsically called the marriage theorem, since if S consists of a collection of n boys and each subset S_i consists of the boys acquainted with a particular girl g_i, then the conditions of the theorem guarantee that each girl could marry a boy of her acquaintance.

Algorithms for finding systems. Algorithms for computers exist which find systems of distinct representatives with reasonable efficiency: as n increases, the time a computer needs to find a system increases as the square of n. *See* DIGITAL COMPUTER.

Permanent. To enumerate the systems of distinct representatives, it is enough to compute the permanent of the incidence matrix defined by $\Sigma m_{1,a\,1}m_{2,a2} \cdots m_{n,an}$, where the sum is taken over all $n!$ permutations $(a_1, a_2, \ldots, a_n)$ of the set of column indices.

Maximal systems. When a complete system of distinct representatives does not exist, the size of a largest possible system is equal to the smallest possible value of the function $n - k + s_{i1\ldots,ik}$ for all possible combinations $S_{i1},\ldots, S_{ik}$ of subsets in the family, where $s_{i1,\ldots,ik}$ is the number of elements in $S_{i1} \cup \cdots \cup S_{ik}$. A related theorem asserts that the minimum number of blocks into which a partially ordered set may be partitioned subject to the constraint that any pair of elements x and y in the same block be related ($x \le y$ or $y \le x$) is equal to the maximum possible size of a set S of pairwise unrelated elements. It is always possible to find such a set S with the further property that any (complete) permutation π which preserves the partial order [if $x \le y$, then $\pi(x) \le \pi(y)$] must take members of S to other members of S. This fact can be used to show that in a boolean algebra the maximum size of S is $C(n, [n/2])$. This number is the middle (largest) binomial coefficient and corresponds to the set S of all subsets of size $[n/2]$.

Assignment problem. Suppose it is desired to assign n workers to do n jobs, and entry a_{ij} of a matrix A measures how well the ith worker does the jth job. An assignment would be a permutation $j_1,\ldots, j_n$ of the jobs so that the ith worker performs the job j_i. The assignment problem requires that one find an assignment maximizing the total utility T, given by Eq. (18).

$$T = \sum_{i=1}^{n} a_{ij_i} \qquad (18)$$

The problem may be solved by introducing auxiliary row and column numbers $u_1,\ldots, u_n$ and $v_1,\ldots,v_n$ subject to the condition $u_i + v_j \ge a_{ij}$ for all i and j. Then Eq. (19) is valid for any assignment,

$$T = \sum_{i=1}^{n} a_{ij_i} \le \sum_{i=1}^{n} u_i + \sum_{j=1}^{n} v_j = R \qquad (19)$$

since in an assignment each row and column is used exactly once. The marriage theorem shows that the maximum utility M of T is equal to the minimum m of R. Further, an algorithm is known which systematically changes the u's and v's to reduce R, arriving at numbers u_i and v_j for which the set of a_{ij}'s such that $a_{ij} = u_i + v_j$ admits a complete system of distinct representatives. For an assignment derived from such a system, $T = R$ and so M is achieved for this T. This method is practical in that the algorithm leads directly to a solution; and since the number of possible assignments is usually very large (for example if $n = 25$, this number is $25! > 10^{25}$), without some guidance there is no practical way to search for the optimal assignment or to recognize it when it is found. Another application of the marriage theorem is to prove topological fixed-point theorems. *See* TOPOLOGY.

Doubly stochastic matrices. A doubly stochastic matrix, a matrix of nonnegative real numbers such that every row sum and every column sum is equal to one, is a real-number analog of a magic square. The set of all n by n doubly stochastic matrices is convex in the sense that if $M_1, \ldots, M_k$ are all doubly stochastic and $a_1, \ldots, a_k$ are nonnegative numbers whose sum is one, then the convex combination

$$\sum_{i=1}^{k} a_i M_i$$

is also doubly stochastic. These matrices in fact form a convex polytope (a generalization of the notion of convex polygon) in euclidean space $\mathbf{R}^{n^2}$, in that their entries are bounded and there are a finite number of vertices (a minimal set of matrices such that every doubly stochastic matrix is a convex combination of elements of this set). The marriage theorem can be used to prove that the $n!$ permutation matrices with exactly one 1 in each row and column are the vertices of the convex polytope of doubly stochastic matrices.

By a theorem in linear programming, linear functions are optimized on the vertices of a convex polytope. For the assignment problem this means that for a more general assignment in which the ith worker spends a fraction m_{ij} of the work time on the jth job and each job is always being worked on (so that the matrix $M = [m_{ij}]$ is doubly stochastic), a maximum utility is obtained when each worker spends all the work time at one job. *See* LINEAR PROGRAMMING.

Upper-bound problem. In a typical problem in linear programming, polytopes in $\mathbf{R}^m$ occur which are defined by n linear constraints, such as those given by (20), where the x_j's are the variables (corresponding to vectors in $\mathbf{R}^m$.

$$\sum_{j=1}^{m} a_{ij} x_j \le b_i \qquad i = 1, \ldots, n \tag{20}$$

Algorithms to maximize linear functions on these polytopes usually involve proceeding from one vertex to another at which the function is greater. [An algorithm was given in 1979 using different (nonlinear) techniques, which guarantees that the number of steps needed to solve any such linear program is no more than a polynomial function of mn, but for most practical applications it has been found that a vertex-to-vertex method such as the simplex algorithm gives a faster answer.] It is important when allocating computer time to place an upper bound on the number of vertices. In 1970 it was shown that the number of vertices of a polytope in $\mathbf{R}^m$ defined by n linear constraints is at most $M(m,n)$, given by Eq. (21).

$$M(m, n) = \binom{n - \left[\frac{m+1}{2}\right]}{n - m} + \binom{n - \left[\frac{m+2}{2}\right]}{n - m} \tag{21}$$

Existence and Construction

In the 1920s R. A. Fisher noted that "the design and analysis of statistical experiments requires the construction of orthogonal Latin squares and balanced incomplete block design." *See* STATISTICS.

Orthogonal Latin squares. A Latin square is a square n by n matrix with entries from the set $N = \{0, 1, \ldots, n-1\}$ so that each number occurs exactly once in each row and exactly once in each column. Two Latin squares are said to be orthogonal if when they are superposed the n^2 cells contain each of the n^2 pairs of numbers from N exactly once. For $n = 3$ one has the superposed orthogonal squares

$$\begin{matrix} 00 & 11 & 22 \\ 12 & 20 & 01 \\ 21 & 02 & 10 \end{matrix}$$

where the first digits form the first square, and the second digits the second square. This square may be used to design an agricultural experiment which tests the interaction of three varieties of grain with three types of fertilizers. A field is divided into nine plots in each of which the choice of grain is made according to the first digit and the choice of fertilizer according to the second digit. The Latin squares assure the even distribution of the varieties of grain and fertilizer in both directions, so that effects such as the variation of the soil are mimimized, and the orthogonality allows the experimenter to try each fertilizer with each variety of grain.

For $n \le 10$ each of these arrays can be viewed as a particular type of magic square whose entries are distinct two-digit numbers and such that each row and column sum is $11n(n-1)/2$ (33 for $n = 3$ and 495 for $n = 10$).

If n is odd, it is easy to construct two orthogonal squares A and B. One takes $A = [a_{ij}]$ and and $B = [b_{ij}]$ where $a_{ij} = i + j$, $b_{ij} = i + 2j$, reducing these sums by n or $2n$ if necessary to put them in the range $0, \ldots, n-1$. If n is a multiple of 4, it is not much more difficult to make a construction. But for n of the form $4m + 2$ it is considerably harder. It is clearly impossible when $n = 2$, and, by an exhaustive trial, G. Tarry showed it to be also impossible for $n = 6$. Euler had

Fig. 1. Two orthogonal Latin squares for $n = 10$. (*Courtesy of Thomas Brylawski*; *Karl Petersen*, *photographer*)

conjectured in 1782 that no pair of orthogonal Latin squares existed for any n of the form $4m + 2$, but in 1959 orthogonal Latin squares were found for every $4m + 2$ greater than or equal to 10 (**Fig. 1**).

Block designs. T. Kirkman posed the following puzzle in the 1850s: Is it possible for 15 schoolchildren to go for walks in 5 groups of 3 every afternoon, so that in seven afternoons every child shall have walked with every other child? This arrangement is indeed possible and the following is a solution, the girls being represented by letters $a, \ldots, o$:

Sun.	Mon.	Tue.	Wed.	Thur.	Fri.	Sat.
abi	*acj*	*adk*	*ael*	*afm*	*agn*	*aho*
cdf	*deg*	*efh*	*fgh*	*ghc*	*hbd*	*bce*
gjo	*hki*	*blj*	*cmk*	*dnl*	*eom*	*fin*
ekn	*flo*	*gmi*	*hnj*	*bok*	*cil*	*djm*
hlm	*bmn*	*cno*	*doi*	*eij*	*fjk*	*glk*

The cited design is a special case of a balanced incomplete block design or (b, v, r, k, λ)-design: an arrangement of v elements or treatments x_i, $i = 1, \ldots, v$, into b subsets or blocks B_j, $j = 1, \ldots, b$, so that each B_j contains exactly k distinct elements, each element occurs in r blocks, and every combination of two elements $x_u x_v$ occurs together in exactly λ blocks.

Counting the total number of plots (incidences of x_i in B_j or symbols in the above arrangement) in two ways—first summing over the blocks and then summing over the treatments, the constraint (22) is obtained.

$$bk = vr \qquad (22)$$

By considering all two-element subsets which contain x, constraint (23) is obtained. The two technical constraints (24) imply that the blocks are incomplete in that none of the blocks contains all or all but one of the treatments and none consists of a single treatment.

$$r(k-1) = \lambda(v-1) \qquad (23)$$

$$2\rangle k\rangle v-1, \lambda\rangle 0 \qquad (24)$$

Steiner triple systems. When $\lambda = 1$ and $k = 3$, such (b, v, r, k, λ)-designs are known as Steiner triple systems, and in this case constraints (22) and (23) imply that v is of the form $6m + 1$ or $6m + 3$. Kirkman himself proved that triple systems exist for all such v.

The schoolchild arrangement has the additional property that the blocks themselves are partitioned into r families called parallel classes of v/k blocks each such that every element occurs in exactly one block of each parallel class. Such designs are termed resolvable. A resolvable Steiner triple system is called a Kirkman triple system, and clearly in this case v must be divisible by three. In 1968 Kirkman triple systems (resolvable balanced incomplete block designs with block size three) were shown to exist for all $v = 6m + 3$.

An application of Steiner triple systems might arise in testing taste preferences among v products if every pair of products is to be compared, but each taster can efficiently taste only three products per day. A Kirkman system will, in addition, give an efficient schedule in which each product is used exactly once each day.

Fisher's inequality. Fisher's inequality states that $b \geq v$ in every design. If $b = v$, then necessarily $k = r$ and the design is called a symmetric (v, k, λ)-design. It is a property of these designs that every two blocks intersect in λ elements, and hence the transpose of the incidence matrix of a (v, k, λ)-design is itself a (v, k, λ)-design. Elementary matrix theory may be used to show that if v is even, then a symmetric design with parameters v, k, λ exists only if $k - \lambda$ is a perfect square; and deep results in number theory have been used to show that when v is odd, there must exist integers c, y, and z not all zero such that Eq. (25) holds.

$$x^2 = (k-\lambda)y^2 + (-1)^{(v-1)/2}\lambda z^2 \qquad (25)$$

See NUMBER THEORY.

Existence for fixed k. If k is fixed, then, for all but finitely many sets of parameters b, v, r, k, λ satisfying Eqs. (22), (23), and (24), there exists a block design having those parameters. When $k \leq 5$, all sets of parameters for which a block design exists have been determined. (A design is simple when $\lambda = 1$.)

Projective planes. When a symmetric design has $\lambda = 1$, condition (23) shows that if $k = n + 1$, then $v = n^2 + n + 1$. In analogy with the points (treatments) and lines (blocks) of a plane in projective geometry, such configurations are called projective planes. In this case, condition (25) states that if the parameter n, called the order of the plane, is of the form $4m + 1$ or $4m + 2$, then integers u and v exist with $n = u^2 + v^2$. Thus an infinite number of possible values of n are excluded, beginning with 6, 14, and 21. Whenever n is a power of a prime (and thus the size of a finite field), a plane exists, namely, the projective plane coordinatized over the field (but these are not the only planes which exist for prime-power orders). In the early part of the twentieth century, planes were constructed over many algebraic systems in which linear equations could be solved, but which were not associative. Planes coordinatized over such systems are different from those coordinatized over fields. The smallest of these planes has order 9 and thus has 91 points. *See* ALGEBRA; PROJECTIVE GEOMETRY.

Non-Desarguesian planes. The theorem of G. Desargues (which states that if corresponding vertices of two triangles lie on three concurrent lines, then the three points of intersection of respective sides of those triangles will lie on a line) holds in general only for those planes which arise from fields, and hence the term non-Desarguesian plane is used for the others. No (necessarily non-Desarguesian) projective plane has been found for any n that is not a prime power [and no n has been excluded except those not satisfying condition (19)]. Whether a projective plane exists for an n that is not a power of a prime is an important unsolved problem in existence theory and projective geometry. Orthogonal Latin squares and projective planes are related in that the existence of a projective plane of order n is equivalent to the existence of a set of $(n - 1)$ n by n Latin squares every pair of which is orthogonal. This would mean that for the first unresolved case, $n = 10$, nine pairwise orthogonal Latin squares must be found to produce a projective plane of order 10. No one has found more than two such squares.

Friendship theorem. Only for trivial projective planes can all the points be paired with all the lines in such a way that the incidence system is dualized, and each line is paired with a point not on that line. Stated differently, this is the friendship theorem: Among n people, if every pair of people has exactly one common friend, then there is someone who knows everyone else.

t-Designs. The concept of a block design in which every pair of elements is in the same number of blocks can be generalized to t-designs with parameters $t - (v, k, \lambda)$, in which each t-element subset of a v-element set is in a fixed number λ of k-element blocks. Every t-design is an s-design for all s such that $0 \leq s \leq t$ where the λ_s are given by Eq. (26), and

$$\lambda_s = \frac{\lambda P(v - s, t - s)}{P(k - s, t - s)} \tag{26}$$

these numbers must all be integers. Formulas (22) and (23) are special cases of Eq. (26), with $\lambda_0 = b$, the number of blocks, and $\lambda_1 = r$, the replication number.

Designs are only known for relatively small values of t. For $t = 3$, there are the inversive planes which, like finite projective planes, combine classical geometry and finite fields. Let P be the points of a finite affine plane coordinatized by a field F with q elements. These points are in correspondence with the elements of an extension field F' with q^2 elements, where each point (r,s) is paired with the element $r + sx$, with x the root of an irreducible quadratic equation (like $\sqrt{-1}$ over the real numbers). An ideal point at infinity, ∞, is added giving $v = q^2 + 1$ points. The blocks are then the images of the set B_0 consisting of the line $\{(s,0)$: s element of $F\}$ along with ∞ under all linear fractional transformations, given by Eq. (27). Here ∞ acts like 1/0 so that Eq. (28)

$$y \to \frac{ay + b}{cy + d} \qquad (a,b,c,d \text{ elements of } F',\ ad = bc) \tag{27}$$

$$\frac{a^{\infty} + b}{c^{\infty} + d} = \frac{a}{c} \tag{28}$$

holds. The blocks (all with $q + 1$ elements) are then called circles (with the original lines in the affine plane corresponding to circles through ∞). Circles have the property that every triple of points determines a unique circle ($\lambda = 1$), and further that if C is a circle which contains p but not q, there is a unique circle which contains q and is “tangent” to C at p.

The construction of t-designs has been closely related to the study of multiply transitive groups. The Mathieu groups give two designs for $t = 5$. One has parameters $5 - (12,6,1)$, and the other has parameters $5 - (24,8,1)$. In the first case, the blocks which contain a fixed three-element subset of points form a design isomorphic to the affine plane of order three, and in the second the blocks through three fixed points form a projective plane of order four.

At present no simple designs are known for $t > 5$. Steiner quadruple systems [designs with parameters $3 - (v,4,1)$] have been constructed for all v congruent to 2 or 4 modulo 6.

Error-correcting codes. The following matrix is the incidence system of a projective plane of order 2 (and symmetric Steiner triple system):

$$\begin{matrix}
1 & 0 & 0 & 0 & 1 & 0 & 1 \\
1 & 1 & 0 & 0 & 0 & 1 & 0 \\
0 & 1 & 1 & 0 & 0 & 0 & 1 \\
1 & 0 & 1 & 1 & 0 & 0 & 0 \\
0 & 1 & 0 & 1 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 & 1 & 1 & 0 \\
0 & 0 & 0 & 1 & 0 & 1 & 1
\end{matrix}$$

Since $k = 3$ and $\lambda = 1$, each row has exactly three 1’s and any two rows overlap in only one of these columns. Thus, any two rows differ in four of their entries. This matrix is an example of a binary block code of distance $m = 4$ and length $n = 7$: a set of codewords, each consisting of a sequence of n binary digits (zeros and ones), such that any two codewords differ in at least m places. If seven messages are coded by rows of the above matrix and one is transmitted to a receiver, the original message can be decoded—even if during transmission one of the 1’s were changed to a 0 or conversely—by choosing the codeword closest to the received sequence. For example, if 1001011 were received, the last codeword was transmitted. On the other hand, if two digits were changed, resulting for example in a received message 1000110, the receiver could not tell whether the intended message corresponded to the first codeword or the second. Such a code will then

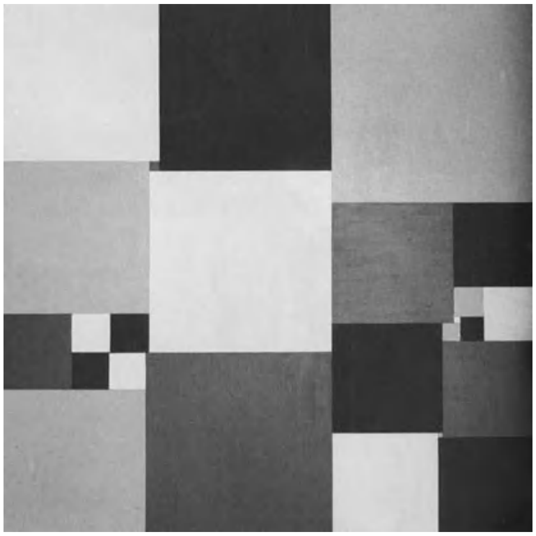

Fig. 2. Subdivision of a square into 26 smaller squares; no two of which are the same size. (*Courtesy of Thomas Brylawski*; *Karl Petersen*, *photographer*)

"correct" one transmission error and decide if an intended codeword with up to three such errors has been correctly transmitted.

In general, a block code will correct up to $[(m-1)/2]$ errors. The fundamental problem in coding theory is to construct codes with a large number of words and large distance but small length. In the example, the size of the code may be increased without decreasing the distance by adding a 1 to the end of all seven codewords, adjoining a new word of eight 1's, and then forming the eight additional words constructed from each of the others by interchanging all 0's and 1's.

Subdivision of square. An elegant combinatorial application of the theories of electrical networks and three dimensional convex polytopes led in the 1940s to the construction of a square subdivided into n smaller squares no two of which are the same size (**Fig. 2**, where $n = 26$). The least number of unequal squares into which a square can be divided is 21, and that, up to symmetry, there is only the following subdivision. A square of length 112 is partitioned into squares of length 50, 35, 27, 8, 19, 15, 17, 11, 6, 24, 29, 25, 9, 2, 7, 18, 16, 42, 4, 37, and 33, respectively, where each square enters the big square as far north as possible and then as far west as possible.

Pigeonhole principle. The pigeonhole (or Dirichlet drawer) principle states that: if a very large set of elements is partitioned into a small number of blocks, then at least one block contains a rather large number of elements. From this result it follows, for example, that any permutation of the numbers from 1 to $mn + 1$ must contain either an increasing subsequence of length $m + 1$ or a decreasing subsequence of length $n + 1$. To see this, associate with each number in the permutation P the pair of numbers (i,d), where i (respectively d) is the length of the longest increasing (respectively decreasing) subsequence in which it is the first element. Then no two numbers in P are associated with the same pair (since if p precedes q, P initiates a longer increasing subsequence if $p < q$ and a longer decreasing subsequence if $p > q$), so that not every number can be associated with one of the mn pairs (i, d), $i = 1, \ldots, m$; $d = 1, \ldots, n$. One can do no better than $mn + 1$, since if the numbers from 1 to mn are arranged sequentially in an n by m array and read off from left to right starting at the bottom, then the longest increasing subsequence has length m and the longest decreasing subsequence has length n. This construction belongs to the field of extremal combinatorial theory, a branch of combinatorics which constructs counterexamples of size n for theorems which hold for all $k \geq n + 1$.

Ramsey's theorem. Ramsey's theorem, proved in the 1930s, generalizes the pigeonhole principle as follows: For any parameters $(r; r_1, \ldots, r_k)$ with each $r_i \geq r$, there exists a number N such that for all $n \geq N$, if S is an n-element set all

$$\binom{n}{r}$$

whose r-element subsets are partitioned into blocks $A_1, \ldots, A_k$, then there is some r_i-element subset S' of S such that all

$$\binom{r_i}{r}$$

of the r-element subsets of S' are in the block A_i. For a given set of parameters, one then asks for the Ramsey number, or smallest N for which the theorem is true. When $r = 1$, by the pigeonhole principle $N = r_1 + \cdots + r_k - k + 1$. For the parameters (2;3,3), the theorem can be interpreted as follows: When the edges and diagonals of a regular polygon with a sufficiently large number N of vertices are all colored red or blue, there are three vertices of the polygon which are also the vertices of a triangle all of whose edges are the same color. One can always find a monochromatic triangle in a hexagon, and the extremal configuration consisting of a pentagon whose edges are red and whose five diagonals are blue shows that the Ramsey number for these parameters is 6.

Analogs of Ramsey's theorem have been proved for graphs, vector spaces, configurations in the Euclidean plane, and (with infinite cardinals as parameters) in set theory. However, very few Ramsey numbers have been computed. For example, when the edges and diagonals of a polygon are colored with four colors, the smallest N which guarantees a monochromatic triangle [that is, for (2;3,3,3,3)] is known only to be between 51 and 63.

Many asymptotic results are known and have interpretations in graph theory. For example, the Ramsey number $(2;3,t)$ is known to be at most $ct^2/\log t$, where c is an absolute constant not depending on t. This means that in any graph with $ct^2/\log t$ vertices and no triangles, there is a subset of t vertices, no two of which are connected by an edge. **Thomas Brylawski**

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Combining volumes, law of

The principle that when gases take part in chemical reactions the volumes of the reacting gases and those of the products, if gaseous, are in the ratio of small whole numbers, provided that all measurements are made at the same temperature and pressure. The law is illustrated by the following reactions:

1. One volume of chlorine and one volume of hydrogen combines to give two volumes of hydrogen chloride.
2. Two volumes of hydrogen and one volume of oxygen combine to give two volumes of steam.
3. One volume of ammonia and one volume of hydrogen chloride combine to give solid ammonium chloride.
4. One volume of oxygen when heated with solid carbon gives one volume of carbon dioxide.

It should be noted that the law applies to all reactions in which gases take part, even though solids or liquids are also reactants or products.

The law of combining volumes was put forward on the basis of experimental evidence, and was first explained by Avogadro's hypothesis that equal volumes of all gases and vapors under the same conditions of temperature and pressure contain identical numbers of molecules. *See* AVOGADRO'S NUMBER.

The law of combining volumes is similar to the other gas laws in that it is strictly true only for an ideal gas, though most gases obey it closely at room temperatures and atmospheric pressure. Under high pressures used in many large-scale industrial operations, such as the manufacture of ammonia from hydrogen and nitrogen, the law ceases to be even approximately true. *See* GAS. Thomas C. Waddington

Combustion

The burning of any substance, in gaseous, liquid, or solid form. In its broad definition, combustion includes fast exothermic chemical reactions, generally in the gas phase but not excluding the reaction of solid carbon with a gaseous oxidant. Flames represent combustion reactions that can propagate through space at subsonic velocity and are accompanied by the emission of light. The flame is the result of complex interactions of chemical and physical processes whose quantitative description must draw on a wide range of disciplines, such as chemistry, thermodynamics, fluid dynamics, and molecular physics. In the course of the chemical reaction, energy is released in the form of heat, and atoms and free radicals, all highly reactive intermediates of the combustion reactions, are generated. *See* FLAME; FREE RADICAL; REACTIVE INTERMEDIATES.

Processes. The physical processes involved in combustion are primarily transport processes: transport of mass and energy and, in systems with flow of the reactants, transport of momentum. The reactants in the chemical reaction are normally a fuel and an oxidant. In practical combustion systems the chemical reactions of the major chemical species, carbon and hydrogen in the fuel and oxygen in the air, are fast at the prevailing high temperatures (greater than 1200 K or 1700°F) because the reaction rates increase exponentially with temperature. In contrast, the rates of the transport processes exhibit much smaller dependence on temperature and are, therefore, lower than those of the chemical reactions. Thus, in most practical flames the rate of evolution of the main combustion products, carbon dioxide and water, and the accompanying heat release depends on the rates at which the reactants are mixed and heat is being transferred from the flame to the fresh fuel-oxidant mixture injected into the flame. However, this generalization cannot be extended to the production and destruction of minor species in the flame, including those of trace concentrations of air pollutants such as nitrogen oxides, polycyclic aromatic hydrocarbons, soot, carbon monoxide, and submicrometer-size inorganic particulate matter. *See* TRANSPORT PROCESSES.

Nitrogen oxides are formed by the capture of atmospheric nitrogen and the oxidation of organically bound nitrogen in fossil fuels in the flame. Both their oxidative formation, and their destruction in high-temperature fuel-rich flame zones are controlled by the chemistry of the interconversions of the nitrogen species in the flame. The oxidation reaction of the trace combustible species may slow down in the tail end of the flame because of the reduced temperature, or it may get quenched in the flow close to cooled walls of the combustion chamber. Hence, the emission of these trace species strongly depends on the rate of their oxidative destruction.

The fine inorganic particulate matter originates from the vaporization of a small fraction of fuel ash, mainly metals in coal and oil ash, and its subsequent condensation to form an aerosol as the combustion products cool down. The chemical transformation of the ash in the course of combustion (for example, the formation of suboxides of reduced melting temperature) has a strong influence on the aerosol formation and emission. *See* AEROSOL.

Types. When the fuel and oxidant are both gaseous, the combustion is called homogeneous. The combustion reactions will commence as the reactants are heated beyond a critical (ignition) temperature. Such a temperature is dependent on the types of the fuel and the oxidant and their mixture ratio, and also on the physical characteristics of the surroundings.

Liquid fuels are usually prepared for combustion by atomization; they are injected into the flame in the form of a spray of fine droplets. The drops vaporize, and the fuel vapor burns in a manner similar to a fuel gas. However, there are two phases present, liquid and gas, and the combustion is called heterogeneous. *See* ATOMIZATION.

The heavy residual fuel oils used in large industrial and utility boilers are not fully vaporizable, and a small fraction (about 10%) of the fuel oil burns in the form of small coke particles in the tail of the flame. Because of the higher carbon-to-hydrogen ratio of petroleum fuels compared to natural gas (the latter being mainly methane), oil flames, with higher concentrations of soot, tend to be more luminous than gas flames. The soot particles, although performing the useful function of increasing the radiating ability of the flame, ought to be completely burned within the combustion chamber to ensure a clean exhaust.

Solid fuels (coal, wood, and agricultural and municipal waste) are often burned on grates, with the fuel lying on the grate as a bed of solids and the air admitted through the openings in the grate. The grate can be stationary or moving, the feed being correspondingly periodic or continuous.

Coal, the most abundant fossil fuel, is burned predominantly in large industrial and utility boilers in pulverized form. After fine grinding, the pulverized coal is pneumatically transported by a fraction of the combustion air or an air–flue-gas mixture to the burner through which it is injected into the combustion chamber. Boiler combustion chambers equipped for burning pulverized coal are large so as to provide ample time for burning even the largest coal particles completely and for cooling the flyash particles below their softening temperature before they leave the combustion chamber. *See* COMBUSTION CHAMBER; FOSSIL FUEL.

Technology. In the early years of the development of modern combustion technology, after World War II, the objectives were to complete combustion in the smallest possible combustion space and with a minimum of air in excess of that which was stoichiometrically required. Environmental concerns changed this agenda, emphasizing the reduction of combustion-generated pollution. This includes emissions of the acid rain precursors, that is, nitrogen oxides and sulfur oxides, and air toxics such as polycyclic aromatic hydrocarbons, soot, and submicrometer-size inorganic particulates. Methods for reducing such emissions include fuel treatment (for example, desulfurization), combustion process modification, and postcombustion fuel-gas cleanup. Of these, the suitable modification of the combustion process is the most cost effective but also the most challenging. Notable examples of the achievements of this method are the significant reduction (up to 95%) of nitrogen oxide emissions from boilers and industrial furnaces obtained by the combination of staged admission of the fuel and the air into the combustion process, the use of flue-gas recirculation, and the use of very fuel lean premixed mixtures in industrial gas turbine combustors. In order to allay environmental concerns and to satisfy tight regulations, it is necessary to combine combustion modifications with fuel treatment and post-combustion cleanup to reduce pollutant emissions further. *See* ACID RAIN; AIR POLLUTION.

Applications. Combustion applications are wide ranging with respect to the fields in which they are used and to their thermal input, extending from a few watts for a candle to hundreds of megawatts for a utility boiler. Combustion is the major mode of fuel utilization in domestic and industrial heating, in production of steam for industrial processes and for electric power generation, in waste incineration, and in propulsion in internal combustion engines, gas turbines, or rocket engines.

Although the specific conditions of the individual applications impose different constraints on technologically acceptable solutions for the common goal of high thermal efficiency with minimal pollutant emission, basic studies of combustion science are a unifying source relevant to the development of clean combustion technologies in diverse fields of practical applications. János M. Beér

Combustion chamber

The space at the head end of an internal combustion engine cylinder where most of the combustion takes place. *See* COMBUSTION.

Spark-ignition engine. In the spark-ignition engine, combustion is initiated in the mixture of fuel and air by an electrical discharge. The resulting reaction moves radially across the combustion space as a zone of active burning, known as the flame front. The velocity of the flame increases nearly in proportion to engine speed so that the distance the engine shaft turns during the burning process is not seriously affected by changes in speed. *See* INTERNAL COMBUSTION ENGINE; SPARK PLUG.

For high efficiency the mixture should burn as quickly as possible while the piston is near top center position (constant-volume combustion). Short burning time is achieved by locating the spark plug in a central position to minimize the distance the flame front must travel. The chamber itself is made as compact as possible for the required volume, to keep the flame paths short (**Fig. 1**). A compact chamber presents less wall area to the enclosed volume, thereby reducing the heat loss from the flame front. Because motion of the flame depends upon transferring heat from the flame to the adjacent layers of unburned mixture, the reduced heat loss increases the flame velocity. One method for increasing flame velocity is to provide small-scale turbulence in the cylinder charge, often by designing the chamber so that part of the piston head comes close to the cylinder head at top center position (Fig. 1*a*). The squish that results forces the mixture in this region into the rest of the combustion chamber at high velocity. The turbulence so produced increases the rate of heat transfer from the flame to the unburned mixture, greatly increasing the flame velocity. Other engines may use high swirl in the intake port and combustion chamber or an auxiliary or precombustion chamber to accomplish the same result (Fig. 1*e*). When a prechamber is used, combustion begins in the richer mixture around the spark plug in the prechamber.

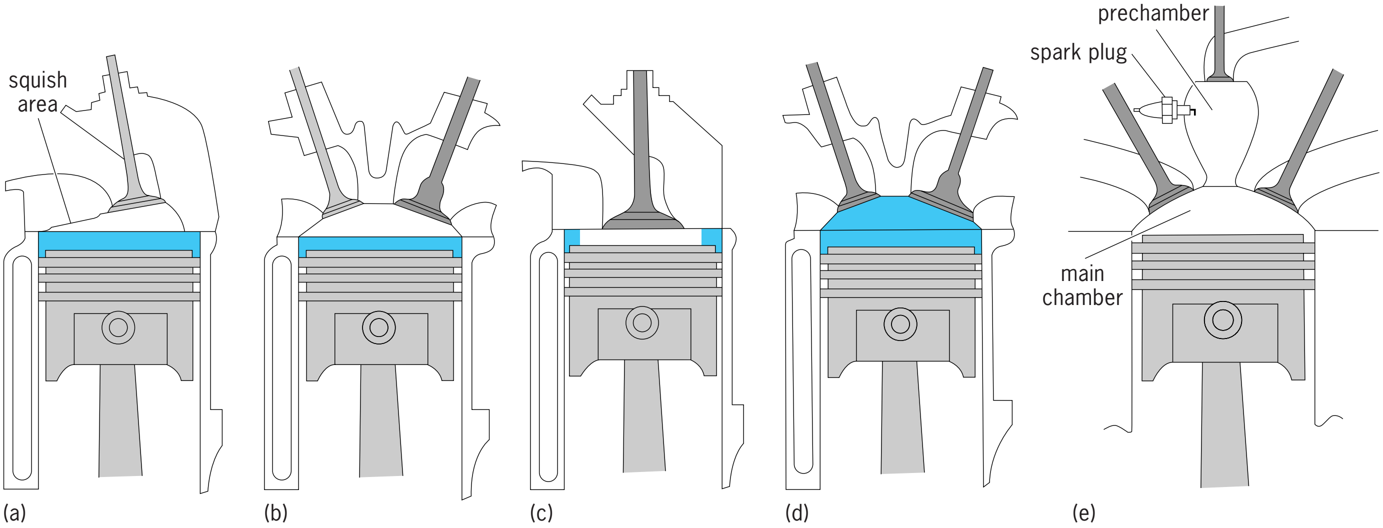

Fig. 1. Various combustion chambers used in spark-ignition engines. (*a*) Wedge. (*b*) Hemispheric (open). (*c*) Bowl-in-piston (cup). (*d*) Crescent (pent-roof). (*e*) Prechamber. (*Automotive and Technical Writing*, *Charlottesville*)

The burning mixture then enters the main chamber, which is filled with a leaner mixture, where combustion is completed. This process is known as stratified charge.

Occasionally a high burning rate, or too rapid change in burning rate, gives rise to unusual noise and vibration called engine roughness. Roughness may be reduced by using less squish or by shaping the combustion chamber to control the area of the flame front. A short burning time is helpful in eliminating knock because the last part of the charge is burned by the flame before it has time to ignite spontaneously. *See* SPARK KNOCK.

For high power output, the shape of the combustion chamber must permit the use of large valves with space around them for unrestricted gas flow. In many engine designs, three and four valves per cylinder are used to provide higher volumetric efficiency. *See* VALVE TRAIN.

Pockets or narrowed sections in the combustion chamber that trap thin layers of combustible mixture between adjacent surfaces interfere with combustion and increase the unburned fuel hydrocarbons normally present in the exhaust gases. Because unburned hydrocarbons are one of the constituents of smog-forming air pollution, the newer combustion chambers have less squish and less surface area per unit of volume. *See* AIR POLLUTION; SMOG.

Compression-ignition engine. In compression-ignition (diesel) engines, the fuel is injected late in the compression stroke into highly compressed air. Mixing must take place quickly, especially in smaller high-speed engines, if the fuel is to find oxygen and burn while the piston remains near top center. After a short delay, the injected fuel ignites from contact with the hot air in the cylinder. There is no flame front travel to limit the combustion rate. Injection may be into either an undivided combustion chamber (direct injection) or a divided combustion chamber (indirect injection) [**Fig. 2**].

During direct injection into an undivided chamber, mixing can be improved by producing a swirl in the intake air so that it is moving relative to the fuel spray (Fig. 2*a*). Swirl velocity increases with higher inlet velocities present at high engine speeds. Therefore, mixing becomes more rapid as the time available for mixing becomes less. Another type of undivided combustion chamber is formed by a narrow cavity in the piston head (Fig. 2*b*). For rapid

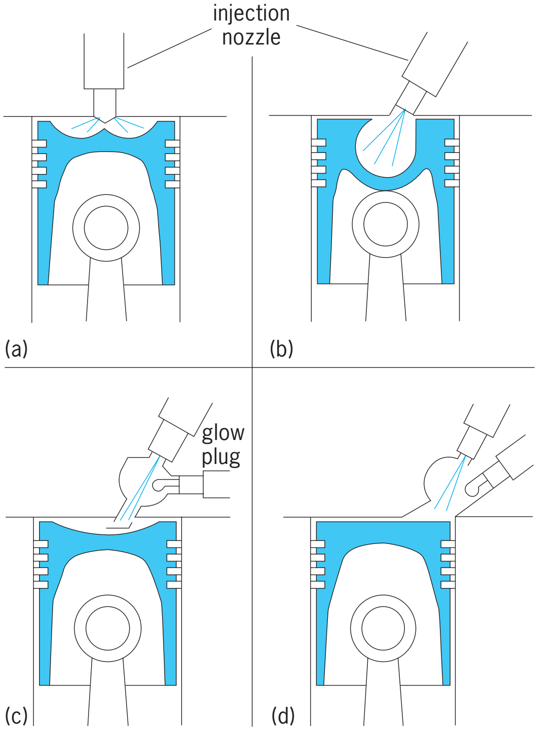

Fig. 2. Various combustion chambers used in compression-ignition (diesel) engines. (*a*) Direct injection. (*b*) MAN M system (German manufacturer). (*c*) Prechamber. (*d*) Swirl chamber. (*Robert Bosch Corp.*)

vaporization, the fuel is sprayed against the hot wall of the combustion chamber in the direction of the swirling air. Smooth combustion with relatively little exhaust smoke results.

Most high-speed diesel engines have indirect injection, in which the combustion chamber is divided into a main and a connected auxiliary chamber. Fuel is sprayed into the auxiliary chamber, where rapid mixing and combustion takes place (Fig. 2*c* and *d*). The burning mixture then issues into the main chamber, where any remaining fuel is burned.

If mixing of fuel and air is too thorough by the end of the delay period, high rates of pressure rise result, and the operation of the engine is rough and noisy. To avoid this condition, the auxiliary chamber in most compression-ignition engines operates at high temperature so that the fuel ignites soon after injection begins. This reduces the amount of fuel present and the degree of mixing at the time that ignition takes place.

High rates of pressure rise can also be reduced by keeping most of the fuel separated from the chamber air until the end of the delay period. Rapid mixing must then take place to ensure efficient burning of the fuel while the piston is near top center. *See* DIESEL ENGINE. Augustus R. Rogowski; Donald L. Anglin

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Comet

One of the major types of objects that move in closed orbits around the Sun. Compared to the orbits of planets and asteroids, comet orbits are more eccentric and have a much greater range of inclinations to the ecliptic (the plane of the Earth's orbit). Physically, a comet is a small, solid body which is roughly 2 mi (3 km) in diameter, contains a high fraction of icy substances, and shows a complex morphology, often including the production of an extensive atmosphere and tail, as it approaches the Sun. *See* ASTEROID; PLANET.

About 10 reasonably bright comets are discovered or rediscovered each year. On the average, one per year is bright enough to be visible to the unaided eye and to generate much interest among the public as well as among comet workers.

Astronomers consider comets to be worthy of detailed study for several reasons: (1) They are intrinsically interesting, involving a large range of physical and chemical processes. (2) They are valuable tools for probing the solar wind. (3) They are considered to be remnants of the solar system's original material and, hence, prime objects to be studied for clues about the nature of the solar system in the distant past. (4) Comets may be required to explain other solar system phenomena.

Present knowledge of comets is heavily influenced by the Halley's Comet campaign in 1986, which included images of the nucleus obtained by spacecraft sent to intercept the comet, and by the extensive studies of the very large Comet Hale-Bopp in 1997. While the data obtained from these comets are invaluable, comets are believed to be highly individualistic. *See* HALLEY'S COMET.

Fig. 1. Comet West as photographed on March 9, 1976, showing the general appearance of a bright comet. The fan-shaped structure emanating from the head or coma is the dust tail, while the single straight structure is the plasma tail. The tails are some 30° in length. (*S. M. Larson*, *Lunar and Planetary Laboratory*, *University of Arizona*)

Appearance. As seen from Earth, comets are nebulous in appearance, and the tail is usually the most visually striking feature. This tail can in some cases stretch along a substantial arc in the sky (**Fig. 1**). Some fainter comets, however, have little or no tail.

The coma or head of a comet is seen as the ball of light from which the tail or tails emanate. Within the coma is the nucleus, the origin of the material in the tail and coma.

Discovery and designation. Comets are discovered by both amateur and professional astronomers. The fainter ones are often discovered by professionals on wide-field images taken for other purposes. In particular, searches for near-Earth objects and other asteroids have dramatically increased the discovery rate of fainter comets. Comets are also being discovered by space-borne solar coronagraphs. Amateurs usually carry out systematic searches of the sky using wide-field binoculars or telescopes. Discoveries are communicated to the Bureau for Astronomical Telegrams, Smithsonian Astrophysical Observatory, Cambridge, Massachusetts, and are then announced by the International Astronomical Union.

In the system for comet designations in use since January 1, 1995, objects are recorded by a letter for the half-month in which they are found; note that the letters I and Z are not used. Thus, the second comet discovered during the second half of February 1995 would be designated C/1995 D2; the C (for comet) is replaced by P if the comet is periodic. The naming of comets carries on the tradition of naming them for their discoverers while striving for fairness and simplicity. For example, Comet C/1995 O1 (Hale-Bopp) was independently discovered by A. Hale and T. Bopp on July 23, 1995, and was the first comet discovered in that half-month period. Comets discovered prior to 1995 retain their old system designation, where the comets in a given year were assigned a letter in order of their discovery. The letter was later replaced by a roman numeral indicating order of perihelion passage. Halley's Comet at its last appearance was first called Comet 1982i, and later became Comet 1986III. Halley's Comet also illustrates the exceptional case of a comet being named after the person who computed its orbit.

Oort Cloud and comet evolution. A major step in understanding the origin of comets was taken in 1950 by J. Oort. He developed the idea that comets are in effect "stored" in a Sun-centered spherical cloud of radius approximately 50,000 AU from the Sun (1 AU is the distance from the Sun to the Earth, 9.3×10^7 mi or 1.50×10^8 km). Occasionally, gravitational perturbations by passing stars or clouds of interstellar gas send comets into the inner solar system, where they are discovered and their phenomena are observed. This process, of course, leads to the eventual destruction of the comet, because passages near the Sun cause a loss of material which is not recovered by the comet. Very rough estimates indicate that a comet loses 0.1% to 1% of its mass at each perihelion passage. Thus, a comet with radius of 0.6 mi (1 km) would lose a layer approximately in the range 1–10 ft (0.3–3 m) thick on each passage. The origin and evolution of comets are discussed in more detail below.

The current view considers the Oort Cloud as a steady-state reservoir which loses comets as just described and gains them from an inner cloud of comets located between the orbit of Neptune and the traditional Oort Cloud. Some comets can enter the inner solar system directly from the innermost part of the inner cloud, called the Kuiper Belt, discussed below. These discoveries mark a trend to expand the study of comets to bodies both larger and smaller than the traditional range. Ideas that periodic comet showers could result from a tenth planet in the inner cloud or a faint solar companion, called Nemesis, are novel but not generally accepted.

Observations. Observations of comets run the gamut of modern observing techniques. These include images in visual and ultraviolet wavelengths, photometry (accurate brightness measurements) in visual and infrared wavelengths, spectral scans in many wavelength regions, radio observations, and observations in extreme ultraviolet wavelengths and x-rays from rockets and orbiting spacecraft above the Earth's atmosphere. Visual wavelength spectra of comets show considerable variation. Ultraviolet spectra, obtained regularly with the *International Ultraviolet Explorer* satellite during its lifetime, have been found to be rather similar. Observations of meteors also contribute to the understanding of comets. *See* ASTRONOMICAL SPECTROSCOPY.

Measurements. The advent of space missions to comets has added an entirely new dimension to obtaining cometary information. A wide variety of direct measurement techniques have already been applied. Mass spectrometers have determined the properties of neutral gases, plasmas, and dust particles (via impact ionization). Dust counters have recorded the fluxes of dust and determined the mass distribution. Magnetometers have measured the strength and orientation of the magnetic field. Further plasma properties have been determined by plasma wave detectors. In addition, detailed imaging of the nucleus was made possible by the space missions. *See* HALLEY'S COMET.

Near-Sun and near-Earth comets. Most comets are observed under so-called normal circumstances; that is, the comet is between 0.5 and 1.5 AU from the Sun and a few tenths of an AU from Earth. Two specific exceptions are discussed here.

While comets have been observed at distances from the Sun of less than 0.1 AU for decades, only in 1979 was it learned that comets occasionally impact the Sun (**Fig. 2**). This fact was determined from a satellite (*SOLRAD*) used to monitor the Sun's corona; hence, the cometary discovery was not planned. The instrument carries an occulting disk which blocks out the bright glare of the Sun's surface, producing

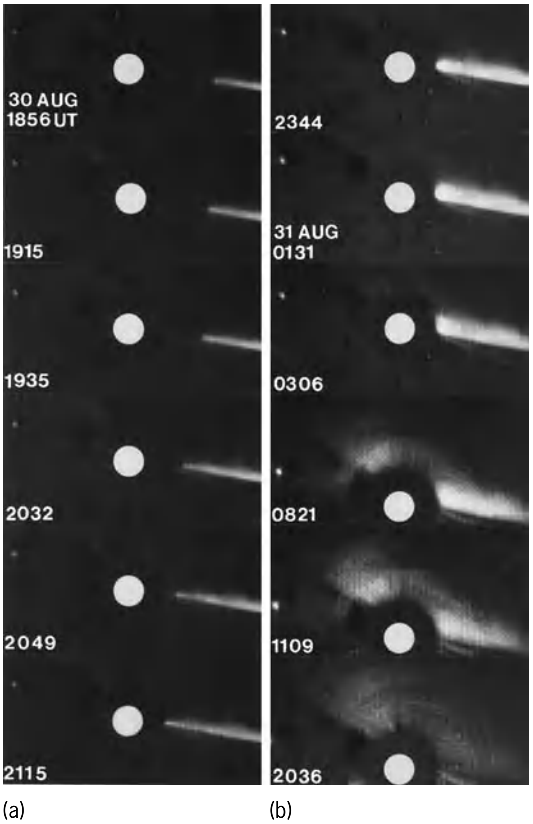


Fig. 2. Sequence of photographs obtained from a *SOLRAD* satellite showing Comet Howard-Koomen-Michels hitting the Sun in August 1979. Captions give date and universal time (Greenwich mean time) of each photograph. (*a*) Before impact. (*b*) After impact. (*Naval Research Laboratory*, *Washington*, *DC*)

a dark circle with an apparent diameter of 5 solar radii. Comet Howard-Koomen-Michels hit the Sun on August 30, 1979; the estimated time of impact was 22^h29^m Greenwich mean time. The comet was clearly photographed (Fig. 2) approaching the Sun, but its reappearance, which would have produced a cometary image on the *SOLRAD* photographs, did not occur. Instead, a brightening of a major portion of the corona was observed which then slowly faded away. The brightening was presumably caused by cometary debris ultimately blown away by the Sun's radiation pressure following the disintegration of the nucleus.

Analysis of the data from this solar monitoring satellite and from other satellites, such as the *Solar Maximum Mission* (*SMM*) and the *Solar and Heliospheric Observatory* (*SOHO*), has turned up many more cometary impacts with the Sun. These results imply that solar impacts by relatively small comets are quite frequent. Observations by *SOHO* led to discovery of many comets and are providing a database for studying cometary phenomena near the Sun.

Comets very near the Earth are rare, but provide unique opportunities for new discoveries. Comet IRAS-Araki-Alcock was another example of a comet being first discovered by a satellite, in this case the *Infrared Astronomical Satellite* (*IRAS*), which also discovered additional comets. This comet passed within 0.031 AU of Earth on May 11, 1983. This distance was only about 12 times the average distance from the Earth to the Moon. Comet Hyakutake passed relatively close to Earth in late March and early April of 1996, thus providing spectacular naked-eye views.

The small distance to Comet IRAS-Araki-Alcock also provided a perfect opportunity to bounce radar waves off the nucleus. The experiment was successful, and the echoes provided evidence for the existence of a solid cometary nucleus with diameter of 0.6 mi (1 km).

The discovery of small comets hitting the Sun and the comets discovered by *IRAS* (including Comet IRAS-Araki-Alcock) imply that small comets are more numerous than had been generally believed. As the details for the origin of comets are worked out, it will be necessary to account for this fact. There has been increasing interest in small comets or comet-like objects, and the number of these objects in the inner solar system may be much larger than previously thought. In the past, the total population of comets might have been an important source of atmospheres for the terrestrial planets as well as a possible source of moderately complex organic molecules necessary for the initial development of life on Earth.

The proposal that the Earth is constantly being bombarded by very large numbers of house-size, icy objects has received considerable public attention. These objects have been called comets, but they are not comets because they do not sublimate. Their origin is unclear, and if they existed, they would have to have extraordinary properties. In sum, their existence is highly unlikely.

Kuiper Belt objects. Observations since 1992 have revealed a major population of large comets in a vast region beyond the orbit of Neptune. This discovery was anticipated about 1950 when K. E. Edgeworth and Gerard Kuiper, working independently, noted that the distribution of mass in the solar system dropped precipitously beyond the orbit of Neptune. They postulated that the missing mass was in a ring of undiscovered bodies in the trans-Neptunian region. These are commonly called Kuiper Belt objects.

Many of these objects, which continue to be discovered, are not small by cometary standards, and they are numerous. Credible estimates place roughly 100,000 objects with diameters larger than 60 mi (100 km) in a ring extending from 30 to 50 AU. Clearly, this is a major, largely unexplored population of cometary objects in this region. *See* KUIPER BELT.

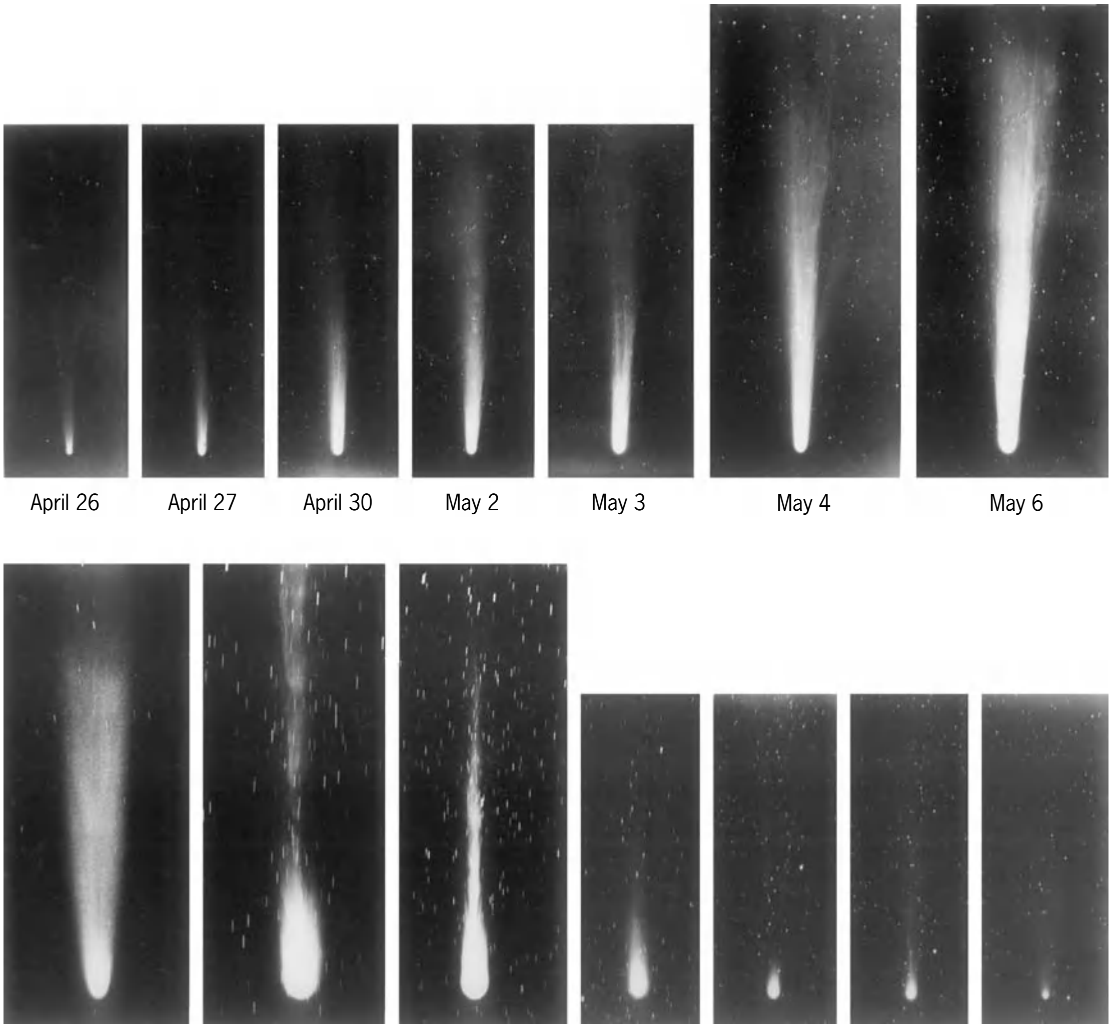
Orbits. The first closed comet orbit to be calculated was Edmond Halley's elliptical orbit for the comet of 1680. This work indicated that comet orbits were ellipses with the Sun at one focus. In subsequent work, Halley noticed the striking similarity of the orbits of what were thought to be three different comets observed in 1531, 1607, and 1682. In 1705 he concluded that these were the same comet with a period of 75 or 76 years, and predicted its return in 1758. This comet is the one bearing Halley's name. It made an appearance in 1910 (**Fig. 3**), and again in 1985 and 1986.

The second comet to have its return successfully predicted was named after J. F. Encke. This comet has the shortest known period, 3.3 years. At its 1838 return, Encke's Comet showed another common property of comets, that is, a steadily changing period. This phenomenon is now known to result from the so-called nongravitational forces which must be explained by any successful comet model.

Six parameters are necessary to describe completely the orbit of a comet. They specify the orientation of the orbital plane in space, the orientation of the orbit in this plane, the size and shape of the ellipse, and the position of the comet along the orbit. In principle, three observations of position on the celestial sphere are sufficient, because each observation consists of independent measures of two coordinates. In practice, definitive orbits are derived from many observations, often hundreds.

While comet orbits are represented by ellipses to a good approximation, there are departures caused by the nongravitational forces and by the gravitational perturbations of the planets. When orbital parameters are listed for a comet, they refer to an ellipse which exactly matches the comet's position and motion at a specific time. Such an osculating orbit, as it is called, forms the starting point for studies of orbital evolution and for accurate predictions of the time and location of a comet's appearance in the sky. *See* CELESTIAL MECHANICS.

Currently, orbital parameters have been determined for roughly 1000 individual comets. Most are classified as long-period comets, that is, comets with


April 26 April 27 April 30 May 2 May 3 May 4 May 6

May 15 May 23 May 28 June 3 June 6 June 6 June 11

Fig. 3. Sequence of photographs showing the changing appearance of Halley's Comet in 1910. (*Carnegie Observatories*)

orbital periods greater than 200 years. The orbital planes of the long-period comets have approximately random inclinations with respect to the ecliptic. This means that there are as many comets with direct orbits (revolving around the Sun in the same sense as the planets) as with retrograde orbits (revolving in the sense opposed to the planets' motion). Careful examination of the original (that is, inbound) orbits of the long-period comets shows none that are hyperbolas; that is, no interstellar comets have yet been observed. This fact strongly implies that the cloud of comets is gravitationally bound to the Sun and therefore is a part of the solar system.

The short-period comets are mostly in direct orbits with inclinations of less than 30°. The distribution of periods shows a peak between 7 and 8 years, and the majority have an aphelion (point of greatest distance from the Sun) near the orbit of Jupiter.

Composition. The many spectroscopic studies and direct spacecraft measurements on the composition of comets have observed numerous species of atoms, molecules, and ions (see **table**). Fairly complex molecules such as polymerized formaldehyde [$(H_2CO)_n$] and methyl cyanide (CH_3CN) are present.

Observations of the gas composition in Halley's coma have found these values by number of molecules: water, approximately 80%; carbon monoxide, roughly 10%; carbon dioxide, approximately 3.5%; complex organic compounds such as polymerized formaldehyde, a few percent; and trace substances, the remainder. These values were obtained from direct measurements, except for that of carbon monoxide, which was determined from a rocket

Atomic and molecular species observed in comets*

Neutrals	Ions
H, OH, O, S, H_2O, H_2CO	CO^+, CO_2^+,
C, C_2, C_3, CH, CN, CO, CS, S_2	H_2O^+, OH^+,
HCN, CH_3CN, NH	H_3O^+
NH_2, Na, Fe, K	CH^+, N_2^+, Ca^+,
Ca, V, Cr, Mn, Co, Ni, Cu	C^+, CN^+
$(H_2CO)_n$	

*Species observed in coma and tail in spectroscopic studies and direct spacecraft measurements.

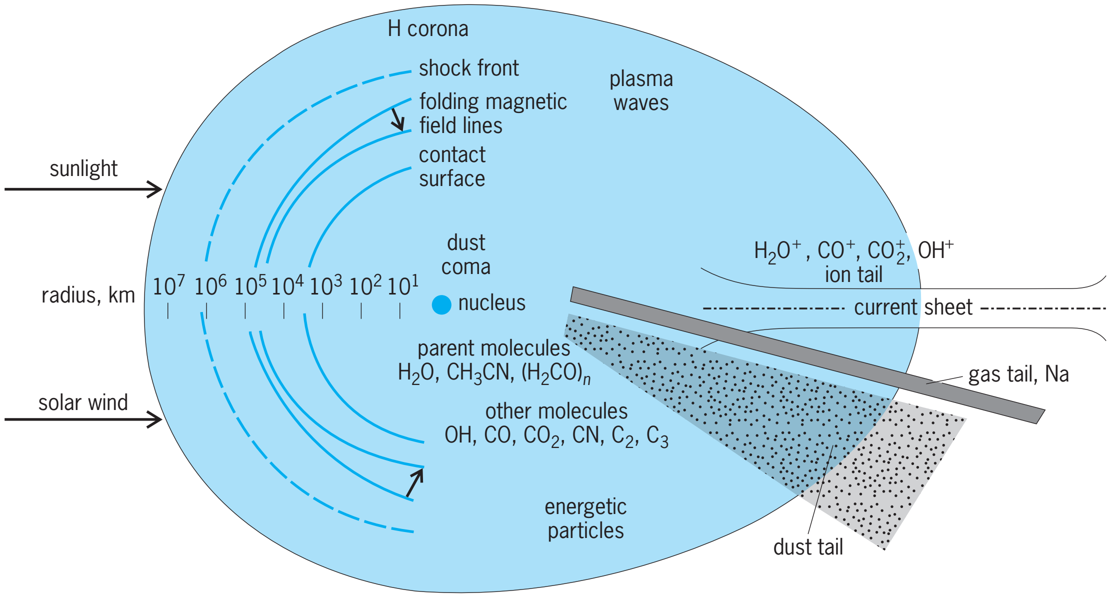


Fig. 4. Cometary features diagrammed on a logarithmic scale. 1 km = 0.6 mi.

experiment. These values are for the outer layers of a comet which has passed through the inner solar system many times. The values of a new comet or the interior of Halley may be different with a higher fraction of carbon dioxide likely.

Measurements of dust composition were made by instruments on the spacecraft sent to Halley's Comet. Some of the particles contain essentially only the atoms hydrogen, carbon, nitrogen, and oxygen; these are the "CHON" particles. Other particles have a silicate composition, that is, they resemble rocks found throughout the solar system. The dominant dust composition is a mixture of these two and resembles carbonaceous chondrites enriched in the light elements hydrogen, carbon, nitrogen, and oxygen.

Structure. The main components of a comet are the nucleus, coma, hydrogen cloud, and tails (**Fig. 4**).

Nucleus. Strong evidence points to the existence of a central nuclear body or nucleus for all comets from which all cometary material, both gas and dust, originates. In the early 1950s, F. L. Whipple proposed an icy conglomerate model of the nucleus. In this model, the nucleus is not a cloud of particles as had previously been thought (the "sandbank" model), but a single mass of ice with embedded dust particles, commonly called a dirty snowball. Such a nucleus could supply an adequate amount of gas to explain cometary phenomena and last through many apparitions because only a relatively thin surface layer would be eroded away (by sublimation) during each passage near the Sun.

The nucleus of Halley's Comet has been directly observed. Its shape was highly irregular, the surface exhibited features and structure, and the albedo (fraction of reflected light) was very low. While the confirmation of the existence of a single, nuclear body is important, Halley is just one comet and generalizations from it may not be valid. *See* ALBEDO.

Fortunately, images of three more nuclei have been obtained. The image of the nucleus of Comet Borelly was taken by the *Deep Space 1* spacecraft on September 22, 2001. The close-up view of the nucleus (**Fig. 5***a*) shows considerable detail and an irregular shape about 5 mi (8 km) long. The image shows smooth terrain around the central part of the nucleus, which is also the part of the nucleus with active jets. The remainder of the terrain is generally inactive and has features identified as pits, troughs, and ridges. The albedo over the surface varies from 0.01 to 0.03; in other words, the surface is very dark.

The image of the nucleus of Comet Wild 2 was taken by the *Stardust* spacecraft on January 2, 2004. The close-up view of the nucleus (Fig. 5*b*) shows detail including an apparent impact crater, and a rounded body with a typical dimension of 2.5 mi (4 km). The albedo is 0.03±0.015; that is, it is also very dark. The surface has high-angle slopes which indicate that the body is cohesive and self-supporting. The images of Comet Wild 2 serve to emphasize the differences with Comets Halley and Borrelly. The diversity of comets is clearly very important.

The generic nuclear body (**Fig. 6**) is irregular, with radius ranging from around 1000 ft (300 m) to 12 mi (20 km). Masses would range in order of magnitude from 10^{11} to 10^{16} kg (10^{11} to 10^{16} lb), with roughly equal parts of snow and dust. The average density would be in the range 0.2 to 2 g/cm^3 (0.2 to 2 times that of water). The interior is probably porous, which means that there are significant voids along with the regions of solid material. Nuclei of comets sometimes split into two or more pieces; Comet West (1976 VI) is an example.

Coma. The coma is observed as an essentially spherical cloud of gas and dust surrounding the nucleus. The principal gaseous constituents are neutral molecules (see table), and the dust composition has

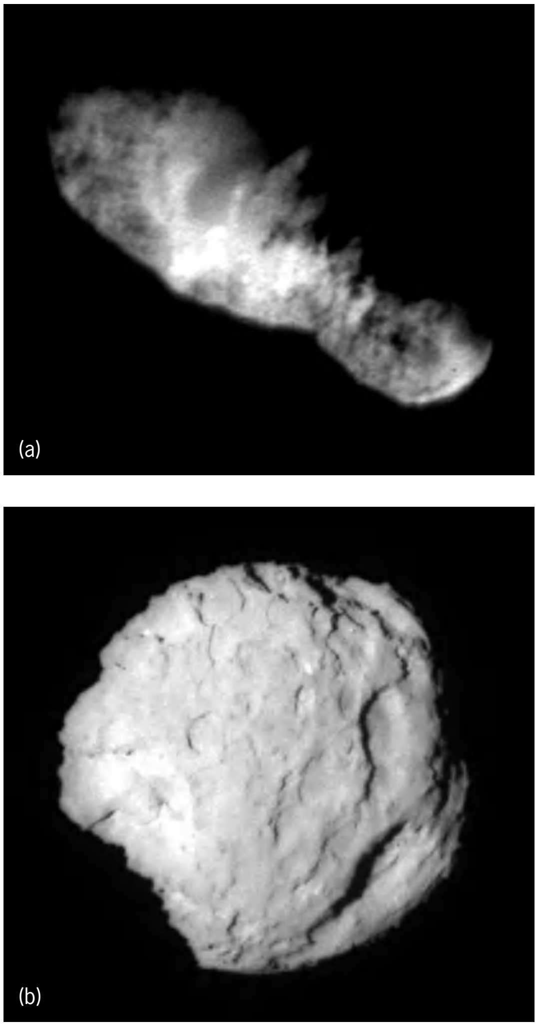


Fig. 5. Images of comet nuclei. (*a*) Close-up image of Comet Borrelly's nucleus taken on September 22, 2001, by the *Deep Space 1* spacecraft (*NASA/JPL*). (*b*) Image of Comet Wild 2's nucleus taken on January 2, 2004, just after closest approach by the *Stardust* spacecraft (*NASA; Stardust mission team*).

been described above. The coma can extend as far as 10^5 to 10^6 km (10^5 to 10^6 mi) from the nucleus, and the material is flowing away from the nucleus at a typical speed of 0.6 mi/s (1.0 km/s). As the gas flows away from the nucleus, the dust particles are dragged along. For comets at heliocentric distances greater than 2.5 to 3 AU, the coma is not normally visible and is presumed not to be present. An exception is Halley's Comet, which displayed an outburst and comalike activity at 14.4 AU.

Hydrogen cloud. In 1970, observations of Comet Tago-Sato-Kosaka and Comet Bennett from orbiting spacecraft showed that these comets were surrounded by a giant hydrogen cloud that extends to distances on the order of 10^7 km (10^7 mi), or a size larger than the Sun. The observations were made in the resonance line of atomic hydrogen at 121.6 nm. Hydrogen clouds have since been observed for many other comets. Fairly bright comets (such as Bennett) have a hydrogen production rate by sublimation from the nucleus at heliocentric distance of 1 AU in the range 3 to 8×10^{29} atoms/s. The size of the hydrogen cloud depends on the velocity of the outflowing hydrogen atoms, and 5 mi/s (8 km/s) has been derived. This velocity would arise (from energy balance considerations) if most of the hydrogen in the cloud were produced by the photodissociation of the hydroxyl radical (OH).

Tails. Photographs of bright comets generally show two distinct types of tails (Fig. 1): the dust tails and the plasma tails. They can exist separately or together in the same comet. In a color photograph, the dust tails appear yellow because the light is reflected sunlight, and the plasma tails appear blue from emission due to ionized carbon monoxide, CO^+.

Studies of features in plasma tails led L. Biermann in 1951 to postulate the existence of a continuous outflow of ionized material from the Sun, which he called the solar corpuscular radiation, now called the solar wind. The interaction of the solar wind and its magnetic field, as suggested by H. Alfvén in 1957, plays an important role in cometary physics and in the formation of plasma tails. The direct measurements on the sunward side by the spacecraft sent to Halley's Comet, on the tailward side by the *International Cometary Explorer* mission to Comet Giacobini-Zinner in 1985, by the *Giotto* spacecraft passing Comet Grigg-Skjellerup in 1992, and by the *Deep Space 1* spacecraft passing Comet Borrelly in 2001 have confirmed these views. *See* SOLAR WIND.

The plasma tails are generally straight and have lengths that range in order of magnitude from 10^7 to 10^8 km (10^7 to 10^8 mi). The Great Comet of 1843 had a plasma tail extending over 2 AU in length. The plasma in these tails is composed of electrons and molecular ions (see table). The dominant visible ion is CO^+. The zone of production for the molecular plasma appears to be in the coma near the sunward side of the nucleus. The material in the plasma tails is concentrated into thin bundles or streamers, and additional structure is found in the tail in the form of knots and kinks. These features appear to move along the tail away from the head at speeds of 6 mi/s (10 km/s) to 120 mi/s (200 km/s). Plasma tails are generally not observed beyond heliocentric distances of 1.5 to 2 AU; an exception is Comet Humason, which showed a spectacular, disturbed plasma tail well beyond normal distances.

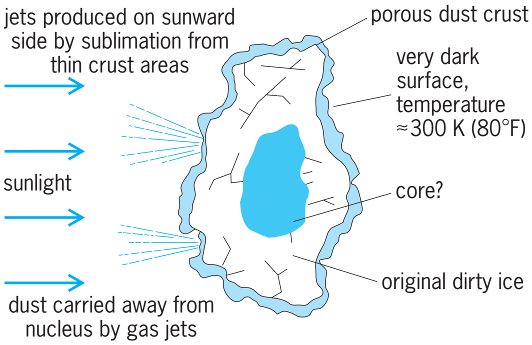


Fig. 6. Schematic model of the cometary nucleus.

The dust tails are usually curved and have lengths that range in order of magnitude from 10^6 to 10^7 km (10^6 to 10^7 mi). Normally, the dust tails are relatively homogeneous; an exception, Comet West, is shown in Fig. 1. Observations indicate that the dust particles are typically 1 micrometer in diameter and are probably silicate in composition. Occasionally dust tails are seen which appear to point in the sunward direction, the so-called antitails. Examples are Comet Arend-Roland in 1957 and Halley's Comet in 1986. These are not truly sunward appendages but are the result of projection effects.

Observations of the bright comet Hale-Bopp have revealed gas tails in the element sodium. One of these is long and narrow (Fig. 4). The other is a diffuse sodium gas tail superimposed on the dust tail. The sodium tails are probably present in all comets but were made more easily visible by Comet Hale-Bopp's large size.

Modern theory. The goal of modern comet theory is to explain the facts about comets outlined above. The broad, theoretical approach appears to be in reasonably good shape and has survived the tests of direct exploration by spacecraft (**Fig. 7**).

Sublimation from nucleus. The cornerstone of the current best ideas is F. L. Whipple's icy conglomerate model of the nucleus. As a comet approaches the Sun on its orbit, sunlight supplies radiant energy to the surface of the nucleus. The energy received heats the nucleus when it is far from the Sun. As the comet

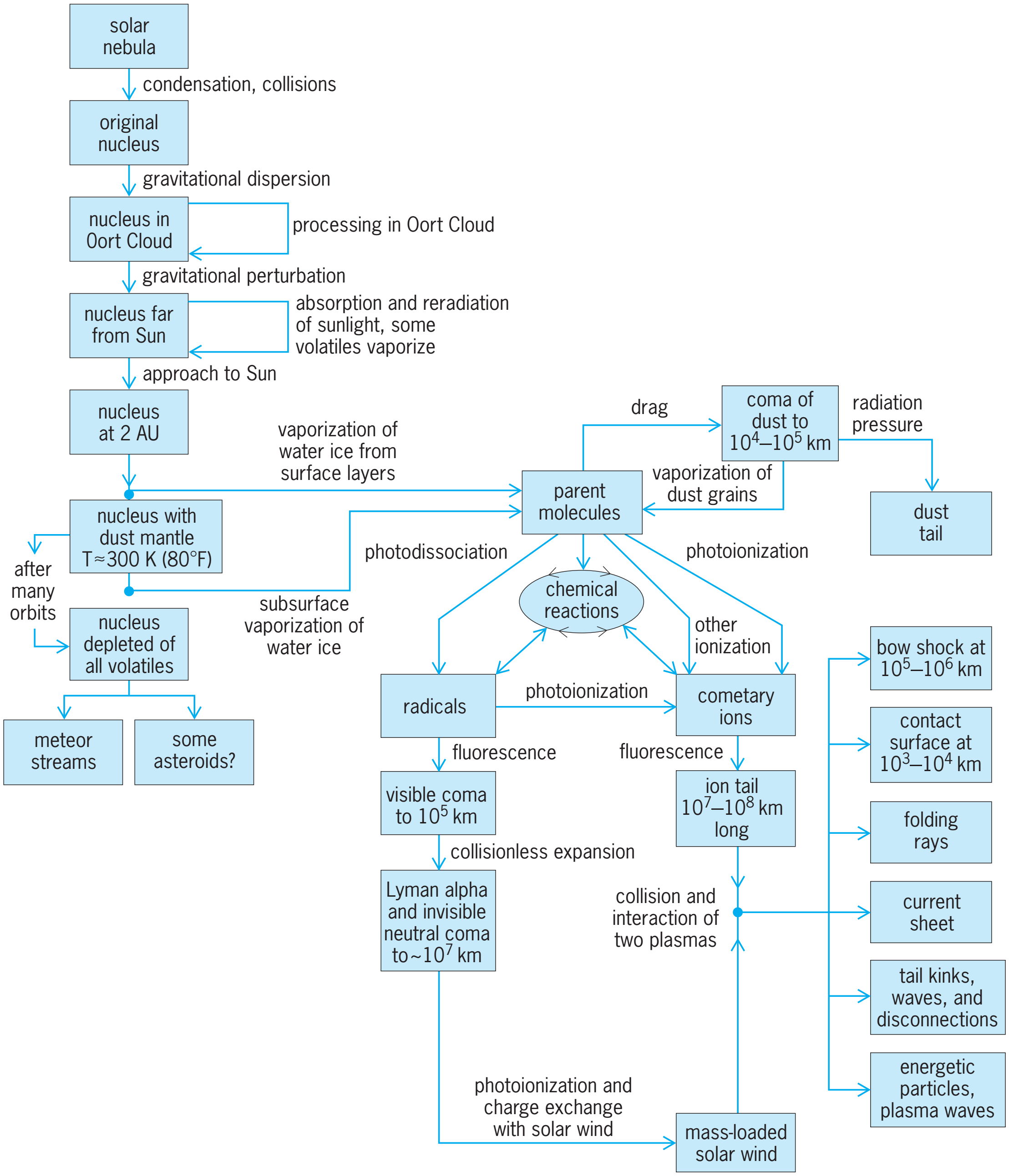


Fig. 7. Summary of processes involved in the formation of comets and the interaction with sunlight and the solar wind. 1 km = 0.6 mi.

continues toward the Sun, the temperature of the surface layers increases to a value, determined by the thermodynamic properties of the ice, where sublimation (passage from the solid state directly to the gaseous state) occurs. Then, most of the incident energy goes to the sublimation of ices. The situation has at least one additional complexity. Sublimation of ice from a dust–ice mixture probably leaves a dust crust which is heated to temperatures higher than the sublimation temperature of water ice. The heat is conducted inward to the ice layers, and the sublimated gases then pass outward through the dust crust. The jets of material seen on Halley's Comet originate in areas of minimal dust crust.

The onset of activity in comets at 2.5 to 3 AU is entirely consistent with water ice as the dominant ice constituent of the nucleus. But a problem still exists. Most other possible constituents are predicted from theory to begin sublimation much farther from the Sun than water ice, but, for example, molecular emissions from CN are visible essentially at the onset of activity.

The solution to this problem lies in the dominant form of water ice found in comets, amorphous ice. Models for the formation of comets treat the process as occurring under low-temperature and low-pressure conditions. When ices form under these conditions, energy is not available to convert the amorphous ice to crystalline ice (a minimum energy state). The transition to crystalline ice takes place at temperatures much higher than the formation temperature. Also, minor constituents are trapped in the amorphous ice. They are partially released when the amorphous ice crystallizes, and the rest is released when the ice sublimates. Some minor constituents may not be trapped in the amorphous ice, and these could be vaporized and released from comets beyond 3 AU, particularly on a comet's first approach to the Sun.

Origin of nongravitational forces. The nongravitational forces have a ready explanation if the cometary nucleus is rotating. The result of radiant energy producing sublimation of ices in an ice-dust mixture is to leave a crust of dusty material. Thus, there is a time lag while the heat traverses the dust layer between maximum solar energy received and maximum loss through sublimation. If the nucleus were not rotating, the maximum mass loss would be directly toward the Sun. For a rotating nucleus, the mass loss occurs away from the sunward direction, toward the afternoon side of the comet. The analogous situation on Earth (that is, the time lag between cause and effect) produces the warmest time of day in the afternoon, not at noon. The mass loss under these circumstances produces a force on the nucleus via the rocket effect (reaction force), and this force can accelerate or retard the motion of the comet in its orbit. Detailed studies of the nongravitational forces in comets show that they are entirely consistent with water ice as the controlling substance.

A possible alternative origin of nongravitational forces is still based on water as the controlling substance. For some comets, simply having a larger mass loss before perihelion compared to after perihelion would produce the nongravitational effects.

Formation of coma. The sublimated gases, mostly neutral molecules, flow away from the nucleus, dragging some of the dust particles with them to form the coma. Close to the nucleus, the densities are high enough that chemical reactions can occur between molecular species. Photodissociation is also important. Thus, the molecules observed spectroscopically far from the nucleus often are not the same as the initial composition.

Formation of dust tails. The dust particles carried away from the nucleus by the flow of coma gases are blown in the antisolar direction by the Sun's radiation pressure to form the dust tails. The detailed theory has been developed through the years, and good agreement can usually be obtained with the observed shapes and sizes of the tails if the emission of dust from the nucleus has a peak before perihelion. The larger particles liberated from the nucleus can orbit the Sun and reflect sunlight to produce the zodiacal light. *See* ZODIACAL LIGHT.

Formation of plasma tails. The gas flowing away from the nucleus has a more involved fate. Under normal circumstances, when a comet's heliocentric distance is about 1.5 to 2 AU or less, significant ionization of the coma molecules occurs (probably by solar radiation), and this triggers a reaction with the solar wind. At the Earth, the solar wind, a fully ionized proton-electron gas, flows away from the Sun at 250–310 mi/s (400–500 km/s) and has an embedded magnetic field. Because of the magnetic field, the ionized cometary molecules cause the solar-wind field lines to slow down in the vicinity of the comet while proceeding at the full solar-wind speed away from the comet. This situation causes the field lines and the trapped plasma to wrap around the nucleus like a folding umbrella, to form the plasma tail. This picture has been completely confirmed by the spacecraft measurements. In addition, the folding can be seen and photographed because of the emission from the trapped ions (such as CO^+) which serve as tracers of the field lines (**Fig. 8**). Thus, while the ionized molecules are indeed swept in the antisolar direction by the solar wind, the plasma tail should be thought of as a part of the comet attached to the near-nuclear region by the magnetic field captured from the solar wind.

Exceptions occur at times apparently when the polarity of the solar-wind magnetic field changes. In terms of solar-wind structure, this polarity reversal takes place when the comet crosses the heliospheric current sheet (HCS). This can disrupt the magnetic connection to the near-nuclear region and literally causes the old plasma tail to disconnect while the new tail is forming. This process is quite common (**Fig. 9**). While the physics of this phenomenon is complex, the observational and theoretical basis is sound.

Fate of comets. When the process of sublimation has been carried out over an extensive period of time, as would be the case for the short-period comets, the ices will be exhausted and the inactive or "dead"

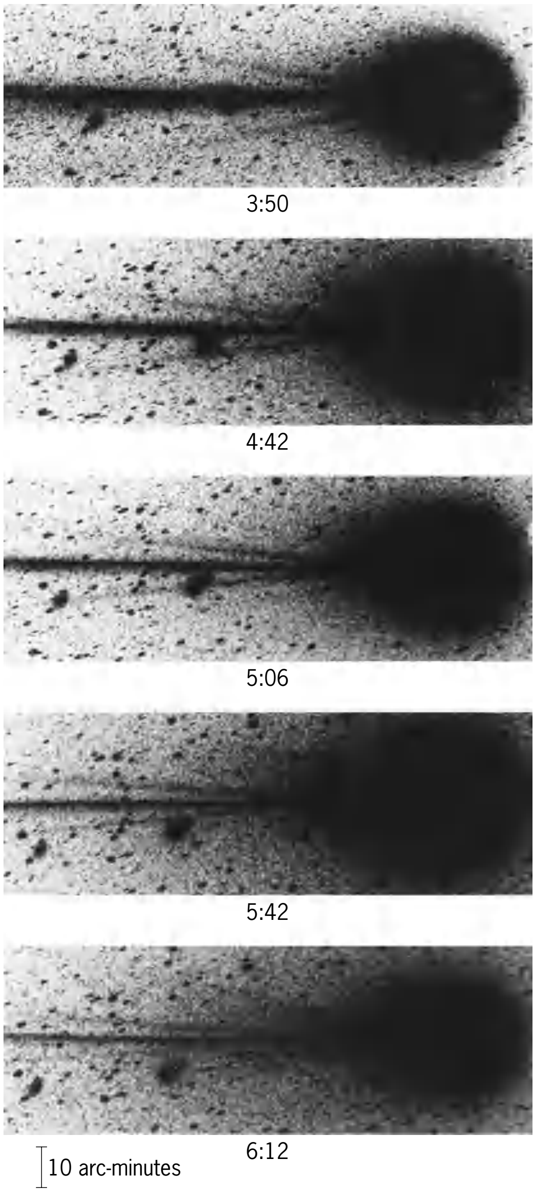


Fig. 8. Sequence of photographs of Comet Kobayashi-Berger-Milon on July 31, 1975, showing the capture of magnetic field from the solar wind. The dominant pair of tail streamers visible on either side of the main tail lengthen and turn toward the tail axis in this sequence. (*Joint Observatory for Cometary Research*, operated by *NASA–Goddard Space Flight Center and New Mexico Institute of Mining and Technology*)

comet should consist of dust particles and larger-sized rocky material. These remnants are dispersed along the comet's orbit by perturbations, and are the particles responsible for producing meteors when they enter the Earth's atmosphere. Small particles, very probably of cometary origin, have been collected by high-flying aircraft. *See* METEOR.

Comet Shoemaker-Levy 9 and Jupiter. Images of Comet Shoemaker-Levy from the Hubble Space Telescope in 1993 and early 1994 show a string of many bright points (**Fig. 10*a***). The comet then consisted of pieces from a larger body torn apart by a close encounter with Jupiter in 1992. This comet's life ended with a spectacular collision with Jupiter over a period of a few days around July 22, 1994 (Fig. 10*b*). These events dramatically illustrate disruption and collisions with other solar system bodies as fates for cometary bodies. *See* JUPITER.

Comet Hyakutake. In late March 1996, Comet Hyakutake came within about 0.1 AU of Earth, providing spectacular views. On the evening of March 25, the plasma tail stretched from near Polaris well to the south. A length of 55° was easily observed, and experienced observers in dark sites reported lengths of 100°, that is, the tail extended more than halfway across the sky.

The comet was very low in dust content, and the plasma was conspicuous. On March 24–25, a superb disconnection event took place (Fig. 9); the disconnected part of the tail could be traced to a distance of at least 35° from the head. The disconnection event and the disturbed appearance of the plasma tail are characteristic of a comet in the stormy equatorial region of the solar wind. The appearance of Comet Hyakutake contrasted with that of Comet Hale-Bopp (**Fig. 11**).

A major unexpected discovery was that Comet Hyakutake is a bright and variable source of x-rays. Searches of databases of satellites observing in x-rays subsequently showed that x-ray emission is a common property of comets. The x-rays are produced when a highly ionized species in the solar wind (such as oxygen ionized six times) exchanges charge (an electron) with neutral molecules in the coma. The

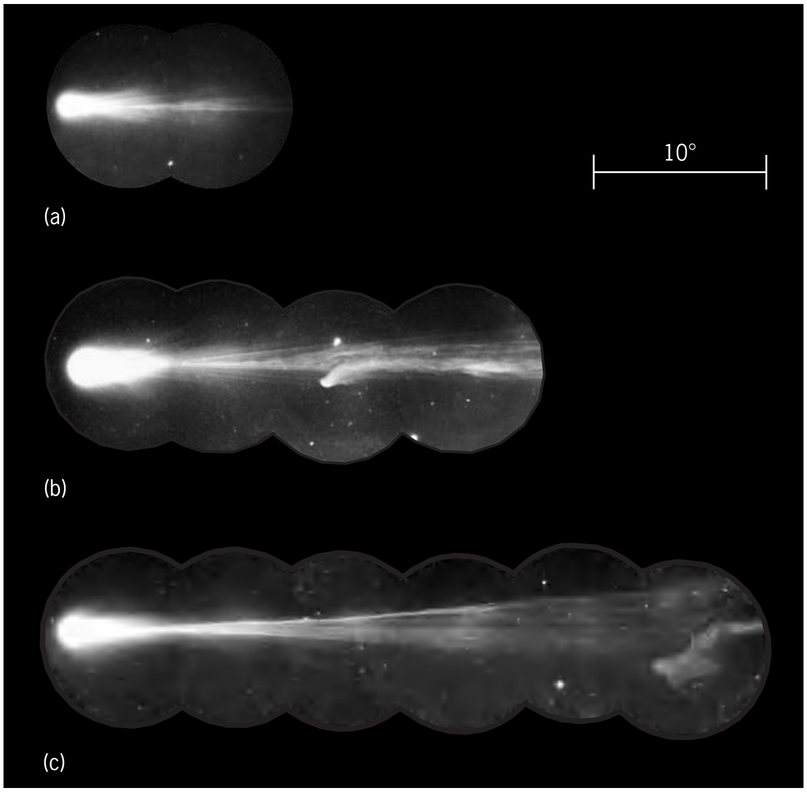


Fig. 9. Photographs of Comet Hyakutake (C/1996 B2) taken on three successive days in March 1996 by Shigemi Numazawa of Niigata, Japan. A spectacular disconnection event is clearly shown, and a new plasma tail immediately forms. (*a*) March 24. (*b*) March 25. (*c*) March 26. (*Courtesy of Sky and Telescope*)

(a) (b)

Fig. 10. Comet Shoemaker-Levy 9. (*a*) Mosaic of three *Hubble Space Telescope* images taken in January 1994. Twenty comet fragments are visible (*H. A. Weaver and T. E. Smith, Space Telescope Science Institute, NASA*). (*b*) Sequence of *Hubble Space Telescope* images of Jupiter showing evolution of impact site of fragment "G," the largest fragment of the comet. From lower left to upper right, the images show the impact plume visible just off the limb about 5 minutes after impact on July 18, 1994; the fresh impact site about 1.5 hours after the impact; the evolved "G" impact site and other impact sites on July 21; and the view on July 23 (*R. Evans, J. Trauger, H. Hammel, HST Comet Science Team, NASA*)

result is a species with reduced ionization (in the previous example, oxygen ionized five times) but in an excited state. These ions spontaneously emit photons in the x-ray wavelength range.

Comet Hale-Bopp. Comet Hale-Bopp provided spectacular views in March and April 1997. Because of the observing circumstances, the comet was often both an evening and a morning object. Its intrinsic brightness can be appreciated by the fact that the comet was never closer to the Earth than 1 AU. Comet Hale-Bopp is clearly the largest comet studied with modern technology, even though no spacecraft was sent to the comet. An extensive body of data was gathered.

Because of the comet's great intrinsic brightness, a large nucleus was suspected. The brightness profile obtained from Hubble Space Telescope images showed a sharp peak that could be identified with light from the nucleus itself. A diameter of about 25 mi (40 km) was inferred. This is a very large nucleus, with roughly 65 times the volume of Comet Halley's nucleus.

Fig. 11. Photograph of Comet Hale-Bopp taken on April 8, 1997, by H. Mikuz and B. Kambik at the Crni Vrh Observatory, Slovenia. The image shows the smooth, white dust tail (right) and the blue plasma tail (left); the latter shows some filamentary structure but is relatively undisturbed. (*Ulysses Comet Watch*)

A wide-field image of Comet Hale-Bopp (Fig. 11) shows large dust and plasma tails. The dust tail was expected because this was a very dusty comet. The appearance of the plasma tail is unusual because of the inclination of the comet's orbit to the plane of the ecliptic of 89.4°. This means that the orbit is almost exactly perpendicular to the Earth's orbit. Comet Hale-Bopp spent months in the calm polar solar wind and was the best-documented comet in the polar region. The relatively undisturbed, almost serene appearance of the plasma tail is a direct consequence of the calm polar-region environment.

Origin. For years, it seemed likely that the population of short-period comets could be produced from the population of the long-period comets—those in Oort's Cloud—by their gravitational interaction with Jupiter. It is now understood that they originate in a ring of comets in the vicinity of the orbits of Neptune and Uranus, and beyond.

The Oort Cloud is the source of the long-period comets. The evidence from the statistics of cometary orbits indicates an essentially spherical cloud of comets with dimensions in the range 10^4 to 10^5 AU. Gravitational perturbations from passing stars and gas clouds have several effects on the cloud. They limit its size and tend to make the orbits random (as observed). Most importantly, the perturbations continually send new comets from the cloud into the inner solar system, where they are observed. Thus, the Oort Cloud can be considered as a steady-state reservoir for new comets. Evidence is mounting for the view that the Oort Cloud is supplied by an inner cloud of comets.

The current consensus on the origin of comets holds that they condensed from the solar nebula at the same time as the formation of the Sun and planets. In other words, although the details are sketchy, comets are a natural by-product of the solar system's origin. They may be remnants of the formation process, and their material may be little altered from the era of condensation to the present time. *See* SOLAR SYSTEM.

The consensus scenario for the origin is as follows. Generally accepted models of the solar nebula have temperature and density conditions suitable for the condensation of cometary materials at solar distances around the orbits of Uranus and Neptune. The condensate could coalesce to produce a ring of comets or cometesimals. Gravitational perturbations by the major planets would disperse the ring of comets, sending some into the inner cloud or Oort's Cloud and sending some inward to become short-period comets.

Some scenarios for formation and evolution assign additional roles to the comets. They may have been a major source of the atmospheres of the terrestrial planets and might even have provided the organic molecules necessary for the evolution of life on Earth. While some of these ideas are speculative, they help show why comets are objects of keen interest and active study, and why several space agencies have launched deep-space probes to comets beginning in the 1980s.

Space missions to comets. Interest in sending a spacecraft to a comet was heightened by the appearance of Halley's Comet in 1985 and 1986. The first mission was the diversion of the third *International Sun-Earth Explorer* (*ISEE 3*) from Earth orbit to pass through the tail of Comet Giacobini-Zinner in September 1985. The spacecraft, renamed *International Cometary Explorer* (*ICE*), measured the properties of the tail, including the magnetic field, and the general plasma environment. For a discussion of the missions to Halley's Comet, also called the Halley armada, *see* HALLEY'S COMET.

One Armada spacecraft, *Giotto*, was diverted to intercept Comet Grigg-Skjellurup in July 1992.

The *Deep Space 1* spacecraft encountered Comet Borrelly in September 2001 and obtained imaging and plasma data, as mentioned above.

The *Stardust* mission was launched in February 1999 and encountered Comet Wild 2 in January 2004. Besides imaging of the nucleus and coma, the mission plan is to bring samples of cometary dust back to Earth. This has been accomplished.

The *Deep Impact* mission to Comet Tempel 1 was launched in January 2005. On July 4, 2005, it sent an 820-lbm (370-kg) impactor spacecraft (mostly copper) into the comet's nucleus. **Figure 12** shows the scene shortly after the impact. Because of the large amount of dust in the plume, the expected crater cannot be seen with certainty. Studies of the plume indicate that the outer layer of the comet (down to tens of meters) consists of fine powdery dust only loosely bound by the gravity of the nucleus.

The *Rosetta* mission to Comet Churyumov-Gerasimenko was launched in March 2004. The journey to the comet takes approximately 10 years, and the plan is highly ambitious. Part of the spacecraft will spend about 2 years near the comet and part will land on the comet's nucleus. The nominal mission end is in 2015.

Fig. 12. Image of Comet Tempel 1, 67 s after the impact, taken from the *Deep Impact* flyby spacecraft. The nucleus and the plume of material from the impact are clearly visible. (*NASA/JPL-Caltech/University of Maryland*)

Comets and the public. There is no scientific evidence for the belief that comets are harbingers, omens, or actual producers of evil, disasters, or natural calamities. Some facts about comets can be distorted to provide an apparent basis for some fears. There are toxic gases in comets, but the amount is very small and, moreover, the cometary gas would not penetrate the Earth's atmosphere. The only real problem would be an impact of a comet on the Earth's surface. The odds of an impact are very small, and studies indicate that the somewhat fragile cometary nucleus would break up high in the Earth's atmosphere. Thus, the Tunguska event, which took place in central Siberia on June 30, 1908, and which produced substantial devastation, is no longer believed to have a cometary origin.

The opportunities for much of the public to view bright comets are becoming increasingly rare due to the combination of atmospheric pollution and bright city lights. In January 1974 there was general public disappointment over the poor visibility of Comet Kohoutek, particularly as viewed from cities in the populous northeastern United States, although it was a conspicuous object to astronomers at mountaintop observatories in the southwestern United States. Halley's Comet was not a spectacular object for public viewing in 1985 and 1986. In part, this was due to the circumstances of the comet's orbit, which led to the comet's times of greatest intrinsic brightness occurring well away from the Earth in contrast to the situation in 1910. The march of light pollution is inexorable, and the interested viewer of comets will require an observing site well away from urban population centers. John C. Brandt

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Comfort heating

The maintenance of the temperature in a closed volume, such as a home, office, or factory, at a comfortable level during periods of low outside temperature. Two principal factors determine the amount of heat required to maintain a comfortable inside temperature: the difference between inside and outside temperatures and the ease with which heat can flow out through the enclosure. *See* CONDUCTION (HEAT).

Heating load. The first step in planning a heating system is to estimate the heating requirements. This involves calculating heat loss from the space, which in turn depends upon the difference between outside and inside space temperatures and upon the heat transfer coefficients of the surrounding structural members.

Outside and inside design temperatures are first selected. Ideally, a heating system should maintain the desired inside temperature under the most severe weather conditions. Economically, however, the lowest outside temperature on record for a locality is seldom used. The design temperature selected depends upon the heat capacity of the structure, amount of insulation, wind exposure, proportion of heat loss due to infiltration or ventilation, nature and time of occupancy or use of the space, difference between daily maximum and minimum temperatures, and other factors. Usually the outside design temperature used is the median of extreme temperatures.

The selected inside design temperature depends upon the use and occupancy of the space. Generally it is between 66 and 75°F (19 and 24°C).

The total heat loss from a space consists of losses through windows and doors, walls or partitions, ceiling or roof, and floor, plus air leakage or ventilation. All items but the last are calculated from $H_l = UA(t_i - t_o)$, where heat loss H_l is in British thermal units per hour (or in watts), U is overall coefficient of heat transmission from inside to outside air in Btu/(h)(ft^2)(°F) (or J/s · m^2 · °C), A is inside surface area in square feet (or square meters), t_i is inside design temperature, and t_o is outside design temperature in °F (or °C).

Values for U can be calculated from heat transfer coefficients of air films and heat conductivities for building materials or obtained directly for various materials and types of construction from heating guides and handbooks.

The heating engineer should work with the architect and building engineer on the economics of the completed structure. Consideration should be given to the use of double glass or storm sash in areas where outside design temperature is 10°F (−12°C) or lower. Heat loss through windows and doors can be more than halved and comfort considerably improved with double glazing. Insulation in exposed walls, ceilings, and around the edges of the ground slab can usually reduce local heat loss by 50–75%. **Table 1** compares two typical dwellings. The 43% reduction in heat loss of the insulated house produces a worthwhile decrease in the cost of the heating plant and its operation. Building the house tight reduces the large heat loss due to infiltration of outside air. High heating-energy costs may now warrant 4 in. (10 cm) of insulation in the walls and 8 in. (20 cm) or more in the ceiling.

Humidification. In localities where outdoor temperatures are often below 36°F (2°C), it is advisable to provide means for adding moisture in heated spaces to improve comfort. The colder the outside air is, the less moisture it can hold. When it is heated to room temperature, the relative humidity in the space becomes low enough to dry out nasal membranes, furniture, and other hygroscopic materials. This results in discomfort as well as deterioration of physical products.

Various types of humidifiers are available. The most satisfactory type provides for the evaporation of the water to take place on a mold-resistant treated material which can be easily washed to get rid of the resultant deposits. When a higher relative humidity is maintained in a room, a lower dry-bulb temperature or thermostat setting will provide an equal sensation

TABLE 1. Effectiveness of double glass and insulation*

		Heat loss, Btu/h†	
Heat-loss members	Area, ft^2 (m^2)	With single-glass weather-stripped windows and doors	With double-glass windows, storm doors, and 2-in. (5.1-cm) wall insulation
Windows and doors	439 (40)	39,600	15,800
Walls	1952 (181)	32,800	14,100
Ceiling	900 (84)	5,800	5,800
Infiltration		20,800	20,800
Total heat loss		99,000	56,500
Duct loss in basement and walls (20% of total loss)		19,800	11,300
Total required furnace output		118,800	67,800

*Data are for two-story house with basement in St. Louis, Missouri. Walls are frame with brick veneer and 25/32-in. (2.0-cm) insulation plus gypsum lath and plaster. Attic floor has 3-in. (7.5-cm) fibrous insulation or its equivalent. Infiltration of outside air is taken as a 1-h air change in the 14,400 ft^3 (408 m^3) of heating space. Outside design temperature is −5°F (−21°C); inside temperature is selected as 75°F (24°C).

†1 Btu/h = 0.293 W.

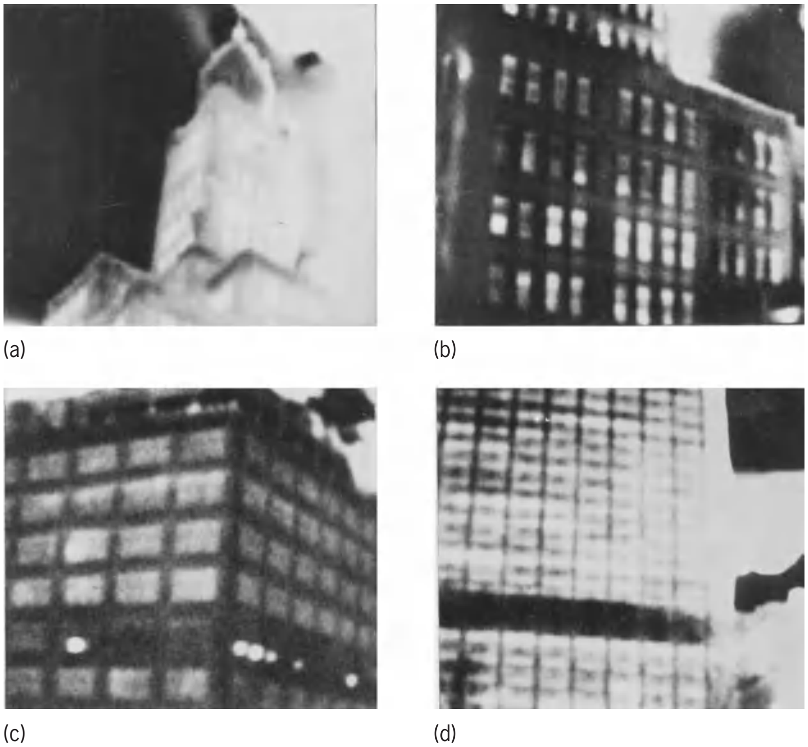
of warmth. This does not mean, however, that there is a saving in heating fuel, because heat from some source is required to evaporate the moisture.

Some humidifiers operate whenever the furnace fan runs, and usually are fed water through a float-controlled valve. With radiation heating, a unitary humidifier located in the room and controlled by a humidistat can be used.

Insulation and vapor barrier. Good insulating material has air cells or several reflective surfaces. A good vapor barrier should be used with or in addition to insulation, or serious trouble may result. Outdoor air or any air at subfreezing temperatures is comparatively dry, and the colder it is the drier it can be. Air inside a space in which moisture has been added from cooking, washing, drying, or humidifying has a much higher vapor pressure than cold outdoor air. Therefore, moisture in vapor form passes from the high vapor pressure space to the lower pressure space and will readily pass through most building materials. When this moisture reaches a subfreezing temperature in the structure, it may condense and freeze. When the structure is later warmed, this moisture will thaw and soak the building material, which may be harmful. For example, in a house that has 4 in. (10 cm) or more of mineral wool insulation in the attic floor, moisture can penetrate up through the second floor ceiling and freeze in the attic when the temperature there is below freezing. When a warm day comes, the ice will melt and can ruin the second floor ceiling. Ventilating the attic helps because the dry outdoor air readily absorbs the moisture before it condenses on the surfaces. Installing a vapor barrier in insulated outside walls is recommended, preferably on the room side of the insulation. Good vapor barriers include asphalt-impregnated paper, metal foil, and some plastic-coated papers. The joints should be sealed to be most effective. *See* HEAT INSULATION.

Thermography. Remote heat-sensing techniques evolved from space technology developments related to weather satellites can be used to detect comparative heat energy losses from roofs, walls, windows, and so on. A method called thermography is defined as the conversion of a temperature pattern detected on a surface by contrast into an image called a thermogram (see **illus.**). Thermovision is defined as the technique of utilizing the infrared radiation from a surface, which varies with the surface temperatures, to produce a thermal picture or thermogram. A camera can scan the area in question and focus the radiation on a sensitive detector which in turn converts it to an electronic signal. The signal can be amplified and displayed on a cathode-ray tube as a thermogram.

Normally the relative temperature gradients will vary from white through gray to black. Temperatures from −22 to 3540°F (−30 to 2000°C) can be measured. Color cathode-ray tubes may be used to display color-coded thermograms showing as many as 10 different isotherms. Permanent records are possible by using photos or magnetic tape.


(a)
(b)
(c)
(d)

Thermograms of building structures: (*a-c*) masonry buildings; (*d*) glass-faced building. Black indicates negligible heat loss; gray, partial loss; and white, excessive loss. (*Courtesy of A. P. Pontello*)

Infrared thermography is used to point out where energy can be saved, and comparative insulation installations and practices can be evaluated. Thermograms of roofs are also used to indicate areas of wet insulation caused by leaks in the roof.

Infiltration. In **Table 2**, the loss due to infiltration is large. It is the most difficult item to estimate accurately and depends upon how well the house is built. If a masonry or brick-veneer house is not well caulked or if the windows are not tightly fitted and weather-stripped, this loss can be quite large. Sometimes, infiltration is estimated more accurately by measuring the length of crack around windows and

TABLE 2. Infiltration loss with 15-mi/h (24 km/h) outside wind

Building item	Infiltration, $ft^3/(ft)(h)$
Double-hung unlocked wood sash windows of average tightness, non-weather-stripped including wood frame leakage	39
Same window, weather-stripped	24
Same window poorly fitted, non-weather-stripped	111
Same window poorly fitted, weather-stripped	34
Double-hung metal windows unlocked, non-weather-stripped	74
Same window, weather-stripped	32
Residential metal casement, $^{1}/_{64}$-in. (0.4-mm) crack	33
Residential metal casement, $^{1}/_{32}$-in. (0.8-mm) crack	52

doors. Illustrative quantities of air leakage for various types of window construction are shown in Table 2. The figures given are in cubic feet of air per foot of crack per hour.

Design. Before a heating system can be designed, it is necessary to estimate the heating load for each room so that the proper amount of radiation or the proper size of supply air outlets can be selected and the connecting pipe or duct work designed. *See* AIR REGISTER; CENTRAL HEATING AND COOLING; HOT-WATER HEATING SYSTEM; OIL BURNER; RADIATOR; STEAM HEATING; WARM-AIR HEATING SYSTEM.

Heat is released into the space by electric lights and equipment, by machines, and by people. Credit to these in reducing the size of the heating system can be given only to the extent that the equipment is in use continuously or if forced ventilation, which may be a big heat load factor, is not used when these items are not giving off heat, as in a factory. When these internal heat gain items are large, it may be advisable to estimate the heat requirements at different times during a design day under different load conditions to maintain inside temperatures at the desired level.

Cost of operation. Design and selection of a heating system should include operating costs. The quantity of fuel required for an average heating season may be calculated from

$$F = \frac{Q \times 24 \times \mathrm{DD}}{(t_i - t_o) \times \ \mathrm{Eff} \ \times H}$$

where F = annual fuel quantity, same units as H
Q = total heat loss, Btu/h (or J/s)
t_i = inside design temperature, °F (or °C)
t_o = outside design temperature, °F (or °C)
Eff = efficiency of total heating system (not just the furnace) as a decimal
H = heating value of fuel
DD = degree-days for the locality for 65°F (19.3°C) base, which is the sum of 65 (19.3) minus each day's mean temperature in °F (or°C) for all the day's of the year

If a gas furnace is used for the insulated house of Table 1, the annual fuel consumption would be

$$F = \frac{56,500 \times 24 \times 4699}{[75-(-5)] \times 0.80 \times 1050} = 94,800\ \mathrm{ft}^3 \ \ (2684\mathrm{m}^3)$$

For a 5°F (3°C), 6–8-h night setback, this consumption would be reduced by about 5%. *See* THERMOSTAT.

Gayle B. Priester

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Comfort temperatures

Air temperatures adjusted to represent human comfort or discomfort under prevailing conditions of temperature, humidity, radiation, and wind. Theoretical formulas attempt to compare the rate of heat loss to surroundings with rate of heat production by work and metabolism. Most modern empirical relations, based on relative comfort expressed by human subjects under differing atmospheric combinations, attempt to indicate the temperature at which air at some standard humidity, air motion, and radiation load would be just as uncomfortable (or comfortable). Many former indices, however, had arbitrary scales.

Heat is produced constantly by the human body at a rate depending on muscular activity. For body heat balance to be maintained, this heat must be dissipated by conduction to cooler air, by evaporation of perspiration into unsaturated air, and by radiative exchange with surroundings. Air motion (wind) affects the rate of conductive and evaporative cooling of skin, but not of lungs; radiative losses occur only from bare skin or clothing, and depend on its temperature and that of surroundings, as well as sunshine intensity.

As air temperatures approach body temperature, conductive heat loss decreases and evaporative loss increases in importance. Hence, at warmer temperature, humidity is the second-most important atmospheric property controlling heat loss and hence comfort, and the various sensible temperature formulas incorporate some humidity measure. *See* BIOMETEOROLOGY.

Temperature and humidity. Almost a century ago, wet-bulb temperature was thought to indicate human comfort under warm conditions, especially in deep mines, ship engine rooms, and steel mills and other factories, on the assumption that sweaty skin approximated a wet bulb. It was superseded after 1923 by the effective temperature, which combined dry- and wet-bulb temperatures, at constant low-ventilation rate, as evaluated by 300 trained subjects walking between controlled-environment rooms. In the 1950s this was approximated by the discomfort index, soon renamed temperature-humidity index (THI) and used by the Weather Bureau (now National Weather Service) for several years. In Canada it was called humidity index. It is calculated by either Eq. (1) or Eq. (2), where the air

$$\mathrm{THI} = 15 - 0.4(t_a + t_w) \qquad (1)$$

$$\mathrm{THI} = t_a - 0.55(1 - \mathrm{RH})(t_a - 58) \qquad (2)$$

and wet-bulb temperatures—t_a and t_w respectively—are expressed in °F and relative humidity (RH) is expressed as a decimal fraction. Except in saturated air (RH = 1.0, that is, 100%), the temperature-humidity index is usually lower than air temperature. A different temperature-humidity index was used in 1980 by another National Weather Service office to compute a heat wave index, ranging from 0 (mild) to 15 (extreme).

A simple average of air temperature in °F and relative humidity in percent was called humiture in 1937, and was changed in 1959 to a simple average of dry- and wet-bulb temperatures in °F. Later, this was further changed to an average of air temperature in °F and excess vapor pressure e, above 10 millibars, with the saturation vapor pressure at 45°F. This index is called humidex in Canada. The originator of humidex opposed raising the threshold to 21 mb (saturation at 65°F), which was being used by at least one television weatherperson. No two of these formulations are equivalent, but each is usually less than air temperature. *See* AIR TEMPERATURE; HUMIDITY; PSYCHROMETRICS.

Wind and radiation. Meanwhile, more refined measurements led to more elaborate formulas involving all aspects of heat loss. Operative temperature modifies effective temperature to include radiation at constant wind speed, and standard operative temperature considers also temperature and heat conduction of skin. The 1955 heat stress index, essentially the ratio of evaporation needed to maintain a stable body temperature to the evaporation possible under existing conditions and working rate, has been evaluated by a detailed computer program. The 1979 apparent temperature, a very complete formulation, is calculated by use of a nomograph or computer as the heat index of the National Oceanic and Atmospheric Administration (see **illus.**). It is a nonlinear combination of air temperature and relative humidity, adjusted for wind.

A less detailed graphic computation yields a similar but not equivalent value known as humisery. Another approach uses the shaded comfort-factor thermometer, which is a large bulb half-covered by a wetted cloth so that air temperature, wet-bulb temperature, wind, and radiation are integrated into a single number similar to a Fahrenheit temperature; most people are said to be comfortable at values from 63 to 72.

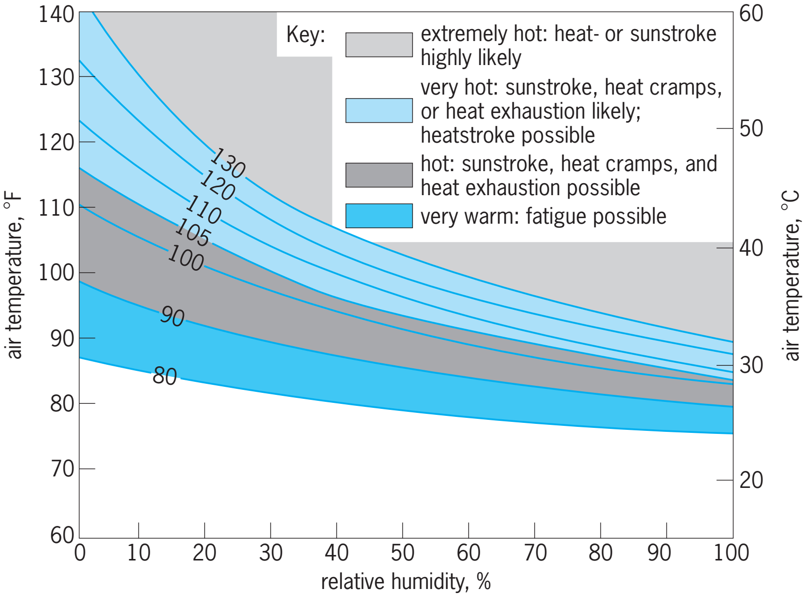
Cold conditions. Under cold conditions, atmospheric moisture is negligible and wind becomes important in heat removal. Wind chill, given by Eq. (3),

$$H = (10.45 + 10\sqrt{v} - v)(33 - t) \qquad (3)$$

where H represents heat loss in kcal/(m^2)(h^2), does not estimate sensible temperature as such, but rather heat loss in kcal/(m^2)(h) for wind speed v in m/s and air temperature t in °C.

The formula was based on the rate of freezing, at various temperature-wind combinations during the Antarctic winter, of water in a plastic cylinder, not on responses of human subjects. It has never been validated by the latter approach. Nevertheless, the temperature at which the estimated heat loss at some reference wind speed equals that at the existing temperature-wind combination is the wind chill temperature. The reference wind speed is variously 3 mi/h, 3 knots, or 4 mi/h, and in a revised formulation is 0.

Arnold Court



Heat index used by the National Weather Service, National Oceanographic and Atmospheric Administration. The numerical values on each curve represent a heat index, that is, apparent temperature in °F.

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Commelinales

An order of flowering plants, division Magnoliophyta (Angiospermae), which is included in the subclass Commelinidae in the class Liliopsida (monocotyledons). It consists of 4 families and about 1000 species, the bulk of which is in the families Commelinaceae (about 700 species) and Xyridaceae (about 200 species). The order is marked by its flowers that ordinarily have the perianth well differentiated into sepals and petals but do not have nectaries or nectar. The ovary is consistently superior and the fruit capsular. The wandering Jew (species of *Tradescantia* and *Zebrina* in the Commelinaceae) belongs to this order. *See* COMMELINIDAE; LILIOPSIDA; MAGNOLIOPHYTA; PLANT KINGDOM.

Arthur Cronquist; T. M. Barkley

Commelinidae

A subclass of the class Liliopsida (monocotyledons) of the division Magnoliophyta (Angiospermae), the flowering plants, consisting of 7 orders, 16 families, and nearly 15,000 species. The orders include Commelinales, Eriocaulales, Restionales, Juncales, Cyperales, Hydatellales, and Typhales. For further information see separate articles on each order.

These monocotyledons are syncarpous (the carpels are united in a compound ovary) or pseudomonomerous (reduced to a single carpel from a syncarpous ancestry). The endosperm is usually starchy, and the perianth is either well differentiated into sepals and petals or more or less reduced and not petallike. The stomates have two or more subsidiary cells, the pollen is either binucleate or more often trinucleate, and the endosperm may be nuclear. Many of the families have well-developed vessels in all vegetative organs. Several of the orders of Commelinidae have often been treated as a single order Farinosae or Farinales. *See* LILIOPSIDA; MAGNOLIOPHYTA; PLANT KINGDOM.

Arthur Cronquist; T. M. Barkley

Common cold

An acute infectious disorder characterized by nasal obstruction and discharge that may be accompanied by sneezing, sore throat, headache, malaise, cough, and fever. The disorder involves all human populations, age groups, and geographic regions; it is more common in winter than in summer in temperate climates. Most people in the United States experience at least one disabling cold (causing loss of time from work or school or a physician visit) per year. Frequencies are highest in children and are reduced with increasing age.

Most, or possibly all, infectious colds are caused by viruses. More than 200 different viruses can induce the illness, but rhinoviruses, in the picornavirus family, are predominant. Rhinoviruses are small ribonucleic acid–containing viruses with properties similar to polioviruses. Other viruses commonly causing colds include corona, parainfluenza, influenza, respiratory syncytial, entero, and adeno. *See* ADENOVIRIDAE; ENTEROVIRUS; PARAINFLUENZA VIRUS; RHINOVIRUS.

Cold viruses are spread from one person to another in either of two ways: by inhalation of infectious aerosols produced by the sneezing or coughing of ill individuals, or by inoculation with virus-containing secretions through direct contact with a person or a contaminated surface. Controlled experiments have not shown that chilling produces or increases susceptibility to colds. Infection in the nasopharynx induces symptoms, with the severity of the illness relating directly to the extent of the infection. Recovery after a few days of symptoms is likely, but some individuals may develop a complicating secondary bacterial infection of the sinuses, ear, or lung (pneumonia).

Colds are treated with medications designed to suppress major symptoms until natural defense mechanisms terminate the infection. Immunity to reinfection follows recovery and is most effective in relation to antibody in respiratory secretions. There is no established method for prevention of colds; however, personal hygiene is recommended to reduce contamination of environmental air and surfaces with virus that may be in respiratory secretions. *See* PNEUMONIA.

Robert B. Couch

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Communications cable

A cable that transmits information signals between geographically separated points. The heart of a communications cable is the transmission medium, which may be optical fibers, coaxial conductors, or twisted wire pairs. A mechanical structure protects the heart of the cable against handling forces and the external environment. The structure of a cable depends on the application.

Optical communications cables. These cables are used in both terrestrial (**Fig. 1**) and undersea (**Fig. 2**) systems. Optical communications cables for terrestrial use may be installed aerially, by direct burial, or in protective ducts. The terrestrial and undersea cables differ in several respects. First, the terrestrial cable requires only enough longitudinal strength to support its own weight over relatively short pole-to-pole spans, or to allow installers to pull the cable into ducts or lay it in a trench. For the undersea

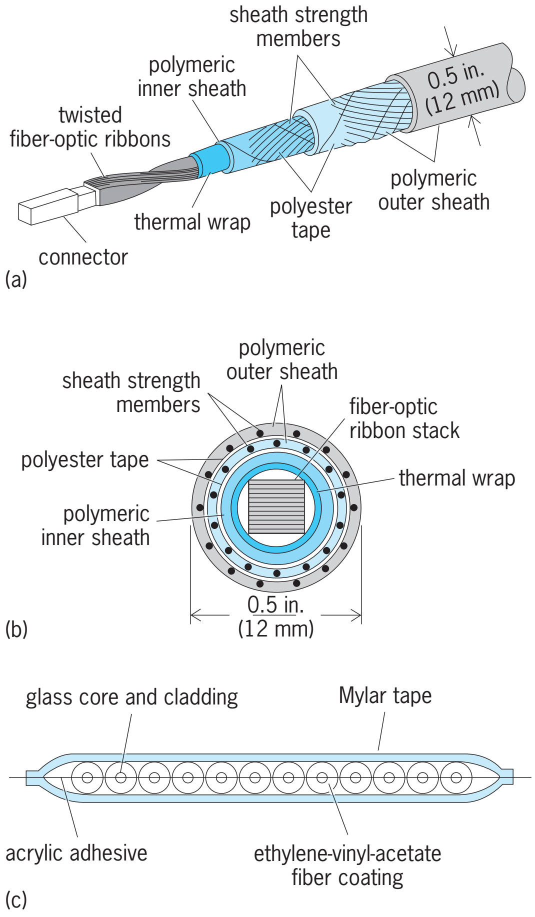

Fig. 1. Multifiber cable for terrestrial use (144 fibers maximum). (*a*) Cutaway view. (*b*) Cross section of cable. (*c*) Cross section of single optical fiber ribbon (12 fibers).

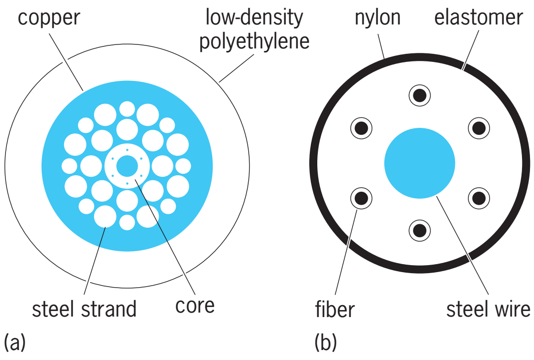

Fig. 2. Optical-fiber cable for undersea systems. (*a*) Cross section. (*b*) Detail of cross section of core.

TABLE 1. Principal characteristics of the first transoceanic fiber-optic United States-to-Europe undersea cable system

Characteristic	Value
Line rate	295.6 megabits/s
Number of service fibers	4
Number of protection fibers	2
Regenerators per repeater	6
Number of voice channels	8000
Number of conversations (with digital circuit multiplication equipment)	40,000
Optical wavelength	1310 nm

cable, the high-strength steel strand allows it to be laid and recovered in ocean depths up to 4.5 mi (7315 m). A second difference is that the undersea cable must deliver as much as 1.6 amperes of direct current to the spaced, series-connected repeaters. Repeaters for the terrestrial system are generally located in buildings, and are powered from locally available sources. A third difference is due to the environment. Terrestrial cables are often installed in ducts. Hence, only limited protection is required against local hazards. The undersea cable, on the other hand, must withstand moderately severe handling in laying, and it sustains the full pressure of ocean depths. At 4.5 mi (7315 m) depth, this pressure is 10,700 lb/in.^{2} (73.8 megapascals). To withstand this pressure, the cable is a filled design (no voids). The thick polyethylene outer layer provides electrical insulation for the power-carrying copper conductor, and is tough enough to resist severe handling. In addition to providing longitudinal strength, the steel strand overlaid with copper acts as a pressure cage to protect the core and fibers. *See* ELECTRICAL INSULATION; POLYOLEFIN RESINS; SUBMARINE CABLE.

Optical communications cables are often used to carry input and output data to computers, or to carry such data from one computer to another. Then they are generally referred to as optical data links or local-area networks. The links are generally short enough that intermediate regeneration of the signals is not needed. *See* FIBER-OPTIC CIRCUIT; LOCAL-AREA NETWORKS.

Optical fibers. Signals in these cables are carried by light pulses which are guided down the optical fiber. In most applications, two fibers make up a complete two-way signal channel. The guiding effect of the fiber confines light to the core of the glass fiber and prevents interference between signals being carried on different fibers. The guiding effect also delivers the strongest possible signal to the far end of the cable. Exceptionally pure silica glass in the fiber minimizes light loss for signals passing longitudinally through the glass fiber. Developers have realized fiber losses of 0.27 dB or less per statute mile (0.17 dB per kilometer), at a wavelength of 1550 nanometers. For such a fiber, the signal can travel 11 mi (18 km) before losing half its power, and can travel 75 mi (120 km) or more before requiring electronic regeneration or amplification. Coaxial cable systems require regeneration at much closer intervals. In the L5 and T4M Coaxial Cable systems, for example, signals are amplified or regenerated every mile (every 1.6 km). *See* OPTICAL FIBERS.

Signal regeneration. Optical cable systems are usually digital. Thus, information is coded into a train of off-or-on light pulses. These are detected by a photodetector at the far end of a cable span and converted into electronic pulses which are amplified, retimed, recognized in a decision circuit, and finally used to drive an optical transmitter. In the transmitter, a laser converts the electric signals back into a train of light pulses which are strong enough to traverse another cable span. By placing many spans in tandem, optical cable systems can carry signals faithfully for thousands of miles.

In TAT-8, the first transoceanic fiber-optic cable, which entered service in 1988 (**Table 1**), six regenerators are mounted in a repeater housing (**Fig. 3**). Thus, the repeater regenerates signals in three pairs of fibers.

Optical-fiber amplifiers. Rather than undersea regenerators, current optical-fiber cable systems use erbium-doped fiber amplifiers (EDFAs) to boost the optical signal on long spans. Conversion from optical to electronic modes and back again is then not needed in the undersea repeaters. Systems using optical amplifiers are simple and reliable, but still deliver a near-perfect, low-noise signal because of signal regeneration at the receiving terminal. With careful design, it is possible to carry a 5-gigabit/s signal across the Pacific Ocean, a 5500-mi (9000-km) distance, with EDFAs before regeneration on shore. Such systems deliver the signal to the distant shore with a bit-error ratio of better than 10^{-10}.

Repeaterless undersea cables. The trend toward lower fiber loss allows the linking of mainland to offshore islands without undersea electronics and optics. Cable systems of over 155 mi (250 km) are feasible (**Table 2**), with future capability trending toward 190 mi (300 km).

Advantages. Optical communications cables have five key advantages over earlier metallic cables: noise- and error-free transmission; greater repeater spacings; enormous information capacity (many individual voice, data, or television channels); immunity

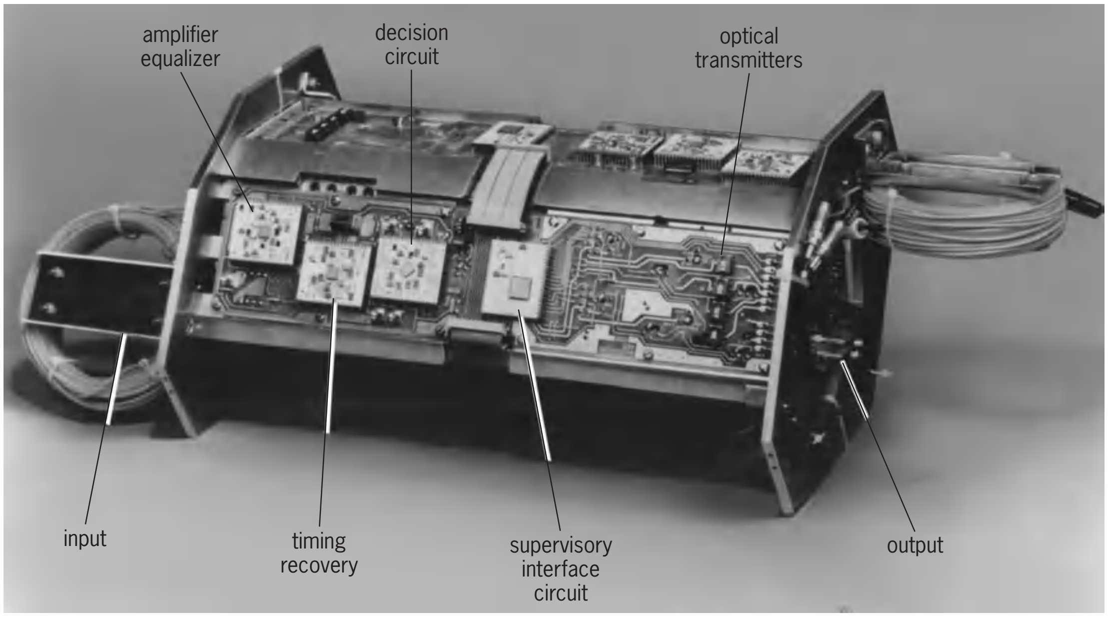

Fig. 3. Regenerator for SL-280 optical undersea cable communications system used in TAT-8.

from outside interference (other signals or noise); and smaller size and lower weight.

Because of these advantages and because optical cable technology is in its infancy, many additional applications can be expected to develop, and the cost of such communications cables can be expected to continue to decrease. *See* OPTICAL COMMUNICATIONS.

Coaxial cable communications systems. Coaxial communication systems evolved before optical systems. Most of these systems are analog in nature. Signals are represented by the amplitude of a wave representing the signal to be transmitted. In a multichannel system, each voice, data, or picture signal occupies its unique portion of a broadband signal which is carried on a shared coaxial conductor or "pipe." In the transmitting terminal, various signals are combined in the frequency-division transmitting multiplex equipment. At the receiving end of a link, signals are separated in the receiving demultiplex equipment. This combining and separation operates much as broadcast radio and television do, and the principles are identical. *See* AMPLITUDE MODULATION; ELECTRICAL COMMUNICATIONS; FREQUENCY MODULATION.

TABLE 2. Repeaterless cable system

Characteristic	Value
System length	188 mi (300 km) maximum
Fiber type	SL, dispersion shifted
Fiber proof stress	200,000 lb/in.^{2} (1.38 GPa)
Cable design	SL, embedded core
Optical wavelength	1.55 μm
Optical source	Buried-heterostructure multiple quantum well laser and EDFA*
Optical detector	EDFA and avalanche photodiode
Line data rate	5 gigabits/s
Line coding	Nonreturn to zero (NRZ)

*EDFA = erbium-doped fiber amplifier.

In order to carry as many channels as possible, the multiplexing and demultiplexing use single-sideband (SSB) transmission. The fixed carrier signals, which do not convey useful information, are suppressed in the transmitting multiplex and reintroduced in the receiving multiplex. This avoids unnecessary load on the system. *See* SINGLE SIDEBAND.

Terrestrial cables. The channel capacity of terrestrial coaxial systems increased dramatically over the years to meet increased long-distance calling (**Table 3**). This resulted in decreased cost per channel, which stimulated still further demand. While demand was the driving force, it is improving technology which allowed such tremendous increases in capacity.

The L1 and L3 systems used electron tubes as the amplifying device, while all later systems used transistors. The L5 system benefited by the use of thin-film integrated circuits. These advances were responsible for the 22-fold increase in the number of channels per coaxial pair (Table 3). Because the number of coaxial pairs per cable was also increased, the total route capacity was increased by a factor of 73 over the 30-year period. *See* ELECTRON TUBE; INTEGRATED CIRCUITS; TRANSISTOR.

Repeater spacing decreases as the capacity rises (Table 3). Multiplying channel capacity by 22 has meant going to higher frequencies, since each additional channel requires another 4 kHz of spectrum. At higher frequencies the cable has higher loss, and therefore such signals must be amplified at closer intervals.

Undersea cables. The history of undersea communications goes back to 1858, when the first transatlantic telegraph cable was completed by C. W. Field. This cable had no repeaters and thus was capable of carrying only a single slow-speed telegraph signal. Nevertheless, it allowed news to be communicated

TABLE 3. L-system characteristics

Characteristic	L1	L3	L4	L5	L5E
Service date	1946	1953	1967	1974	1976
Repeater spacing, mi (km)	8 (12.9)	4 (6.4)	2 (3.2)	1 (1.6)	1 (1.6)
Voice-band channel capacity per 3/8-in. (9.5-mm) coaxial pair	600	1860	3600	10,800	13,200
Coaxial pairs	4	6	10	11	11
Working pairs	3	5	9	10	10
Channel capacity	1800	9300	32,400	108,000	132,000

between North America and Europe without the long delay of surface mail. While telegraph cables were improved over the years, the next major breakthrough occurred in 1956, when the first transatlantic telephone cable was completed from Nova Scotia to Newfoundland, and then across the Atlantic to Scotland.

With the completion of TAT-1 (Transatlantic Telephone-1), callers could for the first time talk across the Atlantic Ocean as easily as they could within the continents. The response was a dramatic increase in use of overseas calling. Since 1956, cables have been installed throughout the world. England, France, Japan, and the United States have been active in designing and installing undersea communications cables.

Low delay is one respect in which undersea cables have a significant edge over satellites in a geosynchronous orbit. Delay is usually evaluated in terms of round-trip message time. For a telephone conversation, it is the extra time added between question and answer because of the transmission time. For the satellite connection, this delay is about 0.5 s. For a 4000-statute-mile (6400-km) undersea cable link, delay is only 0.06 s. Longer delay has two effects: it makes echo more bothersome to voice communications, and it requires more complex and less efficient protocols for data communications. *See* COAXIAL CABLE; TELEPHONE SERVICE; TELEPHONE SYSTEMS CONSTRUCTION. S. Theodore Brewer

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Communications satellite

An artificial device that circumnavigates the Earth, receiving and retransmitting radio-frequency signals to multiple points on Earth. The communications hardware includes antennas, receivers, signal processing, and power amplifiers. The performance is predicted by calculating the power received by the satellite and by the receiving ground station. The satellite has solar arrays and batteries to provide electrical power, thrusters to keep the satellite in the desired position and orientation, and radiators to dissipate heat. The equipment is designed to operate unattended for many years. Many communications satellites are put in a special circular orbit high above the equator.

Communications satellites provide worldwide exchange of voice, text, data, and images to both fixed stations and mobile stations in support of aeronautical, land, and maritime services. With the advent of more powerful satellites and smaller, less powerful, and even portable terminals, satellite broadcasts are accessible to users in both highly populated and remote areas of the world. Applications are proliferating—from distributing network programming to television and radio stations or directly to subscribers, to providing essential communications for disaster relief or medical treatment, supporting Internet access and e-mail, or even to connecting travelers on handheld phones. By providing reliable communications among diverse and geographically distant populations, satellites have helped to make the world a global community. Communications satellites represent at least 40% of the total number of satellites and 30% in cost.

For a communications satellite to provide continuous service 24 h every day, it must remain above the Earth station's horizon, and preferably remain stationary in one spot in the sky so that antennas on the ground do not have to be repointed. As the Earth turns, the satellite moves in a circle, and the center of this circle must be at the center of the Earth. This can happen only if the satellite is above and perpendicular to a spot on the Equator. The height of the satellite is also critical. If the satellite is too low, the attraction of gravity is too strong and the satellite will accelerate toward the Earth. If the satellite is too high, the gravitational attraction is too weak and the satellite will accelerate away from the Earth. If the satellite is 35,786 km (22,237 mi) above the Earth's surface, the attraction of gravity is exactly right. Except for a few small disturbing forces, the satellite will remain at that height, over a point on the Earth's Equator. Such a satellite is called a geostationary satellite and, as the Earth turns, it traverses a path called a geostationary orbit. To an observer on Earth, the satellite remains stationary in the sky.

Basic configuration. Most communications satellites are active repeaters. That is, they receive a signal from an Earth station, amplify it, and retransmit it to one or more earth stations (**Fig. 1**). The signal

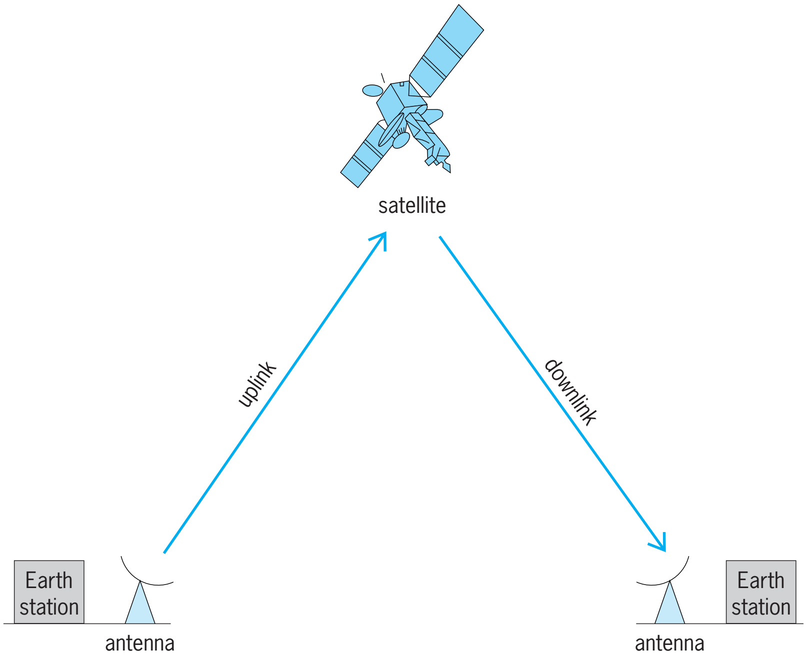


Fig. 1. Communications to and from a satellite.

from the first Earth station to the satellite is called the uplink, and the signal from the satellite back to another Earth station is the downlink. In the satellite, the equipment used to handle the signals is the communications subsystem. The signal is received by an antenna, amplified, processed through many stages, and immediately transmitted through an antenna back to Earth.

A typical communications satellite has a compact, rectangular body, with antennas and solar arrays unfolded in space (**Fig. 2**). The large antennas are used for both transmitting and receiving communications. A smaller antenna is often used to receive commands and to send information about the satellite's status. Before launch, the solar panels are folded next to the body. After launch, they are extended into two long arrays. Other external parts include the thrusters for propulsion, sensors to detect orientation, and radiators to dissipate excess heat.

Inside the satellite, the communications subsystem includes the receiver, the processing equipment, and the power amplifier. The receiver includes a low-noise amplifier to minimize the noise added to the signal, and a downconverter to shift the carrier frequency to another frequency. The processing equipment may include switches, attenuators, and multiplexers. The power amplifiers provide the maximum power to be transmitted.

To support communications, the satellite has several specialized components. These provide the electric power (solar array, batteries, and power conditioning equipment), orientation (sensors and wheels), propulsion (propellant tanks, fuel, and thrusters), structure, and thermal control. Telemetry provides information about the satellite, the command subsystem is used to control the satellite, and tracking is used to help determine its orbit. Since ordinary repairs cannot be done after a satellite is launched, high reliability is essential. Frequently, duplicate equipment is available in the satellite, and used if the primary equipment fails.

Communications Subsystem

The function of a communications satellite is accomplished by the communications subsystem, which receives, amplifies, processes, and transmits

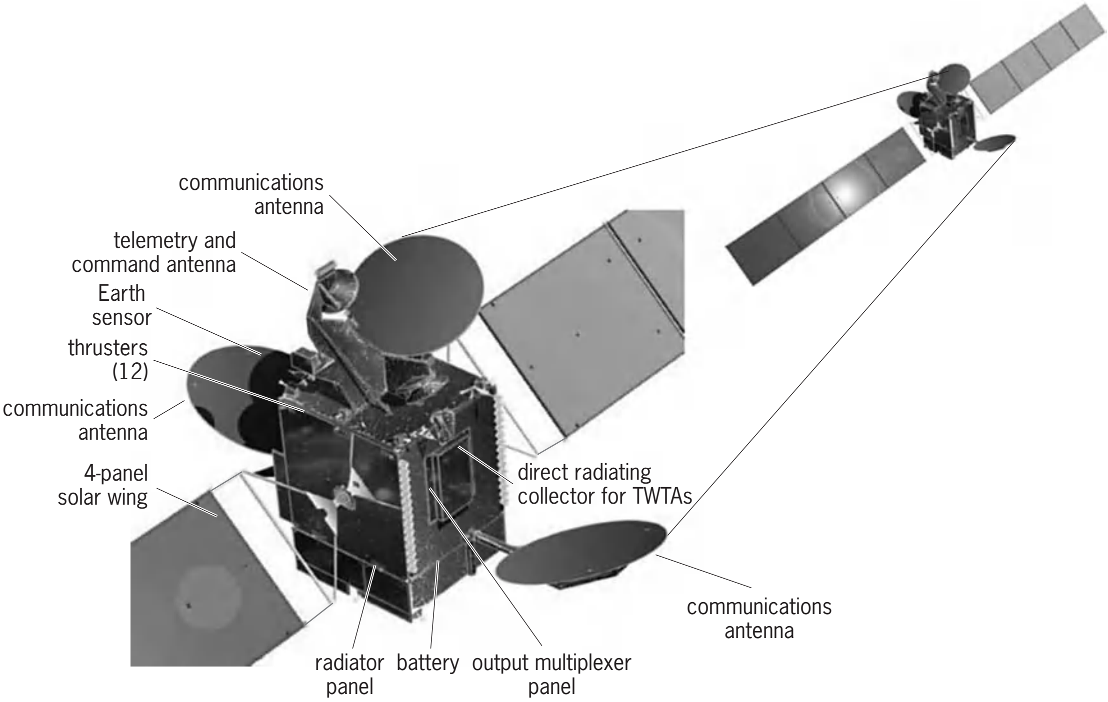


Fig. 2. Typical communications satellite. TWTA = traveling-wave-tube amplifier. (*Space Systems/Loral*)

TABLE 1. Frequencies allocated to communications satellites*

Frequency range, GHz	Letter designation	Typical service usage
1.0–2.0	L-band	Mobile satellite service
1.55–3.9	S-band	Mobile satellite service, digital audio radio service
3.7–6.2	C-band	Fixed satellite service, very small aperture terminal
8.0–12.0	X-band	Military/satellite imagery
11.7–14.5	Ku-band	Fixed satellite service, direct broadcast satellite, very small aperture terminal
17.7–21.2	Ka-band	Fixed satellite service “broadband,” intersatellite link
27.5–31.0	Ka-band	Fixed satellite service “broadband,” intersatellite link

*From Richard Barnett.

information. Hardware includes antennas, receivers, frequency converters, multiplexers, and power amplifiers. The properties of these components depend on the radio frequencies used, and the way the information is imposed on the carrier frequency.

Radio frequencies. A variety of frequencies are received and transmitted by communications satellites (**Table 1**). The fixed satellite service (FSS) provides the major communications between fixed Earth stations. The mobile satellite service (MSS) communicates with ships, vehicles, and airplanes. Direct broadcast satellite (DBS) transmits television directly to homes. Digital audio radio service (DARS) provides continuous radio programs to vehicles. Very small aperture terminals (VSATs) provide communications to very small antennas, often used by businesses. And intersatellite links carry communications from one satellite to another. *See* SATELLITE RADIO; SATELLITE TELEVISION BROADCASTING.

Communications satellites use frequencies above 1 GHz (1,000,000,000 Hz or 1,000,000,000 cycles per second). The commonly used radio frequencies are lower. The AM radio band is around 1000 kHz (or 0.001 GHz) and the FM radio band is around 100 MHz (or 0.1 GHz). Frequencies from 0.3 to 3 GHz are also called ultrahigh frequencies (UHF), and frequencies from 3 to 30 GHz are called superhigh frequencies (SHF).

The amount of radio spectrum (bandwidth) available for space communications is limited. Bandwidth is a measure of how much information can be transmitted. A telephone call, or a modem connection to the Internet, takes only about 10 kHz. A television channel, or a high-speed connection to the Internet for transmission of pictures, requires much more bandwidth. The demand for satellite communications continues to increase, and the lower frequencies are in high demand. The higher frequencies (above 15 GHz) are more available, but are also more attenuated by rain, which can both decrease the signal power and increase the receiver noise level. *See* BANDWIDTH REQUIREMENTS (COMMUNICATIONS); RADIO-WAVE PROPAGATION.

There are different ways to conserve bandwidth by reusing frequencies in a single satellite. One way is to use narrow antenna beams on a satellite. If one beam covers Europe and the other covers North America, different signals can be sent on the different beams at the same frequency, using the antenna directivity for isolation. Another way is to use polarized beams, with the same frequency used for two different polarizations. Antennas can discriminate against an undesired signal, just as polarizing sunglasses can reduce the glare from horizontal surfaces. In each of these ways, the equipment is designed so that the unwanted signal is no more than 1/1000 of the desired signal.

Multiple satellites can use the same frequencies—if the Earth station antennas can discriminate between adjacent satellites. The Earth station antenna must have a beam that includes only a single satellite. This applies to both the uplink and the downlink. The signal from the ground must be received by only one satellite, and the signal to the ground must be received from only one satellite. In geostationary orbit, some neighboring satellites, using identical frequencies, are operated with only a 2° separation, which is 1470 km (915 mi).

Finally, another method, called compression, packs more information into less bandwidth. This technique takes advantage of redundancy in the signal. Voice activation uses a voice channel only when a person is speaking, typically only 40% of the time. Early television compression made use of the time it took an electron beam to return to the start of another scanning line. More compression is possible using the time between frames. With digital data, more efficient modulation methods allow more information bits per unit of time. Packet switching, used in the Internet, allows a variety of different signals originating and destined for different users to share the same communications channel. With many different technical improvements, a single communications satellite can now broadcast a hundred different television channels to small home antennas. Earlier satellites could broadcast only a few channels to Earth stations with large antennas. *See* DATA COMPRESSION; PACKET SWITCHING.

The International Telecommunications Union (ITU), working with various national agencies such as the Federal Communications Commission (FCC), controls the use of radio frequencies by specifying the frequency ranges and imposing limitations on power. Some frequencies used by satellites were first used by microwave relay systems, which transmit a signal through a series of relay towers, typically on the tops of hills. Since microwave relay systems preceded satellites, satellites must limit the power per area incident on these towers to avoid causing harmful interference. *See* RADIO SPECTRUM ALLOCATIONS.

Modulation, multiplexing, and multiple access. To send a signal through a communications satellite, the information must be superimposed on a high-frequency (RF) signal (carrier). This is called modulation. If the carrier is not modulated, no information is transmitted and only a constant signal is received. A satellite will normally relay many signals from an Earth station. Multiplexing is used to combine these signals and demultiplexing to separate them. Finally, a satellite often handles signals from more than one Earth station; this is called multiple access.

There are several methods of modulation, multiplexing, and multiple access that may be used in various combinations. Multiplexing and multiple access require sharing the satellite resources to carry various signals. These resources can be shared by using different frequencies, by taking turns (time division), by using different antenna beams, or by using different polarizations. Signals such as telephone and television may be analog or digital. Theoretically, any method can be used for either type of signal. In practice, time division is easier with digital signals, while frequency division is easier with analog signals.

Modulation. There are three basic modulation methods, which change the amplitude, frequency, or phase of a carrier. In amplitude modulation (AM), the amplitude of the carrier is varied in proportion to the input signal. In frequency modulation (FM), the frequency of the carrier is varied in proportion to the input signal. FM is less susceptible to noise and interference than AM. In phase modulation (PM), also called angle modulation, the phase of the carrier is varied in proportion to the input signal. This also varies the frequency of the carrier, but much less than FM, since the variation is never more than one cycle.

Phase-shift keying (PSK) is a digital version of phase modulation in which the phase of the carrier is changed depending on certain bit sequences. This is the most common form of modulation used on communications satellites today. *See* AMPLITUDE MODULATION; FREQUENCY MODULATION; MODULATION; PHASE MODULATION.

Multiplexing. Most communications satellites handle many signals. Multiplexers are used to combine signals before they reach an Earth station, at the Earth station, or in the satellite. The most common forms of multiplexing used in satellite communications are frequency-division multiplexing (FDM) and time-division multiplexing (TDM). As a simple illustration, in the case of a radio or television receiver, different broadcast stations are transmitted at different frequencies (FDM), while different programs may be on one station, but received at different times (TDM).

Frequency-division multiplexing is often used to combine telephone channels. This may be done before the signals reach the Earth station, and then the resulting trunks may be multiplexed together at the station. Each signal is converted to an assigned frequency band, and then the signals can be combined. For example, if two phone channels have frequencies of 0–10 kHz, one channel can stay at the same frequency and another channel can be converted to 10–20 kHz. These two channels can be combined into one 0–20 kHz signal. Many other channels can be converted to other frequency bands and combined. The combination can then be sent up to a satellite and down to another Earth station, where demultiplexers reverse the process and separate the different telephone channels.

Time-division multiplexers were introduced in telephone networks when voice calls were digitized. At 64,000 bits/second, the voice signal can be sampled 8000 times per second, and each sample digitized to 8-bit accuracy. These digitized voice signals can be multiplexed with other voice channels to form digital streams with many more bits/second, extending to standardized streams as high as billions of bits per second, for use in communications satellites, as well as fiber optic and microwave services. Once information is digitized, it can be multiplexed with any other type of digitized information.

Multiple access. Several Earth stations can send signals, including voice, data, teletype, facsimile, television, and digitized data, simultaneously to the same satellite. This is called multiple access. Multiple access is similar to multiplexing signals into a satellite, but the different Earth stations must coordinate their transmissions. There are several ways to share access to a satellite: dividing the frequency band (frequency-division multiple access or FDMA); dividing access in time (time-division multiple access or TDMA); dividing access in space (space-division multiple access or SDMA) via spot beams or polarizations, for example; or by using different codes to divide the access (code-division multiple access or CDMA).

In FDMA, each Earth station has exclusive use of an assigned bandwidth between specified frequencies. The strength of the signals must be balanced, so that a strong signal at one frequency does not interfere with a weak signal at a neighboring frequency. Individual carriers may also have different power, bandwidth, and quality requirements, which all must be balanced so that each station is satisfied.

In TDMA, each Earth station has an assigned time to use the entire bandwidth or a portion of it. A prearranged schedule is used to avoid overlapping transmissions so that at any time the satellite has only one signal present within each TDMA channel. TDMA systems are flexible, and can accommodate traffic variations among stations by increasing or decreasing the duration of each station's bursts to match the traffic flow.

Random multiple access (RMA) is a variation of TDMA in which the available time is not assigned to individual stations. This system, also called ALOHA, was devised at the University of Hawaii. It allows small, inexpensive Earth stations to communicate through a satellite with a minimum of protocols and no network supervision. When a station needs to transmit, it sends a burst of data pulses, and then watches the downlink. If it sees a corrupted signal, it knows that another station is transmitting. It then waits a short, random time before trying again. If there is not too much traffic, the signal is eventually transmitted with no interference.

In CDMA, the transmitting Earth station uses a unique digital code to spread each signal over a bandwidth much wider than is actually needed. The receiving station uses the same code to retrieve the information. Other networks may operate simultaneously within the same bandwidth, as long as different, noninterfering (orthogonal) codes are used for different signals. *See* MULTIPLEXING AND MULTIPLE ACCESS.

Antennas. Antennas are passive devices used to collect the signal (radio-frequency power) incident on a satellite, and to radiate an amplified signal from the satellite. Inside the satellite, radio-frequency power is often guided by waveguides, or hollow metal pipes with circular or rectangular cross section. If a waveguide is open at one end, it will radiate some power, but not very efficiently. If the open end is flared out like a cone, it will be more efficient as a radiator. *See* WAVEGUIDE.

If an antenna is a good radiator, it is also a good receiver. Its properties are reciprocal. At the same frequency, it has the same pattern for transmitting and receiving. If it transmits a lot of power in a certain direction, it will also be good at receiving power from that same direction.

Types of antennas. A horn is an open waveguide designed to radiate maximum power. Close to the radiating end, the opening increases in size. The angles and surfaces (smooth, steps, or corrugations) are chosen for maximum performance. A horn is simple and reliable. Communications satellites use horns for global beams, which radiate over the entire Earth, facing the satellite. Horns may also be used for telemetry and command signals, which radiate in many directions.

A parabolic antenna is the type most commonly used in communications satellites. It has a feed, similar to a horn, and a parabolic reflector. The feed radiates a wide beam, aimed toward the reflector. The reflector surface has the shape of a paraboloid, made by rotating a parabola around its axis. The feed is at the focus of the parabola so that the reflector focuses the radiation into a narrow beam. Like the reflecting telescopes used by astronomers, parabolic reflectors work over a wide range of frequencies. That is, they have the same focus for different colors (they are free of chromatic aberration).

For Earth stations, large parabolic antennas usually have an on-axis feed located in the reflected beam (**Fig. 3***a*). Since the feed is small compared to the reflector diameter, it obstructs only a small part of the reflected beam. On small antennas, an offset feed may be placed outside of the reflected beam (Fig. 3*b*). The reflector is still part of a paraboloid, and the feed is still at the focus, but the reflector is part of one side of a paraboloid.

Antenna gain. The gain of an antenna is the ratio of how much better it radiates in one direction (beam center) than an ideal isotropic radiator, which radiates equally in all directions. The antenna gain G of a parabolic reflector is given by Eq. (1), where A is

$$G = 4\pi \eta A/\lambda^2 \qquad (1)$$

the physical area of the reflector, η is the antenna efficiency, and λ is the wavelength. The antenna efficiency accounts for imperfections in the antenna, and is always less than unity. The gain can also be calculated as $109\eta D^2 f^2$, where the diameter, D, is in meters (m), and the frequency, f, is in gigahertz (GHz). Thus, the gain of a parabolic antenna is higher for larger reflectors and for higher frequencies. As an example, an INTELSAT Earth station may have a 30-m (98-ft) antenna, transmitting at 6 GHz, with an efficiency of 0.60. Its antenna gain, G, is a ratio greater than 2,000,000.

Antenna beamwidth. A good antenna focuses the power in one direction, but only at the expense of power in other directions. The antenna is a passive device. It does not amplify the total power. With a good parabolic antenna, the power decreases rapidly as the angle from the beam axis increases. A useful definition of beamwidth is the angle over which the power has dropped to one-half of the peak value. This is called a half-power beamwidth. An approximate, but useful, equation for the half-power beamwidth of a parabolic antenna (in degrees) is given by Eq. (2), where, again, frequency, f, is in

$$\theta = 21/(fD) \qquad (2)$$

gigahertz and antenna diameter, D, is in meters. The number 21 is not a true constant, but may vary somewhat for different antennas. The INTELSAT antenna just described would have a beamwidth of 0.1°.

Antenna coverage. An Earth station antenna usually transmits to and receives from a single satellite. The maximum gain is desired in one direction, and a simple parabolic antenna often provides excellent performance. However, a satellite antenna often communicates with several Earth stations. In this case, the aim is to achieve a minimum gain anywhere in a given region. This region may be a country, a group of

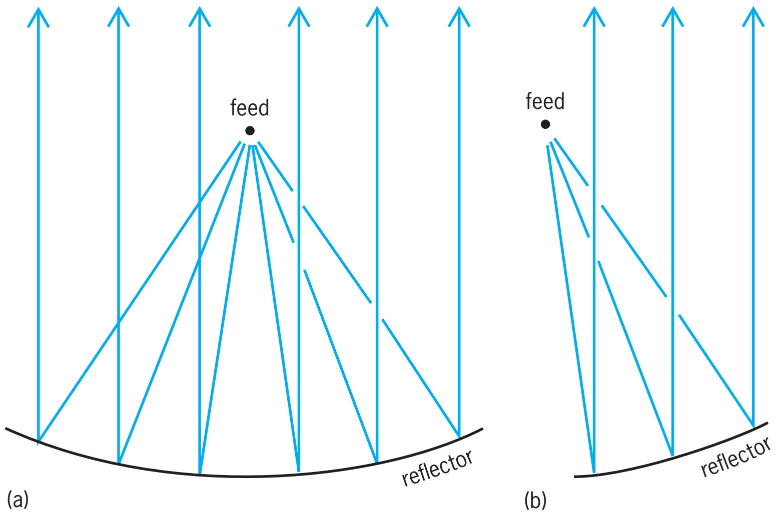


Fig. 3. Parabolic antennas. (*a*) On-axis feed. (*b*) Offset feed.

countries, or a time zone within a country. Because the power outside the desired region is wasted, it should be minimized. Circular and elliptical patterns can be generated with a single feed and a reflector. More complicated patterns can be generated with a single parabolic reflector and several feeds, or a single feed and a specially distorted reflector. In the case of a multifeed antenna, the designer often varies the number of feeds, their location, the power in each feed, and the phase. A computer is used to calculate the pattern for each variation, and the variables are adjusted until a near-optimum pattern is obtained. *See* ANTENNA (ELECTROMAGNETISM).

Receivers. The signal from the Earth station enters the satellite receive antenna and is amplified by the satellite receiver. Because the received signal is at a very low power level, the first few stages should amplify the signal without introducing additional noise. These initial amplifier stages are called a low-noise amplifier. After the signal has been amplified by the initial stages, its higher power level is less likely to be affected by noise.

The receiver also shifts the carrier frequency of the received signal. In a satellite it must be shifted to a different frequency before it is transmitted. Otherwise, the high-power transmitter would overwhelm the sensitive receiver. In an Earth station the frequency is often shifted to a lower frequency for ease of handling. It is most efficient to shift the frequency of the signal at low power levels. After the initial amplification stages, the frequency is changed, followed by additional amplification.

Power amplifiers. Traveling-wave tubes (TWTs) are often used in satellites to generate the high levels of radio-frequency power required. The power output of a traveling-wave tube increases as the power input is increased. As in any amplifier, the power output has a practical maximum; at this maximum, the traveling-wave tube is operating in a nonlinear mode called saturation. In satellite communications, maximum power is often desired, but it sometimes does not result in the best performance. For some operations, it is necessary to "back off" from the maximum, to find a linear portion of the output versus input curve. This decreases the distortion near saturation, and reduces crosstalk, when one user's communications cross over to a different user's channel at a different frequency. *See* CROSSTALK; SATURATION; TRAVELING-WAVE TUBE.

Solid-state power amplifiers (SSPAs) are also used in satellites when they can supply the desired power output. SSPAs have several stages of amplification. The maximum power is often limited by the heat dissipated by the amplifier. This heat can be conducted to larger surfaces and then radiated away. If enough heat cannot be dissipated, the temperature increases and may lead to failure of the amplifier. *See* POWER AMPLIFIER; MICROWAVE SOLID-STATE DEVICES.

Satellite Performance (Link Budget)

A communications satellite is built to be operated with specified Earth stations. Its communications performance, described in terms of a link budget, is evaluated as the power of the received signal relative to the sources of noise in the link between two Earth stations. The total link budget represents both parts of the link: the uplink from Earth station to satellite and the downlink from satellite to a second Earth station.

For each link a "good" signal must be received. The system designer must decide whether to spend more money for a more powerful transmitter, larger antennas, or a better receiver. To find the best system, the designer must work with a budget for each of the two links. One example of a downlink budget starts with a transmitter power of 180 W (**Fig. 4**, right). An antenna increases the power to an apparent 180,000 W, a loss in space drops this to 4×10^{-16} W, and the Earth station antenna increases this to a received power of about 10^{-12} W. A similar calculation is made for the uplink budget (Fig. 4, left). The other part of the calculation for each link, is to see if this is a "good" signal, that is, if it is larger than the noise by a sufficient margin.

Decibels. In both the uplink and the downlink, the power transmitted, P, is a large number of watts, and the carrier power received, C, is usually a very small number of watts. It is easier to express these numbers in decibels rather than in absolute quantities. Ratios were first expressed as decibels in measurements of sound intensity. The bottom of the scale was determined (the minimum intensity that can be heard), and any measured sound intensity could then be expressed in decibels, as an absolute measurement.

To express a quantity in decibels, the common logarithm of the absolute quantity is taken, and the result multiplied by ten, that is, $10 \log_{10}(\ )$. There are two main reasons for using decibels: (1) decibel notation makes it easy to write and understand very small and very large numbers, and (2) it is easier to calculate the cumulative effects of gains and losses along the link path by addition rather than multiplication.

In calculating link budgets, the unit abbreviation is attached to "dB." For example, 10 million watts, or 10^7 W, is expressed as 70 dBW. In calculating satellite performance, not only are many numbers expressed in decibels, but equations are often written in decibel format, with addition and subtraction symbols, instead of multiplication and division notation. *See* DECIBEL; LOGARITHM.

Transmitter performance. The start of any radio-frequency transmission in space is the output of the power amplifier from either the satellite or the Earth station. The transmitter should transmit the maximum power in the direction of the intended receiver. This is done by using an amplifier with maximum output power, P, and a transmit antenna with maximum antenna gain, G_t. The product of the transmitter power (in watts) and the antenna gain (as a ratio) is known as the equivalent isotropically radiated power or EIRP (in watts or dBW). From the receiver's point of view, the transmitter appears to be radiating this amount of power (and, it would be radiating this amount of power if it were radiating equally in all directions).

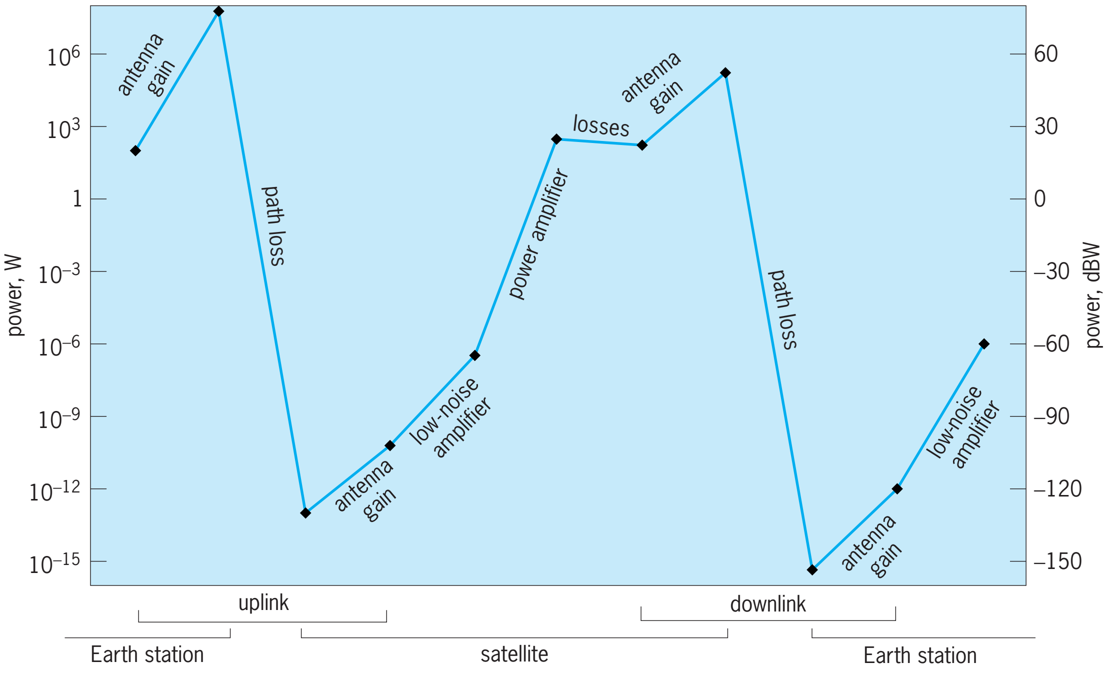


Fig. 4. Power levels for a broadcast satellite (link budget). (*Data from Space Systems/Loral*)

Free-space path loss. In almost any transmission of radio frequencies, most of the power is lost in space. In transmission to and from communications satellites, the distances are larger, so the losses are larger. The distance S from an Earth station to a satellite is enormous—more than 35,000 km (22,000 mi) for a geostationary satellite. The power will spread over a large area of $4\pi S^2$, and the receive antenna only intercepts a small area A, reduced by the receive antenna efficiency η. The received carrier power C is then given by Eq. (3). If the value of ηA from Eq. (1)

$$C = \frac{PG_t\eta A}{4\pi S^2} \tag{3}$$

is substituted in Eq. (3), the received carrier power C can be written as Eq. (4), where P is the transmitter power, and G_t and G_r are the gains of the transmit antenna and receive antenna. The transmitter power, P, is increased by the two antenna gains, and reduced by the loss in space. The free-space path loss, L, is found to be $(4\pi S)^2/\pi^2$. Since the wavelength λ of the carrier is very small and the distance S is very large, the free-space path loss is a very large ratio.

$$C = PG_t(1/L)G_r \tag{4}$$

The reason for introducing the receive antenna gain G_r into Eq. (3) is to treat both antennas in the same way. Antennas are reciprocal: an antenna used to receive has the same gain as it would to transmit, providing that gain is measured at the same frequency. A numerical example of Eq. (4) is given at the top of **Table 2**. The transmitter power per channel is 180 W. The transmit antenna increases this by a factor of 1000. The reciprocal of the free-space path loss is a factor of 2.3×10^{-21}, which with a receive antenna gain of 2500 results in a carrier power received of 1.04×10^{-12} W.

TABLE 2. Performance of the downlink, from a broadcast satellite[*]

Symbol	Description	Number	In decibels[†]
P	Transmitter power per channel	180 W	22.5 dBW
G_t	Transmitter antenna gain	1000	30.0 dB
$1/L$	1/Free space path loss[‡]	2.3×10^{-21}	−206.3 dB
G_r	Receiver antenna gain	2500	34.0 dB
C	**Carrier power received**	**1.04×10^{-12} W**	**−119.8 dBW**
T_s	Noise temperature	125.0 K	21.0 dBK
k	Boltzmann's constant	1.381×10^{-23} W/Hz-K	−228.6 dBW/Hz-K
B	Bandwidth	24,000,000 Hz	73.8 dBHz
kT_sB	**Noise received**	**4.1×10^{-14} W**	**−133.8 dBW**
C/kT_sB	Carrier-to-noise ratio	25	14.0 dB

[*] Data from Space Systems/Loral.
[†] Decibels are explained in the text. Example: $10 \log_{10}(180\text{W}) = 22.5$ dBW.
[‡] Path is 39,500 km (22,544 mi) from satellite to Earth; radio frequency is at 12.5 GHz.

Noise. The carrier power received is important only when compared to the noise present in the system. Without additional information, it is difficult to determine whether the received carrier power of 1 trillionth of a watt is sufficient. If no noise is present, the signal can be amplified to any desired power; however, if there is too much noise present, the received signal is useless. The noise may come from many sources. The noise may be directly incident on the antenna (such as the Sun in the antenna beam axis), it may leak in from the sides (from antenna sidelobes), it may be added between the antenna and receiver (waveguides may not be perfect), or it may be inherent in the receiver (from the "low-noise amplifier").

In satellite communications, the noise power is often expressed as a system noise temperature T_s, equivalent to that radiated by a blackbody at the specified temperature. This noise is usually present over a broad band of frequencies, and most of it can be filtered out. However, the desired signal occupies a narrow band, and the noise in that band cannot be filtered out. For an audio signal the bandwidth might be only 10 kHz, while for a television channel it might be 24 MHz. When the noise temperature, T_s, the bandwidth, B, and Boltzmann's constant, k (a fundamental physical constant), are multiplied together, the result is the noise received, in watts. In the example in Table 2, the noise temperature is 125 K ($-148°$C), and the bandwidth is 24 MHz, so the noise power received is 4.1×10^{-14} W. Usually, the noise temperature is lower for a downlink, since the receive antenna on the ground "sees" cold space as background, while in an uplink, the receive antenna "sees" the warmer earth. *See* BOLTZMANN CONSTANT; HEAT RADIATION.

The values in the right column of Table 2 are in decibel notation. To calculate the carrier power received, the first four numbers are added instead of multiplied. To find the noise power, the decibel values of T_s, k, and B are added. The final carrier-to-noise ratio, 14.0 dB, is determined by subtracting the noise (-133.8 dBW) from the carrier power (-119.8 dBW).

In this example, the ratio of carrier to noise is 25, which means that the signal is 25 times stronger than the noise. The minimum ratio required depends on the specific application. During the design phase, if the ratio is too low, some changes must be made in the link to achieve an acceptable value. For example, the transmitter power or the size of one of the antennas might be increased.

System performance. Usually, a communications satellite receives a signal from an Earth station and sends it back to another Earth station. The system performance depends on the uplink (Earth to satellite), and the downlink (satellite to Earth). To combine the two ratios, the noise per carrier for each link must be added. Therefore, the reciprocals of the carrier-to-noise ratios must be added, and then the reciprocal taken of the result. If the uplink carrier-to-noise ratio (C/N_u) is 240 and the downlink carrier-to-noise ratio (C/N_d) is 25, then the total carrier-to-noise ratio (C/N_t) is 22.6. In general, the combined ratio is less than that of either of the links.

Losses. In addition to free-space path loss, there may be many other losses in power. Some are negligible, while others are significant. The transmitter and the transmit antenna are usually connected with a waveguide that may have losses. Similarly, there may be losses between the receive antenna and the receiver; to minimize these, the receiver is mounted as close to the antenna as possible.

Geometric loss results from spreading the signal over a large area. Additional losses may be incurred in going through the Earth's atmosphere. At certain frequencies, especially above 10 GHz, there are absorption bands from oxygen and water vapor in the air. For low-elevation angles from the Earth station to the satellite, these bands produce more absorption because the beam has a longer path in the atmosphere. The presence of raindrops in the atmosphere can increase both the attenuation and the noise level in the signal. Both the decrease in the carrier signal and the increase in the noise result in a decrease of the all-important ratio of carrier to noise power.

Margin. Some losses are fixed, some slowly increase with time, and others fluctuate with time. Some losses are known, and some are unknown. To compensate for all these losses, a system is designed with a margin. This means that the system has more capability (a higher total carrier-to-noise ratio) than needed. When a loss is larger than expected, the margin decreases, but the system continues to operate according to specifications. The power of Earth station transmitters can usually be adjusted, especially when several stations are transmitting to one satellite at the same or adjacent frequencies. The satellite transmitted power can also be adjusted by ground-controlled attenuators.

Space Technology

Much of the space technology used in communications satellites is also used in many other satellites in near-Earth orbit. This section deals primarily with the technology specially for communications satellites. *See* SPACE PROBE; SPACE TECHNOLOGY.

Orientation. Many communications satellites are three-axis body-stabilized, that is, they have one axis pointed north, one axis pointed toward Earth, and the third more or less parallel to the velocity vector along the orbit. The orientation is measured with Sun sensors (the simplest method), Earth sensors (or horizon sensors), or radio-frequency sensors. Any error in attitude is corrected by actuating wheels with rotational inertia. The simplest arrangement to visualize is three reaction wheels, each used to correct for errors around the three axes. For redundancy, four reaction wheels may be used, with each axis at the same angle from the other three (109.5°). Some satellites have either a fixed momentum wheel or a gimballed momentum wheel that always turns in the same direction. Note that gyroscopes are wheels used only as sensors, reaction wheels rotate in either direction, and momentum wheels rotate always in the same direction. When a wheel reaches its maximum allowed rotation speed, a thruster is fired to exert a torque that causes the wheel to slow down. *See* GYROSCOPE.

Structure. A typical communications satellite has a compact rectangular body, with various antennas, thrusters, and solar arrays mounted on external surfaces. After launch, the two solar arrays are unfolded (deployed) in the north and south directions, and mounted so that they can rotate around this north-south axis to face the Sun continually. Usually, there is no correction for the annual north- south motion of the Sun. The structure needs to be light, strong enough to withstand the acceleration and vibration of launch, and stiff enough to keep antennas pointed accurately. Therefore, it is made of light metals (aluminum, beryllium, magnesium, or titanium) or a composite (boron/epoxy or graphite/epoxy). *See* SPACECRAFT STRUCTURE.

Propulsion. Thrusters are used for both attitude control (satellite orientation) and station keeping (satellite positioning). The most common propellant is hydrazine (N_2H_4). This monopropellant needs no oxidizer; when heated, it decomposes and generates more heat. The simplest system has pressurized nitrogen inside the tank with the hydrazine to expel the fuel from the tank (blow-down system). There is no apparent gravity in orbit, so either a bladder or a surface tension system is needed to ensure that fuel rather than nitrogen comes out of the tank. *See* HYDRAZINE; ROCKET PROPULSION; SPACECRAFT PROPULSION.

Electric power. A communications satellite uses most of the available power for the power amplifiers: either traveling-wave tubes or solid-state power amplifiers. Primary electrical power is provided by solar cells mounted on solar arrays, and secondary power is provided by rechargeable batteries. These components must be connected with appropriate regulation, conversion, and distribution. Deployed solar arrays get cold during eclipse, and generate excess voltage when they come out of eclipse. Batteries require a higher voltage during charge, and provide a lower voltage during discharge. Solid-state power amplifiers need only a few volts. Traveling-wave tubes require a few volts for the filament heater, but over 1000 V for acceleration of the electron beam. Because solar arrays lose power due to particle radiation in space over many years, they are built with excess power. Some batteries have a limited life, but with careful construction, testing, and operation, they provide excellent service. *See* RADIATION DAMAGE TO MATERIALS; SPACE POWER SYSTEMS.

Thermal control. In many communications satellites, the majority of the electric power is used by the power amplifiers. While these amplifiers generate lots of radio-frequency power, they are not 100% efficient, so they also generate heat. Dissipation of this heat is a key element in the thermal control of communications satellites. The north and south faces are often used for heat dissipation, since they receive less sunlight than the other surfaces. These surfaces have low absorptivity to visible light, including sunlight, and high thermal emissivity to radiate the heat into space. The heat is conducted to these faces with solid metal or with heat pipes. The power amplifiers are mounted on or near the inside of these surfaces. With solid-state power amplifiers, the small integrated circuit chip is mounted on a metal heat sink that absorbs and spreads the heat to limit the chip temperature.

Telemetry and command. The objective of the telemetry subsystem is to provide information about the spacecraft for operational use, failure analysis, and prediction of spacecraft performance. The command subsystem receives commands from the spacecraft control center and executes them. Some commands are used to reconfigure the communications subsystem, to fire thrusters, and to switch to redundant equipment when needed.

Since telemetry and command are essential for failure recovery, the antenna coverage must be nearly omnidirectional. This enables recovery even when control of orientation has been lost, and the main antennas no longer point at the Earth. If the available power decreases, other equipment is turned off automatically so that the telemetry and command subsystems will still have power. *See* TELEMETERING.

Tracking. The location of a satellite can be measured by determining its distance from two or three Earth stations. The distance is determined from the transit time of radio signals. This measurement is independent of the processing of telemetry and command signals, but uses the same command receiver and telemetry transmitter. The transit times may be measured by transmitting tones of different frequencies and finding the phase relations of the returned signals. The transit times can also be measured by transmitting a pseudorandom series of bits, and measuring the time delay for which there is most correlation between the transmitted and received signal—when they match. From a series of measurements, the location of the satellite at various times can be determined. Thruster firings are then scheduled to keep the satellite in the desired location.

Reliability. Large velocity changes are needed to launch satellites into space. Once launched, satellites are difficult to repair and expensive to replace. Therefore, satellites must function when they are first launched, and continue to perform for many years. This task is similar to building a car that will go over 200,000 km (over 125,000 mi) without maintenance or repair. Satellites achieve a long life by having inherently reliable components, redundant subsystems, and a rigorous test schedule before launch.

Communications satellites have an excellent record. The launch reliability, including both the launch vehicle and initial operation of the satellite, may be 75% for early launch vehicles and new programs and as high as 95% for mature operations. The probability of their reaching a design lifetime of 12 or 15 years may be calculated as 75%, and is often exceeded. This excellent record, in addition to larger satellites handling lots of traffic, has drastically reduced the cost of communications, including overseas phone calls. For example, a computer

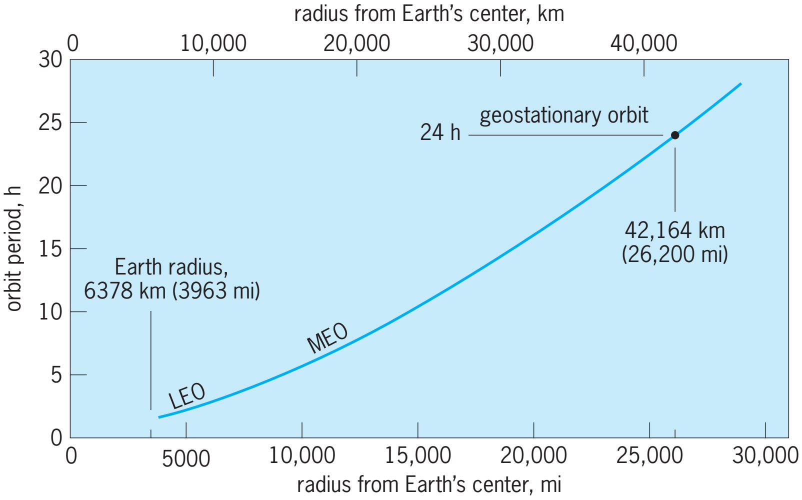


Fig. 5. Orbit periods of circular orbits.

may be purchased at a nearby store, but the technical assistance may be halfway around the world, via satellite. *See* RELIABILITY, AVAILABILITY, AND MAINTAINABILITY.

Orbits

Communications satellites circumnavigate the Earth in a path called an orbit. The majority are in a very special orbit, called a geostationary orbit. Other orbits are also used, due to advantages in launching the satellite, keeping the satellite in place (stationkeeping), or communicating with desired earth stations.

Geostationary orbit. The first characteristic of a geostationary orbit is that the path is circular (eccentricity is near zero), so the satellite is always the same distance (radius) from the center of the Earth. When the radius is larger, the time to go around increases, both because of the larger distance and because the satellite has a smaller velocity (**Fig. 5**). The second characteristic is that the geostationary orbit have a period of rotation exactly equal to the time it takes the Earth to rotate around its axis (23 h, 56 min, 4.1 s). This occurs for a satellite 35,786 km (22,237 mi) above the Earth's surface, or 42,164 km (26,200 mi) from the center of the Earth. For low Earth orbits (LEO), the period is only a few hours; for medium Earth orbits (MEO) it is longer. For a very large radius of 384,300 km (238,860 mi), the orbit period would be 27.3 days, which corresponds to the Moon's orbit around the Earth.

A third characteristic of a geostationary orbit is that the orbit must be in the equatorial plane. Otherwise, the satellite would have a north-south oscillation. Since the satellite orbit period is the same as the time it takes for the Earth to complete a rotation, the satellite is always over the same point (longitude) on the Equator. And, most importantly, since the satellite is always at the same height over the same point on the Equator, it appears to be stationary in the sky to an observer on the Earth. Once an Earth station antenna is pointed at the satellite, it will remain pointed at the satellite.

Different points along the Equator can be identified by their longitude. Longitudes may range from 0 to 360° E, or they can be written from −180° to +180° E. Negative east longitudes are simply west longitudes (west from the Greenwich meridian). The longitude of a geostationary satellite is the longitude of the point on the equator directly underneath the satellite.

Azimuth and elevation. To point an antenna at a satellite, it is useful to know the satellite's azimuth and elevation as seen by an observer on Earth. The azimuth is the direction of the satellite, measured in the horizontal plane from geographic north in a clockwise direction (starting eastward). The elevation is the angle between a satellite and the observer's horizon plane.

For an observer in the Northern Hemisphere, geostationary (GEO) satellites appear placed in an arc in the southern sky, as shown in **Fig. 6**. The top curve in the figure is for an observer at 10° N latitude. Satellites are shown for differences of 2° longitude (satellite longitude minus station longitude). The lower curves are for observers at other latitudes (30° N, 50° N, and 70° N), with satellites having 10° spacing. The azimuths are between 90° and 270°. For an observer in the Southern Hemisphere, the geostationary arc appears in the northern sky, and the azimuths are in the ranges 270° to 360°, and 0° to 90°.

If the longitude of the satellite is equal to the longitude of the observer (Earth station), then an observer in the Northern Hemisphere would find the satellite directly south (azimuth = 180°). When the longitudes of the satellite and observer are different, then the elevations are lower, and the azimuth (direction) is no longer due south.

Stationkeeping. If the Earth were perfectly spherical and there were no other perturbing forces, a satellite inserted into geostationary orbit would remain there indefinitely. But there are perturbing forces, and over time the orbit of a satellite changes. For a communications satellite to perform its mission, small thrusters must be used to counteract these forces and keep the satellite in its desired location. This is called stationkeeping. Without these thrusters, a geostationary satellite would have significant longitudinal drift, north-south oscillations, east-west oscillations, and radial oscillations.

The longitudinal drift is caused by irregularities in the Earth's shape around the Equator, unknown until artificial satellites were launched. Specifically, the equatorial cross section is not circular. This causes a change in the longitudinal drift, which can be a longitude acceleration of as much as 0.002 (degree)/(day)^2. This is small, but over many days the satellite would move to a different longitude. The change in longitude can be pictured as a weight sliding downhill, as in **Fig. 7**. The figure shows two low points, around 75°E and 252°E. A satellite at one of these stable longitudes will stay there, and a satellite near that longitude will oscillate about that longitude. The first commercial communications satellite, *Early Bird*, was stationed at 310°E and kept there by use of its thrusters. When it ran out of fuel, it "slid down the hill" to 252°E, and up the other side to 200°E. Around 200°E, it reversed,

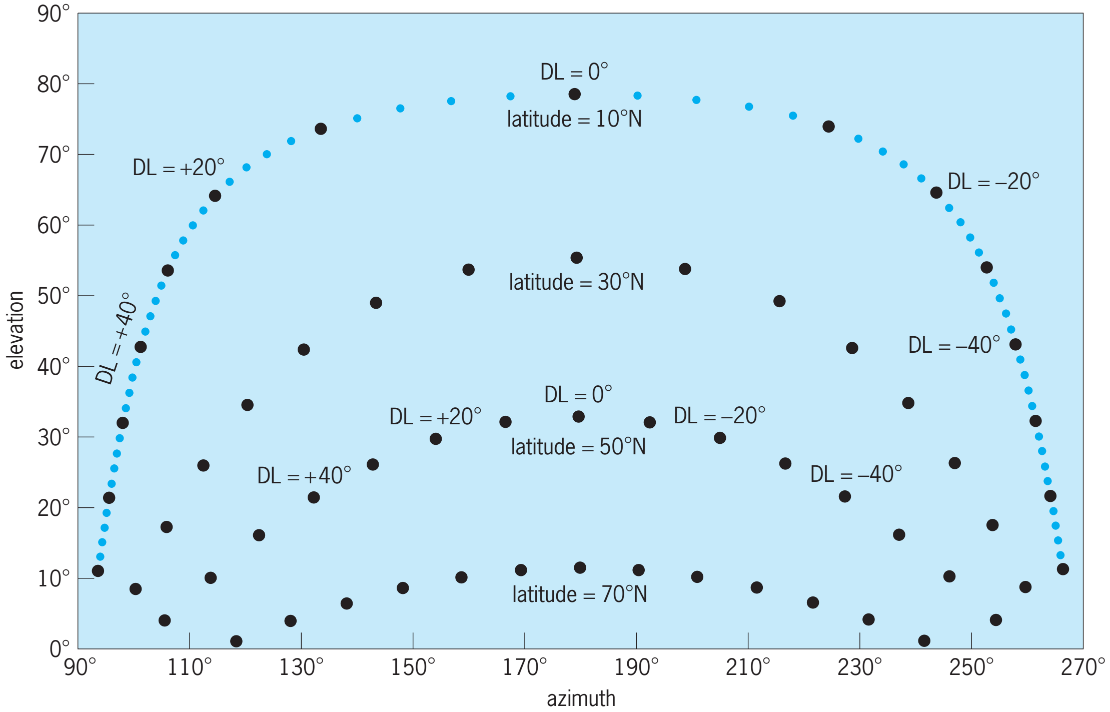


Fig. 6. Azimuth and elevation of geostationary satellites. DL = satellite east longitude − station east longitude.

and came back to 310°E. It continues to go back and forth every 3 years. *See* EARTH, GRAVITY FIELD OF.

The daily north-south oscillations of the satellite are caused by gravitational attractions of the Sun and Moon. These cause the orbit plane to tip with respect to the equatorial plane. Instead of remaining over one spot on the Equator, the satellite shows a daily cycle of going into the Northern Hemisphere and then the southern hemisphere. If unchecked, this north-south oscillation will increase to 15° in about 26 years, and then return to zero. In practice, controlling these north-south oscillations takes the major part of a satellite's fuel. Near the end of the satellite's life, the fuel may be reserved for longitudinal control, and the north-south oscillations allowed to increase.

The daily east-west oscillations of a satellite are caused by solar radiation pressure, which is 4.57×10^{-6} N/m^2 (6.6×10^{-10} psi) at the Sun-to-Earth distance. On one side of the orbit, the force increases the velocity, and on the other side it decreases it. These forces change an initially circular orbit into an elliptical orbit. On one side the satellite is going faster than the Earth, and the satellite moves eastward in longitude, and on the other side, 12 h later, the satellite is moving westward. The eccentricity would continue to increase, except that after 6 months the sunlight comes from the opposite direction, and the effect is reversed. Satellite maneuvers are usually not done just to control eccentricity. When thrusters are fired to control the mean longitude, they also affect the orbit eccentricity. Choosing the best time of day for these maneuvers usually allows the orbit eccentricity to be kept within acceptable limits.

Daily radial oscillations also take place with eccentric orbits, as the distance between the satellite and the center of Earth varies. In terms of actual distance (kilometers or miles), the daily radial oscillation is exactly one-half of the east-west oscillation. For antenna pointing, the radial oscillations are usually not important. In a few applications, involving digital communications, radial oscillations may become significant, as both the frequency received and the time delay have a daily variation.

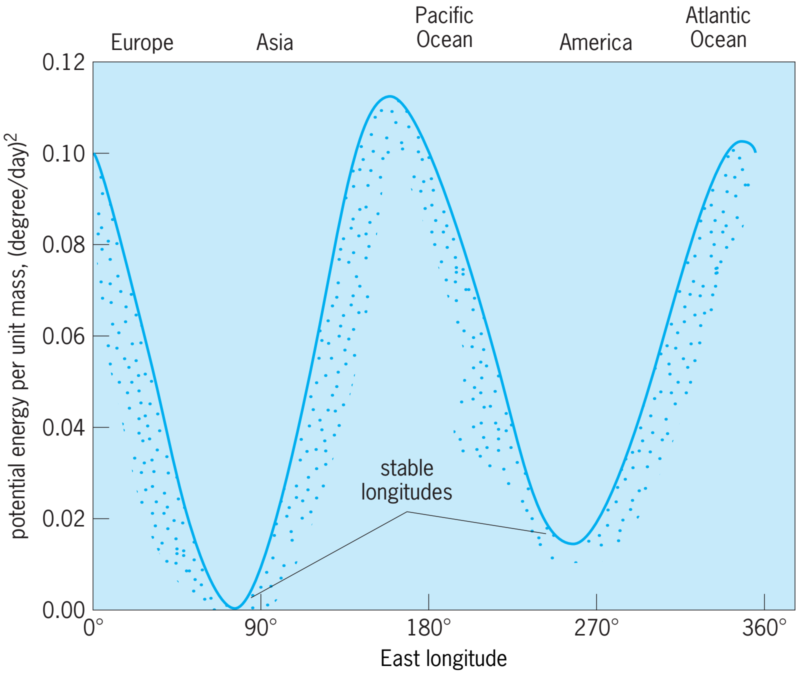


Fig. 7. Longitudinal acceleration pictured as hills and valleys. A satellite tends to "slide downhill." (The vertical scale, which is the potential energy per unit mass, is also the integral of the longitude acceleration with respect to longitude.)

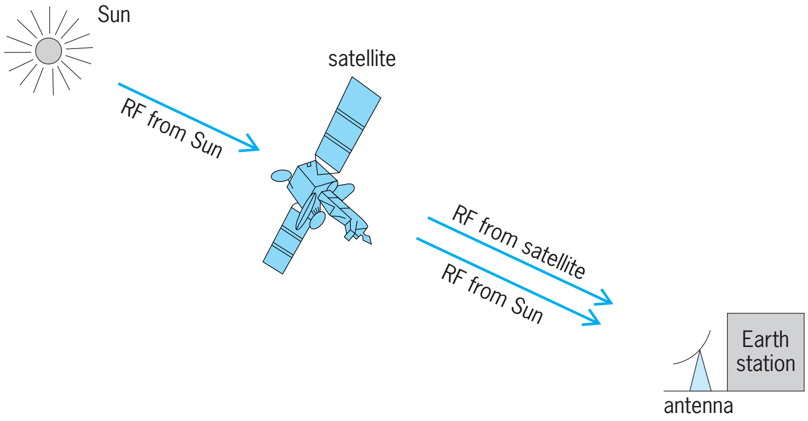


Fig. 8. Sun-station interference. Radio-frequency (RF) signals from the Sun interfere with those from the satellite.

Satellite link delays. A signal goes from Earth to a satellite at the speed of light, which is 299,792 km/s (186,282 mi/s). This means that there is a time delay between sending and receiving a signal. The distance to a communications satellite in geostationary orbit can vary from 35,786 km (22,237 mi) to 41,679 km (25,898 mi), so the time delay is from 0.12 to 0.14 s. The usual phone conversation through a satellite includes an uplink and a downlink from one speaker to another, and then a return through another uplink and downlink. Therefore, there are four time delays in sequence. The total delay is about half a second. This time delay can be a problem when the two speakers start speaking at the same time. It also produces an echo if equipment is not operating properly. Suppressing the echo requires special equipment because local phones have only a pair of wires to transmit and receive. Lower-altitude satellites, not in geostationary orbit, will have less time delay.

Sun, Earth, and Moon effects. The Sun emits radio-frequency radiation at microwave frequencies. This radiation can produce noise in a communications downlink, when the Sun is in the beam of the Earth station antenna receiving the satellite signal. The worst interference occurs when the satellite is directly between the Earth station and the Sun (**Fig. 8**). At different times, this condition may affect the downlink of every geostationary communications satellite to any Earth station. This Sun-generated noise may be a minor annoyance, or may completely overwhelm the transmitted signal. However, interference occurs only a few consecutive days in the spring and a few days in the fall, and it lasts only several minutes each day.

The Earth casts a shadow into space. Except for a few minutes at the start and end of the shadow period, these are total eclipses. When a geostationary satellite is in the shadow, the solar array output drops to zero. To continue operation, power is furnished by rechargeable batteries. These eclipses occur in two 6-week periods in the spring and in the fall. The duration of the eclipse increases to a maximum of 70 min (which occurs on the vernal and autumnal equinox), and then decreases again to zero over that period.

The Moon also casts a shadow in space. When a satellite is in the shadow, the solar array output also drops. These eclipses are mostly partial eclipses (the satellite is in the penumbra). The occurrences are irregular, and can occur during any month of the year. Most last less than an hour. A very small number of eclipses are much longer. On September 23, 2014, for example, an unusual partial eclipse on a geostationary satellite at 180° E will last over 3 h. A few similar eclipses of long duration occur every 18.6 years (when the Moon's orbit plane is closest to the equatorial plane). *See* ECLIPSE; MOON.

Launching into geostationary orbit. A communications satellite is often launched into geostationary orbit in three steps, which requires three firings of rockets or thrusters. The first step is a launch into a parking orbit, a low circular orbit. The second step is from the parking orbit into a transfer orbit, which has a high point (apogee) near geostationary orbit, and a third step circularizes the orbit and puts the satellite into geostationary orbit. Each rocket firing starts with an initial velocity, produces a change in velocity (called Delta-V), and ends with a final velocity (**Table 3**). The change in velocity is related to the mass ratio, that is, the ratio of the combined rocket, fuel, and satellite masses to the rocket and satellite mass after the fuel mass is used up. The actual numbers depend on various factors, including the launch site, launch vehicles, and height of the parking orbit. If a 1000-kg (2200-lb) satellite is needed in geostationary orbit, the mass in parking orbit is about five times as much, or 5000 kg (11,000 lb).

Constellations of satellites at lower altitudes. Compared to satellites in geostationary orbit, satellites at lower altitudes have smaller orbit periods. This means they cannot continuously communicate with an Earth station. Eventually they will disappear below the horizon. With a number of satellites, it is possible to always have one or more above the horizon. The Earth station can maintain continuous communications by switching from one satellite to another, just as a cell phone in a car switches from one tower to another. *See* MOBILE RADIO.

TABLE 3. Launching into geostationary orbit, from Kennedy Space Center (Florida)

	Initial velocity, km/s (mi/s)	Final velocity, km/s (mi/s)	Delta-V, km/s (mi/s)	Mass ratio
Achieve parking orbit	0.4 (0.25)	7.7 (4.8)	7.3 (4.5)	10 to 1
Perigee firing	7.7 (4.8)	10.1 (6.3)	2.4 (1.5)	5 to 2
Apogee firing*	1.6 (1.0)	3.1 (1.9)	1.8 (1.1)	2 to 1

*Cape Kennedy launch requires extra Delta-V of 0.3 km/s (0.2 mi/s) for 30° orbit plane change.

The advantages of these constellations include ease of communication to a satellite that is closer, ease of launch to lower altitudes, and antenna beams that can focus on smaller areas (thus serving higher-density populations). The major disadvantages are the large number of satellites required, and the large initial cost of manufacturing and launching all the satellites. Many different constellations of satellites have been studied. Usually a symmetrical constellation is planned, with each satellite carefully positioned with respect to the others.

One system, called Globalstar, uses 48 satellites. There are eight circular orbits, each with six satellites. The orbits are inclined at 52° to the Equator, and the ascending nodes (where the satellites pass the Equator going from south to north) are separated by 45°. In each orbit, there are six satellites equally spaced around the orbit. Each satellite provides communications between a handheld phone and a base station that connects to landlines, undersea cables, or satellites that handle international traffic. Technically, this system has been successful, but in the initial phases it has not generated the expected traffic and revenue. Another similar system, Iridium, included intersatellite links, so that any communications path could be established through a series of these satellites to any point in the world.

Other orbits. To meet special needs, other orbits are used by some communications satellites. The former Soviet Union established *Molniya* satellites in a Molniya orbit. This elliptical orbit is inclined 62.9° to the Equator, with a high point (apogee) at the most northern latitude. Special parameters were chosen so that the apogee did not precess to the Southern Hemisphere. Also, the orbit period was one-half of a sidereal day (11 h, 58 min), so every other apogee would always be at the same longitude. Earth stations usually had two tracking antennas, so that they could switch between satellites without a break in communications. The *Molniya* orbit has high-elevation-angle coverage of the Northern Hemisphere, and advantages of long dwell times and economical launches. During the Cold War, there were two hotlines between Washington and Moscow, one using a *Molniya* satellite, the other using a geostationary satellite.

More recently, variations on the Molniya orbit have been proposed for certain communications satellites. These all have in common the use of an inclined, elliptical orbit, with the satellites dwelling at the apogee over the geographic area they are intended to serve. In ITU terminology, they are referred to as HEO (highly elliptical orbit) satellites. Some systems have their orbit period as a submultiple of a sidereal day in order to keep the apogee at an constant Earth longitude. For continuous service, more satellites are required in the constellation because the orbit period is reduced (for example, three satellites for an 8-h orbit).

Satellites for mobile communications are sometimes designed without north-south stationkeeping. These are sometimes called geosynchronous satellites because, while the orbit period is equal to a sidereal day, the orbit inclination results in a daily north-south excursion of several degrees. This reduces consumption of satellite fuel. These orbits are applicable to mobile communications because the beamwidth of the mobile Earth stations tends to be wider, and able to encompass the north-south movement of the satellite without losing signal strength. Mobile applications with narrow-beamwidth Earth-station antennas must be equipped to constantly repoint their antennas because the mobile user may move in different directions and sometimes with pitch and roll. In this case, the additional movement of the satellite by a few degrees in a north-south direction can be easily accommodated. The *Marisat* satellite, for example, started with an inclination of several degrees (resulting in north-south oscillations of several degrees), which over the years first decreased to zero and then started increasing.

Stations in polar regions cannot use geostationary satellites. For those very close to a pole, the satellites are below the horizon, and for those a little farther away, it is difficult to communicate with a satellite at a low elevation. After 25 years, the *Marisat* satellite has an inclination of 15°, so each day it is above the horizon for a few hours. It has outlived its design lifetime, but still has some communications capability. Therefore, the research station at the South Pole can use it for a few hours each day, and other similar satellites at other times. *See* CELESTIAL MECHANICS; ORBITAL MOTION.

History and Present-Day Satellites

During World War II, the development of rockets and radar (using microwaves) made satellite communications a feasible concept. Launch vehicles would be required to place the satellites into orbit, and microwave components to make wideband communications possible. In 1945, Arthur C. Clarke wrote about the possibility of communications satellites in geostationary orbit. Transistors had not yet been invented, so he thought "in terms of large manned space stations. . . perhaps half a century" latter. In 1958, a battery-operated tape recorder (project SCORE) transmitted the first satellite message to the whole world—a Christmas message by President Eisenhower from a low-orbit satellite.

Active repeater satellites. In 1962, the first repeating communications satellites were launched: *Telstar* and *Relay*. These satellites received a signal, amplified it, and retransmitted it. For the first time, television signals could be transmitted across the Atlantic Ocean, but these satellites were in low orbit, and after 20 or 30 min disappeared below the horizon. Then *Syncom I* was launched into geosynchronous orbit. Due to launch constraints, it was in a 33° inclined orbit, so that each day the subsatellite point (the point directly under the satellite) oscillated between 33° N and 33° S.

Led by COMSAT, a multinational consortium of nations, the International Telecommunications Satellite (INTELSAT) Organization, was formed to establish global commercial satellite communications. In 1965, *Early Bird* was launched by COMSAT into a geostationary orbit, in which it remained stationed over the mouth of the Amazon River. It could thus

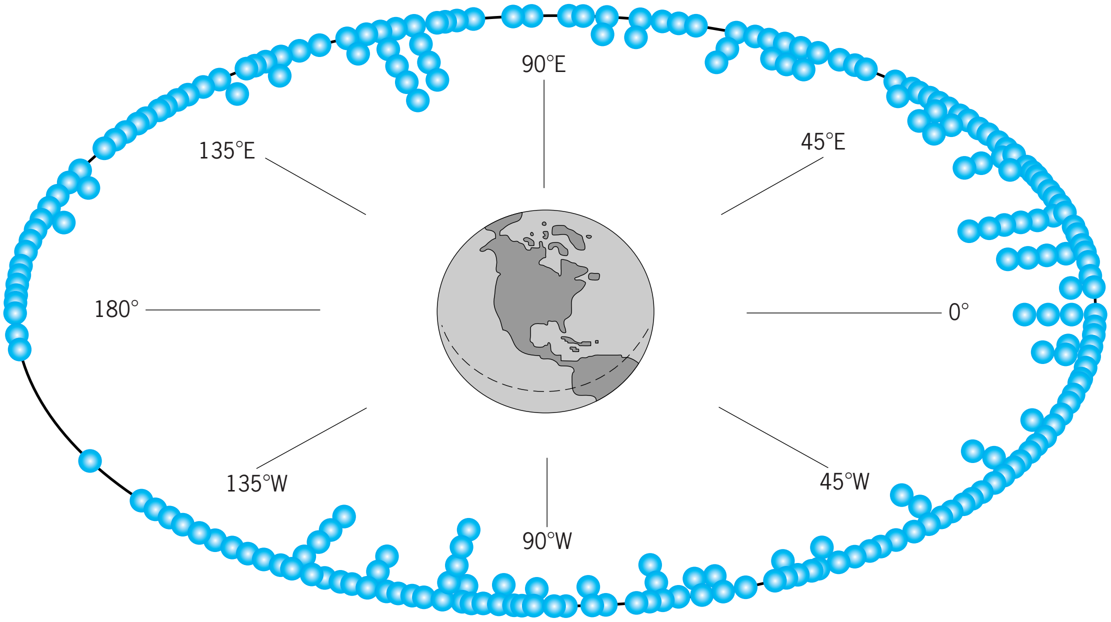


Fig. 9. Commercial communications satellites in geostationary orbit. (*Boeing Company*)

provide continuous communications between the eastern United States and western Europe 24 h a day. An INTELSAT satellite launched in 1967 brought commercial service to the Pacific area. Additional satellites later provided more communications to achieve a commercial global system.

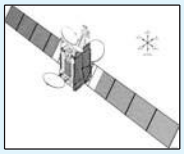
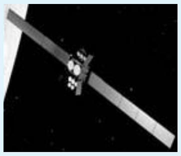
Meanwhile, the U.S. Department of Defense developed the Initial Defense Communications Satellite Program (IDCSP), whose satellites were in near synchronous orbits. The Soviet Union launched communications satellites into Molniya orbits, which provided better coverage at high latitudes (far from the equator). Many Communist countries used the system initiated by the Soviet Union called Intersputnik.

Technical progress. Early earth stations were large and powerful so that they could communicate with small and weak satellites. As the capabilities of satellites increased, the Earth terminals could be smaller and less powerful. From specialized sites they moved to business premises and to homes. From communications to ships they progressed to other mobile communications, with airplanes, cars, and handheld phones. Satellite antennas became larger, with higher gains. Low-noise amplifiers made it easier to detect faint signals. Traveling-wave tubes and solid-state power amplifiers became more powerful. Silicon solar cells tripled in efficiency. Nickel-cadmium batteries were replaced by nickel-hydrogen and other batteries.

The number of active commercial communications satellites in geostationary orbit is now over 200 (**Fig. 9**), not including communications satellites in lower orbit or military communications satellites in geostationary orbit. With a variety of methods of frequency reuse, there is still room for more satellites.

Communications satellites are designed for specific missions, but have many common features (**Table 4**). A large, modern communications satellite may communicate with large fixed Earth stations (INTELSAT), it may broadcast to a large number

TABLE 4. Characteristics of a few communications satellites in use*

Spacecraft type:	Fixed satellite service	Broadcast	Mobile	Ka-band spot	Military
					
Spacecraft name:	INTELSAT IX	Echostar 9	Thuraya 2	iPSTAR	Wideband Gapfiller
Launch year	2001 to 2003	2003	2003	2005	2007
Procurement agency	INTELSAT	EchoStar	Thuraya/Etisalat	Shin	U.S. Military
Satellite contractor	Space Systems/Loral	Space Systems/Loral	Boeing	Space Systems/Loral	Boeing
Launch vehicle	Ariane-44L, Ariane 5, Proton-M	Zenit-3SL	Zenit-3SL	Ariane-5GS	Delta-4M + (5,4)
Orbital slot	64°E to 34.5°W	121°W	44°E	120°E	
Satellite mass, kg (lb)	4725 (10,395)	4737 (10,421)	5177 (11,389)	6775 (14,905)	5987 (13,171)
Transponders per frequency band	44 C, 12 Ku	2 Ka, 32 Ku, 24 C	128-element L, 2 C	53 Ku, 18 Ka	× Ka
Mission life, years	15	15	12	15	14

*From Space Systems/Loral.

of television users (Echostar and Direct TV), or it may communicate directly with handheld telephones (Thruraya). Satellites may be launched from the Kennedy Space Center in the United State (using the Delta or Atlas launch vehicle), Korou in French Guiana (Ariane), or Russia (Zenit or Proton). Many have a mass of around 5000 kg (10,000 lb), 50 to 100 power amplifiers (transponders), and design lifetimes of 12–15 years.

Since the beginnings of communications satellites in the 1960s, advances in communications have included fiber-optic cables and cellular telephones. However, these technologies are unlikely to completely replace satellites since these services complement each other. Satellites can never provide adequate cell phone service for large cities, but cellular phone towers may never be built in sparsely populated areas, and certainly not in ocean regions. Satellites are well suited to mobile communications, including aeronautical, maritime, and land applications. Fiber-optic cables are ideal for wideband communications from point to point, but when undersea cables break, satellites are often used to restore traffic. And satellites are particularly useful for broadcasting to a large number of points, whether for distributing network programs to television stations, or directly to television subscribers. Satellites also have the flexibility to switch their capability from one area to another. Spot beams can be repositioned to accommodate changing traffic needs for coverage of special events such as the Olympics or compelling news, such as disasters and other national and international developments. Gary D. Gordon; Denis J. Curtin

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Communications scrambling

The methods for ensuring the privacy of voice, data, and video transmissions. Various techniques are commonly utilized to perform such functions.

Voice. Analog methods typically involve splitting the voice frequency spectrum into a number of sections by means of a filter bank and then shifting or reversing the sections for transmission in a manner determined by switch settings similar to those of a combination lock; the reverse process takes places at the receive end. The strength of these methods depends on the number of switch settings available (often called the key size) and the rate at which the switch settings are changed. *See* ELECTRIC FILTER.

Digital methods first convert the analog voice to digital form by a number of digital coding techniques such as pulse code modulation (PCM), delta modulation, or linear predictive coding (LPC). The digital voice data are then scrambled or encrypted by one of the many methods discussed below and are transmitted digitally. After the data are received, they are descrambled or deciphered and then converted back to analog form by the appropriate voice decader. *See* ANALOG-TO-DIGITAL CONVERTER; DIGITAL-TO-ANALOG CONVERTER; MODULATION; PULSE MODULATION.

Data. A simple data-scrambling method involves the addition of a pseudorandom number sequence to the data at the transmit end. The same sequence must be subtracted at the receive end to recover the data. The strength of the method depends on the period of the sequence and the way the sequence is generated, as well as the number of different pseudorandom number sequences available. Devices using this method are known as stream ciphers. Typically, the pseudorandom number sequences are in binary form; and the addition and subtraction are performed in binary form also.

A second method partitions the data into blocks. Data within a block may be permutated bit by bit or substituted by some other data in a manner determined by the switch setting, which is often called a key. At the receive side, the reverse permutation or substitution is performed to recover the data. Devices using this method are known as block ciphers. An example of block ciphers is the Data Encryption Standard (DES), accepted as a standard by the National Bureau of Standards in 1977. DES, which uses both permutation and substitution iteratively, is approved for nonmilitary, nondiplomatic governmental use.

The National Security Agency established a commercial communication security endorsement program under which encryption devices suitable for different applications are developed and certified by the government. *See* CRYPTOGRAPHY.

Video. Typical video scrambling devices used for cable television applications involve modifying the amplitude or polarity of the synchronization signals, thereby preventing the normal receiver from detecting the synchronization signals. A device capable of undoing the modifications is used to recover the signal. Some devices also invert the polarity of the video signal so that the black and white levels are reversed. *See* CLOSED-CIRCUIT TELEVISION.

A more sophisticated technique, used in satellite transmission, introduces a random delay to the active video signal on a line-by-line basis which is determined by a pseudorandom number sequence. Knowing the sequence, the receiver can compensate for the delay and recover the signal. An even more advanced technique called cut-and-rotate has been proposed. This method selects a random point of time in a scan line and cuts the line into two sections. The second section of the line is transmitted first, followed by the first section. By knowing exactly where the cut takes place, the receive side can perform the reverse process and reconstruct the signal.

Video signals can also be digitized by a number of coding techniques and then scrambled by any of the data-scrambling techniques discussed above to achieve high security. *See* TELEVISION. Lin-Nan Lee

Communications systems protection

The protection of wire and optical communications systems equipment and service from electrical disturbances. This includes the electrical protection of lines, terminal equipment, and switching centers, and inductive coordination, or the protection against interference from nearby electric power lines.

Sources of disturbance. The principal sources of destructive electrical disturbances on wire communications systems are lightning and accidental energization by power lines. Lightning that directly strikes aerial or buried communication cable may cause localized thermal damage and crushing. Simultaneously, it energizes the communication line with a high-level voltage transient that is conducted to terminal equipment. Indirect strikes are more common than direct strikes and, although they normally do not cause mechanical damage, they propagate electrical transients along the line. The rate of occurrence of these transients is geographically dependent, increasing with the level of thunderstorm activity (keraunic level) and earth resistivity. The distance over which a buried cable collects a lightning strike, and the resulting voltage produced within a cable, both increase as resistivity of the earth increases. The duration of the lightning-caused voltage transient on shielded communication cable is typically less than 1 or 2 milliseconds. The magnitude of the voltage between conductors and shield of a cable can reach several thousand volts. In regions of high thunderstorm activity and earth resistivity, a communication line several miles long may experience annually more than 1000 voltage transients of magnitude greater than 250 V. The accompanying current surge usually is less than 100 A, but much higher currents can result from a direct strike to the cable. *See* LIGHTNING.

During fault conditions on commercial power lines, high voltages may occur in nearby communication lines by several mechanisms. The most common is magnetically induced voltage caused by the high unbalanced currents of a phase-to-ground power-line fault. During such an event, an aerial or buried communication line that is parallel to the faulted power line intercepts its time-varying magnetic field, incurring a high longitudinal voltage. In effect, the system is a one-turn to one-turn air-core transformer. This inductively coupled voltage may be several hundred volts, with current limited by the impedance of the communication line and its terminations. Another source of high voltage is a damaged aerial power line that falls and directly contacts an aerial communication cable, or a digging machine that simultaneously contacts power and communication cable jointly buried in a common trench. In these cases, currents conductively enter the communication lines and are limited in magnitude only by fusing capabilities. Finally, communication lines near a power station or transmission-line tower may be subjected to high voltages from the rise in ground potential as power fault currents return through the ground mat of the power station. In each of these mechanisms, power-line fault-clearing devices are intended to limit duration of conduction to a few seconds. However, if the power-line fault impedance is high, the automatic clearing devices may not operate, and the overvoltage can last indefinitely. *See* ELECTRIC POWER SYSTEMS; ELECTROMAGNETIC INDUCTION; GROUNDING; TRANSFORMER; TRANSMISSION LINES.

In city centers, the diversion of lightning strikes by steel-framed buildings, and the shielding effect of the many underground metallic utility systems, considerably reduce the probability of high-voltage transients from lightning or induction from power lines. Since communication and power facilities are routed in separate conduits, the possibility of a power contact is remote. *See* ELECTRICAL INTERFERENCE; ELECTRICAL NOISE.

Electrical protection. The components of a communications system requiring electrical protection include both metallic and optical-fiber lines, terminal equipment, and switching centers.

Metallic lines. Metallic communication lines often are made up of many closely spaced pairs of wires arranged as a cable. A grounded circumferential metallic shield on the cable reduces the magnitude of electrical transients from nearby lightning strikes, and also can intercept a low-current direct strike, minimizing damage to the internal conductors. The effectiveness of the shield is improved if its resistance per unit length is low and if the dielectric strength of the insulation between the shield and the internal conductors is high. Frequent grounding of the shield eases the return of lightning currents to earth, thereby reducing voltages in the cable. Voltage breakdown within the cable can be avoided by installing surge protective devices between the pairs and shield at stress points along the cable. The devices may be air gaps consisting of carbon electrodes separated by a few thousandths of an inch (about 0.1 mm), or gas tube surge arresters, which use metallic electrodes separated by a gap in an enclosed discharge medium. They limit voltages at their terminals to the capabilities of the cable insulation, and are used principally in areas of high lightning activity. *See* COMMUNICATIONS CABLE; ELECTRICAL SHIELDING; GAS TUBE; LIGHTNING AND SURGE PROTECTION; SURGE SUPPRESSOR.

A special case for this type of protection arises on lines that serve antennas of wireless telecommunications systems. Lightning striking an antenna tower propagates voltage surges along the cable. If the cable is not well shielded and insulated, damage can occur, sometimes at considerable distance from the tower. Surge protectors placed between lines and shield at several locations within about a mile (1–2 km) of the tower help avoid this damage.

The localized damage caused by a direct strike to buried shielded cable can be reduced or eliminated by the burial of one or more wires at least 1 ft (0.3 m) above the cable. These shield wires divert all or much of the lightning current from the cable.

Damage to cable plant from a power-line contact is minimized by providing frequent bonds between the cable shield or aerial support strand and the neutral conductor of the power line. These bonds create low-resistance paths for fault currents returning to the neutral, and hasten deenergization by power-line fault-clearing devices. Closely spacing the bonds limits the length of communication cable that is damaged by the contact.

The outer metallic shields of belowground cables may be attacked by electrolytic action and require protective measures against corrosion. Electrolysis occurs where direct current leaves the shield. Severe sources of electrolytic currents include stray direct current from electrified railways and from industries using large amounts of direct current in grounded circuits. An effective remedial measure is to install a gap, known as an insulating joint, in the cable shield to interrupt the current. This gap can hinder the electrical protection and noise mitigation function of the shield unless it is bridged with a capacitor that provides a bypass for lightning and power-frequency currents. *See* CORROSION.

Optical-fiber lines. Optical-fiber communication lines are enclosed in cables that may contain metallic components to provide mechanical strength, waterproofing, local communications, or a rodent barrier. Though the cables otherwise would be immune to the effects of lightning or nearby power lines, such metallic components introduce a measure of susceptibility that is made all the more important by the high information rates carried by the fibers. A direct lightning strike to a metallic component of buried optical-fiber cable can cause localized thermal damage, arcing, and crushing that together may damage the fibers. Electrical protection is provided by cable designs that withstand these effects. As with metallic lines, the probability of this damage can be reduced by burying one or more shield wires at least 1 ft (0.3 m) above the cable.

Alternating currents may be conducted on the metallic sheath components of optical-fiber cables during an accidental contact with power-line conductors. Cable damage is minimized in extent by bonding the sheath to the neutral conductor of the power line, and by providing enough conductivity to carry the currents without damage to the fibers. *See* OPTICAL COMMUNICATIONS; OPTICAL FIBERS.

Some networks provide high-speed data via optical lines between a communication center and a pedestal near the served premises, and then use metallic lines to enter the premises (fiber-to-curb system). Often the power for equipment in the pedestals comes from a centralized powering node over metallic lines. Surge protectors are placed at each end of these powering lines to help avoid equipment damage. Because the power on these lines may exceed those of ordinary telephony, care should be taken to ensure that the protectors can reset after conducting a surge. These protectors, and the protectors on the lines between pedestal and premises, should not have too low a limiting voltage or they may needlessly cause data disturbances during thunderstorms or power-line malfunctions.

Terminal equipment. To protect the users, their premises, and terminal equipment, communication lines that are exposed to lightning or contacts with power lines are usually provided with surge protectors. Article 800 of the National Electrical Code requires that communication lines exposed to contact with power lines of voltages greater than 300 V be equipped with a protector at the entrance to the served premises. Interbuilding lines that are exposed to lightning also have protectors. Although not required, it is common practice to minimize equipment damage by so equipping communication lines in an area of significant lightning exposure even if there is no power-contact hazard. Article 830 extends similar requirements to coaxial circuits that provide network-powered broadband communications. *See* ELECTRICAL CODES.

For the most part, the protector contains a voltage-limiting device, such as a gap-type or solid-state surge protector, connected between each wire of the line and a local ground electrode. Any voltage surge on the wires thereby is limited with respect to local ground. Voltages between the communication lines, power lines, and other grounded systems within the premises are limited by bonds between the protector ground, the power neutral, and other metallic systems.

Sparking between communication lines and nearby objects, and electric shock hazard to the user, are minimized if the insulation of the lines and terminal equipment withstands voltages at least as great as the limiting voltage of the protector (plus an allowance for voltage drop of grounding conductors). Service interruptions are avoided if electronic circuits within the equipment also are able to withstand these surge voltages. Within some equipment, surge immunity is achieved by applying additional voltage limiters, such as varistors, avalanche diodes, or special low-voltage gas tubes. *See* MICROWAVE SOLID-STATE DEVICES; VARISTOR.

Sustained currents from power-line contacts can overheat the network-side wires connected to the protector unless interrupted by a current-limiting device. A short length of fine-gage wire in series with the communication line, or a fuse at the protector, is usually installed for that purpose. If the terminal equipment contains an internal voltage limiter, an additional fuse may be needed to protect the premises wire connecting the equipment to the protector. *See* FUSE (ELECTRICITY).

Switching centers. Switching centers contain electronic equipment that routes communications to their proper destinations. This equipment is protected from the effects of electrical transients appearing at interfaces with external communication lines in a similar way as for terminal equipment. In addition to these effects at external interfaces, communication equipment within centers may be subjected to transient voltages resulting from lightning strikes to nearby objects or from direct strikes to the building. Such events cause rapidly varying currents in metallic structural members and in the grounding system. These currents can be conductively and magnetically coupled to wires interconnecting equipment in the building. Depending on the relative paths taken by the lightning currents and the wiring, transient differences in voltage may appear between nearby ground and conductors that extend between internal locations.

One method of controlling these voltages is to bond, as often as possible, all metallic equipment frame members and grounded circuits to the floor ground of the building. This technique, known as an integrated ground (or mesh bonding network), reduces potential differences, but permits surge currents to circulate throughout the system. Sensitive electronics can be damaged by the local potential differences caused by these circulating currents, so some designs avoid circulating currents by isolating the entire system from ground except at one location, which is deliberately grounded. This system, known as the isolated ground plane (or isolated bonding network), has found effective use in many switching centers. *See* ELECTRIC PROTECTIVE DEVICES; ELECTROMAGNETIC COMPATIBILITY; ELECTRONIC EQUIPMENT GROUNDING; SWITCHING SYSTEMS (COMMUNICATIONS).

Inductive coordination. Inductive coordination refers to measures that reduce the magnitudes and effects of steady-state potentials and currents induced in metallic communication lines from paralleling power facilities. Where power and communication lines are parallel for long distances, normal-load power currents returning to the power generator via the neutral conductor or earth induce voltages into the communication lines. Malfunction of terminal equipment may result. The induced voltages appear equally in each wire of a pair; electrical asymmetries in the lines or terminal equipment convert them to a voltage between the wires of a pair and may cause background noise or data errors. Remedial measures that reduce the induction effect are (1) balancing the power-line currents to reduce the neutral component returning to the generator; (2) using a grounded metallic shield on the communication cable so that shield currents partly cancel the field from the disturbing power line; (3) using well-balanced communication line and terminal equipment to minimize conversion to voltages between wires; (4) installing reactive components in the communication line to reduce induced currents; and (5) using terminal equipment that is tolerant of induced voltages. *See* INDUCTIVE COORDINATION.

Solar magnetic storms. Solar magnetic storms, which occur with varying intensity over an 11-year cycle, produce strong currents in a predominantly east-west direction of the earth surface. They cause a voltage difference between a conductor and the earth that increases at higher latitudes and with earth resistivity. The voltage typically lasts for several minutes and is low frequency (below 0.1 Hz); it can be treated as a direct-current voltage on telecommunication and power-line circuits.

Long-distance metallic lines are susceptible to these storms to the extent that they have conductive connections to earth, either deliberately or by means of surge protective devices that are operated by the storm. The increasing use of optical-fiber lines for long-distance telephony largely removes this threat. Where protectors are used on long metallic lines, they should be capable of continuously conducting up to 1.0 A without posing a fire hazard. Short metallic lines are unlikely to experience enough voltage to operate surge protectors. If terminals on these lines have conductive connections to earth, ability to operate in the presence of 3-V direct current between ends of the line accommodates all but extreme magnetic storms.

Power utilities have had widespread outages during magnetic storms, and this loss of utility power poses a threat to metallic and optical-fiber communication systems. Reserve power systems using batteries in conjunction with engine alternators help provide uninterrupted telecommunications service for the duration of an extended power outage. *See* GEOELECTRICITY; GEOMAGNETIC VARIATIONS; UNINTERRUPTIBLE POWER SUPPLY.

Nuclear electromagnetic pulse. A nuclear burst at altitudes higher than about 25 mi (40 km) generates an electromagnetic field pulse over a large area of the earth surface; a burst at 300 mi (500 km) would illuminate most of the contiguous United States. The magnitude of the electric field would peak at tens of kilovolts per meter in a few nanoseconds and would last a few hundred nanoseconds. It would affect communication systems by causing high-voltage transients on wires that enter electronic equipment at telecommunications centers. The field would couple to the wires by two mechanisms: direct penetration through walls of the building into the wiring; and coupling of current pulses onto conductors that enter the building (such as power lines, telecommunications cables, and antenna leads), which in turn couple surges to the internal wiring. The surges, though brief, may be much larger than normal signal levels and can cause malfunctions or damage. The protection measures summarized here are among those considered to be reasonable and practical for public communication networks.

Direct field penetration through the structure is reduced by enhancing its shielding. This is done by selecting construction methods with electrically interconnected components in walls, floors, and roof. Poured concrete with interconnected steel reinforcement is preferred. The interconnected steel should be bonded to the common bonding network of the building. Where this construction is unavailable, interior metallic structures, such as cable racks, supports, raceways, and equipment cabinets, should be interconnected and bonded to the common bonding network. Critical equipment and its wiring should be distant from unshielded windows.

The effect of surge currents entering via penetrating conductors is best reduced by diverting to ground much of the surge current before it enters the building. This is largely done by directly bonding to the grounding system all entering telecommunication cable shields and antenna lead-ins, and by installing surge protectors on mains conductors at the service entrance. Because these means do not completely remove penetrating currents, critical equipment and its wiring should be separated from penetrating conductors. *See* ELECTROMAGNETIC PULSE (EMP). Michael Parente

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Commutation

The process of transferring current from one connection to another within an electric circuit. Depending on the application, commutation is achieved either by mechanical switching or by electronic switching.

Mechanical switching. Commutation was conceived over a century ago through the invention of the direct-current (dc) motor. When direct current is supplied to a winding on a rotor that is subjected to a stationary magnetic field, it experiences a rotational force and resulting output torque. As the stator north and south poles are reversed relative to the rotating winding, the rotor current is reversed by a commutator in order to maintain the unidirectional torque required for continuous motor action. *See* DIRECT-CURRENT MOTOR; WINDINGS IN ELECTRIC MACHINERY.

The principle is illustrated in **Fig. 1**. In its simplest form, a single rotor winding is connected between two segments of a cylindrical copper commutator which is mounted axially on the rotor. Connection to the external dc supply is through sliding carbon contacts (brushes). The segments have small insulated gaps at *A* and *B*. As *A* and *B* pass the brushes, the current in the rotor winding reverses. In the short interval where the brushes short-circuit the segments, the rotor current decays before building up in the reverse direction. The angular position of the brushes is selected to reverse the current at the appropriate rotor position. *See* COMMUTATOR.

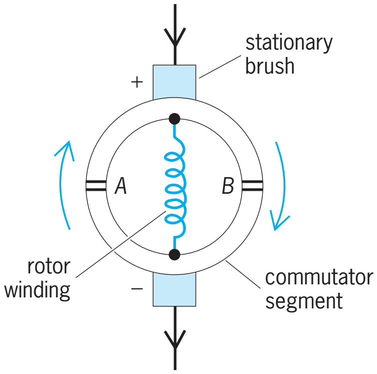

Fig. 1. Basic commutator for a dc motor.

Commutation not only reverses the current but automatically synchronizes the timing of the reversal with the rotor position, irrespective of motor speed. The process can also be considered as a mechanical alternating-current/direct-current converter with the frequency of the rotor current being matched to the speed. The same commutation permits the reverse conversion in a dc generator where alternating-current (ac) voltages induced in a driven rotor are converted to a dc output voltage. *See* DIRECT-CURRENT GENERATOR.

Practical dc motors and generators typically incorporate several winding sections positioned around the rotor and connected to a correspondingly increased number of commutator segments to produce smoother performance.

The same principle of commutation applies to the ac commutator motor and universal ac/dc motor, which are common in variable-speed kitchen appliances and electric hand tools. The commutator still reverses the connection to the rotor to accommodate rotor position. When ac voltage is supplied to both commutator and stator winding, current reversals in the ac waveform are common to both the rotor and the stator thus torque remains unidirectional. *See* ALTERNATING-CURRENT MOTOR; UNIVERSAL MOTOR.

Electronic commutation. The equivalent of mechanical commutation occurs in solid-state converter circuits such as those used for rectifying ac to dc or inverting dc to ac. **Figure 2** shows a three-phase converter widely used in industry. For simplicity, the ac supply network is represented by equivalent phase voltages in series with the effective supply inductance. (Often this inductance is mainly the inductance per phase of a converter transformer that interfaces the converter and the three-phase supply.) Usually, supply resistance is relatively low and plays a negligible role in the converter action. As shown, thyristors 1 and 2 are conducting the dc current from phase *a* to phase *c*. A smooth dc current does not produce a voltage across the inductance *L* in each phase.

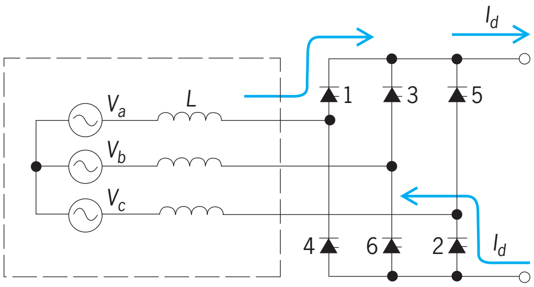

Fig. 2. Three-phase converter.

In the cyclic conduction sequence, the dc current is commutated from phase *a* and thyristor 1 to phase *b* and thyristor 3. To achieve this, thyristor 3 is gated in a region of the ac waveform when its forward voltage is positive. Turning it on applies a reverse voltage to thyristor 1 (phase *b* being more positive than phase *a*), which ceases conduction to complete the commutation of the dc current. This is repeated in sequence for the other thyristors in each ac cycle. *See* CONVERTER; SEMICONDUCTOR RECTIFIER.

In practice, the commutation is not instantaneous because of the inductance, which is referred to as commutation inductance or commutation reactance when considered as an ac impedance. The buildup of current in the incoming phase matches the reduction of current in the outgoing phase over a certain electrical angle until commutation is complete. The angle is referred to as the overlap or commutation angle and may typically be 20–30 electrical degrees. *See* INDUCTANCE.

Meanwhile the dc waveform, which is composed of segments of the ac waveform as selected by the switching action, is affected by the overlap because of the transient commutation voltage drop in the inductances. On average, with consideration of six commutations per ac cycle, the dc voltage may be reduced by several percent, sufficient for commutation to be incorporated into conversion calculations. The overlap angle is a variable and becomes larger for a larger dc current to be commutated, for a larger commutation reactance, and for a smaller ac voltage. It also depends on the actual values of ac voltage at the point-on-wave at which a thyristor is gated to turn on.

Artificial (forced) commutation. The ac supply voltages in Fig. 2 provide a natural commutation voltage. In some other circuits, additional circuit means are necessary to provide a reverse voltage for the outgoing thyristor (or other solid-state switching device). They include charged capacitors, voltage reversals from resonant inductance–capacitance circuits, and additional thyristors.

Electrical noise. Commutation, whether natural or forced, creates abrupt transitions in the converter waveforms, with high-frequency components as an unwanted by-product. This is a factor in assessing radio-frequency interference in the vicinity of power electronic equipment and supply leads. *See* ELECTRICAL INTERFERENCE; ELECTRICAL NOISE.

Commutation with dc converter stations. Converters at the very high power levels of dc transmission are based on natural commutation of the converters shown in Fig. 2. As for many industrial applications of the same circuit, the timing of the commutation process is determined by real-time automatic control. In controlling the dc voltage and current, the commutation must be confined to points in the ac waveform for which the commutating voltage is conducive to successful completion of the commutation. Theoretically, the gating of a thyristor can be delayed by a half cycle (180°) from the point-on-wave where its voltage becomes positive, in order to have a controlled transition from full dc voltage as a rectifier to full reverse dc voltage as an inverter. In practice, commutation imposes constraints at both extremes of control: delay with a minimum value of 5–7° provides a sufficient commutation voltage to avoid hesitant thyristor turn-on; at the other extreme, the delay must still leave sufficient time for the overlap angle together with a period for the outgoing thyristor to recover its ability to hold off conduction. *See* DIRECT-CURRENT TRANSMISSION.

In establishing the maximum permitted delay (firing angle) for inverter operation, the control has to take into account variations in the overlap angle (as noted previously) to maintain the recovery period referred to as the extinction or commutation margin angle, typically 15–18°. Should a delayed commutation extend into this margin, there is the prospect of commutation failure, which implies that the orderly converter switching is disturbed, resulting in a collapse of the converter dc voltage. This power interruption is temporary if the control returns the firing angle to a safe region. A disturbance in the ac system adjacent to a converting station may depress the ac voltage to a level at which commutation cannot be completed. This is also designated as a commutation failure. The recovery of the converter to the previous power level commences when the voltage is restored. John Reeve

Bibliography. J. Arrillaga, *High Voltage Direct Current Transmission*, 2d ed., 1998; B. J. Chalmers, *Electric Motor Handbook* 1988; C. W. Lander, *Power Electronics*, 3d ed., 1994; M. A. Rashid, *Power Electronics*, 3d ed., 2003.

Commutator

That part of a dc motor or generator which serves the dual function, in combination with brushes, of providing an electrical connection between the rotating armature winding and the stationary terminals, and of permitting the reversal of the current in the armature windings. For explanation of the necessity of this function *see* COMMUTATION.

A commutator (**Fig. 1**) is composed of copper bars assembled to form a drumlike cylinder which is concentric with the axis of rotation. Insulation, commonly mica, to provide exceptional mechanical and electrical stability, is placed between commutator bars and between the bars and the shaft.

Conducting brushes (**Fig. 2**), commonly carbon, sufficient in size and number to carry the current, are spaced at intervals of 180 electrical degrees about the surface of the commutator and held in contact with the surface of the commutator by spring tension. In special cases, as when only the top or bottom half of a dc motor is accessible, only one positive brush set and one negative brush set are used when the armature is wave-wound. This is permissible, as wave windings characteristically have two parallel paths between any two commutator bars separated 180 electrical

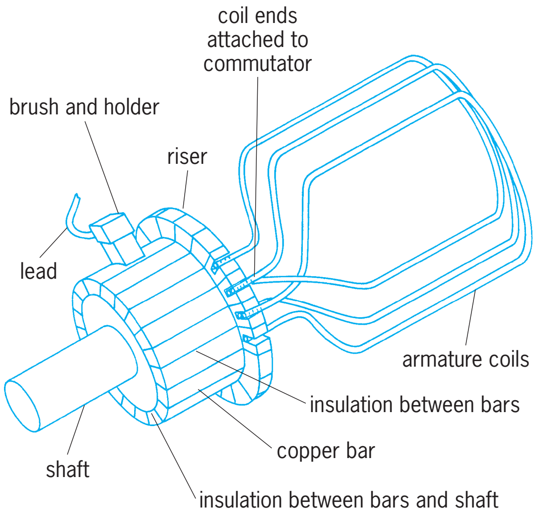

Fig. 1. Commutator and brush assembly with coil connections for lap winding.

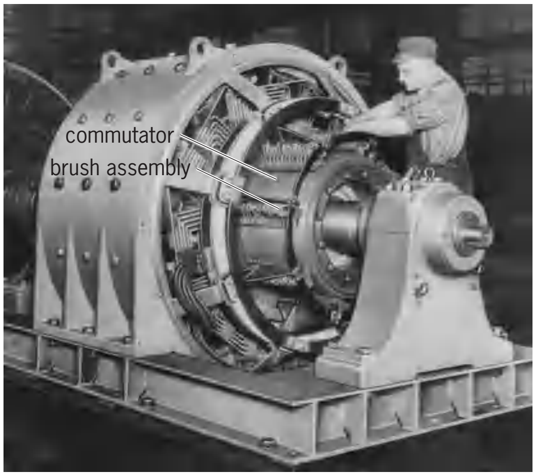

Fig. 2. Direct-current generator showing the typical brush assembly. (*Allis-Chalmers*)

degrees. Machines employing commutators are usually restricted to voltages below the kilovolt range because flashover between the closely spaced commutator segments may result from deposition of carbon dust from the brushes and from uneven voltage distribution between commutator bars under heavy loading. For machines using commutators *see* DIRECT-CURRENT GENERATOR; DIRECT-CURRENT MOTOR; REPULSION MOTOR; UNIVERSAL MOTOR; WINDINGS IN ELECTRIC MACHINERY.

Arthur R. Eckels

Compact disk

A system for data storage in which digitally encoded information in the form of microscopic pits on a rotating disk is accessed by optical readout. The compact disk was originally developed as a music carrier providing high fidelity, random access, convenience, durability, and low cost. Its attributes made it suitable for storing diverse data such as video programs and computer software, and improvements allowed recordability and erasability. Greater storage capacity and more sophisticated integration of features is provided in the DVD optical disk format.

Operating Principles

An acoustic signal waveform is stored on the disk in the form of a binary code, as a series of 0's and 1's. This is done by forming pits along spiral tracks on a transparent plastic disk, overlaying this with a reflective coating, and covering this coating with a protective layer. The light from a semiconductor laser is focused onto the pits from below (**Fig. 1**). The presence or absence of pits within the laser spot changes the intensity of the reflected beam (pits diffract the light, reducing reflected intensity). The reflected light strikes a light-detecting photodiode that converts the varying-intensity light beam into a binary electrical signal. *See* LASER.

With the light focused on the pits, the outer lower surface of the transparent disk is out of focus; hence dust, fingerprints, and minor scratches on this surface are blurred and do not affect the detection process. Even more important, the use of an optical pickup means that there is no mechanical contact and hence no wear on pickup or disk.

Because the focused laser spot size is extremely small, a considerable amount of information can be placed on the data surface. Adjacent tracks of the spiral of pits are nominally 1.6 micrometer apart (track pitch), and hence about 22,200 such tracks are placed across a 35.5-mm radius on a 120-mm-diameter (4.75-in.) disk. The track is optically scanned at a nominal constant linear velocity of about 1.4 m/s. The pits, and the separations between pits along a track, vary in length from about 0.97 to 3.56 μm (**Fig. 2**). Smaller track pitch and lower linear velocities (and shorter pit and land lengths) may be used for greater storage capacity.

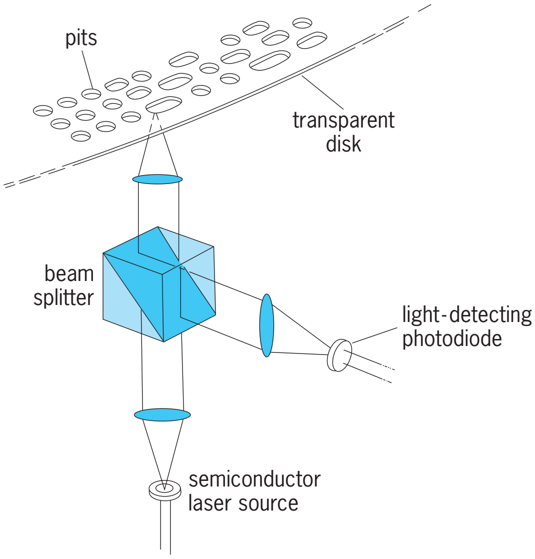

Fig. 1. Optical readout system for an audio compact disk.

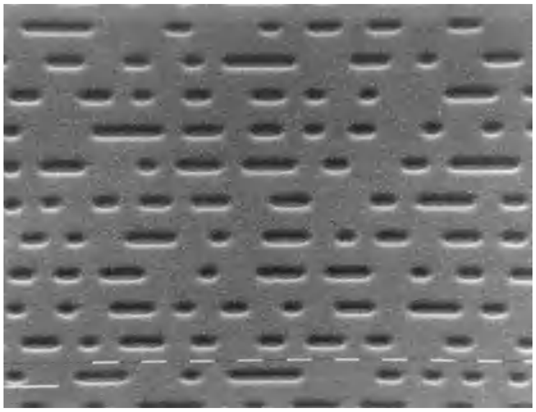

Fig. 2. Pits on an audio compact disk. (*From M. G. Carasso et al., Compact disc: Digital audio, Philips Tech. Rev., 40(6):151–180, 1982*)

Digitally encoded waveform. The human ear is insensitive to sounds with frequencies higher than about 20,000 Hz. The Shannon (or Nyquist) sampling theorem specifies that a waveform can be exactly reproduced from samples taken at a uniform rate of at least twice that of the highest signal frequency. The standard sampling rate for audio compact disks is 44.1 kHz; thus, the highest audio frequency encoded is 22.05 kHz. The amplitude of each sample is represented by a 16-bit binary word. Thus, the amplitude of each original audio sample is approximated to the nearest of 2^{16} (65,536) equally spaced levels in a process known as quantization. With stereo channels, the data rate stored on the disk is $2 \times 16 \times 44{,}100 = 1{,}411{,}200$ bits/s. *See* INFORMATION THEORY; PULSE MODULATION.

An important audio performance figure is the signal-to-noise ratio. If it is assumed that all unwanted noise and interference have been eliminated, the remaining noise will be that due to the quantization process, with an amplitude of the order of one-half of a quantization level. The theoretical signal-to-noise ratio, the amplitude of the largest undistorted signal to the amplitude of the noise, is $S/N = 6.02(16) + 1.76 = {\sim}98$ dB. This is comparable, for example, to the figure of 90 dB for the dynamic range of a symphony orchestra. As a comparison, the best signal-to-noise ratio figure for professional magnetic tapes is about 80 dB, and acceptable signal-to-noise ratios for conventional audio systems are about 70–80 dB.

Disk mastering and replication. In the disk mastering and replication process (**Fig. 3**), a glass disk is covered by a uniform coating of photoresist material. A laser exposes portions of the photoresist where pits are to be formed. The photoresist is then developed and washed, leaving the master recording. A nickel mother is derived from this master and is then used as a mold to produce multiple copies of the disk in transparent polycarbonate plastic. These substrates are coated with a thin metallic reflecting layer (usually aluminum), with a protective plastic coating on top of that.

Data is coded on a compact disk using an EFM (eight-to-fourteen modulation) code. In EFM, single binary 1's are represented by both the beginning and end of a pit length; otherwise the signal is a sequence of 0's. This correspondence between the channel bit stream (the signal represented on the disk) and the cross section of a disk is shown in Fig. 3*e* and *f*.

Electromechanical control. Advanced control systems in the compact disk player are designed to retrieve data from the disk surface reliably. The laser spot on the pit track must stay focused to within $+/-0.5\ \mu$m. But since the vertical movement of the disk might be as much as 1000 times this, automatic focusing must be provided. In some designs, this is accomplished by inserting a cylindrical lens in the path of the reflected beam and allowing the beam to impinge on a four-quadrant segmented photodiode. The changing ellipticity of the focused spot is registered as a differential signal between two opposite pairs of photodiode segments, which provides the control signal for the focusing servomechanism. *See* SERVOMECHANISM.

The laser spot must track the pits with a tolerance of $\pm 0.1\ \mu$m. However, track eccentricity might be 100 μm or more. Thus, an automatic tracking system

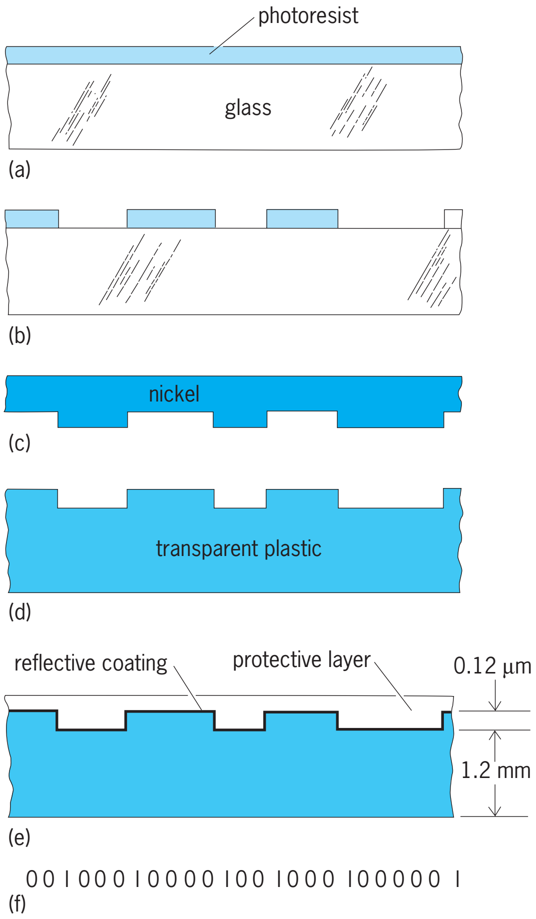

Fig. 3. Mastering and replication process for an audio compact disk. (*a*) Glass disk covered by a uniform layer of photoresist. (*b*) Pits formed by a focused laser in the photoresist, which is developed and washed away, giving the master. (*c*) Nickel mother, formed from the master. (*d*) Transparent plastic disk stamped from the nickel mother. (*e*) Disk with the reflective coating and the protective layer added. (*f*) Associated binary electrical signal (channel bit stream).

is required. In some designs, lateral tracking control is achieved by generating two tracking laser spots, with one straddling each edge of the track when the main spot is properly centered. The differential signal from two photodiodes positioned to pick up the reflection from the tracking spots provides the lateral position control signal.

The constant linear velocity of the beam along the track is ensured by synchronizing the data read off the disk with a quartz-crystal oscillator. *See* OSCILLATOR.

Signal processing. Since the information that is read off the disk is in digital form, as a sequence of 0's and 1's, it can be processed in many ways that are not possible with analog systems. To enable this, information can be passed through a buffer memory, and then output at a rate that is controlled by the player's quartz-crystal (oscillator) clock, hence entirely eliminating the wow and flutter of conventional systems.

Error correction. Errors in the information read off the disk fall into two broad categories: (1) An error in an individual bit may be due to an imperfectly formed pit or random imperfection formed in the plastic disk during the molding process. (2) A burstlike error produced by severe scratches or dirt on the outer layer of the transparent disk affects many adjacent tracks.

In principle, the detection and correction of errors is achieved by adding extra check bits known as parity bits. The bit stream can be divided into blocks and the bits in a block arranged in the form of a rectangular grid or matrix. If a parity bit is assigned to every row and every column, then, on the assumption that only one bit per block is in error, it is possible to identify precisely which bit is in error, and hence to correct it. In practice, extensions of this idea are used in the detection and possible correction of compact disk data errors, but implementation is more complex. In particular, an algorithm known as the cross interleave Reed-Solomon code (CIRC) is used.

Conversion of signal to analog form. To recreate the original music signal, the binary data on the disk must be passed through a digital-to-analog (D/A) converter and a low-pass filter. The digital-to-analog converter accepts each 16-bit sample and outputs a voltage corresponding to its value. The series of samples forms a staircase waveform that is applied to a low-pass filter that removes all frequencies above the half-sampling frequency. In this way, the filter reconstructs the original waveform. A steep (high-order) analog filter can be used, with a flat amplitude to the half-sampling frequency, at which point the amplitude falls to zero. *See* DIGITAL-TO-ANALOG CONVERTER; ELECTRIC FILTER.

In practice, low-pass filtering is accomplished using a technique called oversampling, in which the output sampling rate is increased by a factor of, say, 8, from 44.1 to 352.8 kHz, with a digital filter. This technique has the effect of requiring only a mild (low-order) analog filter while the audio bandwidth remains limited to 20 kHz. Oversampling yields an output signal characteristic with essentially flat frequency response and phase linearity.

Diverse Formats

The compact disk was originally designed as a music carrier. Subsequently, the format was extended to include the CD-ROM (read-only memory) format for computer applications. Newer formats that use the compact disk as their basis include the recordable CD-R and erasable CD-RW formats, and the multimedia DVD format.

CD-R. The CD-R (recordable) format allows users to record audio or other digital data on a compact disk; it is also called the CD-WO (write-once) format. The recording is permanent and may be read indefinitely, but cannot be erased. CD-R disks with up to 80 min (or about 700 megabytes) of playing time are available. A recording is complete when a leadin area (with table of contents), user data, and leadout area have been written.

CD-R disks are built on a polycarbonate substrate and contain a reflective layer and a protective top layer. Sandwiched between the substrate and the reflective layer is a recording layer composed of an organic dye polymer, generally either cyanine or phthalocyanine. To achieve appropriate reflectivity, a gold or silver reflective layer is used. Unlike regular compact disks, CD-R disks are manufactured with a pregrooved track, which is used to guide the recording laser. This practice simplifies recorder hardware design and promotes disk compatibility. The organic dye recording layer is a photoabsorption surface that absorbs energy from the recording laser as heat. The laser passes through the polycarbonate substrate and heats this layer, causing the substrate layer to expand into the absorption layer and mix with the dye materials there. The polycarbonate mixed with dye, which has been decomposed from the heat, acts to form a pit in the substrate. These pits create the change in reflectivity required by compact disk player pickups. During readout, the same laser, reduced in power, is reflected from the pits and its changing intensity is monitored at a photodiode. In this way, CD-R disks can be played in most CD audio and CD-ROM drives.

CD-RW. The CD-RW (rewritable) format allows data to be written, read, erased, and rewritten. A CD-RW drive can read, write, and erase CD-RW media, read and write CD-R media, and read CD audio and CD-ROM media. The data can comprise computer programs, text, pictures, video files, or audio files. Altogether, five layers are built on a transparent polycarbonate substrate: a dielectric layer, a recording layer, another dielectric layer, a reflective metal (aluminum) layer, and a top acrylic protective layer. As in the CD-R, the writing and reading laser follows a pregroove across the disk radius. However, whereas the CD-R uses a dye recording layer, the CD-RW format employs a phase-change mechanism. The recording layer is composed of an alloy of silver, indium, antimony, and tellurium, which exhibits a reversible crystalline-amorphous phase change when recorded at one temperature and erased at another. Data are recorded by directing a laser to heat an area of the crystalline layer to a temperature slightly above its melting point. When the area solidifies rapidly, it becomes amorphous, and the decreased change in reflectivity can be detected. Because the crystalline form is more stable, the material will tend to change back to this form. Thus, when the area is heated again (at a slightly lower laser power) and cooled gradually, it will return to a crystalline state, providing rewritability. A very low power laser is used to read data.

This phase-change recording technology allows thousands of rewrite cycles. The disk capacity is 650 megabytes. Since the reflectivity of CD-RW disks is only about 15 and 25% in the amorphous and crystalline states respectively, they cannot be played in conventional compact disk players. A CD-RW drive is required, or a multiread drive capable of reading lower-reflectivity disks. The CD-UDF (universal disk format) specification modifies the CD Red Book file format so that nonaudio data can be written in data packets. With CD-UDF-compliant drives, CD-R and CD-RW disks can be used in a personal-computer environment much like other storage media; in addition to audio recording, nonaudio data files can be dragged and dropped from the personal computer to disk storage.

DVD. The DVD (digital video disk or digital versatile disk) standard includes formats for video, audio, and computer applications. DVD-video was the first DVD format to be developed. One disk digitally stores a complete feature film with digital audio sound tracks. As with compact disks, DVD-video disks use a pit-and-land structure to store data. The track pitch is 0.74 μm, compared to 1.6 μm on a compact disk. The pits and lands are as short as 0.4 μm, compared to 0.83 μm on a compact disk. These reduced dimensions are possible because the laser beam uses a visible red wavelength of 635 or 650 nanometers, compared with 780 nm in a compact disk. The standard specifies a lens with a numerical aperture of 0.6, compared with 0.45 in the compact disk standard. These specifications provide a large storage capacity.

Data storage. A DVD-video disk is the same diameter (120 mm or 4.75 in.) and thickness (1.2 mm or 0.05 in.) as a compact disk. Whereas a compact disk uses a single polycarbonate substrate, a DVD-video disk employs two 0.6-mm substrates, bonded together, with the data layers placed near the internal interface.

A single-layer, single-sided DVD-video disk uses one substrate with a data surface, and one blank substrate; the disk holds 4.7 gigabytes of data. Two substrates with data surfaces can be bonded together to form a single-layer, double-sided disk holding 9.4 gigabytes of data; the disk is turned over to access the opposite layer.

The DVD-video standard also allows data to be placed on two layers in a substrate, one embedded beneath the other to create a dual-layer disk that is read from one side. The layers are separated by a semitransparent (semireflective) metal layer. Both layers can be read from one side by focusing the reading laser on either layer. The beam either reflects from the lower semireflective layer or passes through it and reflects from the top reflective layer. Together, the dual layers hold 8.5 gigabytes of data. The DVD-video standard allows for a double-sided, double-layer disk, in which two dual-layer substrates are bonded together, creating a capacity of 17 gigabytes.

Data compression. A motion picture may comprise 200 gigabytes of data; to fit this program on a single disk, data reduction must be employed. The DVD-video standard uses the MPEG-2 (Motion Picture Experts Group-2) algorithm to encode its video program. Image data that are redundant, not perceived, or marginally perceived are removed or coarsely quantized. This analysis is carried out for both individual video frames and series of frames. MPEG-2 allows for a variable bit rate. Simple pictures are given a low bit rate, and complex pictures a high bit rate. The maximum output bit rate is 10.08 megabits per second, and the average bit rate might be 4.7 megabits per second, in contrast to the compact disk's fixed rate of 1.41 megabits per second. With MPEG-2, a single-layer DVD-video disk can store up to 133 min of high-quality digital video with digital audio sound tracks; longer motion pictures can use the dual-layer disk design. The video program is stored at 4:2:0 component video; 4:2:0 refers to the ratios of frequencies used to record the different video components (one luminance and two color-difference), and the luminance and color-difference data are kept separate for higher fidelity. *See* DATA COMPRESSION.

Audio. The audio portion of the DVD-video standard provides both multichannel and stereo sound tracks. DVD-video disks can accommodate three independent 5.1-channel sound tracks, each with five main channels and a low-frequency effects channel. The DVD-video standard recognizes two multichannel formats. Disks can carry a digital sound track with a sampling frequency of 48 kHz; using audio data compression, the normal output bit rate is 384 kilobits per second. Disks also carry linear pulse-code-modulation (PCM) digital stereo sound tracks employing sampling rates of either 48 or 96 kHz, and word lengths of 16, 20, or 24 bits. Up to eight independent pulse-code-modulation channels are permitted.

Features. A DVD-video player is often connected to a home theater system and can also play CD music disks. DVD-video disks cannot be played in compact disk players. The DVD-video standard provides features such as normal (4:3) and wide-screen (16:9) aspect ratios, an automatic pan-scan feature, up to nine camera angles and interactive story lines, up to eight language tracks, and up to 32 sets of subtitles. These features are options, and implementation is left to the content provider. The DVD-video format also uses copy protection to prevent digital or analog dubbing of disks. Disks and players are tagged with regional flags so that players will play only disks intended for certain geographical markets.

Formats. In addition to the DVD-video format (formally known as Book B), the DVD family includes

DVD-read only (Book A), DVD-audio (Book C), DVD-write once (Book D), and DVD-rewritable (Book E) as well as other formats and extensions. The DVD format uses the UDF file structure. The DVD-audio format is used to store high-quality multichannel music programs at a variety of sampling frequencies and quantization word lengths. In addition, the DVD-audio format can employ lossless audio data compression to increase storage capacity effectively without degrading audio file content. The other DVD formats are employed in computer applications; Books A and E are often called DVD-ROM and DVD-RAM (random access memory), respectively. DVD-ROM and DVD-RAM drives are connected to personal computers, and function much like CD-ROM drives.

Other optical disk formats under development provide greater capacity and performance. The compact disk and the DVD will further integrate audio and video technologies with the technology of the computer. *See* COMPUTER STORAGE TECHNOLOGY; OPTICAL RECORDING.

Ken C. Pohlmann

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Comparator

An electronic circuit that produces an output voltage or current whenever two input levels simultaneously satisfy predetermined amplitude requirements. A comparator circuit may be designed to respond to continuously varying (analog) or discrete (digital) signals, and its output may be in the form of signaling pulses which occur at the comparison point or in the form of discrete direct-current (dc) levels.

Linear or analog comparator. A linear comparator operates on continuous, or nondiscrete, waveforms. Most often one voltage, referred to as the reference voltage, is a variable dc or level-setting voltage and the other is a time-varying waveform. When the signal voltage becomes equal to the reference voltage, a discrete output level is obtained. If the time-varying (signal) voltage approaches the reference voltage from a more negative level the output voltage is of one polarity; if it approaches the reference from a more positive value the output is of the opposite polarity.

Operational-amplifier voltage comparator. A very high-gain operational amplifier whose output is inverting with respect to one input terminal and noninverting with respect to the other and whose output voltage is limited at upper and lower levels (usually at voltages near the supply voltage levels, $+V_{\text{supply}}$) may be used as a voltage comparator (**Fig. 1**). The upper and lower output levels are designated as V_{OH} and V_{OL}, respectively. When the input signal υ_i equals V_{REF}, the output is approximately in the center of this range. The change in input voltage around V_{REF} required to drive the output to its respective limits is given by Eq. (1), where A is the voltage gain of the

$$\Delta \upsilon_i = \frac{V_{OH} - V_{OL}}{A} \qquad (1)$$

amplifier. If A is very large, $\Delta \upsilon_i$ approaches 0; as υ_i approaches V_{REF} from the negative side, the output switches abruptly from V_{OL} to V_{OH} as soon as υ_i becomes bigger than V_{REF}; and as υ_i approaches V_{REF} from the positive side, the output switches abruptly to V_{OL} as soon as υ_i becomes less than V_{REF}. If υ_i and V_{REF} are interchanged, the output polarity shifts are reversed.

Comparators are often designed with a built-in offset voltage; that is V_{OH} and V_{OL} need not be symmetrical about V_{REF}. For example, high and low output levels may be designed as $V_{OH} = +5$ V and $V_{OL} = 0$, which would be compatible with standard saturated logic levels; or as $V_{OH} = 0$ and $V_{OL} = 15$ V, for outputs compatible with standard emitter-coupled logic levels. *See* LOGIC CIRCUITS.

The high-gain operational-amplifier comparator used in the open-loop mode is designated as a nonregenerative comparator because there is no positive feedback path from the output back to the input.

An operational-amplifier comparator connected in a positive-feedback mode (**Fig. 2**) is referred to as a regenerative comparator. If the voltage gain A is

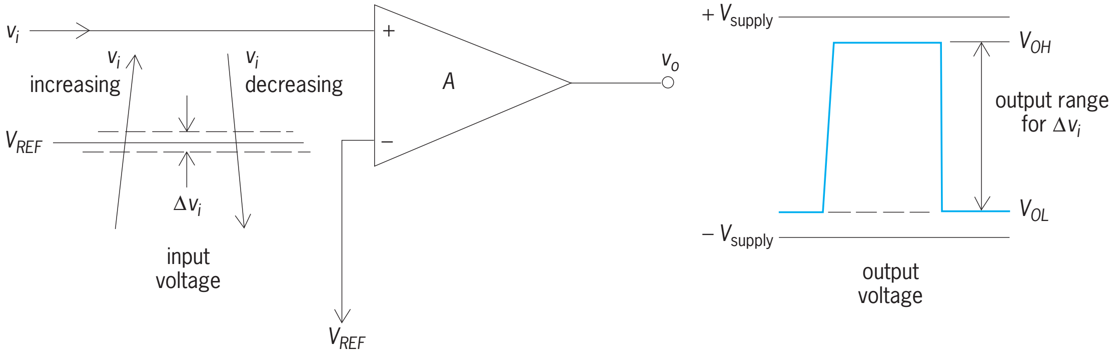

Fig. 1. High-gain nonregenerative operational amplifier as voltage comparator.

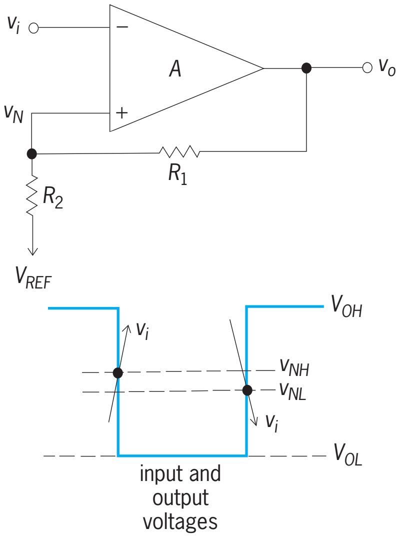

Fig. 2. Regenerative operational amplifier as comparator (Schmitt trigger). The input and output voltages are superimposed, showing hysteresis.

very high, then the feedback voltage v_N is given by Eq. (2) when the output voltage is $v_o = V_{OH}$; and

$$v_N = v_{NH} = \frac{R_2 V_{OH} + R_1 V_{REF}}{R_1 + R_2} \qquad (2)$$

when $v_o = V_{OL}$ the feedback voltage is given by Eq. (3).

$$v_N = v_{NL} = \frac{R_2 V_{OL} + R_1 V_{REF}}{R_1 + R_2} \qquad (3)$$

For this circuit there is a difference between the input levels which will cause the output to switch, given by Eq. (4).

$$v_{NH} - v_{NL} = \frac{R_2}{R_1 + R_2}(V_{OH} - V_{OL}) \qquad (4)$$

This difference in input levels is referred to as the hysteresis of the circuit. Such regenerative comparators are generically referred to as Schmitt triggers. Historically, they were first implemented as discrete two-vacuum-tube devices, which were later replaced by transistors and then by the operational amplifier feedback circuit. *See* AMPLIFIER; FEEDBACK CIRCUIT; HYSTERESIS; OPERATIONAL AMPLIFIER.

Digital comparator. The term digital comparator has historically been used when the comparator circuit is specifically designed to respond to a combination of discrete level (digital) signals, for example, when one or more such input signals simultaneously reach the reference level which causes the change of state of the output. Among other applications, such comparators perform the function of the logic gate such as the AND, OR, NOR, and NAND functions. More often, the term digital comparator describes an array of logic gates designed specifically to determine whether one binary number is less than or greater than another binary number. Such digital comparators are sometimes called magnitude or binary comparators.

Applications. Comparators may take many forms and can find many uses, in addition to those which have been discussed. For example, the electronically regulated dc voltage supply uses a circuit which compares the dc output voltage with a fixed reference level. The resulting difference signal controls an amplifier which in turn changes the output to the desired level. In a radio receiver the automatic gain control circuit may be thought of broadly as a comparator; it measures the short-term average of the signal at the output of the detector, compares this output with a desired bias level on the radio-frequency amplifier stages, and changes that bias to maintain a constant average level output from the detector. *See* AUTOMATIC GAIN CONTROL (AGC).

Regenerative comparators (Schmitt triggers) are often used as the key element in the voltage-controlled oscillator (VCO), which in turn is the control element in the phase-locked loop (PLL). Nonregenerative comparators are often used in parallel analog-to-digital converters where a number of comparators (equal to the desired bit rate) are used at a succession of higher V_{REF} levels. *See* ANALOG-TO-DIGITAL CONVERTER; PHASE-LOCKED LOOPS.

Glenn M. Glasford

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Complement

A group of proteins in the blood and body fluids that are sequentially activated by limited proteolysis and play an important role in humoral immunity and the generation of inflammation. When activated by antigen–antibody complexes, or by other agents such as proteolytic enzymes (for example, plasmin), complement kills bacteria and other microorganisms. In addition, complement activation results in the release of peptides that enhance vascular permeability, release histamine, and attract white blood cells (chemotaxis). The binding of complement to target cells also enhances their phagocytosis by white blood cells. The most important step in complement system function is the activation of the third component of complement (C3), which is the most abundant of these proteins in the blood. *See* IMMUNITY.

There are two mechanisms for the activation of C3, the classical and the alternative pathways. The classical pathway requires calcium and is activated when the C1q component binds to immunoglobulin antibodies IgG or IgM. In contrast, activation of the alternative pathway requires magnesium and is not dependent on antibodies. The activation of C3 by either pathway results in the cleavage of C3 to a small fragment, C3a, and a large fragment, C3b. The latter binds to a bimolecular enzyme, and a new trimolecular complex is formed which cleaves C5 into a small fragment, C5a, and a large fragment, C5b. This is the final enzymatic step in complement activation; the rest of the activation process is nonenzymatic. An amphiphilic macromolecular complex is formed by the binding of one molecule of C5b to one molecule each of C6, C7, and C8, and 12 or more molecules of C9. This so-called membrane attack complex invades the membrane of target cells and kills them. At first these complexes become embedded in target-cell membranes without inflicting any damage. After a molecule of C8 binds to the C5b,6,7 complex, a transmembrane channel (pore) is formed, and the complex can destroy target cells, although very slowly. The process is much accelerated by polymerization of C9 into the complexes, forming a cylindrical structure. The top of the cylinder is hydrophilic and capped by a ring or annulus that remains outside the target cell. The other end is lipophilic; it becomes embedded in the cell membrane and forms large transmembrane channels which coalesce into so-called leaky patches. The target cell loses potassium, imbibes sodium and water, swells, and bursts. This is called cell lysis, or hemolysis in the case of a red blood cell.

As mentioned earlier, several small fragments are enzymatically generated during complement activation, and these act to release histamine from mast cells. The C5a fragment is potent in chemotaxis and in activating phagocytes. The C2b fragment contains a peptide that, upon release by further proteolysis, markedly enhances vascular permeability. Phagocytes and red blood cells have a receptor for fragments C4b and C3b, called complement receptor (CR1), which appears to play an important role in clearing immune complexes from blood. Phagocytes also have a complement receptor 3 (CR3) which, when engaged, stimulates phagocytes to produce superoxide and enhances phagocytic killing of ingested bacteria. A third complement receptor (CR2) is found only on B lymphocytes. *See* ALLERGY; CELLULAR IMMUNOLOGY; HISTAMINE.

Genetic deficiencies of certain complement subcomponents, including properdin, have been found in humans, rabbits, guinea pigs, and mice. All are inherited as autosomal recessives, except for properdin deficiency, which is X-linked recessive, and C1 inhibitor deficiency, which is autosomal dominant. Certain deficiencies lead to immune-complex diseases, such as systemic lupus erythematosus; other deficiencies result in increased susceptibility to bacterial infections, particularly those of the genus *Neisseria* (for example, gonorrhea and meningococcal meningitis), and hereditary angioneurotic edema. *See* COMPLEMENT-FIXATION TEST.

Fred S. Rosen

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Complement-fixation test

A sensitive reaction used in serology for the detection of either antigen or antibody, as in the diagnosis of many bacterial, viral, and other diseases, including syphilis. It involves two stages: stage I is the binding or fixation of complement if certain antigen-antibody reactions occur, and stage II is detection of residual unbound complement, if any, by its hemolytic action on the sensitized erythrocytes subsequently added. This is shown in the **illustration**. *See* ANTIBODY; ANTIGEN; COMPLEMENT.

In the first stage either the antigen or the antibody must be supplied as a reagent, with the other of the pair as the test unknown. Fresh guinea pig serum is normally used as a complement source. Sheep erythrocytes which are coated with their corresponding antibody (amboceptor or hemolysin) are used in the second stage.

The controls A, B, and C in the illustration demonstrate that sufficient complement is present to effect hemolysis of the sensitized indicator cells and that

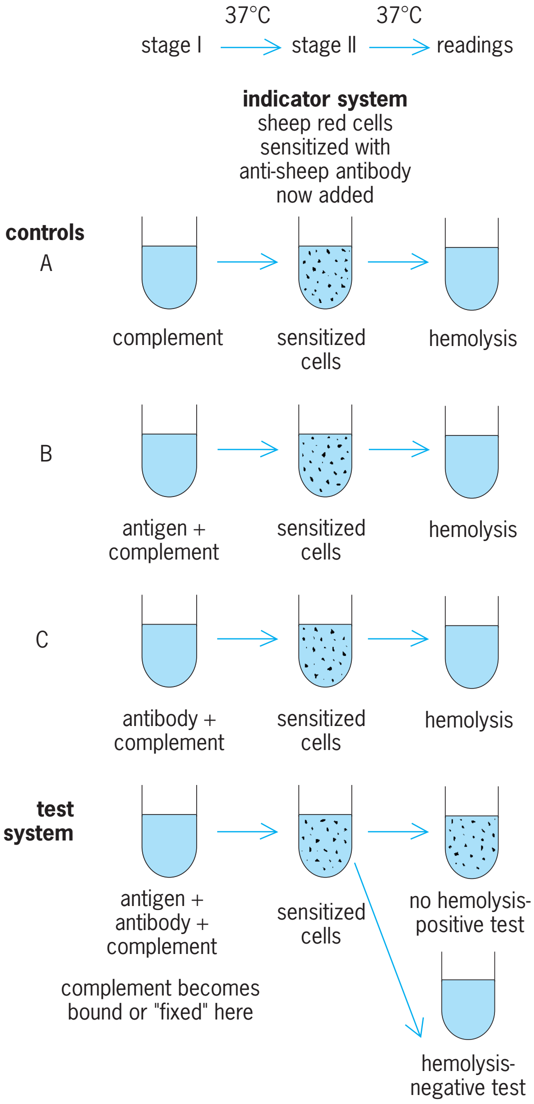

Diagram of the complement-fixation reaction. 37°C = 98.6°F.

neither antigen nor antibody added alone will interfere with this by binding complement. In the test system the combination of a suitable antigen and antibody in the presence of complement will bind the complement to the complex so that the complement becomes unavailable for the hemolysis of the indicator cells added in stage II. If either antigen or antibody is added as a reagent in stage I, then the presence of the other in the test unknown that is added can be detected through its ability to complete the antigen-antibody system. A lack of hemolysis denotes that the complement is bound. This result is termed a positive complement-fixation reaction and, if the system is controlled against false reactions, implies that the antigen (or antibody) assumed to be in the test unknown was actually present. Conversely, complete hemolysis of the sensitized erythrocytes implies, ultimately, absence of antigen or antibody and is termed a negative complement-fixation reaction. In its most sensitive form the microcomplement-fixation test can distinguish the minute antigenic difference that results from the shift in a single amino acid between hemoglobins A and S. *See* IMMUNOLOGY; LYTIC REACTION; SEROLOGY. **Henry P. Treffers**

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Complementation (genetics)

The correction of a cellular defect caused by mutations in a gene by the addition of the normal gene or its product (protein). In cell cultures, complementation can be accomplished by transfer of deoxyribonucleic acid (DNA) or messenger ribonucleic acid (mRNA) that encodes this protein. Another way to "complement" a cellular defect is by joining two chromosome sets in the same cell, each defective due to a different mutation but together able to correct the cellular defect. This principle is used in somatic cell hybridization (or cell fusion), in which cells are fused to generate hybrid cells that possess all chromosomes from both fusion partners. Such hybrids are usually viable and can be examined for the presence of the cellular deficiency via complementation analysis. *See* CHROMOSOME; DEOXYRIBONUCLEIC ACID (DNA); MUTATION.

Complementation analysis. Complementation analysis is used to study the relationships between different genes or alleles which individually cause functional defects in the organism when mutated but in combination restore the wildtype phenotype. It has been very helpful in elucidating the genetic heterogeneity of hereditary diseases, such as Zellweger syndrome, which is caused by malfunctioning peroxisomes (intracellular organelles involved in the metabolism of hydrogen peroxide); xeroderma pigmentosum, which is associated with defective repair of DNA damage caused by ultraviolet light; and Fanconi anemia, a blood disorder associated with chromosomal breakage and a high susceptibility to cancer. These are recessive diseases, which means that both copies of the disease gene are defective; patients inherit a defective copy from each parent, who themselves are carriers of only one defective copy and are asymptomatic.

A condition for carrying out complementation analysis is that a specific disease feature should be recognizable at the cellular level. In the case of Fanconi anemia, for example, this feature is the hypersensitivity of patient cells to DNA cross-linking agents (which promote the joining of two DNA strands or a DNA strand with a protein strand) such as mitomycin C (MMC). When cell lines derived from two unrelated patients with Fanconi anemia are fused, the resulting hybrid cell line may continue to show MMC sensitivity (indicating a lack of complementation), or the cell line may show MMC resistance (indicating that complementation has taken place). *See* PEROXISOME; SOMATIC CELL GENETICS.

Complementation groups. Patients whose cell lines—when combined in a fusion hybrid—fail to complement each other's defect are said to belong to the same "complementation group," whereas when complementation does occur, the cell lines belong to different groups (**Fig. 1**). When multiple complementation groups exist for a disease, each group is thought to represent a distinct disease gene. The explanation is that certain proteins may function as essential components of a specific biochemical pathway and that a defect in any one of these components may cause disruption of that pathway, each defect having essentially the same consequence for the organism. In the case of Fanconi anemia, 12 complementation groups have been distinguished. The disease gene has been identified for 11 of these groups. Eight of these genes encode proteins that aggregate into a multi-subunit complex that protects the cell against certain types of DNA

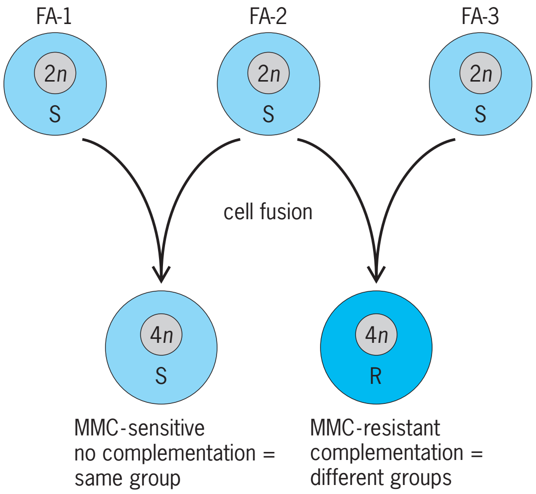

Fig. 1. Complementation analysis by cell fusion. FA, Fanconi anemia; MMC, mitomycin C. [*Reproduced with permission from Nature Reviews Genetics (http://www.nature.com/reviews): H. Joenje and K. J. Patel, The emerging genetic and molecular basis of Fanconi anaemia, Nature Rev. Genet., 2(6):446–457,* © *2001 Macmillan Magazines Ltd.*]

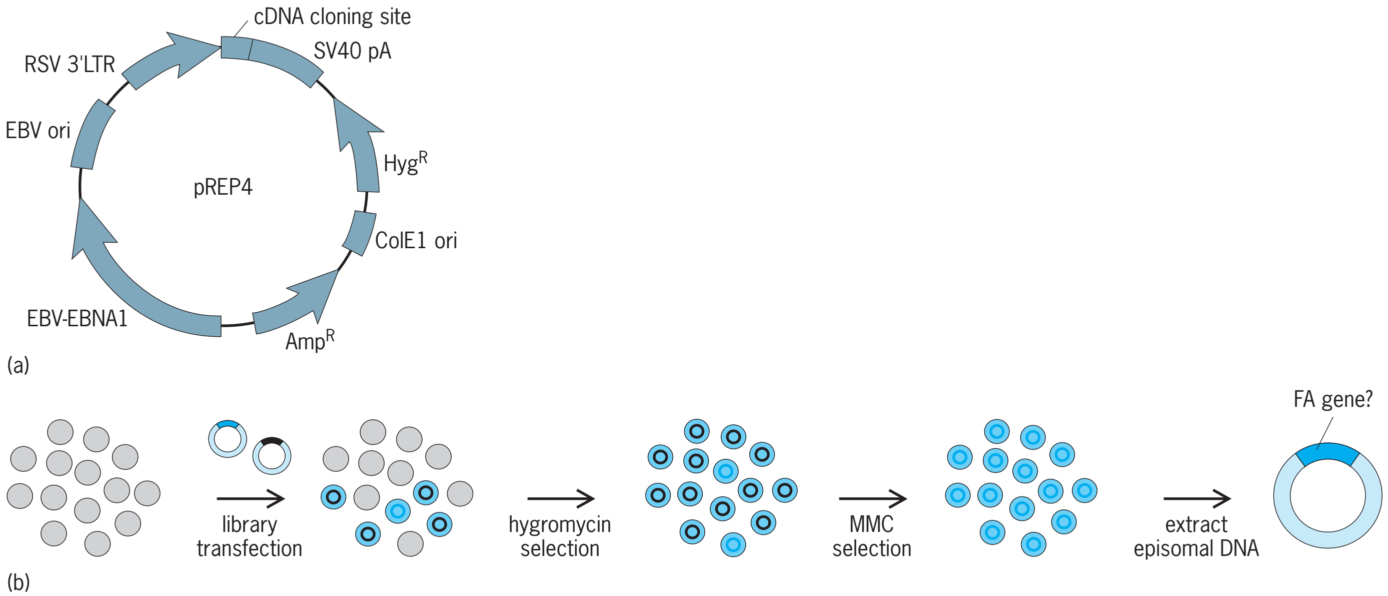

Fig. 2. Example of complementation cloning of an FA gene. (*a*) The vector containing various cDNAs. (*b*) The plasmid with the various inserts is introduced into lymphoblasts derived from a patient with FA (library transfection). Selection with hygromycin causes only cells that contain a plasmid to survive. Selection with MMC causes cells to survive that are complemented for the FA defect. The cDNA present in the plasmid extracted from surviving cells is likely the gene that is defective in the lymphoblasts. [*Reproduced with permission from Nature Reviews Genetics (http://www.nature.com/reviews): H. Joenje and K. J. Patel, The emerging genetic and molecular basis of Fanconi anaemia, Nature Rev. Genet., 2(6):446–457, © 2001 Macmillan Magazines Ltd.*]

damage. Each protein is important for the function of this complex, which explains why defects in any one of them cause Fanconi anemia.

Complementation cloning. A procedure known as complementation cloning has been instrumental in the identification of most of the genes underlying Fanconi anemia. This method makes use of an expression plasmid (a vector that expresses the gene) that is able to replicate in bacteria as well as in human cells (**Fig. 2**). When introduced into human B lymphoblasts (white blood cells), the plasmid is constructed in such a way that it cannot be integrated into the cellular DNA. A wide variety of human genes (cDNAs) are placed into multiple copies of this plasmid, which ensures expression of all these individual genes. After the plasmids with the inserted human genes are introduced into lymphoblasts from a patient with Fanconi anemia, the cells are selected for plasmid uptake by using a selection marker present in the plasmid. Further selection with a concentration of MMC that kills Fanconi anemia cells but not wild-type cells (normal functioning cells) allows survival of cells that have been complemented for the defect. These complemented cells are likely to harbor a plasmid that expresses the gene that is defective in the lymphoblasts. Extraction of the plasmid allows the identification of its insert, which is a candidate for representing the defective gene. Finding pathogenic mutations in this gene in patients belonging to the same complementation group finally should provide proof of identity for this disease gene.

Intragenic complementation. Sometimes combinations of different defects in a single gene may lead to partial or complete complementation (intragenic complementation). This might occur when the protein functions exclusively by forming a homodimer. In such cases, deficiencies in different regions of the individual proteins may be compensated in the dimeric structure, resulting in a preserved function. *See* GENE; GENE ACTION; HUMAN GENETICS.

M. Levitus; H. Joenje

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Complex numbers and complex variables

A natural and extremely useful extension of the familiar real numbers. They can be introduced formally as follows. Consider the two-dimensional real vector space consisting of all ordered pairs (a_1, a_2) of real numbers. Geometrically this space can be identified with the ordinary euclidean plane, viewing the real numbers a_1, a_2 as the coordinates of a point in the plane.

The addition of vectors is defined by $(a_1, a_2) + (b_1, b_2) = (a_1 + b_1, a_2 + b_2)$ and is just the usual addition of vectors by the parallelogram law (**Fig. 1**). The multiplication of a vector (a_1, a_2) by a real number c is defined by $c(a_1, a_2) = (ca_1, ca_2)$, and is just the uniform dilation of the plane by the factor c. It

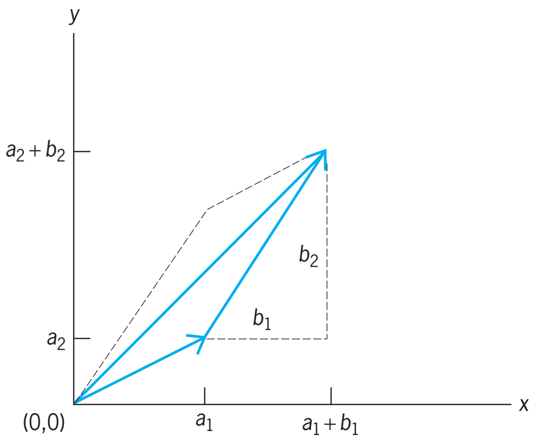

Fig. 1. Vector addition of two complex numbers by the parallelogram law.

may be asked whether it is possible to define a multiplication of one vector by another in such a manner that this multiplication is linear and satisfies the same formal rules as multiplication of real numbers. That is to say, it may be asked whether it is possible to associate to any two vectors (a_1, a_2) and (b_1, b_2) a product vector $(a_1, a_2) \cdot (b_1, b_2)$ in such a manner that:

1 The multiplication is linear in the sense that

$$(a_1, a_2) \cdot [(b_1, b_2) + (c_1, c_2)] = (a_1, a_2) \cdot (b_1, b_2) + (a_1, a_2) \cdot (c_1, c_2)$$

2 It is associative,

$$(a_1, a_2) \cdot [(b_1, b_2) \cdot (c_1, c_2)] = [(a_1, a_2) \cdot (b_1, b_2)] \cdot (c_1, c_2)$$

3 It is commutative,

$$(a_1, a_2) \cdot (b_1, b_2) = (b_1, b_2) \cdot (a_1, a_2)$$

4 There is an identity vector (e_1, e_2) such that

$$(e_1, e_2) \cdot (a_1, a_2) = (a_1, a_2)$$

for all vectors (a_1, a_2).

5 For each vector (a_1, a_2) other than (0, 0) there is a vector (b_1, b_2) for which

$$(b_1, b_2) \cdot (a_1, a_2) = (e_1, e_2)$$

There does exist such a multiplication, given by Eq. (1), and it is essentially unique in the sense that

$$(a_1, a_2) \cdot (b_1, b_2) = (a_1 b_1 - a_2 b_2, a_1 b_2 + a_2 b_1) \quad (1)$$

any multiplication satisfying all the desired properties can be reduced to Eq. (1) by a suitable choice of coordinates in the plane. The plane with the ordinary addition and scalar multiplication of vectors and with the vector multiplication in Eq. (1) is the complex number system. It is not possible to introduce a corresponding multiplication on vector spaces of higher dimensions, although, for example, if the commutativity condition is dropped, there is a multiplication satisfying the remaining conditions on the four-dimensional vector space (the quaternions).

Geometric interpretation. The multiplication in Eq. (1) can be interpreted most easily geometrically by introducing polar coordinates in the plane and writing $(a_1, a_2) = (r \cos \theta, r \sin \theta)$, where r is the length of the vector (a_1, a_2), or the modulus of the complex number (a_1, a_2), defined by $r^2 = a_1^2 + a_2^2$, and θ is the angle between the vector (a_1, a_2) and the first coordinate axis, or the argument of the complex number (a_1, a_2), defined by $\tan \theta = a_2/a_1$. It follows immediately from Eq. (1), by using the familiar addition formulas for the sine and cosine functions, that

$$(r_1 \cos \theta_1, r_1 \sin \theta_1) \cdot (r_2 \cos \theta_2, r_2 \sin \theta_2) = [r_1 r_2 \cos (\theta_1 + \theta_2), r_1 r_2 \sin (\theta_1 + \theta_2)]$$

Thus multiplication of complex numbers amounts to multiplying their moduli and adding their arguments (**Fig. 2**). *See* TRIGONOMETRY.

Real and imaginary parts. Introducing the basis vectors $l = (1, 0)$ and $i = (0, 1)$, any vector (x, y) can be written uniquely as the sum $(x, y) = xl + yi$. Since the multiplication given by Eq. (1) is linear, the product of any two vectors is determined by giving the multiplication table for the basis vectors l and i. It follows readily from Eq. (1) that $l \cdot l = l$, $l \cdot i = i \cdot l = i$, and $i \cdot i = -l$, so that in particular the vector l is the identity element for the multiplication of complex numbers. Furthermore, the addition and multiplication of vectors of the form xl for all real numbers x reduce to the ordinary addition and multiplication of real numbers. There is consequently a natural imbedding of the real numbers into the complex numbers by associating to any real number x the complex number xl. The complex number l can be identified with the ordinary real number 1, and reflecting this identification the notation can be simplified by writing a complex number $z = (x, y) = xl + yi$ merely as $z = x + iy$. The component x is called the real part of the complex number

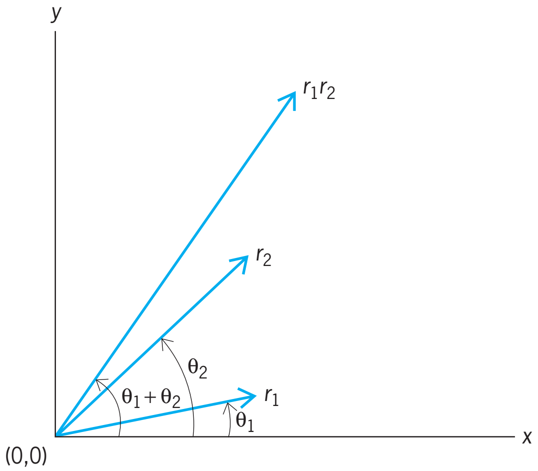

Fig. 2. Multiplication of complex numbers.

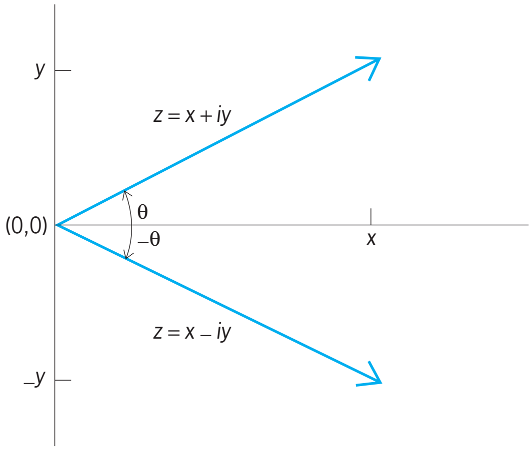

Fig. 3. Complex conjugate numbers.

z, and the component y is called the imaginary part. The modulus of the complex number z is denoted by $|z|$.

Complex conjugates. The vectors l and $-i$ are also a basis and satisfy exactly the same multiplication table as the vectors l and i, so the mapping which associates to any complex number $z = x + iy$ the complex number $\bar{z} = x - iy$ is a one-to-one mapping preserving the algebraic structure of the complex number system; thus $\overline{(z_1 + z_2)} = \bar{z}_1 + \bar{z}_2$ and $\overline{(z_1 \cdot z_2)} = \bar{z}_1 \cdot \bar{z}_2$. The complex number $\bar{z}$ is called the conjugate of z. It has the properties that $z = \bar{z}$ precisely when z is a real number, that $z \cdot \bar{z} = x^2 + y^2 = |z|^2$, and that in polar coordinates $\bar{z}$ is a complex number with the same modulus as z but with the negative argument (**Fig. 3**).

Polynomials. An ordinary real polynomial function $f(x) = x_n + a_1x^{n-1} + \cdots + a_n$ can be extended to a function of a complex variable z in the obvious manner, merely setting $f(z) = z^n + a_1z^{n-1} + \cdots + a_n$ and using the algebraic operations as defined for complex numbers. The advantage of this extension is that the fundamental theorem of algebra then holds: a nontrivial polynomial function over the complex numbers always has a root α, a complex value for which $f(\alpha) = 0$. The same result is true for polynomials with complex coefficients $a_1, \ldots, a_n$. A simple consequence of this result is that any polynomial function of degree n can be written as a product $f(z) = (z - \alpha_1)(z - \alpha_2) \cdots (z - \alpha_n)$ where the complex numbers $\alpha_1, \alpha_2, \ldots, \alpha_n$ are precisely the roots of this polynomial repeated according to multiplicity. Thus passing from the real to the complex number system simplifies the analysis of polynomial functions and clarifies many of their properties. This was in a sense the original motivation for introducing the complex number system.

Power series. In a somewhat similar manner, passing from the real to the complex number system simplifies and clarifies the analysis of more general functions than polynomials. Many of the familiar functions treated in elementary calculus have convergent Taylor series expansions and so can be written for all real numbers x sufficiently near a real number a in the form of a convergent infinite series

$$f(x) = \sum_{n=0}^{\infty} a_n(x - a)^n$$

where $n!a_n = f^{(n)}(a)$. If this series converges when the real number x is replaced by nearby complex numbers z, there results a natural extension of the function f to a complex-valued function of the complex variable z.

The question of convergence can be handled rather easily. A series of the form

$$\sum_{n=0}^{\infty} a_n(z - a)^n$$

where a_n, a, z are complex numbers is called a complex power series centered at the point a. For any such series there is a value r, a nonnegative real number or ∞, such that the power series converges for all complex numbers z satisfying $|z - a| < r$ and diverges for all complex numbers z satisfying $|z - a| > r$; r is called the radius of convergence of the power series. If $r = 0$, the power series diverges for all complex numbers z other than $z = a$, while if $r = \infty$, the power series converges for all complex numbers. Otherwise, the series converges for all complex numbers lying within a circle of radius r centered at the point a and diverges for all complex numbers outside that circle. The series may or may not converge at complex numbers on the circle itself. The radius of convergence can be determined by Hadamard's formula: $1/r = \limsup_{n\to\infty} |a_n|^{1/n}$. Alternatively and generally more simply the radius of convergence satisfies

$$\liminf_{n\to\infty} |a_n|/|a_{n+1}| \leq r \leq \limsup_{n\to\infty} |a_n|/|a_{n+1}|$$

If r is the radius of convergence of a power series, then that series converges absolutely and uniformly on the set of all complex numbers z satisfying $|z - a| \leq \rho$ whenever $\rho < r$.

Using these observations it is easy to see, for example, that the exponential function can be extended to a complex-valued function of the complex variable z defined for any z by

$$e^z = \sum_{n=0}^{\infty} z^n/n!$$

Among the trigonometric functions the sine and cosine functions also can be defined for arbitrary complex numbers z by their Taylor series. Moreover, these functions satisfy the identity $e^{iz} = \cos z + i \sin z$ for all complex numbers z, an interesting relation among the elementary functions only apparent when passing to complex numbers. *See* SERIES.

Analytic functions. A complex-valued function f of a complex variable defined on some region Ω in the complex plane is analytic or holomorphic in Ω if for each point a in Ω the values of the function at all points z sufficiently near a are given by a power series expansion

$$f(z) = \sum_{n=0}^{\infty} a_n (z - a)^n$$

This power series then must be the Taylor series expansion of the function f at the point a and must converge in at least the largest circle centered at a and contained in Ω. An analytic function in a region Ω is necessarily a continuous function in Ω moreover, as a function of the two real variables (x, y), an analytic function has partial derivatives of all orders.

Characterization by differentiability. There are a number of alternative characterizations of analytic functions, all of which are useful. The most common and perhaps the most surprising characterization, which is often taken as the definition of an analytic function, is that a function f is analytic in Ω precisely when the limit given by (2) exists at all points a in Ω. This limit is

$$\lim_{z\to a}\frac{f(z)-f(a)}{z-a} \tag{2}$$

the complex analog of the ordinary derivative and is therefore called the complex derivative and written $f(a)$. If the power series

$$f(z)=\sum_{n=0}^{\infty}a_n(z-a)^n$$

converges in a disc Δ centered at a, then

$$f'(z)=\sum_{n=0}^{\infty}na_n(z-a)^{n-1}$$

and this series also converges in the disc Δ. *See* CALCULUS.

Cauchy-Riemann equation. If f is analytic near a point a, then the complex derivative (2) can be calculated by letting z approach a through a sequence of points having the same imaginary value as a, hence $f'(a) = \partial f/\partial x$. Alternatively, the complex derivative can be calculated by letting z approach a through a sequence of points having the same real value as a, hence $f'(a) = -i\,\partial f/\partial y$. Upon comparing these two results it follows that an analytic function f must satisfy the Cauchy-Riemann equation

$$\frac{\partial f}{\partial x}+i\frac{\partial f}{\partial y}=0$$

which is sometimes written $\partial f/\partial\bar{z}=0$. Conversely if f is a complex-valued function defined in a region Ω of the complex plane, and if f has continuous first partial derivatives with respect to the real coordinates x and y, and if they satisfy the Cauchy-Riemann equation at all points of Ω, then f is analytic in Ω. It is not enough merely to require the existence of the first partial derivatives, and so this is not such a clean characterization of analytic functions as the preceding one, but it is nonetheless very useful. Weaker regularity conditions than the continuity of the first partial derivatives are possible. For instance, if the function f has first partial derivatives in the sense of distributions and if they satisfy the Cauchy-Riemann equation, then f is analytic.

Relation to harmonic functions. Setting $f(x, y) = u(x, y) + iv(x, y)$, where u and $v$are real-valued functions, the Cauchy-Riemann equation can be written equivalently as the pair of equations

$$\frac{\partial u}{\partial x}=\frac{\partial v}{\partial y},\quad \frac{\partial u}{\partial u}=-\frac{\partial v}{\partial x}$$

It follows immediately from this that $\partial^2u/\partial x^2 + \partial^2v/\partial y^2 = 0$ and similarly for v, so that the real and imaginary parts of an analytic function are harmonic functions. Conversely if u is harmonic in a simply connected region Ω of the complex plane, the pair of real Cauchy-Riemann equations determines a harmonic function v such that $u + iv$ is analytic in Ω, and v is unique up to an additive constant; if Ω is not simply connected, the function v may not be single-valued. *See* DIFFERENTIAL EQUATION; LAPLACE'S DIFFERENTIAL EQUATION.

Morera's theorem. If f is an analytic function in a region Ω of the complex plane, then it follows from the Cauchy-Riemann equation that, using the terminology and notation of differential forms, the differential form $fdz = fdx + ifdy$ is closed, since

$$d(f\,dx+i\,f\,dy)=\left(i\frac{\partial f}{\partial x}-\frac{\partial f}{\partial y}\right)dx\wedge dy=0$$

Therefore

$$\int_{\gamma} f\,dz=0$$

for any closed path γ homologous to zero in Ω. Conversely Morera's theorem asserts that if f is a continuous complex-valued function in Ω and if

$$\int_{\gamma} f\,dz=0$$

for all closed paths γ homologous to zero in Ω, then f is necessarily analytic in Ω. From this characterization of analyticity it follows immediately that the limit of a uniformly convergent sequence of analytic functions is also analytic.

Conformal mapping. An analytic function f in a region Ω of the complex plane can be viewed as a mapping from the plane region Ω into the complex plane. If $f(z) = u(z) + iv(z)$, this mapping is described in real terms by the pair of functions $u(x, y)$, $v(x, y)$. It follows readily from the Cauchy-Riemann equation that the jacobian determinant of this real mapping is

$$\det\begin{pmatrix}u_x\ u_y\\ v_x\ v_y\end{pmatrix}=u_x^2+v_x^2=\left|f'(z)\right|^2 \tag{3}$$

Since the jacobian determinant is thus always nonnegative, the mapping always preserves orientation. Moreover, the mapping is locally one-to-one whenever $f'(z) \neq 0$, and its inverse is readily seen also to satisfy the Cauchy-Riemann equation and therefore to be analytic. By analyzing further the condition imposed by the Cauchy-Riemann equation it follows that if $f'(a) \neq 0$, if γ_1 and γ_2 are two differentiable paths through the point a, and if the tangent vectors to γ_1 and γ_2 at the point a are at an angle θ apart, then the tangent vectors to the paths $f(\gamma_1)$ and $f(\gamma_2)$ at the point $f(a)$ are also at an angle θ apart. The mapping

Fig. 4. A conformal mapping that preserves angles at a.

f thus preserves angles at a, and is therefore said to be conformal at a (**Fig. 4**). Conversely any continuously differentiable conformal mapping is an analytic function with a nonzero complex derivative, thus providing a very geometric characterization of analytic functions. *See* CONFORMAL MAPPING; PARTIAL DIFFERENTIATION.

For completeness, something should be said about the mapping property of an analytic function at a point at which the complex derivative is zero. The analytic function $f(z) = z^n$, for example, has a zero derivative at $z = 0$ whenever $n > 1$. The mapping is not conformal but increases angles at the origin by a factor of n (**Fig. 5**) and so can be viewed as a mapping which wraps each circle about the origin in its domain n times about the origin in its range. Now if f is any analytic function at the origin with $f(0) = f'(0) = 0$, then this function can be written in the form $f(z) = g(z)^n$ for some integer $n > 1$, where g is analytic at the origin, $g(0) = 0$ but $g'(0) \neq 0$. Therefore the change of variable $w = g(z)$ reduces the function f to the form $f(w) = w^n$ just considered. It is clear from this that an analytic function takes open sets to open sets even when its derivative is zero and that any analytic function satisfies the maximum modulus theorem: if f is analytic at a and $|f(a)| \geq |f(z)|$ for all points z in some neighborhood of a, then f must actually be a constant. This seemingly simple property has a considerable range of applications.

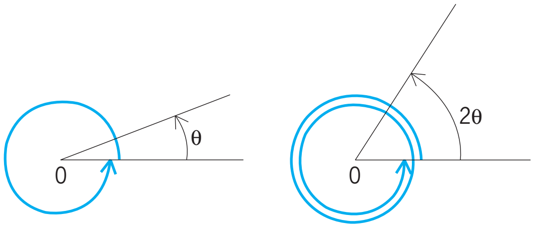

Fig. 5. The mapping z^2 at the origin.

Cauchy integral formula. An integral representation formula due to A. Cauchy plays a fundamental role in complex analysis and is traditionally the principal tool used in proving the equivalence of some of the alternative characterizations of analytic functions given above. The formula asserts that if γ is the smooth boundary curve of a finite region Ω in the complex plane (**Fig. 6**) and if f is analytic in an open neighborhood of the closed region $\Omega \cup \gamma$ (the union of Ω and γ), then

$$\frac{1}{2\pi i}\int_\gamma \frac{f(\zeta)d\zeta}{\zeta - z} = \begin{cases} f(z) & \text{whenever } z \text{ is a member of } \Omega \\ 0 & \text{whenever } z \text{ is not a member of } \Omega \cup \gamma \end{cases} \quad (4)$$

This shows, for example, that the values of the analytic function f in Ω are completely determined by the values of that function on the boundary of Ω. Equation (4) can be differentiated under the integral sign to yield the companion formula (5)

$$f^{(n)}(z) = \frac{n!}{2\pi i}\int_\gamma \frac{f(\zeta)\,d\zeta}{(\zeta - z)^{n+1}} \quad (5)$$

for the derivatives of the function f at any point z in Ω. In particular, if Ω is a disk of radius r centered at a point a and if $|f(z)| \leq M$ on the boundary γ of Ω, then (5) implies that $|f^n(a)| \leq Mr^{-n}n!$. Thus the derivatives of an analytic function cannot grow faster than $r^{-n}n!$ for some r as n tends to infinity. An immediate consequence of this estimate is Liouville's theorem, the assertion that the only functions analytic and bounded in the entire plane are the constant functions.

Relation to Green's integral theorem. The Cauchy integral formula (4) can be considered as a special case of a more general integral representation formula, following fairly directly from Green's integral theorem. If Ω and γ are as before and if f is any continuously differentiable complex-valued function of the real variables (x, y) in an open neighborhood of the closed region $\Omega \cup \gamma$, then

$$f(z) = \frac{1}{2\pi i}\int_\gamma f(\zeta)\frac{d\zeta}{\zeta - z} + \frac{1}{2\pi i}\int\int_\gamma \frac{\partial f(\zeta)}{\partial\bar{\zeta}}\frac{d\zeta \wedge d\bar{\zeta}}{\zeta - z} \quad (6)$$

is valid for all z in Ω. Since analytic functions are characterized by the Cauchy-Riemann equation $\partial f/\partial\bar{z} = 0$, it is evident that (6) reduces to (4) for analytic functions. The more general formula (6) is useful in investigating solutions of the partial differential equation $\partial f/\partial\bar{z} = g$ for a given function g. This equation has many applications in complex analysis.

Relation to Poisson integral formula. The Cauchy integral formula (4) is also closely related to the Poisson integral formula for harmonic functions, which can be

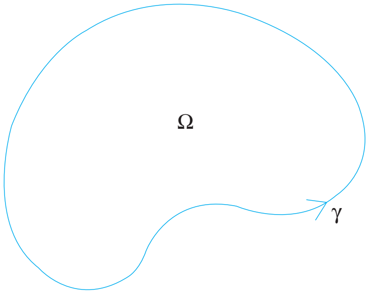

Fig. 6. The geometric situation in which the Cauchy integral formula holds.

derived from Eq. (4). The Poisson formula is useful in solving boundary-value problems for harmonic functions. For any continuous function on the smooth boundary γ of a bounded region Ω, there exists a harmonic function u in Ω with the given boundary values. If Ω is simply connected, the function u is the real part of an analytic function in Ω, so there thus exists a holomorphic function in Ω with an arbitrarily specified real part on γ. The imaginary part of this analytic function is determined uniquely up to an additive constant by the real part, so there cannot exist an analytic function in Ω with arbitrarily specified values on the boundary curve γ. On the other hand, if g is any sufficiently smooth function on γ, the integral

$$\int_\gamma \frac{g(\zeta)}{\zeta - z} d\zeta$$

represents an analytic function $f_i(z)$ at all points z in Ω and another analytic function $f_0(z)$ at all points outside $\Omega \cup \gamma$. These functions have well-defined boundary values on γ, and $f_i(z) - f_0(z) = 2\pi i g(z)$ whenever z is on γ; the function $f_0(z)$ vanishes only when g is the boundary value on γ of an analytic function in Ω.

Isolated singularities. If a function f is analytic at all points of a disk Δ centered at a, except perhaps at the point a itself, a is called an isolated singularity of the function f. There are three mutually exclusive possibilities for the nature of such a singularity.

1. It may happen that $|f(z)|$ remains bounded near the point $a(14)$. In that case the function can be extended to an analytic function even at the point a by suitably choosing the value of $f(a)$; the point a is then called a removable singularity.

2. It may happen that $\lim_{z\to a}|f(z)| = \infty$. In that case a is a removable singularity for the function $g(z) = 1/f(z)$, so that $f(z) = 1/g(z)$ where $g(z)$ is an analytic function vanishing at the point a; and if $g(z) = (z - a)^k g_0(z)$, where $g_0(z)$ is analytic and $g_0(a) \neq 0$, then $f(z) = (z - a)^{-k} f_0(z)$ where $k > 0$ and $f_0(z)$ is analytic and $f_0(a) \neq 0$. The function $f(z)$ is said to have a pole of order k at the point a. The function $f_0(z)$ has a Taylor expansion at the point a as usual, so the function $f(z)$ has an expansion given by Eq. (7).

$$f(z) = a_{-k}(z-a)^{-k} + \cdots + a_{-1}(z-a)^{-1} + a_0 + a_1\,(z-a) + a_2\,(z-a)^2 + \cdots \quad (7)$$

The portion

$$\sum_{n=-k}^{-1} a_n(z-a)^n$$

of this expansion is called the principal part or singular part of the function $f(z)$ at the point a, while the remainder of the series represents an analytic function near a.

3. If neither of the two preceding cases arises, the function $f(z)$ is said to have an essential singularity at the point a. A function having an essential singularity admits a Laurent series expansion near the point a of the form

$$f(z) = \sum_{n=-\infty}^{+\infty} a_n(z-a)^n \quad (8)$$

in which infinitely many terms involving negative powers of the variable $(z - a)$ appear. Singularities of this type can occur and do so frequently. For example, whenever $f(z)$ has a pole at a point a, then $e^{f(z)}$ has an essential singularity at the point a. The behavior of a function near an essential singularity is rather complicated. A theorem of K. Weierstrass asserts that in any neighborhood of an essential singularity the values taken by the function come arbitrarily near any complex value. A much deeper theorem of E. Picard asserts that in any neighborhood of an isolated singularity a function actually takes all complex values with at most one possible exception.

Global properties. The zeros of an analytic function are isolated, in the sense that if f is analytic near a point a and $f(a) = 0$, then f has no other zeros in some neighborhood of a. That leads quite easily to the identity theorem: if $f(z)$ and $g(z)$ are analytic in a connected-region Ω and if $f(a_n) = g(a_n)$ for an infinite sequence of points a_n having a limit point inside Ω, then $f(z) = g(z)$ at all points z in Ω. On the other hand, if a_n is any sequence of points in Ω having no limit point inside Ω, there are analytic functions in Ω having zeros precisely at the points a_n. This result is particularly easy in case that Ω is the entire complex plane. Indeed, in that case any analytic function having zeros at the points a_n can be written as a product given

$$f(z) = z^m e^{h(z)} \prod_n \left(1 - \frac{Dz}{a_n}\right) e^{P_n(z)} \quad (9)$$

where $h(z)$ is an analytic function in the entire plane and $P_n(z)$ are suitably chosen polynomials ensuring that the product converges when there are infinitely many points a_n. There is a good deal of quite detailed information relating the growth of the function $f(z)$, the distribution of the zeros a_n, and the canonical product formula (9). This area of investigation is called the theory of entire functions. The infinite product expansions of even the elementary functions are quite interesting. For example, the expansion of $\sin \pi z$ is given by

$$\sin \pi z = \pi z \prod_{n=1} \left(1 - \frac{z^2}{n^2}\right) \quad (10)$$

Meromorphic functions. A function analytic in a region Ω of the complex plane, except possibly for poles at some points of Ω, is called a meromorphic function in Ω. The points at which the function has poles can of course have no limit point inside Ω. Near any pole a function can be written as the quotient of two analytic functions, as already noted. There is an analogous global result: any meromorphic function in Ω can be written as the quotient of two functions each analytic in Ω. If $a_1, a_2, \ldots$ is any sequence of points in Ω having no limit point inside Ω and if

$f_1(z), f_2(z), \ldots$ are principal parts of poles at these points, so that

$$f_v = \sum_{n=-kv}^{-1} a_{v,n}(z - a_v)^n$$

There exists a meromorphic function $f(z)$ in Ω having poles with the specified principal parts at the specified points and no other singularities. This is the analog of the familiar partial fraction expansion for quotients of polynomials. The resulting expansions of even the elementary functions are quite interesting, as for example the expansion

$$\pi \cot \pi z = \frac{1}{z} + \sum_{n=1}^{\infty} \frac{2z}{z^2 - n^2} \tag{11}$$

Rational functions. Those functions that have at most finitely many zeros and poles in the entire complex plane, and that either have a well-defined limit or tend to infinity as the variable approaches infinity, are rational functions; that is, they are quotients of polynomial functions. These functions extend naturally to the Riemann sphere, the set that arises by adjoining to the complex plane a single point at infinity. The change of variable $\zeta = 1/z$ transforms the complement of a large circle in the plane of the variable z to the interior of a small circle in the plane of the variable ζ; the point at infinity in the variable z corresponds to the origin in the variable ζ, and that makes it possible to speak of the behavior of a rational function at the point at infinity. The rational functions are precisely those functions that are meromorphic on the entire Riemann sphere, including the point at infinity. Although they are in some senses the simplest of analytic functions, their study leads to extremely complicated problems. Any such function can be viewed as a mapping of the Riemann sphere to itself; and this mapping can be iterated, beginning with the function $f(z)$ and then passing to the iterates $f^2(z) = f(f(z))$, and so on. The behavior of the iterates can be very complicated even for the simplest such functions, second-degree polynomials. The sphere can be decomposed into two disjoint sets: the Fatou set, an open subset of the Riemann sphere on which the iterates form an equicontinuous family of functions and generally converge; and the Julia set, usually a very complicated closed set, even a fractal set, on which the iterates form a family exhibiting the phenomenon of chaos (**Fig. 7**). *See* CHAOS; FRACTALS.

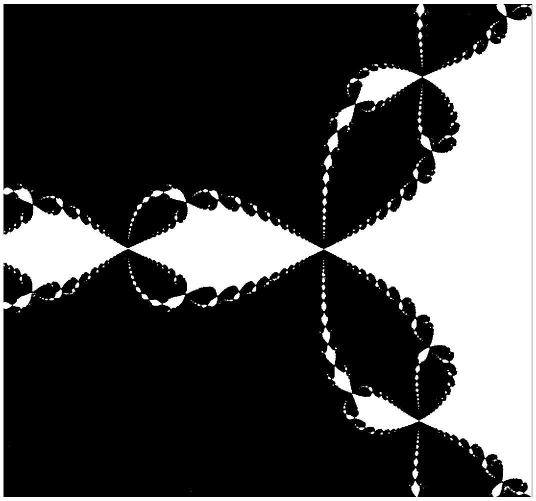

Fig. 7. $z \mapsto z^3 - 1$**. Fractal image. (*Reprinted with permission from H.-O. Peitgen and P. H. Richter, The Beauty of Fractals, Springer-Verlag, New York, 1986*)**

Analytic functions of several variables. A complex-valued function depending on several complex variables $f(z_1, \ldots, z_n)$ is called analytic at a point $(a_1, \ldots, a_n)$ if the values of that function at all points z_j sufficiently near a_j are given by a multiple power series expansion

$$f(z_1, \ldots, z_n) = \sum_{i_1=0}^{\infty} \cdots \sum_{i_n=0}^{\infty} a_{i_1 \ldots i_n}(z - a_1)^{i_1} \cdots (z - a_n)^{i_n} \tag{12}$$

If this series converges at a point $(z^0{}_1, \ldots, z^0{}_n)$ with $|z^0{}_1 - a_i| = r_i > 0$, then it is absolutely and uniformly convergent on the set of all points $(z_1, \ldots, z_n)$ for which $|z_i - a_i| \leq \rho_i$ whenever ρ_i are any positive constants such that $\rho_i < r_i$. This series thus converges to the same value for any ordering of the terms. For example, it can be rewritten as the power series

$$f(z_1, \ldots, z_n) = \sum_{i_n=0}^{\infty} a_{i_n}\left(z_1, \ldots, z_{n-1}\right) \cdot (z_n - a_n)^{i_n} \tag{13}$$

in the variable z_n with coefficients which are analytic functions of the variables $z_1, \ldots, z_{n-1}$. Hence holding $z_1, \ldots, z_{n-1}$ constant, the function $f(z_1, \ldots, z_n)$ is analytic in the variable z_n alone, or more generally the function $f(z_1, \ldots, z_n)$ is analytic in each variable separately. Conversely a surprisingly nontrivial theorem of F. Hartogs asserts that a function $f(z_i, \ldots, z_n)$ that is analytic in each variable separately at all points of a region Ω is an analytic function of all n variables $z_1, \ldots, z_n$ in Ω.

It follows from this result that analytic functions of several variables can be characterized in many of the same ways as are analytic functions of one variable, since it suffices to show that a function is analytic in each variable separately. Thus, if a function of several complex variables has a complex derivative in each variable separately, or satisfies the Cauchy-Riemann equations in each variable separately, then it is analytic. It is convenient to extend the Cauchy-Riemann characterization by associating to any function f of n complex variables the differential form

$$\bar{\partial} f = \sum_{i=1}^{n} \frac{\partial f}{\partial \bar{z}_i} d\bar{z}_i$$

A function of n complex variables that is continuously differentiable in the underlying real variables is analytic if $\bar{\partial} f = 0$. The analysis of this differential operator plays a significant role in a great deal of research on properties of analytic functions of several variables.

Extension of results from one variable. Some results extend quite directly from one to n complex variables: the uniform limit of analytic functions is analytic; the maximum modulus theorem holds; and there is an extension of the Cauchy integral formula, asserting that if $f(z_1, \dots, z_n)$ is analytic whenever z_j is a member of $\Omega_j \cup \gamma_j$ where Ω_j is a plane domain with smooth boundary γ_j, then

$$f(z_1, \dots, z_n) = \left(\frac{1}{2\pi i}\right)^n \int_{\zeta_1 \epsilon \gamma_1} \cdots \int_{\zeta_n \epsilon \gamma_n} \frac{f(\zeta_1, \dots, \zeta_n)}{(\zeta_1 - z_1) \cdots (\zeta_n - z_n)} d\zeta_1 \cdots d\zeta_n \qquad (14)$$

holds whenever z_j is a member of Ω_j for all indices j. However, for the most part, the theory of analytic functions of several complex variables is far from being merely an extension of the standard results of the classical theory of functions of a single complex variable, by considering one variable at a time. Indeed, the theory of functions of several complex variables has quite a distinctive character with a considerable variety of results which perhaps are not the expected generalizations of the classical results but which shed new light on the familiar theory of analytic functions of a single variable.

Integral formulas. In addition to the direct extension of the classical Cauchy integral formula from one to several variables in (14), there are a variety of other integral representation formulas that reflect the higher-dimensional situation and that have significant applications. Some of these formulas, such as those due to André Weil and Stefan Bergman, follow the extended Cauchy integral formula (14) in that they involve integration over only part of the boundary of the domain. Others, such as those of Salomon Bochner and E. Martinelli, involve an integration over the full boundary, and are particularly useful for examining the behavior of functions on smoothly bounded domains. Yet others, such as those due to W. Koppelman and I. Lieb, extend the analysis to functions that are not complex analytic, by providing explicit solutions f of the system of partial differential equations $\bar{\partial} f = \phi$, where ϕ is a differential form. These solutions also are important in the analysis of the boundary values of analytic functions of several variables. The integral formulas themselves are rather complicated.

Analytic continuation. An examination of the extended Cauchy integral formula (14) indicates some of the differences between the cases $n = 1$ and $n > 1$. When $n = 1$, either formula (14) or (4) expresses the values of an analytic function inside a domain Ω in terms of the values of the analytic function on the boundary of Ω, whereas when $n > 1$, formula (14) expresses the values of an analytic function inside a domain $\Omega_1 \times \cdots \times \Omega_n$ in terms of the values of the analytic function on a very small piece of the boundary. For example, when $n = 2$ the domain $\Omega_1 \times \Omega_2$ can be viewed as an open set of the four-dimensional euclidean space, its boundary is the three-dimensional subset $(\Omega_1 \times \gamma_2) \cup (\gamma_1 \times \Omega_2)$, but the integration in (14) is extended across the two-dimensional part $\gamma_1 \times \gamma_2$ of the boundary. This difference is not superficial; it reflects the greater possibilities for analytic continuation of functions of $n > 1$ variables than of functions of a single variable.

For any domain Ω in the complex plane there are functions which are analytic in that domain but which cannot be extended as analytic functions across any part of the boundary of Ω. For example, there exist nontrivial analytic functions vanishing at any infinite sequence of points $a_1, a_2, \dots$ of Ω having no limit point inside Ω, and if every boundary point of Ω is a limit of a subsequence of these points $a_1, a_2, \dots$ then such an analytic function cannot be continued across any boundary point. However, there are domains Ω in the space of $n > 1$ complex variables such that any function analytic in Ω extends to an analytic function in a properly larger domain. For example, it was shown by Hartogs that if Ω is an open neighborhood of the boundary of a compact subset K in the space $n > 1$ complex variables, then every function analytic in Ω extends to a function analytic in the union of K and Ω (**Fig. 8**).

Thus in the study of functions of $n > 1$ complex variables there arise the problems of characterizing the natural domains of existence of analytic functions (called domains of holomorphy) and of determining for those domains which are not domains of holomorphy the largest domains to which all analytic functions can be extended (called the envelopes of holomorphy). Both problems have been extensively studied, the first one particularly so. Perhaps the most surprising result is that the domains of holomorphy can be characterized purely locally: a domain Ω in the space of n complex variables is a domain of holomorphy if and only if each point on the boundary of Ω has an open neighborhood $\cup$ such that the intersection of $\cup$ and Ω is a domain of holomorphy. The determination of the envelope of holomorphy of a domain is generally rather difficult, the situation being complicated by the fact that the envelope of holomorphy may not be realizable as a domain in the space of n complex variables.

Zeros and singularities. Another and not entirely unrelated difference between functions of $n > 1$ and functions of one complex variable is that in the case $n > 1$ the zeros and singularities of an analytic function are never isolated. The set of zeros of an analytic function of $n > 1$ variables is a set of topological dimension $2n - 2$ and is in most places locally euclidean but can have very complicated singularities. Strange spaces, such as the exotic seven spheres,

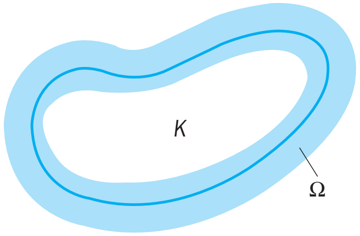

Fig. 8. Analytic continuation in $n > 1$ dimensions according to the theorem of Hartogs.

manifolds which are topologically but not differentiably equivalent to the ordinary seven-dimensional sphere, arise in this context. Even the purely local study of functions of several complex variables thus presents a considerable challenge. *See* TOPOLOGY.

Applications. The general theory of analytic functions of several complex variables has a wide range of applications in other parts of mathematics. It is a standard tool in the examination of function algebras and of special spaces of functions, the subject of harmonic analysis. The techniques also arise in geometric problems in various parts of differential geometry. *See* DIFFERENTIAL GEOMETRY. Robert C. Gunning

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Complexity theory

The theory of complex systems. Complexity theory arises from the need to understand the richness in structure and behavior often seen in large systems. The property that distinguishes complex systems from systems that are large but simple is the emergence of global features from local interactions, as captured in the popular saying "the whole is greater than the sum of its parts." For example, a flock of birds emerges when individual birds coordinate their behavior with each other.

Complexity often appears as unpredictability, or as a tendency for a system to undergo sudden, rapid change. Typically, it arises within systems that have strong interrelationships between components. For instance, the coordinated action of millions of individual cells, all tightly bound together, produces the action of muscles in the body. Epidemics emerge from the spread of infection from individual to individual.

Complexity theory has its roots in many fields of research, including biology, computer science, ecology, engineering control systems, nuclear physics, and operations research. In physics, for instance, there is a need to understand properties that emerge within large ensembles of atoms and other particles. General systems theory, developed by the biologist Ludwig von Bertalanffy in the 1950s, identified the role of internal interactions and processes in self-organization. In the 1960s, W. Ross Ashby and Norbert Wiener developed cybernetics, which concerned communications and feedback in the control of systems. Complexity theory came into its own during the late 1980s, as increasing computing power made large-scale simulation studies practical. The formation of specialist research centers, such as the Santa Fe Institute, did much to promote the new science during the 1990s. *See* CYBERNETICS; ECOLOGY; NUCLEAR STRUCTURE; OPERATIONS RESEARCH.

Several fields of research have become closely linked to complexity theory. The link to graph theory is assured by the network model of complexity (discussed below). The relevance of chaos theory arises because complexity in dynamic systems often leads to nonlinear and chaotic behavior. Another related field is artificial life (Alife), which concerns lifelike features found in artificial systems. By addressing complexity in living systems, this field has influenced the development of theory in evolution, ecology, and sociobiology. Evolutionary computing concerns computational processes that address complex problems by mimicking species evolution. The best-known example is the genetic algorithm, introduced by John Holland in 1975. This solves complex optimization problems by treating key parameters as genes within a population of potential solutions. Complex adaptive systems (CAS) are systems, such as brains or societies, composed of interacting elements that adapt or change in response to experience. *See* CHAOS; EVOLUTIONARY COMPUTATION; GENETIC ALGORITHMS; GRAPH THEORY.

Network model. In most cases, complexity can be understood in terms of networks. This model treats systems as sets of objects ("nodes") with connections ("edges") linking them. For instance, within a flock of birds the nodes would be birds and their interactions would be the edges. In a nuclear chain reaction, the nodes would be atoms and the edges would be moving neutrons. The network model also applies to processes and behavior. In a game of chess, for instance, each arrangement of pieces on the board is a node in a network of board arrangements, and moves by the players provide the edges that link different arrangements. In many games, for instance, a general strategy is to restrict your opponent's moves while maximizing the number of possible moves that you can make.

Strictly speaking, a set of nodes linked by edges forms a graph (for example, people who are neighbors of each other). A directed graph is a graph in which each edge has direction (for example, descendants in a family), and a network is a graph in which the nodes or edges have attributes associated with them (for example, people have names).

In any network, some features arise from the nature of the objects and their relationships, and some emerge from the underlying network. A network is connected if there is a path (a sequence of edges) leading from any one node to any other. For example, the edges A-B, B-C, C-D form a path between nodes A and D. Attributes that are often used to express the structure of different networks include:

Connectivity (the number of edges that must be removed to break the network apart).

Edge density (the number of edges as a fraction of the total number possible).

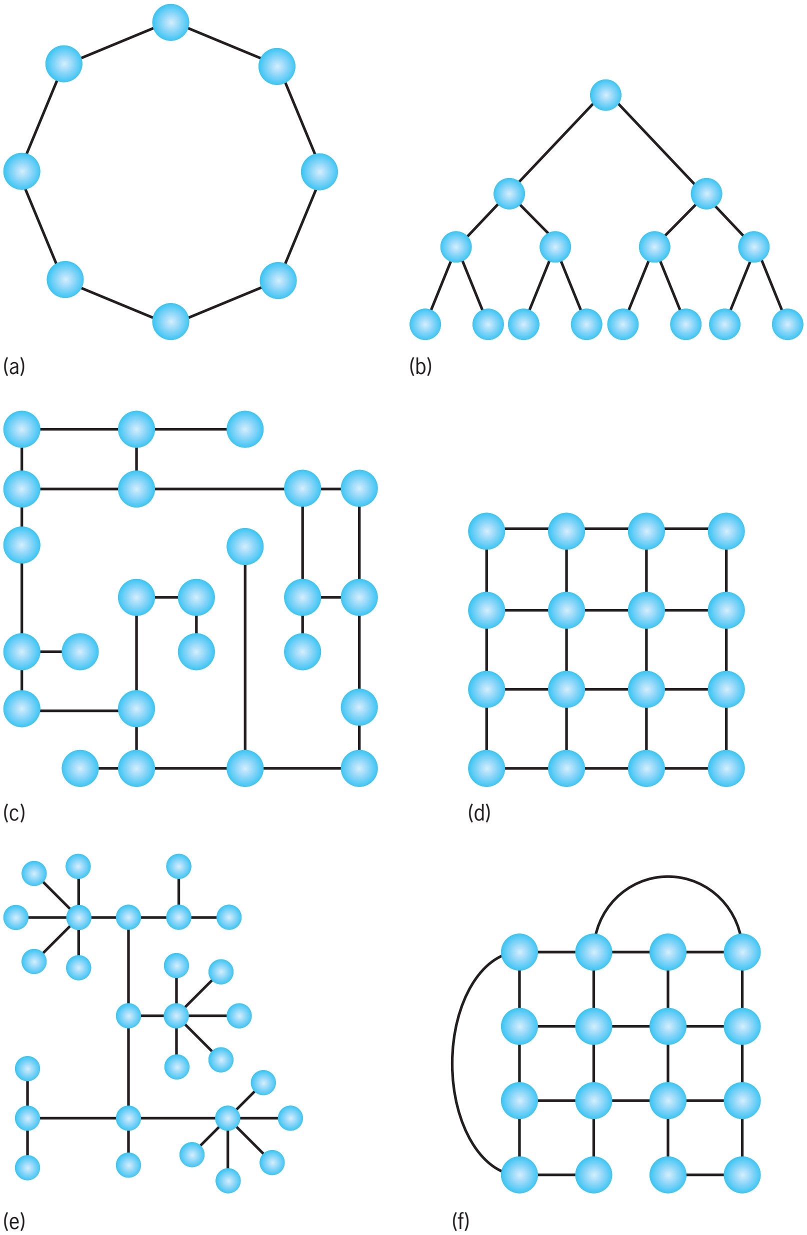

Fig. 1. Structure of some common kinds of networks. (*a*) Cycle. (*b*) Tree. (*c*) Random. (*d*) Regular. (*e*) Scale-free. (*f*) Small world.

Clustering (the density of links between sets of nodes linked to a given node).

Diameter (the greatest separation between pairs of nodes, where separation is taken to mean the shortest path between a given pair of nodes).

Several kinds of network structure are common because they confer important properties:

1. Cycles or circuits (**Fig. 1*a***) are regular networks in which a single path joins every node. The sequence of edges A-B, B-C, C-D, D-A forms a cycle linking the nodes A, B, C, and D.

2. Trees (Fig. 1*b*) are connected networks that contain no cycles. Hierarchies are trees with a root node, a node that all edges lead away from (for example, a common ancestor in a family tree). In computing, objects can form hierarchies in two ways: whole-part hierarchies (for example, in a whole book, the parts are chapters), and gen-spec hierarchies (for example, a novel is a special kind of book, and a book is a special kind of publication).

3. Random networks (Fig. 1*c*) are networks in which edges are distributed randomly between nodes.

4. Regular networks (Fig. 1*d*) are connected networks in which the edges form a pattern (for example, a lattice or grid).

5. Scale-free networks (Fig. 1*e*) form when new nodes in a growing network attach preferentially to existing nodes with highest connectivity. The resulting distribution of links per node obeys an inverse power law. That is, some nodes have many connections, but most have few. Web sites on the Internet, connected by hypertext links, provide a good example.

6. Small worlds (Fig. 1*f*) are connected graphs that contain both local clusters and long-range interactions. They fall between random networks at one extreme and regular networks at the other. Social networks often take this form.

Phase transitions. Complex systems have a tendency to undergo sudden change. Examples include crystallization, water freezing, and epidemics. In all cases, these phase changes occur at a fixed value (the critical point) of some order parameter (for example, water freezes at a temperature of 0°C). Phase transitions can usually be understood as connectivity avalanches in an underlying network (**Fig. 2**). If a network is formed by adding edges at random to a set of N nodes, then a phase change (connectivity avalanche) occurs when the number of edges reaches the critical density $N/2$ (**Fig. 3**): the nodes become absorbed into a unique giant component. This connectivity avalanche translates into many physical processes. In crystallization, for instance, it involves small crystal seeds merging to form large structures. In all epidemic phenomena, the process requires a certain critical level of interaction to sustain itself. Nuclear fission, for instance, starts when the fuel reaches a critical mass. *See* CRITICAL MASS; CRITICAL PHENOMENA; CRYSTALLIZATION; EPIDEMIC; PHASE TRANSITIONS.

Automata whose state spaces lie close to the phase change in connectivity (the so-called edge of chaos) often exhibit interesting behavior, leading to speculation that only these automata are capable of universal computation and the ability to evolve.

Self-organized criticality occurs when internal processes maintain a system in a critical state (for example, a sand pile). Characteristically, the frequency (f) of events in such a system (for example, the sand pile collapses) follows an inverse power law $f(s) = s^{-\tau}$, where s is the size of the event and τ is a self-similarity exponent.

Encapsulation. Encapsulation involves grouping nodes in a network into modules that are highly connected internally, but with limited connections to the rest of the network. In both natural and artificial systems, encapsulation is the most common way of coping with complexity. It appears in many different guises. In human activity, large tasks are usually

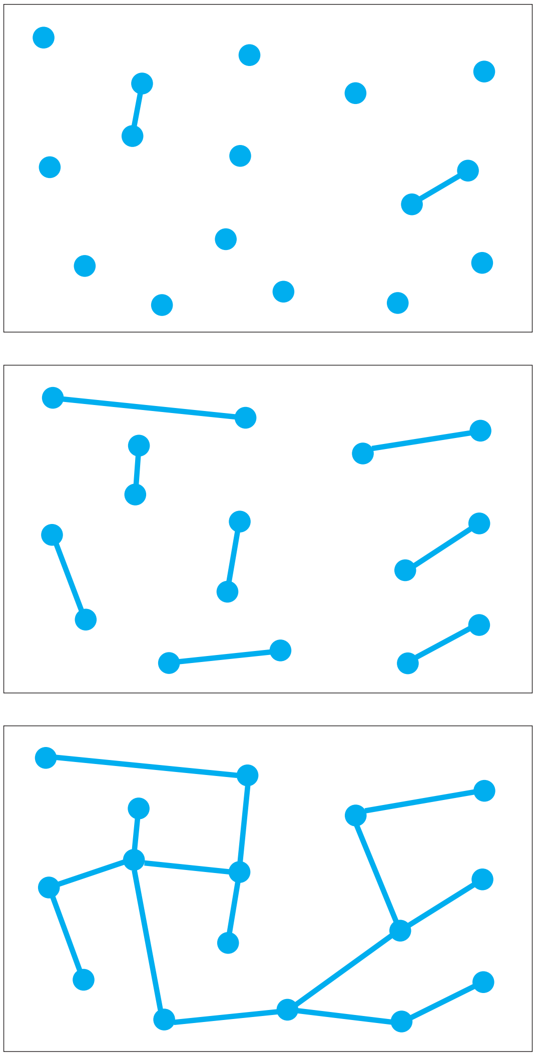

Fig. 2. Formation of a unique giant component as edges are added to a random network.

broken down into managable parts: Large corporations are typically divided into work units such as divisions, departments, and sections. Likewise, filing systems are divided into cabinets, drawers, files, and folders.

Modular design simplifies construction. Computer software typically consists of self-contained, reusable objects and modules. Living trees grow by the repeated addition of modules, such as buds, leaves, and branches. Engineering systems are often designed around modular components. A motor car, for instance, has electrical, fuel, and steering systems, and so on.

Encapsulation reduces complexity by eliminating long-range connections. In a human organization, for instance, specialization reduces the scope of problems that each person needs to deal with. On the other hand, modular designs can be brittle, often failing when long-range connections occur, such as by placing a library book back on the wrong shelf.

Modular structures often form into hierarchies of organization. A book, for instance, is a hierarchy of modules consisting of chapters, sections, paragraphs, sentences, and words. In management, hierarchies arise from the dual desires to simplify complex tasks and to control complex organizations ("divide and rule").

Self-organization. Internal interactions can lead to the emergence of order within complex systems, even in the absence of external influences. Several processes are known to promote self-organization. Ilya Prigogine introduced the term "dissipative systems" to describe systems (including living things) that are far from equilibrium and share energy with their environment. He argued that in dissipative systems local irregularities can grow and spread, allowing large-scale patterns and order to emerge. Crystal growth is an example. *See* CRYSTAL GROWTH.

Feedback plays an important role in self-organization. It occurs where the output of a system is fed back as input to the same system. Negative feedback dampens disturbances and stabilizes local patterns and behavior. Familiar examples include thermostats, speed governors, and other control devices that maintain systems in a steady state (sometimes called homeostasis). Positive feedback amplifies local effects, allowing them to grow and spread. Control systems are designed to avoid positive feedback because of its destabilizing effect. In contrast, positive feedback plays an important role in natural systems by contributing to the formation of large-scale order. In interstellar gas clouds, for instance, gravity leads to the formation of large centers of mass. These centers gather material faster, and at the expense of smaller ones, eventually forming stars and planets. Within an ant colony, piles of food, eggs, and waste grow in a similar way. Eventually this sorting of materials creates the order seen in ant colonies. Firing of a laser occurs when groups of atoms synchronize their outputs by "enslaving" other atoms. *See* CONTROL SYSTEMS; HOMEOSTASIS; LASER; MOLECULAR CLOUD.

Other processes that promote self-organization include encapsulation, adaptation, and evolution within living systems.

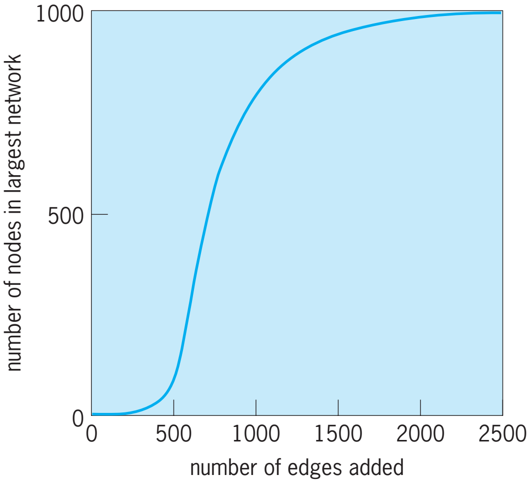

Fig. 3. Connectivity avalanche. Edges, each joining a pair of nodes, are added at random to a set of 1000 nodes. The avalanche begins when about 500 edges are added.

Emergence. In a system of objects, interactions lead to self-organization, which results in the emergence of large-scale features. An ant colony emerges from the joint activity of thousands of individual ants interacting with each other and with their environment. Emergent properties are not predictable from the properties of the individuals, but often involve the imposing of constraints on individuals. In module formation, for instance, individual interactions with the outside could disrupt the module's integrity.

Module formation is a crucial mechanism in the emergence of order in many complex systems. In a growing embryo, for instance, cells differentiate at a very early stage of development, forming modules that grow into separate limbs and organs. *See* CELL DIFFERENTIATION.

A related problem is the paradox of self-replication. This originated during the seventeenth century with attempts to explain human reproduction. Human eggs or sperm were thought to contain homunculi, tiny bodies from which children would grow. However, this idea led to a paradox: a single homunculus would need to have nested within it smaller homunculi from which future generations would spring. The paradox of self-replication arises because some part a self-replicating system apparently needs to contain a copy of the whole system. How is it possible, for instance, for a plant or animal to reproduce without including a complete description of itself? The paradox is resolved by observing that only information about the process of replication needs to be embedded within the system, not the entire system itself. The rest of the information can be derived from interaction of the system with its environment. John von Neumann suggested that there is a threshold of complexity below which automata are too simple to be capable of self-replication. However, later researchers, such as Lionel and Roger Penrose, demonstrated that even certain simple block structures could replicate themselves. Tom Ray's Tierra model provided a practical demonstration of a computational environment within which programs emulated organisms by containing code for reproducing themselves.

Computational complexity. In computing, the complexity of a problem is measured by the time (or space) required to solve it, and the way that time increases as the size of the input increases. For instance, given a list of the locations of n towns, the time needed to find the most northerly town increases in proportion to n [denoted $O(n)$], but the time required to find the shortest distance between pairs of towns increases in proportion to n^2 [denoted $O(n^2)$].

In problem solving, an important advantage of modularity is to reduce combinatorial complexity. In a rail network linking, say, 100 stations, separate fares for every pair of stations would require a table with 4950 entries, but grouping the stations into, say, 3 zones would reduce the table to no more than 6 different fares.

Problems are often classified according to their computational complexity. Conventional terminology defines the class P to consist of all problems that can be solved by a deterministic algorithm for which the time complexity is a polynomial function of the input (for example, the towns examples above). The class NP consists of problems that a nondeterministic machine can solve in polynomial time. An unresolved theoretical question is whether the classes P and NP are identical. *See* CRYPTOGRAPHY.

Hard problems occur when the time complexity increases faster than any polynomial of the input. In the traveling salesman problem, for instance, a salesperson needs to find a route that minimizes the total distance traveled while visiting a number of towns (without doubling back). The solution involves checking all possible orderings of a list of the towns.

Attempts to link complexity to thermodynamics and information theory led to the Kolmogorov-Chaitin definition of algorithmic complexity, which is the length of the shortest program needed to compute a given pattern. For example, a table of sports scores in general contains more or less random entries and cannot be compressed. In contrast, a table of logarithms can be condensed to a formula that calculates all the entries. Describing the path of a flock of birds greatly reduces the detail needed to describe the paths of all the individual birds. These ideas extend into many aspects of computing. Methods such as minimum message length (MML) adapt them to provide practical methods of classification and problem solving. Data compression algorithms typically employ a fixed program and reduce a file to the data needed to regenerate the original pattern. Fractals may be regarded as patterns that are produced by repeating a given algorithm on different scales. *See* DATA COMPRESSION; FRACTALS; INFORMATION THEORY.

As information technology has spread throughout society, the idea of natural computation has been increasingly influential. This idea treats natural processes as forms of computing. For instance, scientific studies sometimes employ computational analogies (for example, animals as programmed robots) to understand complex processes in natural systems. Likewise, computing has borrowed ideas from nature, which has evolved ways of solving complex problems. This practice has resulted in a proliferation of biological terms such as cellular automata, genetic algorithms, neural networks, and swarm intelligence. *See* NEURAL NETWORK.

Role of simulation. Complex systems usually behave in nonlinear fashion. They are often mathematically intractable, and the richness of their behavior can make them inherently unpredictable. Simulation models provide a practical way of representing them. Certain representations are widely used to simulate specific kinds of complex systems, notably cellular automata, spin glasses, and agent-based models.

Cellular automata are grids of cells, each of which is an automaton that interacts with its neighbors. First introduced by John von Neumann, cellular automata became popular during the 1970s as a result of John Conway's cellular automaton Game of Life.

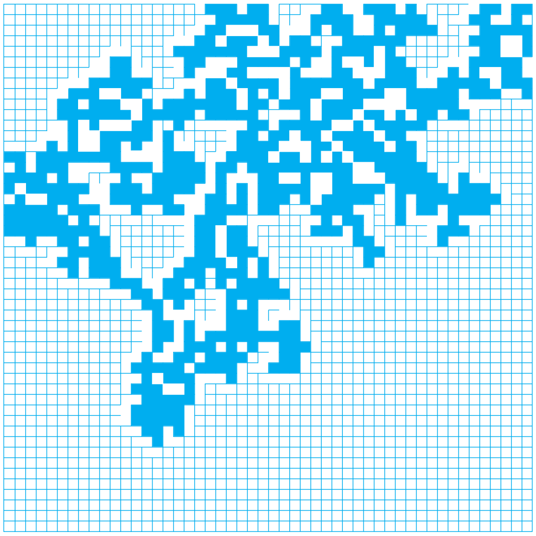

Fig. 4. Cellular automaton simulation of epidemic spread through a landscape. The cells represent areas of the land surface. Filled cells have been infected.

They have been applied to many physical processes, such as flows and spread of epidemics (**Fig. 4**). In a simple cellular automaton model of disease spread, for instance, each cell would denote an area within a landscape, and the cell's state at any given time might be "susceptible," "infected," or "immune." The epidemic would spread from infected cells to neighboring susceptible cells. The virulence of the disease would determine the chances of a susceptible cell becoming infected; otherwise it would become immune. *See* CELLULAR AUTOMATA.

Spin glasses (regular lattices, in which each node has a "spin") have been used to study processes, such as glass formation, involving transitions from incoherent to coherent configurations of spin states in magnetic materials. *See* SPIN GLASS.

Agent-based models consist of many independent agents (for example, people, animals, or companies) that interact with one another and behave according to defined sets of rules. Cellular automata are a subclass of agent-based models. Early examples of this approach included Paulien Hogeweg's work on the emergence of social order within bumblebee colonies and Craig Reynold's "boids" models of flocking behavior in birds.

Simulation models provide several practical advantages for dealing with complexity. One is the potential to perform "virtual experiments" for problems where real-world experiments are impractical. Another is the ability to explore "what-if" scenarios when complexity makes prediction impossible. *See* SIMULATION.

Future challenges. Complexity theory is becoming more important as the problems faced by science and society grow more complex. Is it possible to evolve designs to specification for huge networks that are both robust and efficient? The Internet, for instance, poses enormous challenges as a self-organizing system for gathering, storing, and distributing information. *See* INTERNET.

In biology perhaps the greatest challenge at present is to understand how genetic regulatory networks control growth and development. During the 1970s, Stuart Kauffmann proposed a switching model of genetic control that was based on Boolean networks. Research has increasingly pointed to modular organization within the genome. Development of the eye, for instance, is encoded by a set of genes whose activity is controlled by a single "eyeless gene." *See* DEVELOPMENTAL GENETICS; MOLECULAR BIOLOGY.

One far-reaching impact of communications and globalization is that the world is increasingly rich in interactions. Cascading interactions often mean that events in one part of the world can affect events on the other side of the globe.

David G. Green; Tania Bransden

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Composite beam

A structural member composed of two or more dissimilar materials joined together to act as a unit. An example in civil structures is the steel-concrete composite beam in which a steel wide-flange shape (I or W shape) is attached to a concrete floor slab (**Fig. 1**). The many other kinds of composite beam include steel-wood, wood-concrete, and plastic-concrete or advanced composite materials–concrete. Composite beams as defined here are different from beams made from fiber-reinforced polymeric materials. *See* COMPOSITE MATERIAL.

There are two main benefits of composite action in structural members. (1) By rigidly joining the two parts together, the resulting system is stronger than the sum of its parts. A simple example is a pair of timber 2 by 4 in. (5 by 10 cm) studs joined by

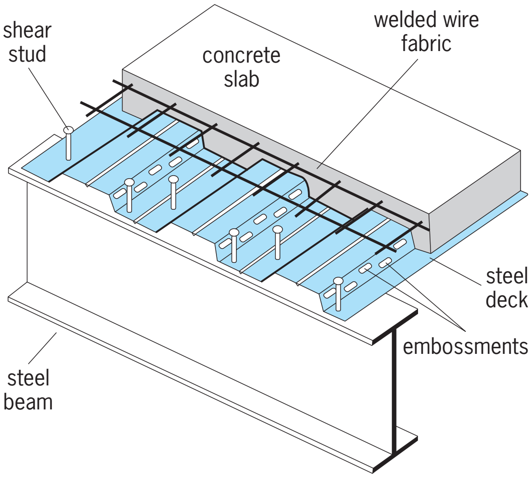

Fig. 1. Typical composite floor system.

nails. The two timber pieces connected together are far stronger and more rigid than the two individual pieces stacked together. A key feature of this system is the connecting elements, nails in this case, which provide the transfer of horizontal (shear) forces in the system. (2) Composite action can better utilize the properties of each constituent material. In steel-concrete composite beams, for example, the concrete is assumed to take most or all of the compression while the steel takes all the tension. Since concrete is very strong in compression but weak in tension (the ratio of tensile to compressive strength being approximately 1:10), and steel is prone to instability (buckling) in compression, the composite beam represents the most efficient use of these two materials. *See* CONCRETE; SHEAR; STEEL.

In general, it is assumed that these composite beams are loaded primarily in flexure and that the steel beam carries all of the tension and the slab part or all of the compression. The bending forces on the beam give rise to large horizontal (shear) forces at the interface of the materials. To transfer this force, several mechanisms can be considered, including adhesion, friction, and bearing. The first two are generally disregarded because of their lack of reliability, and in most composite systems the shear connection is provided by steel elements welded to the steel beam. These elements transfer the shear forces by bearing against the concrete. The most common type of shear connector is a shear stud, which resembles a bolt but has no threads and a smaller head (Fig. 1). Shear studs typically range from $\frac{1}{2}$ to $\frac{3}{4}$ in. (13 to 19 mm) in diameter, and from $3\frac{1}{2}$ to 5 in. (8 to 13 cm) in length. A typical $\frac{3}{4}$ -in. shear stud can transfer about 20 kips (90 kilonewtons) of horizontal force (1 kip = 1000 lb or 454 kg load). The shear stud requires a head to resist any tendency of the slab and beam to separate vertically. The studs typically are distributed evenly along the length of the beam, with spacing ranging from 6 to 16 in. (150 to 400 mm). Because typical steel decks have troughs at 12 in. (150 mm) spacing, this is the most common spacing for shear studs. It is also common to see several studs side by side in the direction perpendicular to the main axis of the beam. This arrangement is necessary in steel bridges, because the size of the steel beam is large and thus the shear forces are large. *See* STRESS AND STRAIN.

There are numerous reasons why steel-concrete composite beams have long been recognized as one the most economical structural systems for both multistory steel buildings and steel bridges. Buildings and bridges require a floor slab to provide a surface for occupants and vehicles, respectively. Concrete is the material of choice for the slab because its mass and stiffness can be used to reduce deflections and vibrations of the floor system and to provide the required fire protection. The supporting system underneath the slab, however, is often steel because it offers superior strength-weight and stiffness-weight ratio, ease of handling, and rapid construction cycles. Since both the steel and concrete are already present in the structures, it is logical to connect them together to better utilize their strength and stiffness. The typical steel-concrete composite beam is 60 to 80% stronger and stiffer than the steel beam alone. The stiffness and strength gains are greater for shallow beams [16 to 24 in. (40 to 60 cm) in depth] and less for deeper sections.

Three important developments have contributed to the widespread use of steel-concrete composite beams. (1) Automated systems were developed to provide the connection between the steel beam and the concrete. This connection was originally provided by welding steel channels, spirals, or serpentines to the top of the steel beam. In the 1950s a system utilizing shear studs that could be welded with a portable system (stud gun) was developed, and is in almost universal use today. (2) In the 1960s and 1970s, steel floor decking was developed. Steel decking consists of thin corrugated metal sheets that are laid between the steel beams and used as the formwork to cast the concrete. This made concrete casting much simpler, as the formwork was left in place to provide much of the tensile capacity of the slab. (3) Alternative types of steel beams were developed. Due to height limitations and the need for complex HVAC (heating, ventilation, and air conditioning), electrical, and communication installations, several variations on the traditional composite beam have been developed. They include composite joists, composite trusses, and stub-girders (**Fig. 2**). These systems are intended to provide high span/depth ratios while retaining flexibility in relocating building services. Systems using joists and trusses are popular since they avoid the need to make expensive penetrations in the beam web. *See* CONCRETE SLAB.

Composite beams in buildings have spans ranging typically from about 20 to 40 ft (6 to 12 m) for traditional beams but can be as large as 80 to 100 ft (24 to 30 m) for systems using trusses rather than I sections for the steel portion. Until recently, most

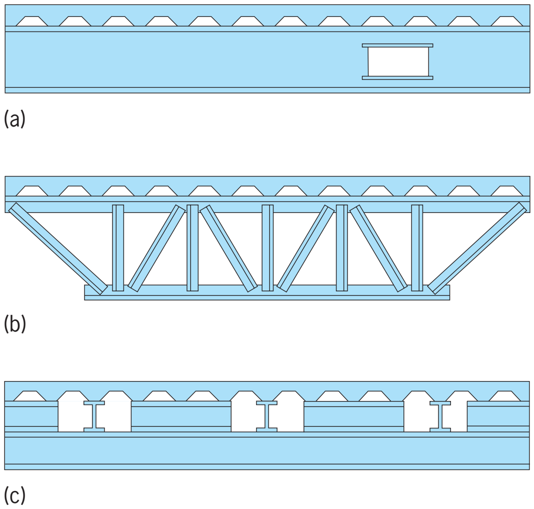

Fig. 2. Types of composite beams. (*a*) Composite beam showing reinforced web opening. (*b*) Composite joist or truss with double angle members. (*c*) Stub-girder system showing perpendicular floor beams.

composite beams were designed for full interaction, meaning that enough studs were provided to transfer the full capacity of the steel beam or concrete slab, whichever was lower. Today, composite beams are often designed for partial interaction; that is, they use fewer studs than needed to transfer the full capacity of the steel or concrete. Unlike composite beams in buildings, where the design of the shear connection is controlled by strength, the design of shear studs for composite beams in bridges is controlled by the fatigue capacity of the studs.

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Composite laminates

Assemblages of layers of fibrous composite materials (**Fig. 1**) which can be tailored to provide a wide range of engineering properties, including inplane stiffness, bending stiffness, strength, and coefficients of thermal expansion.

The individual layers consist of high-modulus, high-strength fibers in a polymeric, metallic, or ceramic matrix material. Fibers currently in use include graphite, glass, boron, and silicon carbide. Typical matrix materials are epoxies, polyimides, aluminum, titanium, and alumina. Layers of different materials may be used, resulting in a hybrid laminate. The individual layers generally are orthotropic (that is, with principal properties in orthogonal directions) or transversely isotropic (with isotropic properties in the transverse plane) with the laminate then exhibiting anisotropic (with variable direction of principal properties), orthotropic, or quasi-isotropic properties. Quasi-isotropic laminates exhibit isotropic (that is, independent of direction) inplane response but are not restricted to isotropic out-of-plane (bending) response. Depending upon the stacking sequence of the individual layers, the laminate may exhibit coupling between inplane and out-of-plane response. An example of bending-stretching coupling is the presence of curvature developing as a result of inplane loading. *See* COMPOSITE MATERIAL; METAL MATRIX COMPOSITE; POLYMERIC COMPOSITE.

Lamination theory. Classical lamination theory describes the mechanical response of any composite laminate subjected to a combination of inplane and bending loads. The laminate in Fig. 1 uses a global x-y-z coordinate system with z perpendicular to the plane of the laminate and positive downward. The origin of the coordinate system is located on the laminate midplane. The laminate has N layers numbered from top to bottom. Each layer has a distinct fiber orientation denoted θ_k. The z coordinate to the bottom of the kth layer is designated z_k with the top of the layer being z_{k-1}. The thickness, t_k, of any layer is then $t_k = z_k - z_{k-1}$. The top surface of the laminate is denoted z_0, and the total thickness is $2H$.

Assumptions. It is assumed that (1) there is perfect bonding between layers; (2) each layer can be represented as a homogeneous material with known effective properties which may be isotropic, orthotropic, or transversely isotropic; (3) each layer is in a state of plane stress; and (4) the laminate deforms according to the Kirchhoff (1850) assumptions for bending and stretching of thin plates: (a) normals to the midplane remain straight and normal to the deformed midplane after deformation, and (b) normals to the midplane do not change length.

Strain-displacement relationships. The Kirchhoff assumptions require the out-of-plane strains ε_z, γ_{zx}, and γ_{zy} to be identically zero. The nonzero strains, $\{\varepsilon\}$, at any z location can then be expressed in terms of the midplane strains, $\{\varepsilon^0\}$, and curvatures, $\{\kappa\}$, in Eq. (1).

$$\{\varepsilon\} = \{\varepsilon^0\} + z\{\kappa\} \tag{1}$$

Stresses. The stresses, $\{\sigma\}^k$, at any z location in the kth layer are now determined from the strains [Eq. (1)] and the stress-strain constitutive equations expressed in terms of the stiffness matrix $[\overline{Q}]^k$ of the kth layer. The result is shown in Eq. (2).

$$\{\sigma\}^k = [\overline{Q}]^k(\{\varepsilon^0\} + z\{\kappa\}) \tag{2}$$

Inplane forces per unit length. The inplane forces per unit length $\{N\}$ (**Fig. 2**) are defined as the through-thickness integrals of the planar stresses in the laminate. After integration, the results are shown in Eq. (3), where $[A]$ and $[B]$ are coefficient matrices

$$\{N\} = [A]\{\varepsilon^0\} + [B]\{\kappa\} \tag{3}$$

that are functions of the layer material properties and laminate stacking sequence. The $[A]$ matrix represents the inplane stiffness, and the $[B]$ matrix defines the bending-stretching coupling. $[A]$ is a function of the layer thicknesses, but is independent of the stacking sequence of the layers. In contrast, $[B]$ is dependent on both the layer thicknesses and the stacking sequence of the individual layers. If the laminate

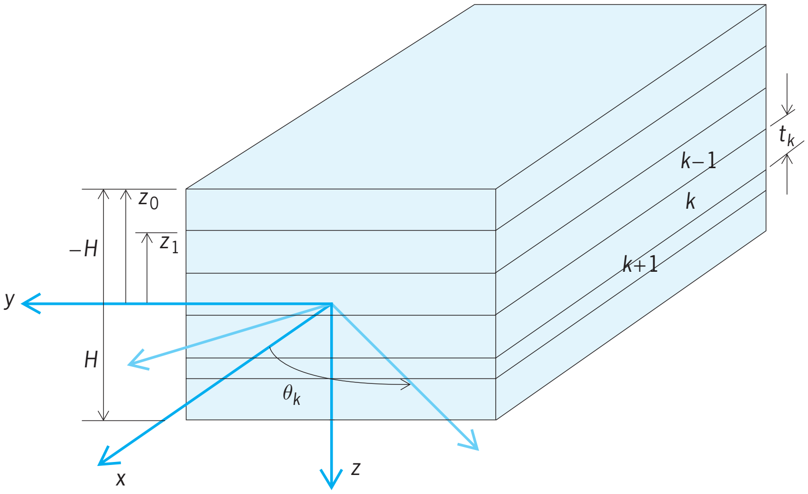

Fig. 1. Composite laminate consisting of layers with varying thickness.

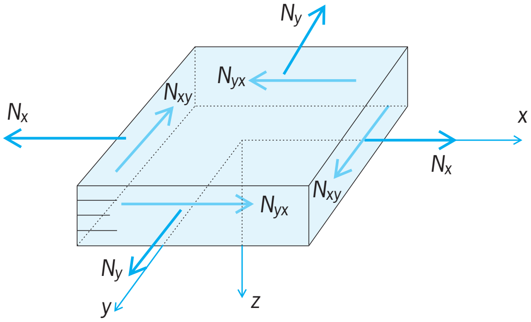

Fig. 2. Inplane forces per unit length, {*N*}.

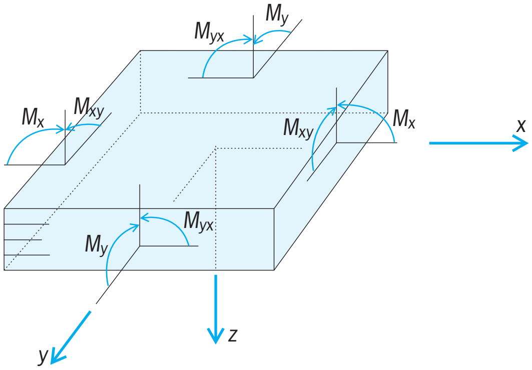

Fig. 3. Moments per unit length, {*M*}.

stacking sequence is symmetric about the laminate midplane, then $[B] = 0$.

Moments per unit length. The moments per unit length, $\{M\}$ (**Fig. 3**), are defined as the integrals of the differential forces, $\sigma_i dz$, times the moment arm, z, integrated over the laminate thickness, resulting in Eq. (4). Here the stacking sequence–dependent

$$\{M\} = [B]\{\varepsilon^0\} + [D]\{\kappa\} \tag{4}$$

bending stiffness matrix, $[D]$, is a coefficient matrix similar to $[A]$ and $[B]$.

Laminate constitutive relations. Equations (3) and (4) can be combined to give the fundamental equations of lamination theory, Eqs. (5) and (6). Equations (5)

$$\{N\} = [A]\{\varepsilon^0\} + [B]\{\kappa\} \tag{5}$$

$$\{M\} = [B]\{\varepsilon^0\} + [D]\{\kappa\} \tag{6}$$

and (6) exhibit coupling between the bending and stretching response of a laminate through the $[B]$ matrix. If $[B] = 0$, then the inplane (stretching) response is decoupled from the bending response. Indeed, there is no bending-stretching coupling for laminates which are symmetric about their midplane since $[B] = 0$ for symmetric laminates.

Laminate engineering constants. Expressions for the effective engineering constants of symmetric laminates can be determined from consideration of inplane forces applied individually. The laminate compliance, $[a^*]$, is defined in Eq. (7), where $[A]^{-1}$

$$[a^*] \equiv 2H[A]^{-1} \tag{7}$$

is the inverse of the $[A]$ matrix and $2H$ is the total thickness of the laminate. The engineering constants of symmetric laminates can be expressed as functions of the individual coefficients of the laminate compliance.

Examples demonstrating the variability of the effective engineering constants as a function of fiber orientations and laminate stacking sequence are provided in the following paragraphs for unidirectional off-axis and symmetric angle-ply laminates. A unidirectional laminate (also called a lamina) consists of layers all having the same fiber orientation. A symmetric angle-ply laminate has an equal number of layers at $+\theta$ and $-\theta$ fiber orientations located symmetrically about the laminate midplane. These results demonstrate one of the major advantages of fibrous composite materials, namely, the ability to tailor the material properties through the choice of fiber orientations, layer thicknesses, and materials. Most of the results discussed are for a typical carbon-epoxy composite, T300/5208. This composite consists of T300 carbon fibers in an epoxy matrix (5208).

Axial modulus. Predictions for the effective axial modulus (stiffness in the direction of 0° fiber orientation) E_x of angle-ply laminates are compared to the predictions for unidirectional off-axis lamina. The angle-ply laminate has higher stiffness than the off-axis lamina for fiber angles ranging from 0° to approximately 60°. Experimental results for T300/5208 angle-ply laminates exhibit very good correlation with the theoretical predictions. The higher axial stiffness for the angle-ply laminate is a result of the constraining effect (and resulting multiaxial state of stress) that the adjacent layers of the laminate have on each other.

Axial Poisson's ratio. The coupling between the transverse strain (strain perpendicular to the direction of applied stress) and the strain in the direction of applied stress is called Poisson's ratio. It is an important engineering material property. The comparison of Poisson's ratios (**Fig. 4**) is one of the most interesting

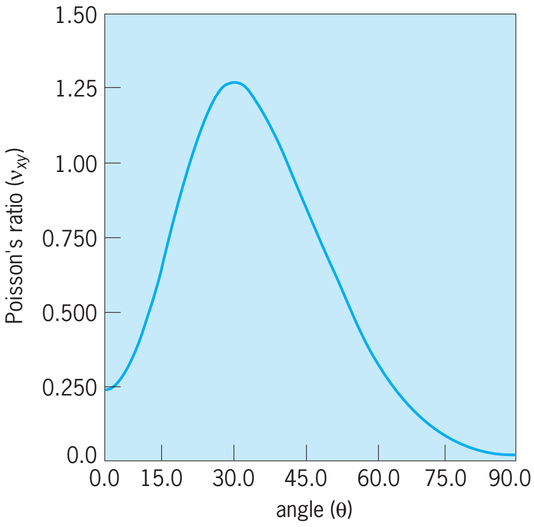

Fig. 4. Poisson's ratio comparisons for the composite laminate T300/5208.

and surprising results for laminated fibrous composites. There is a very large increase in Poisson's ratio when an off-axis ply is laminated with another off-axis ply of opposite sign. This is the case for a wide range of fiber orientations. The angle-ply laminate exhibits a maximum Poisson's ratio in excess of 1.25 (for this particular carbon/epoxy) at an angle of approximately 27°. That the Poisson's ratio can be in excess of 1.0 is very surprising to those accustomed to working with metals, where the maximum Poisson's ratio is 0.5. The high Poisson's ratio in these laminates is due to the internal state of stress in the individual layers. The laminates behave more like structures with variable internal mechanisms as compared with homogeneous materials with uniform stress states. *See* STRESS AND STRAIN.

Through-thickness Poisson's ratio. The ratio of the strain through the thickness of the laminate with that in the direction of the applied stress is called the through-thickness Poisson's ratio. For the unidirectional lamina, the through-thickness Poisson's ratio increases monotonically from the axial value to the transverse value as the fiber orientation angle increases. In sharp contrast, the through-thickness Poisson's ratio for angle-ply laminates initially decreases with increasing angle, passing through zero at approximately 13°, attains a minimum negative value at approximately 25°, then passes through zero again at approximately 40° as it increases to the transverse value at 90° (**Fig. 5**). This is another example of the variety of material properties that are possible with fibrous composites. The minimum value and the angles corresponding to zero through-thickness Poisson's ratios can be altered by modification of the laminate configuration.

Shear modulus. Shear modulus is a measure of the materials resistance (stiffness) to shear loading. The angle-ply laminate is much stiffer than the unidirectional lamina for essentially all fiber orientations. At $\theta = 45^\circ$ where the shear stiffnesses of both the lamina and the laminate are largest, the stiffness of the laminate is more than 3.5 times that of the lamina for the carbon/epoxy under consideration. The results clearly indicate that ±45° fiber orientations are desired in structures requiring high shear stiffness. *See* SHEAR.

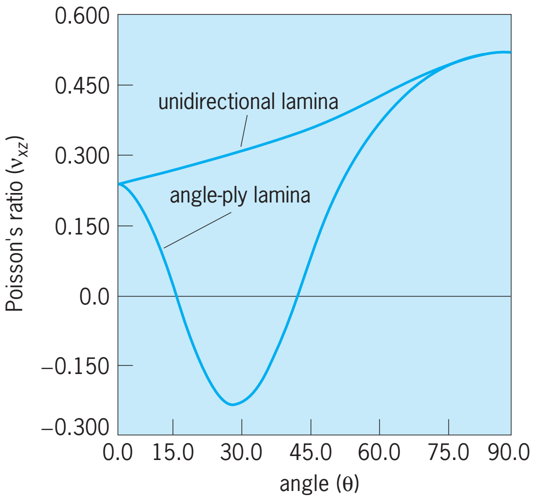

Fig. 5. Through-thickness Poisson's ratios for composite laminate T300/5208.

Coefficients of mutual influence. For anisotropic materials such as fibrous composites, there are additional important engineering properties that describe material behavior. These properties are called coefficients of mutual influence. They are similar to Poisson's ratios in that they provide an indication of the coupling between normal and shear components of strain. This type of coupling is not present in isotropic materials. One of the coefficients of mutual influence for unidirectional off-axis lamina of two different materials (T300/5208 carbon/epoxy and SCS6/Ti-15-3, a metal matrix composite) is the ratio of shear strain to axial strain for applied stress in the axial direction. The most significant features of the results are that the coefficient exhibits vary large gradients and magnitudes for the carbon/epoxy in the vicinity of $\theta = \pm 12^\circ$, and that there is a major difference in maximum values between the two materials. The coefficient of mutual influence can be nearly twice as large as Poisson's ratio. Thus the coupling between axial and shear response can be twice as large as the coupling between axial and transverse response for unidirectional lamina. The effective coefficient of mutual influence is zero for angle-ply laminates because the $+\theta$ and $-\theta$ fiber orientations have the effect of offsetting one another.

Laminate design. A wide variety of effective material properties can be obtained with one type of fibrous composite simply through changes in the stacking arrangement (layer thicknesses and fiber orientations of the individual layers) of the laminate. For example, changing the type of composite provides even more variety in the properties. Thus, material properties of the laminate can be tailored. This is a very important feature of fibrous composites because the material can be designed to have specific material properties.

Coefficient of thermal expansion. The wide variety of coefficients of thermal expansion are possible through changes in the stacking arrangement of a given carbon/epoxy. The coefficient of thermal expansion is the strain associated with a change in temperature of 1°. Most materials have positive coefficients of expansion and thus expand when heated and contract when cooled. The effective axial coefficient of thermal expansion of the carbon/epoxy can be positive, negative, or zero, depending upon the laminate configuration. Laminates with zero coefficient of thermal expansion are particularly important because they do not expand or contract when exposed to a temperature change. Composites with zero (or near zero) coefficient of thermal expansion are therefore good candidates for application in space structures where the temperature change can be 500°F (from −250 to +250°F) [278°C (from −157 to +121°C)] during an orbit in and out of the Sun's proximity. There are many other applications where thermal expansion is a very important consideration.

Carl T. Herakovich

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Composite material

A material system composed of a mixture or combination of two or more macroconstituents that differ in form or material composition and are essentially insoluble in each other. This definition is considered to be too broad by some engineers because it includes many materials that are not usually thought of as composites. For example, in many of the particulate-type composites, such as dispersion-hardened alloys and cermets, the composite structure is microscopic rather than macroscopic. Also, this definition does not draw the line between composite materials and composite structures. However, instead of trying to establish a distinction between materials and structures, it is more useful to make a distinction between mill composites (such as nonmetallic laminates, clad metals, and honeycomb) and specialty composites (such as tires, rocket nose cones, and glass-reinforced plastic boats).

Constituents and Construction

In principle, composites can be constructed of any combination of two or more materials—metallic, organic, or inorganic; but the constituent forms are more restricted. The matrix is the body constituent, serving to enclose the composite and give it bulk form. Major structural constituents are fibers, particles, laminae or layers, flakes, fillers, and matrices. They determine the internal structure of the composite. Usually, they are the additive phase.

Because the different constituents are intermixed or combined, there is always a contiguous region. It may simply be an interface, that is, the surface forming the common boundary of the constituents. An interface is in some ways analogous to the grain boundaries in monolithic materials. In some cases, however, the contiguous region is a distinct added phase, called an interphase. Examples are the coating on the glass fibers in reinforced plastics and the adhesive that bonds the layers of a laminate together. When such an interphase is present, there are two interfaces, one between the matrix and the interphase and one between the fiber and the interface.

Interfaces are among the most important yet least understood components of a composite material. In particular, there is a lack of understanding of processes occurring at the atomic level of interfaces, and how these processes influence the global material behavior. There is a close relationship between processes that occur on the atomic, microscopic, and macroscopic levels. In fact, knowledge of the sequence of events occurring on these different levels is important in understanding the nature of interfacial phenomena. Interfaces in composites, often considered as surfaces, are in fact zones of compositional, structural, and property gradients, typically varying in width from a single atom layer to micrometers. Characterization of the mechanical properties of interfacial zones is necessary for understanding mechanical behavior.

Nature and performance. Several classification systems for composites have been developed, including classification by (1) basic material combinations, for example, metal-organic or metal-inorganic; (2) bulk-form characteristics, such as matrix systems or laminates; (3) distribution of the constituents, that is, continuous or discontinuous; and (4) function, for example, electrical or structural.

There are five classes under the classification by basic material combinations: (1) fiber composites, composed of fibers with or without a matrix; (2) flake composites, composed of flat flakes with or without a matrix; (3) particulate composites, composed of particles with or without a matrix; (4) filled (or skeletal) composites, composed of a continuous skeletal matrix filled by a second material; and (5) laminar composites, composed of layer or laminar constituents.

There is also a classification based on dimensions. The dimensions of some of the components of composite materials vary widely and overlap the dimensions of the microstructural features of common conventional materials (**Fig. 1**). They range from extremely small particles or fine whiskers to the large aggregate particles or rods in reinforced concrete. *See* CRYSTAL WHISKERS; REINFORCED CONCRETE.

The behavior and properties of composites are determined by the composition, form and arrangements, and interaction between the constituents. The intrinsic properties of the materials of which the constituents are composed largely determine the general order or range of properties of the composite. Structural and geometrical characteristics—that is, the shape and size of the individual constituents, their structural arrangement and distribution, and the relative amount of each—contribute to overall performance. Of far-reaching importance are the effects produced by the combination and interaction of the constituents. The basic principle is that by using different constituents it is possible to obtain combinations of properties and property values that are different from those of the individual constituents.

A performance index is a property or group of properties that measures the effectiveness of a material in performing a given function. The values of performance indices for a composite differ from those of the constituents.

Fiber-matrix composites. Fiber-matrix composites have two constituents and usually a bonding phase as well.

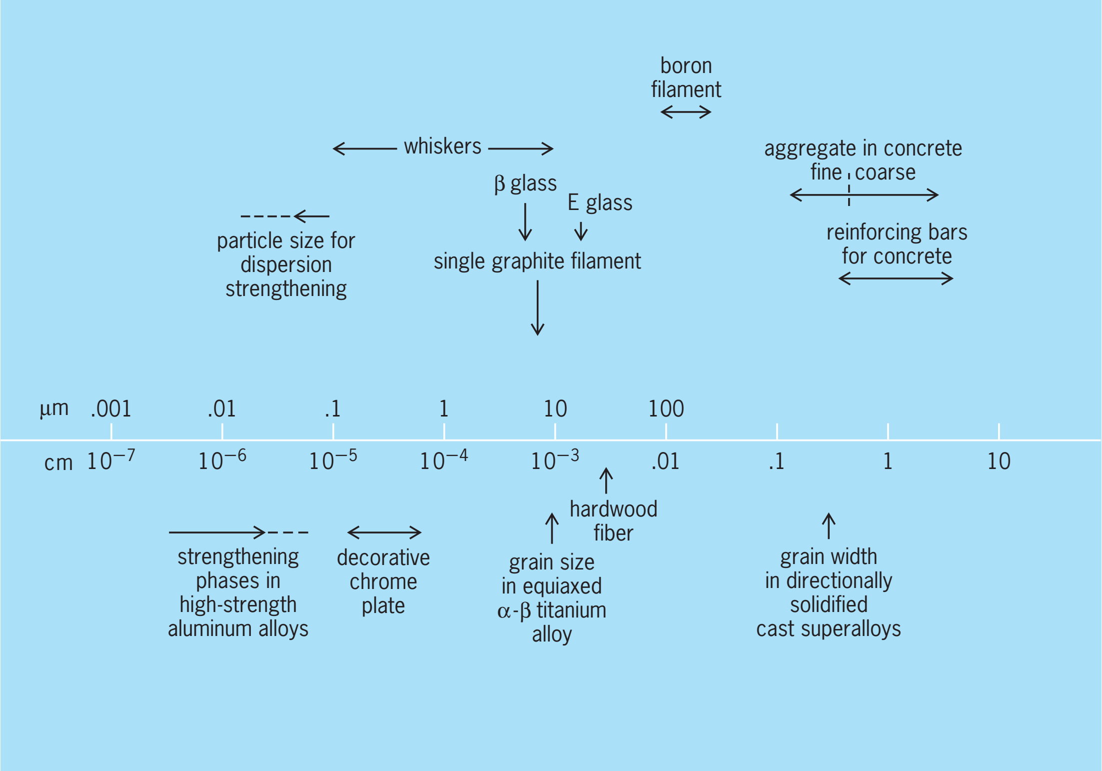

Fig. 1. Dimensional range of microstructural features in composite and conventional materials. Filament and fiber dimensions are diameters. 1 cm = 0.39 in.

Fibers. The performance of a fiber-matrix composite depends on orientation, length, shape, and composition of the fibers; mechanical properties of the matrix; and integrity of the bond between fibers and matrix. Of these, orientation of the fibers is perhaps most important.

Fiber orientation determines the mechanical strength of the composite and the direction of greatest strength. Fiber orientation can be one-dimensional, planar (two-dimensional), or three-dimensional. The one-dimensional type has maximum composite strength and modulus in the direction of the fiber axis. The planar type exhibits different strengths in each direction of fiber orientation; and the three-dimensional type is isotropic but has greatly decreased reinforcing values. The mechanical properties in any one direction are proportional to the amount of fiber by volume oriented in that direction. As fiber orientation becomes more random, the mechanical properties in any one direction become lower.

Fiber length also impacts mechanical properties. Fibers in the matrix can be either continuous or short. Composites made from short fibers, if they could be properly oriented, could have substantially greater strengths than those made from continuous fibers. This is particularly true of whiskers, which have uniform high tensile strengths. Both short and long fibers are also called chopped fibers. Fiber length also has a bearing on the processibility of the composite. In general, continuous fibers are easier to handle but have more design limitations than short fibers.

Bonding. Fiber composites are able to withstand higher stresses than their individual constituents because the fibers and matrix interact, resulting in redistribution of the stresses. The ability of constituents to exchange stresses depends on the effectiveness of the coupling or bonding between them. Bonding can sometimes be achieved by direct contact of the two phases, but usually a specially treated fiber must be used to ensure a receptive adherent surface. This requirement has led to the development of fiber finishes, known as coupling agents. Both chemical and mechanical bonding interactions occur for coupling agents.

Voids (air pockets) in the matrix are one cause of failure. A fiber passing through the void is not supported by resin. Under load, the fiber may buckle and transfer stress to the resin, which readily cracks. Another cause of early failure is weak or incomplete bonding. The fiber-matrix bond is often in a state of shear when the material is under load. When this bond is broken, the fiber separates from the matrix and leaves discontinuities that may cause failure. Coupling agents can be used to strengthen these bonds against shear forces. *See* SHEAR.

Reinforced plastics. Probably the greatest potential for lightweight high-strength composites is represented by the inorganic fiber–organic-matrix composites, and no composite of this type has proved as successful as glass-fiber-reinforced plastic composites. As a group, glass-fiber–plastic composites have the advantages of good physical properties, including strength, elasticity, impact resistance, and dimensional stability; high strength-to-weight ratio; good electrical properties; resistance to chemical attack and outdoor weathering; and resistance to moderately high temperatures (about 260°C or 500°F).

A critical factor in reinforced plastics is the strength of the bond between the fiber and the polymer matrix; weak bonding causes fiber pullout and delamination of the structure, particularly under adverse environmental conditions. Bonding can be improved by coatings and the use of coupling agents. Glass fibers, for example, are treated with silane (SiH_4) for improved wetting and bonding between the fiber and the matrix.

Generally, the greatest stiffness and strength in reinforced plastics are obtained when the fibers are aligned in the direction of the tension force. Other properties of the composite, such as creep resistance, thermal and electrical conductivity, and thermal expansion, are anisotropic. The transverse properties of such a unidirectionally reinforced structure are much lower than the longitudinal. Seven mechanical and thermal properties are of direct interest in assessing the potential of a new composite: density, modulus, strength, toughness, thermal conductivity, expansion coefficient, and heat capacity; others, such as fracture toughness and thermal diffusivity, are calculated from them.

Advanced Composites

Advanced composites comprise structural materials that have been developed for high-technology applications, such as airframe structures, for which other materials are not sufficiently stiff. In these materials, extremely stiff and strong continuous or discontinuous fibers, whiskers, or small particles are dispersed in the matrix. A number of matrix materials are available, including carbon, ceramics, glasses, metals, and polymers. Advanced composites possess enhanced stiffness and lower density compared to fiber-glass and conventional monolithic materials. While composite strength is primarily a function of the reinforcement, the ability of the matrix to support the fibers or particles and to transfer load to the reinforcement is equally important. Also, the matrix frequently dictates service conditions, for example, the upper temperature limit of the composite.

Reinforcements. Continuous filamentary materials that are used as reinforcing constituents in advanced composites are carbonaceous fibers, organic fibers, inorganic fibers, ceramic fibers, and metal wires. Reinforcing inorganic materials are used in the form of discontinuous fibers and whiskers. *See* STRENGTH OF MATERIALS.

Carbon and graphite fibers offer high modulus and the highest strength of all reinforcing fibers. These fibers are produced in a pyrolysis chamber from three different precursor materials—rayon, polyacrylonitrile (PAN), and pitch. High-modulus carbon fibers are available in an array of yarns and bundles of continuous filaments (tows) with differing moduli, strengths, cross-sectional areas, twists, and plies. *See* CARBON; GRAPHITE.

Almost any polymer fiber can be used in a composite structure, but the first one with high-enough tensile modulus and strength to be used as a reinforcement in advanced composites was an aramid, or aromatic polyamide, fiber. Aramid fibers have been the predominant organic reinforcing fiber; graphite is a close second. *See* MANUFACTURED FIBER; POLYMER.

The most important inorganic continuous fibers for reinforcement of advanced composites are boron and silicon carbide, both of which exhibit high stiffness, high strength, and low density. Continuous fibers are made by chemical vapor deposition processes. Other inorganic compounds that provide stiff, strong discontinuous fibers that predominate as reinforcements for metal matrix composites are silicon carbide, aluminum oxide, graphite, silicon nitride, titanium carbide, and carbon carbide. *See* BORON.

Polycrystalline aluminum oxide (Al_2O_3) is a commercial continuous fiber that exhibits high stiffness, high strength, high melting point, and exceptional resistance to corrosive environments. One method to produce the fibers is dry spinning followed by heat treatment.

Whiskers are single crystals that exhibit fibrous characteristics. Compared to continuous or discontinuous polycrystalline fibers, they exhibit exceptionally high strength and stiffness. Silicon carbide whiskers are prepared by chemical processes or by pyrolysis of rice hulls. Whiskers made of aluminum oxide and silicon nitride are also available. Particulates vary widely in size, characteristics, and function; and since particulate composites are usually isotropic, their distribution is usually random rather than controlled. *See* PYROLYSIS.

Organic-matrix composites. In many advanced composites the matrix is organic, but metal matrices are also used. Organic matrix material are lighter than metals, adhere better to the fibers, and offer more flexibility in shaping and forming. Ceramic matrix composites, carbon-carbon composites, and intermetallic matrix composites have applications where organic or metal matrix systems are unsuitable.

Materials. Epoxy resins have been used extensively as the matrix material. However, bismaleimide resins and polyimide resins have been developed to enhance in-service temperatures. Thermoplastic resins, polyetherketone, and polyphenylene sulfide are in limited use.

The continuous reinforcing fibers for organic matrices are available in the forms of monofilaments, multifilament fiber bundles, unidirectional ribbons, roving (slightly twisted fiber), and single-layer and multilayer fabric mats. Frequently, the continuous reinforcing fibers and matrix resins are combined into a nonfinal form known as a prepreg.

Fabrication. Many processes are available for the fabrication of organic matrix composites. The first process is contact molding in order to orient the unidirectional layers at discrete angles to one another. Contact molding is a wet method, in which the reinforcement is impregnated with the resin at the time of molding. The simplest method is hand lay-up, whereby the materials are placed and formed in the mold by hand and the squeezing action expels any trapped air and compacts the part.

Molding may also be done by spraying, but these processes are relatively slow and labor costs are high, even though they can be automated. Many types of boats, as well as buckets for power-line servicing equipment, are made by this process.

Another process is vacuum-bag molding, where prepregs are laid in mold to form the desired shape. In this case, the pressure required to form the shape and achieve good bonding is obtained by covering the lay-up with a plastic bag and creating a vacuum. If additional heat and pressure are desired, the entire assembly is put into an autoclave. In order to prevent the resin from sticking to the vacuum bag and to facilitate removal of excess resin, various materials are placed on top of the prepreg sheets. The molds can be made of metal, usually aluminum, but more often are made from the same resin (with reinforcement) as the material to be cured. This eliminates any problem with differential thermal expansion between the mold and the part.

In filament winding, the resin and fibers are combined at the time of curing. Axisymmetric parts, such as pipes and storage tanks, are produced on a rotating mandrel. The reinforcing filament, tape, or roving is wrapped continuously round the form. The reinforcements are impregnated by passing them through a polymer bath. However, the process can be modified by wrapping the mandrel with prepreg material. The products made by filament winding are very strong because of their highly reinforced structure. For example, filament winding can be used directly over solid-rocket-propellant forms.

Pultrusion is a process used to produce long shapes with constant profiles, such as rods or tubing, similar to extruded metal products. Individual fibers are often combined into a tow, yarns, or roving, which consists of a number of tows or yarns collected into a parallel bundle without twisting (or only slightly so). Filaments can also be arranged in a parallel array called a tape and held together by a binder. Yarns or tows are often processed further by weaving, braiding, and knitting or by forming them into a sheetlike mat consisting of randomly oriented chopped fibers or swirled continuous fibers held together by a binder.

Weaving to produce a fabric is a very effective means of introducing fibers into a composite. There are five commonly used patterns (**Fig. 2**). Although weaving is usually thought of as a two-dimensional process, three-dimensional weaving is often employed.

Knitting is a process of interlooping chains of tow or yarn. Advantages of this process are that the tow or yarn is not crimped as happens in weaving, and higher mechanical properties are often observed in the reinforced product. Also, knitted fabrics are easy to handle and can be cut without falling apart.

In braiding, layers of helically wound yarn or tow are interlaced in a cylindrical shape, and interlocks can be produced at every intersection of fibers. During the process, a mandrel is fed through the center of a braiding machine at a uniform rate, and the yarn or tow from carriers is braided around the mandrel at a controlled angle. The machine operates like a maypole, the carriers working in pairs to accomplish the over-and-under sequencing. The braiding process is most effective for cylindrical geometries. It is used for missile heat shields, lightweight ducts, fluid-sealing components such as packings and sleevings, and tubes for insulation.

Carbon-carbon composites. A carbon-carbon composite is a specialized material made by reinforcing a carbon matrix with continuous carbon fiber. This type of composite has outstanding properties over a wide range of temperatures in both vacuum and inert atmospheres. It will even perform well at elevated temperatures in an oxidizing environment for short times. It has high strength, modulus, and toughness up to 2000°C (3600°F); high thermal conductivity; and a low coefficient of thermal expansion. A material with such properties is excellent for rocket motor nozzles and exit cones, which require high-temperature strength as well as resistance to thermal shock. Carbon-carbon composites are also used for aircraft and other high-performance brake applications that take advantage of the fact that carbon-carbon composites have the highest energy-absorption capability of any known material. If a carbon-carbon composite is exposed to an oxygen-containing atmosphere above 600°C (1100°F) for an

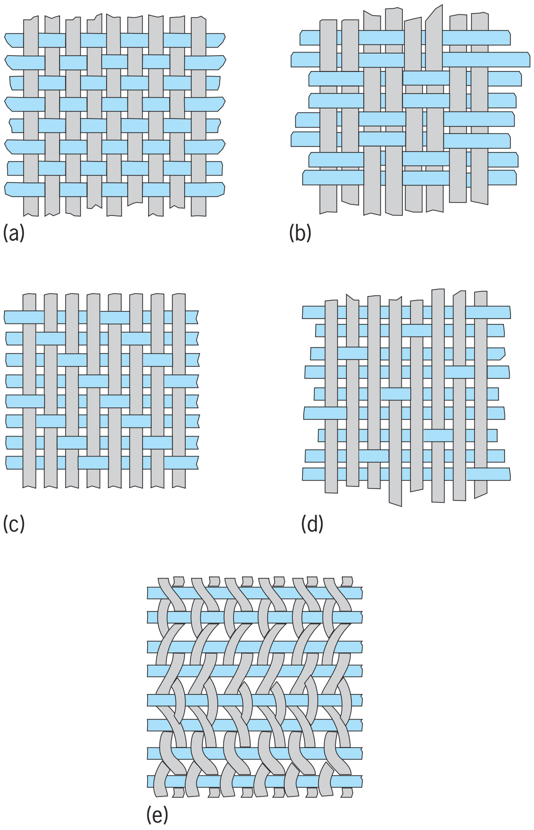

Fig. 2. Common weave patterns: (*a*) box or plain weave, (*b*) basket weave, (*c*) crowfoot, (*d*) long-shaft, and (*e*) leno weave.

appreciable time, it oxidizes, and therefore it must be protected by coatings.

Metal-matrix composites. Metal-matrix composites are usually made with alloys of aluminum, magnesium, or titanium; and the reinforcement is typically a ceramic in the form of particulates, platelets, whiskers, or fibers, although other systems may be used. Metal-matrix composites are often classified as discontinuous or continuous, depending on the geometry of the reinforcement. Particulates, platelets, and whiskers are in the discontinuous category, while the continuous category is reserved for fibers and wires. The type of reinforcement is important in the selection of a metal-matrix composite, because it determines virtually every aspect of the product, including mechanical properties, cost, and processing method. The primary methods for processing of discontinuous metal-matrix composites are powder metallurgy, liquid metal infiltration, squeeze or pressure casting, and conventional casting; however, most of these methods do not result in finished parts. Therefore, most discontinuously reinforced metal-matrix composites require secondary processing, which includes conventional wrought metallurgy operations such as extrusion, forging, and rolling; standard and nonstandard machining operations; and joining techniques such as welding and brazing. *See* BRAZING; MACHINING; METAL CASTING; POWDER METALLURGY; WELDING AND CUTTING OF MATERIALS. Mel M. Schwartz

Ceramic-matrix composites. In general, ceramics are brittle engineering materials with limited reliability. Brittleness is connected with the structure and chemical bonding of the main constituents, and reliability is connected with the stochastic character of main phases and defect distribution within the polycrystalline ceramic body. In spite of the generally high strength, hardness, and chemical and shape stability of ceramics, these two negative properties disqualify their wider application in industry. Ceramic-matrix composites are designed as materials with higher fracture resistance (less brittleness), higher reliability, and in particular cases higher strength compared to monolithic ceramics. These attributes are required for high technologies, especially in the aircraft, automotive, engineering, and energy industries. *See* BRITTLENESS; CERAMICS.

Ceramic composites are materials with at least two constituents, the ceramic-matrix phase and reinforcing-toughening filaments. The filaments cover a wide range of dimensions, from nanoinclusions, through micro-whiskers, to fibers that are several centimeters to a few meters long.

Ceramic nanocomposites. These composites have at least one of the main constituents at the nanometer scale (from one to several hundred nanometers). Typical examples of such ceramic nanocomposites are silicon carbide–silicon nitride (SiC/Si_3N_4) and silicon carbide–alumina (SiC/Al_2O_3). Benefits from the design of these materials are better mechanical properties at room temperature or high temperature, as well as improved electric and magnetic properties. *See* NANOSTRUCTURE.

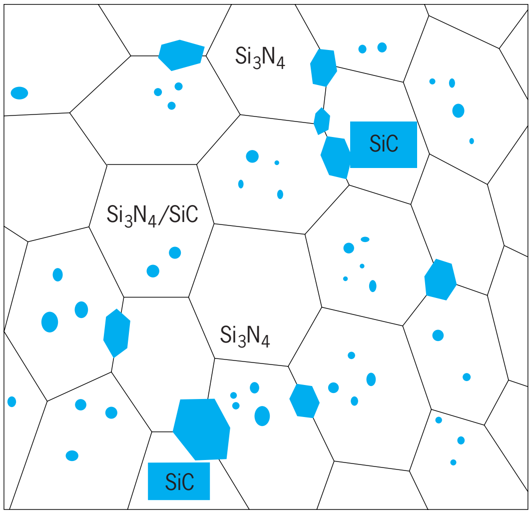

Fig. 3. Schematic of a SiC/Si_3N_4 nanocomposite. This microstructure consists of silicon carbide inclusions within silicon nitride grains, and silicon carbide grains located at the grain boundaries.

Examples of some properties of nanocomposites are as follows: A SiC/Si_3N_4 nanocomposite containing 20 vol % SiC has a bending strength greater than 1 GPa (10000 atm) up to 1400°C (2552°F), and a fracture toughness of 7 $MPa \cdot m^{1/2}$. Silver–ferrite oxide nanocomposite (Ag/Fe_2O_3) exhibits a superparamagnetic state at temperatures greater than 100 K (−173°C; −280°F).

Based on distribution of nanograins within the matrix, ceramic nanocomposites can be formally divided into intra type, inter type, intra/inter type, and nano/nano type. The SiC/Si_3N_4 nanocomposite (**Fig. 3**) can be considered an intra/inter type, because of distribution of SiC grains at grain boundaries as well as within the Si_3N_4 grains.

Whisker/platelet-reinforced composites. This ceramic composite contains whiskers or platelets. The whiskers are randomly distributed within the composite matrix. Silicon carbide or silicon nitride whiskers are usually embedded in a silicon carbide, silicon nitride, or alumina matrix. Improvement of the mechanical properties of these composites is reached by dissipation of the crack tip energy on a whisker or platelet. Whisker length varies between several micrometers and hundreds of micrometers. A typical parameter that determines a whisker shape is the aspect ratio, or the length-to-thickness ratio. Platelets are single crystals of flake shape. Their aspect ratio is the diameter-to-thickness ratio. Despite lower effectivity of platelets in dissipating crack tip energy compared to the whiskers, their application is forced due to the environmental unacceptability of whiskers. The bending strength of Si_3N_4/Si_3N_4 ceramics is 0.8–1 GPa (8000–10,000 atm), and fracture toughness is 6 $MPa \cdot m^{1/2}$ at room temperature.

Ceramic fiber-matrix composites. In principle, these composites are similar to fiber-matrix composites. The difference is in the composition of fibers, the matrices, and the processing routes.

The typical examples of fibers are the silicon carbide or alumina fibers. Fibers are polycrystalline materials with high tensile strength. Silicon carbide fiber tensile strength for Hi-Nicalon-S fiber is greater than 3 GPa (30,000 atm).

Silicon carbide, silicon nitride, and alumina ceramics are typically used as the matrices. Carbon as a constituent of these composites is also used either in the form of fibers or as a matrix.

There are several processes of embedding the continuous fibers into the ceramic matrix: polymer impregnation and pyrolysis, slurry impregnation and hot pressing, and chemical vapor infiltration.

These materials exhibit a high tensile strength when the fibers are oriented in the direction of the tensile force, and a very high work of fracture, which means a high fracture toughness. For example, the tensile strength of a SiC/Si_3N_4 composite is 0.5 GPa (5000 atm), and the fracture toughness is 26.5 $MPa{\cdot}m^{1/2}$.

Laminate/layered ceramic composites. These ceramic composites consist of two or more different ceramic sheets which are repeated several times through the ceramic body. These materials are usually produced by tape casting in order to built the ceramic "green" body, which is densified by hot pressing or gas pressure sintering. The properties of this type of ceramics are highly anisotropic in different directions, parallel and perpendicular to the layer area. The layers can differ by composition or by microstructure. Mechanical properties of silicon nitride–based layered composite are in particular cases exceptional; for example, a bending strength of 1.2 GPa (12,000 atm) and a fracture toughness of 10 $MPa{\cdot}m^{1/2}$ are reported. *See* SINTERING.

Layered materials offer a possibility to design materials with multifunctions, exhibiting excellent mechanical properties and improved electrical, thermal, or magnetic properties. Pavol Šajgalík

Applications

The use of fiber-reinforced materials in engineering applications has grown rapidly. Selection of composites rather than monolithic materials is dictated by the choice of properties. The high values of specific stiffness and specific strength may be the determining factor, but in some applications wear resistance or strength retention at elevated temperatures is more important. A composite must be selected by more than one criterion, although one may dominate.

Components fabricated from advanced organic-matrix–fiber-reinforced composites are used extensively on commercial aircraft as well as for military transports, fighters, and bombers. The propulsion system, which includes engines and fuel, makes up a significant fraction of aircraft weight (frequently 50%) and must provide a good thrust-to-weight ratio and efficient fuel consumption. The primary means of improving engine efficiency are to take advantage of the high specific stiffness and strength of composites for weight reduction, especially in rotating components, where material density directly affects both stress levels and critical dynamic characteristics, such as natural frequency and flutter speed.

Composites consisting of resin matrices reinforced with discontinuous glass fibers and continuous-glass-fiber mats are widely used in truck and automobile components bearing light loads, such as interior and exterior panels, pistons for diesel engines, drive shafts, rotors, brakes, leaf springs, wheels, and clutch plates.

The excellent electrical insulation, formability, and low cost of glass-fiber-reinforced plastics have led to their widespread use in electrical and electronic applications ranging from motors and generators to antennas and printed circuit boards.

Composites are also used for leisure and sporting products such as the frames of rackets, fishing rods, skis, golf club shafts, archery bows and arrows, sailboats, racing cars, and bicycles.

Advanced composites are used in a variety of other applications, including cutting tools for machining of superalloys and cast iron and laser mirrors for outer-space applications. They have made it possible to mimic the properties of human bone, leading to development of biocompatible prostheses for bone replacements and joint implants. In engineering, composites are used as replacements for fiber-reinforced cements and cables for suspension bridges. *See* MATERIALS SCIENCE AND ENGINEERING. Mel M. Schwartz

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Composition board

A wood product in which the grain structure of the original wood is drastically altered. Composition board may be divided into several types. When wood serves as the raw material for chemical processing, the resultant product may be insulation board, hardboard, or other pulp product. When the wood is broken down only by mechanical means, the resultant product is particle board. Because composition board can use waste products of established wood industries and because there is a need to find marketable uses for young trees, manufacture of composition board is one of the most rapidly developing portions of the wood industry. *See* PAPER.

Fiberboard. One form of fiberboard is produced by loading a batch of wood chips into a chamber which is then heated and pressurized by steam. After about 2 min, the 1000-lb/in.^{2} (6.9-megapascal) pressure is abruptly released to hydrolyze and fluff the chips into a brown fiber. The fiber is refined, washed, and felted into a mat on a wire conveyor so that some of the water can drain out, and then the mat is cut to length for loading on a screen into a press. At controlled temperature in the press, the lignin rebonds the material while water is driven off as steam through the screen. The finished reconstituted wood product is a hard isotropic board as a consequence of the felting of the fibers and the ligneous bonding, possibly augmented by synthetic adhesive.

Alternatively, a similar board is produced by a continuous process. A screw feed delivers wood chips from a hopper to a steam preheater where the chips partially hydrolyze in the vicinity of 150 lb/in.^{2} (0.11 MPa). The hot chips pass between grinding disks to discharge as pulp, which is then formed into sheets essentially as described above. The wood chips may also be processed entirely by grinding. A further variation is to deliver the pulp slurry into a deckle box, in which case most of the water is removed by suction applied below the box before the mat is compressed into the finished sheet.

Instead of conveying the wet fiber or pulp to the mat, it can be dried sufficiently to be conveyed by air; it is then introduced between chrome-plated cauls and pressed. Because of the low-moisture content, no screen is needed; the finished sheet is smooth on both sides. Most new plants use variants of the dry process.

In any of the foregoing methods synthetic resin may be added as a binder before the board is formed. After the board is formed, it may be impregnated with drying oils and heated in a kiln at 300°F (150°C) until the oils are completely polymerized to produced tempered board. *See* DRYING OIL; RESIN.

If insulating board is required instead of hardboard, the material is less compacted, the degree of compaction being described by the specific gravity of the finished board.

Particle board. When formed from wood particles that retain their woody structure, the product is termed particle board. Properties of such boards depend on the size and orientation of the particles, which may be dimensioned flakes, random-sized shavings, or splinters. After the particular type of particles are produced, they are screened to remove fines and to return oversizes for further reduction. Graded particles are dried, mixed with synthetic adhesive and other additives such as preservatives, and delivered to the board-forming machine.

Forming machines are basically of two types. In one type mixed materials are metered by weight or volume onto an open flat tray, prepressed at room temperature, and finally consolidated under heat at high pressure to the finished dimension. Whether carried out as a batch or a continuous process, this flat-press method tends to orient the particles with their long dimensions approximately parallel to the face of the board. In the second type of machine the mixed materials are extruded under pressure between heated platens. Thick boards made this way may have hollow cores produced by rods fixed in the aperture ahead of the platens. Particles in extruded boards are randomly oriented. Boards formed by either method may be layered, with different-sized particles at the surfaces from those in the center, which are also usually coarser.

Characteristics. Hardboards produced by a continuous process can be formed to great length, although a finished length of 16 ft (5 m) is usual stock maximum. Standard thicknesses range from $^1/_8$ to $^5/_{16}$ in. (3.2 to 7.9 mm); standard densities range from a specific gravity of 0.80 to 1.15, with boards up to 1.45 available if needed.

Tensile strength parallel to the face ranges from 1000 lb/in.^{2} (6.9 MPa) for untreated board to 5500 lb/in.^{2} (37.9 MPa) for tempered hardboard; perpendicular to the face it ranges from 125 to 400 lb/in.^{2} (0.86 to 2.76 MPa). Compression strength parallel to the face ranges from 2000 to 5300 lb/in.^{2} (13.8 to 36.5 MPa).

Lengths and widths of particle boards are similar to those of hardboards; thicknesses range from $^1/_4$ to 1 in. (6 to 25 mm); thicker sheets are most economically produced by laminating sheets of standard thicknesses. Properties of flat-pressed particle board vary more than do those of hardboard. They have low density: 0.4–1.2 specific gravity. Tensile strength parallel to their faces ranges from 500 to 5000 lb/in.^{2} (3.4 to 34.5 MPa) and perpendicular from 40 to 400 lb/in.^{2} (276 kPa to 2.76 MPa). Extruded particle board has low bending strength; it is used chiefly as the core of plywood-type panel. Development of adhesives specifically for composition boards has extended their utilitarian value, and variety of textures has increased their esthetic appeal. *See* WOOD PRODUCTS.

Frank H. Rockett

Compound (chemistry)

A substance composed of two or more elements that do not vary in composition from sample to sample, and that have fixed and definite physical properties, such as density and refractive index. The elements in compounds cannot be separated by simple physical or mechanical means, but only by chemical treatment. When compounds are formed from their elements, heat is generated or absorbed. These properties distinguish them from mixtures.

For example, if iron filings and sulfur powder are mixed together, the two elements can be separated, either by removing the iron filings with a magnet or by dissolving the sulfur in an appropriate solvent, and the individual particles of each element are distinguishable under a magnifying glass. If iron filings and sulfur are heated together, a chemical reaction takes place and a new substance is formed, iron sulfide, with properties totally different from iron or sulfur. *See* DENSITY; ELEMENT (CHEMISTRY).

Most chemical compounds are formed in fixed and definite proportions by weight from their elements, and they obey the laws of chemical combination. However, a number of solid compounds, known as nonstoichiometric compounds, exhibit departures from the law of definite proportions. *See* DEFINITE COMPOSITION, LAW OF; EQUIVALENT WEIGHT; INORGANIC CHEMISTRY; MULTIPLE PROPORTIONS, LAW OF; NONSTOICHIOMETRIC COMPOUNDS; ORGANIC CHEMISTRY. Thomas C. Waddington

Compressible flow

Flow in which density changes are not negligible. Pressure changes normally occur throughout a fluid flow, and these pressure changes, in general, induce a change in the fluid density. In a compressible flow, the density changes that result from these pressure changes have a significant influence on the flow. The changes in the flow that result from the density changes are often termed compressibility effects. All fluids are compressible. However, compressibility effects are more frequently encountered in gas flows than in liquid flows.

Compressibility. The compressibility of a fluid is defined by Eq. (1), where ρ is the density, and $\Delta\rho$ is the

$$\tau = \frac{\Delta\rho/\rho}{\Delta p} \qquad (1)$$

density change that results from a pressure change of Δp. From Eq. (1) it follows that the relative density change is given by Eq. (2). If the product $\tau\,\Delta p$ is very

$$\frac{\Delta\rho}{\rho} = \tau\,\Delta p \qquad (2)$$

small, then the change in density, $\Delta\rho$, will be negligible and the effect of the density changes on the flow can be neglected. Such flows that are effectively at constant density are termed incompressible flows. For a flow in which the product $\tau\,\Delta p$ is moderate or large, the changes in density in the flow cannot, in general, be neglected. Such flows in which the density changes are significant are termed compressible flows. As a rough guide, if the density changes by less than 5% in the flow, that is, $\Delta\rho/\rho < 0.05$, the flow can be treated as incompressible. The speed of sound in the fluid, a, is approximately given by Eq. (3). Using this in Eq. (1) gives Eq. (4). The larger the

$$a^2 = \frac{\Delta p}{\Delta\rho} \qquad (3)$$

$$\tau = \frac{1}{\rho a^2} \qquad (4)$$

value of ρa^2, the less compressible is the fluid. Thus a liquid, which has a large value of ρa^2, will have a much smaller compressibility than a gas, which has a small value of ρa^2. For example, water has a value of ρa^2 that is about 15,000 times greater than that of air and so is much less compressible than air. *See* SOUND.

Mach number. An important dimensionless parameter in compressible flows is the Mach number, M. This is defined by Eq. (5), where a is the speed of

$$M = \frac{V}{a} \qquad (5)$$

sound and V is the velocity of the flow. For a gas, the speed of sound is given by Eq. (6), where R is the

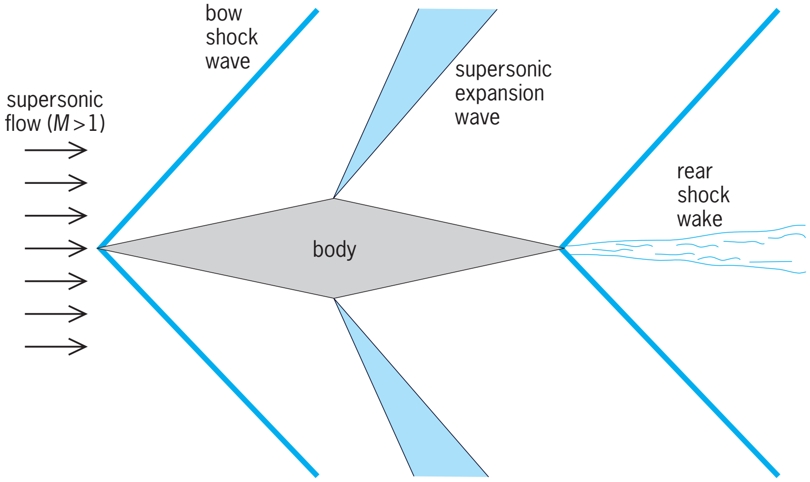
$$a = \sqrt{kRT} \qquad (6)$$

gas constant, $k = c_p/c_v$, c_p and c_v being the specific heats at constant pressure and constant volume respectively, and T is the temperature. If $M < 0.3$ in a flow, the density changes in the flow will usually be negligible; that is, the flow can be treated as incompressible. Compressible flows are, therefore, as a rough guide, associated with Mach numbers greater than 0.3.

When $M < 1$, the flow is said to be subsonic; when $M = 1$, the flow is said to be sonic; when M varies from slightly below 1 to slightly above 1, the flow is said to be transonic; and if $M > 1$, the flow is said to be supersonic. When the Mach number is very high, this usually being taken to mean $M > 5$, the flow is said to be hypersonic.

Properties. Compressible flows can have features that do not occur in low-speed flows. For example, shock waves and expansion waves can occur in supersonic flows (*see* **illus.**). Another important phenomenon that can occur due to compressibility is choking, where the mass flow rate through a duct system may be limited as a result of the Mach number being equal to 1 at some point in the flow. *See* CHOKED FLOW; SHOCK WAVE; SONIC BOOM.

Another effect of compressibility is associated with the acceleration of a gas flow through a duct. In incompressible flow, an increase in velocity is associated with a decrease in the cross-sectional area of the duct, this in fact being true as long as $M < 1$. However, when $M > 1$, that is, when the flow is supersonic, the opposite is true; that is, an increase in the velocity is associated with an increase in the cross-sectional area. Therefore, in order to accelerate



Waves in supersonic flow over a double-wedge body.

a gas flow from subsonic to supersonic velocities in a duct, it is necessary first to decrease the area and then, once the Mach number has reached 1, to increase the area, that is, to use a so-called convergent-divergent nozzle. An example is the nozzle fitted to a rocket engine. *See* FLUID FLOW; MACH NUMBER; NOZZLE; SUPERSONIC FLOW. Patrick H. Oosthuizen

Bibliography. J. D. Anderson, Jr., *Modern Compressible Flow: With Historical Perspective*, 3d ed., McGraw-Hill, 2003; P. H. Oosthuizen and W. E. Carscallen, *Compressible Fluid Flow*, McGraw-Hill, 1997.

Compression ratio

In a cylinder, the piston displacement plus clearance volume, divided by the clearance volume. This is the nominal compression ratio determined by cylinder geometry alone. In practice, the actual compression ratio is appreciably less than the nominal value because the volumetric efficiency of an unsupercharged engine is less than 100%, partly because of late intake valve closing. In spark ignition engines the allowable compression ratio is limited by incipient knock at wide-open throttle. Knock in turn depends on the molecular structure of the fuel and on such engine features as the temperature of the combustible mixture prior to ignition, the geometry and size of the combustion space, and the ignition timing. For example, isooctane, benzene, and alcohol can be burned at much higher compression ratios than *n*-heptane. In compression ignition engines critical compression ratio is that necessary to ignite the fuel and depends on fuel and cylinder geometry. *See* COMBUSTION CHAMBER; DIESEL ENGINE; INTERNAL COMBUSTION ENGINE; SPARK KNOCK; VOLUMETRIC EFFICIENCY. Neil MacCoull

Compressor

A machine that increases the pressure of a gas or vapor (typically air), or mixture of gases and vapors. The pressure of the fluid is increased by reducing the fluid specific volume during passage of the fluid through the compressor. When compared with centrifugal or axial-flow fans on the basis of discharge pressure, compressors are generally classed as high-pressure and fans as low-pressure machines.

Compressors are used to increase the pressure of a wide variety of gases and vapors for a multitude of purposes (**Fig. 1**). A common application is the air compressor used to supply high-pressure air for conveying, paint spraying, tire inflating, cleaning, pneumatic tools, and rock drills. The refrigeration compressor is used to compress the gas formed in the evaporator. Other applications of compressors include chemical processing, gas transmission, gas turbines, and construction. *See* GAS TURBINE; REFRIGERATION.

Characteristics. Compressor displacement is the volume displaced by the compressing element per unit of time and is usually expressed in cubic feet per minute (cfm). Where the fluid being compressed flows in series through more than one separate compressing element (as a cylinder), the displacement of the compressor equals that of the first element. Compressor capacity is the actual quantity of fluid compressed and delivered, expressed in cubic feet per minute at the conditions of total temperature, total pressure, and composition prevailing at the compressor inlet. The capacity is always expressed in terms of air or gas at intake (ambient) conditions rather than in terms of arbitrarily selected standard conditions.

Air compressors often have their displacement and capacity expressed in terms of free air. Free air is air at atmospheric conditions at any specific location. Since the altitude, barometer, and temperature may vary from one location to another, this term does not mean air under uniform or standard conditions. Standard air is at 68°F (20°C), 14.7 lb/in.^{2} (101.3 kilopascals absolute pressure), and a relative humidity of 36%. Gas industries usually consider 60°F (15.6°C) air as standard.

Types. Compressors can be classified as reciprocating, rotary, jet, centrifugal, or axial-flow, depending on the mechanical means used to produce compression of the fluid, or as positive-displacement or dynamic-type, depending on how the mechanical elements act on the fluid to be compressed. Positive-displacement compressors confine successive volumes of fluid within a closed space in which the pressure of the fluid is increased as the volume of the closed space is decreased. Dynamic-type compressors use rotating vanes or impellers to impart velocity and pressure to the fluid.

Reciprocating compressors are positive-displacement types having one or more cylinders, each fitted with a piston driven by a crankshaft through a connecting rod. Each cylinder also has intake and discharge valves, and a means for cooling the mechanical parts (**Fig. 2**). Fluid is drawn into the cylinder during the suction stroke. At the end

Fig. 1. Mobile air compressor unit which is driven by engine in the forward compartment. (*Ingersoll-Rand*)

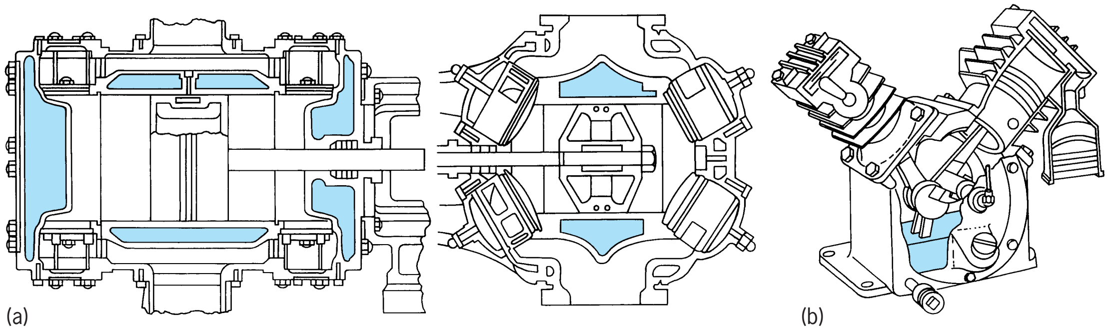


Fig. 2. Compressor cylinders, (*a*) water-cooled and (*b*) air-cooled.

of the suction stroke, motion of the piston reverses and the fluid is compressed and expelled during the discharge stroke. When only one end of the piston acts on the fluid, the compressor is termed a single-acting unit. When both ends of the piston act on the fluid, the compressor is double-acting. The double-acting compressor discharges about twice as much fluid per cylinder per cycle as the single-acting.

Single-stage compressors raise the fluid pressure from inlet to discharge on each working stroke of the piston in each cylinder. Two-stage compressors use one cylinder to compress the fluid to an intermediate pressure and another cylinder to raise it to final discharge pressure. When more than two stages are used, the compressor is called a multistage unit.

Some reciprocating compressors provide variable displacement. Instead of use of a crankshaft, the length of the piston stroke is controlled by a rotating swash plate, or wobble plate, that can change angle while the compressor is running. This design allows the compressor to operate continuously while providing only the displacement needed.

Vertical and horizontal compressors may be single-cylinder or multicylinder units. The angle type is multicylinder with one or more horizontal and vertical compressing elements (**Fig. 3**). Single-frame (straight-line) units are horizontal or vertical, double-acting, with one or more cylinders in line with a single frame having one crank throw, connecting rod, and crosshead. The V or Y type is a two-cylinder, vertical, double-acting machine with cylinders usually at a 45° angle with the vertical. A single crank is used. Semiradial compressors are similar to V or Y type, but have horizontal double-acting cylinders on each side. Duplex compressors have cylinders on two parallel frames connected through a common crankshaft. In duplex-tandem steam-driven units, steam cylinders are in line with air cylinders. Duplex four-cornered steam-driven compressors have one or more compressing cylinders on each end of the frame and one or more steam cylinders on the opposite end. In four-cornered motor-driven units, the motor is on a shaft between compressor frames.

Reciprocating compressors are built to handle fluid capacities ranging to 100,000 ft^3/min (2800 m^3/min); pressures range to over 35,000 lb/in.^{2} (240 megapascals). Special units can be built for larger capacities or higher pressures. Water is the usual coolant for cylinders, intercoolers, and aftercoolers, but other liquids, including refrigerants, may also be used.

Compressor thermodynamics. Compression efficiency in any compressor is compared against two theoretical standards—isothermal and adiabatic. Neither occurs in an actual compressor because of unavoidable losses. Isothermal compression has perfect cooling—air remains at inlet temperature while being compressed. The work input to the compressor is the least possible. Adiabatic compression has no cooling; the temperature rises steadily during compression. Discharge pressure is reached sooner than with isothermal compression. Since air pressure is higher during every part of the piston's stroke, more work input is needed. *See* THERMODYNAMIC PROCESSES.

If compression is divided into two or more steps or stages, air can be cooled between stages. This intercooling brings the actual compression efficiency closer to the isothermal standard.

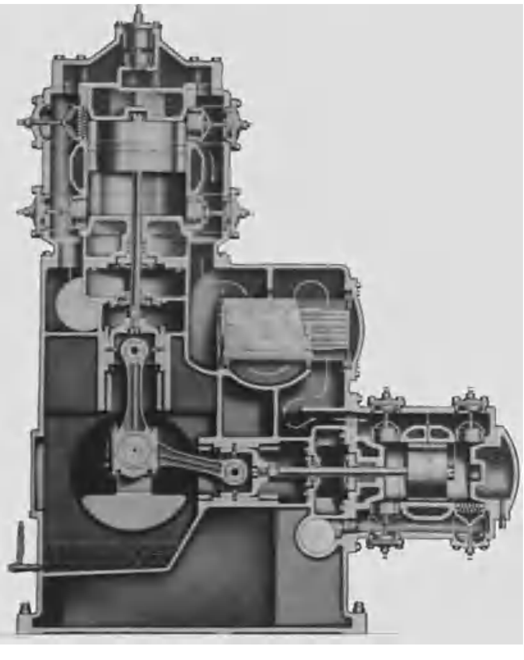


Fig. 3. Cross section of stationary angle-type compressor with first stage vertical and second stage horizontal.

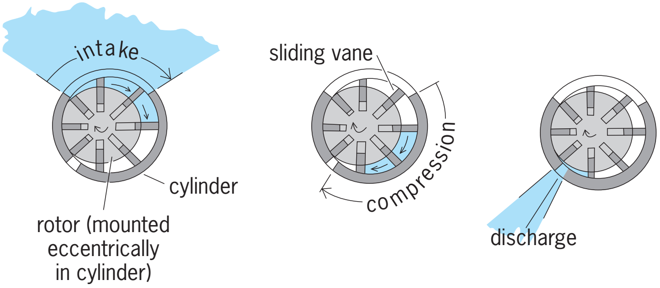


Fig. 4. Operation of sliding-vane rotary compressor.

Water vapor in air entering the compressor leaves as superheated vapor, because its temperature is in excess of that corresponding to its pressure. It can be converted to water only by cooling to a temperature below the saturation temperature corresponding to its pressure. Immediate cooling of air after it leaves the compressor proves best, because this prevents vapor from reaching the distribution system. Either air- or water-cooled heat exchangers, called aftercoolers, are used for this.

The usual single-stage reciprocating compressor is built for pressures to about 150 lb/in.^{2} (1.0 MPa); two-stage types for up to about 500 lb/in.^{2} (3.4 MPa); three-stage for up to about 2500 lb/in.^{2} (17 MPa); four- and five-stage for up to 15,000 lb/in.^{2} (100 MPa), and higher.

Rotary compressors. Other forms of positive-displacement compressor are the rotary types.

Sliding-vane type. In the sliding-vane rotary compressor, fluid is trapped between vanes as the rotor passes the inlet opening (**Fig. 4**). Further rotation of the rotor reduces the volume of the space in which the fluid is trapped. Fluid pressure rises until the discharge port is reached, when discharge occurs.

Depending on design, the compressor may be cooled with atmospheric air, oil, or water. For low pressures one stage of compression is used; for higher pressures, two stages. Capacities range to about 5000 ft^3/min (140 m^3/min). Some compressors of this type have rings around the vanes to keep them from bearing on cylinder walls. Others have vanes bearing against the cylinder.

Lobe type. In the lobed rotary compressor, fluid is trapped between two or more rotors held in fixed relationship to each other. Rotation of the impellers reduces the volume in which the fluid is trapped, producing a pressure rise. Fluid is discharged when the rotors pass the outlet port. Either two or three rotors are used. Capacities range about 5–50,000 ft^3/min (0.1–1400 m^3/min). Pressures above about 15 lb/in.^{2} (100 kPa) are obtained by operating two or more lobe-type compressors in series. Rotors are straight or slightly twisted.

Liquid-piston type. In the liquid piston rotary compressor, a round multiblade rotor revolves in an elliptical casing partly filled with liquid, usually water. When the rotor turns, it carries liquid around with it, the blades forming a series of buckets. Because the liquid follows the casing contours, it alternately leaves and returns to the space between blades (twice each revolution). As the liquid leaves the bucket, the fluid to be compressed is drawn in. When the liquid returns, it compresses the fluid to discharge pressure.

Liquid-piston compressors handle up to about 5000 ft^3/min (40 m^3/min). Single-stage units can develop pressures to about 75 lb/in.^{2} (520 kPa); multistage designs are used for higher pressures. Water or almost any other low-viscosity liquid serves as the compressant. For exacting services, the compressor may be sealed with chilled water to prevent condensation in lines.

Radial-flow units. Dynamic-type centrifugal compressors use rotating elements to accelerate the fluid radially. By diffusing action, velocity is converted to static pressure. Thus, the static pressure is higher in the enlarged section. Centrifugal compressors usually take in fluid at the impeller eye (or central inlet of the circular impeller) and accelerate it radially outward. Some static-pressure rise occurs in the impeller, but most of the pressure rise occurs in the diffuser section of the casing, where velocity is converted to static pressure. Each impeller-diffuser set is a stage of the compressor. Centrifugal compressors are built with from 1 to 12 or more stages, depending on the final pressure desired and the volume of fluid to be handled. The pressure ratio, or compression ratio, of a compressor is the ratio of the absolute discharge pressure to the absolute inlet pressure. *See* BERNOULLI'S THEOREM; DIFFUSER.

In the typical compressor, centrifugal action of the impeller produces a pressure rise and a large increase in air velocity. In the diffuser, velocity energy is converted to static pressure.

Pressure delivered by a centrifugal compressor is practically constant over a relatively wide range of capacities. Pumping limit, also called surge point or pulsation point, is the lower limit of stable operation. Percentage stability is 100 minus the pumping limit in percent of design capacity.

Multistage centrifugal compressors handle from 500 to more than 150,000 ft^3/min (14 to 4300 m^3/min) at pressures as high as 5000 lb/in.^{2} (35 MPa), but are limited to compression ratios in the order of 10.

Axial-flow units. Compressors that accelerate the fluid in a direction generally parallel to the rotating shaft consist of pairs of moving and stationary blade-rows, each pair forming a stage. The pressure rise per stage is small, compared with a radial-flow unit. Therefore, the usual axial-flow compressor has more stages than a centrifugal compressor working through the same pressure range. Single-stage axial compressors have capacities from a few to more than 100,000 ft^3/min (2800 m^3/min) at pressures from less than 1 to several pounds per square inch. Multistage axial-flow compressors compress air to 150 lb/in.^{2} (1 MPa) or more. Some special machines handle over 2,000,000 ft^3/min (60,000 m^3/min). Pressure rise per stage is generally relatively small, so units for higher pressures frequently have a considerable number of stages—20 or more.

While centrifugal machines deliver practically constant pressure over a considerable range of capacities, axials have a substantially constant delivery at variable pressures. In general, centrifugals have a wider stable operating range than axials. Because of their more or less straight-through flow, axials tend to be smaller in diameter than centrifugals and to be longer. Efficiency of axials usually runs slightly higher.

To prevent surging at extremely low loads, large-capacity axials are sometimes fitted with a blowoff system that discharges excess air to the atmosphere. Then there is always enough air passing through the machine to keep it in its stable range.

Because of difficulty in accurately predicting the performance curves of centrifugal and axial compressors, only one capacity and one discharge-pressure rating, together with corresponding power input, are normally guaranteed. Shape of the curve may be indicated but is never guaranteed. *See* FAN; PUMPING MACHINERY. Tyler G. Hicks; Donald L. Anglin

Bibliography. Business Trend Analysts, *Pumps and Compressors,* 1982; Compressed Gas Association Staff, *Handbook of Compressed Gases*, 4th ed., 1999; *Compressor Handbook for the Hydrocarbon Processing Industries*, 1979; Ingersoll-Rand, *Compressed Air and Gas Data*, 1980.

Compton effect

The increase in wavelength of scattered electromagnetic radiation that is determined by the angle of scattering when gamma rays or energetic x-rays are scattered by electrons. When the scattering electron is assumed to be unbound and at rest, analysis leads to a wavelength increase approximated by Eq. (1).

$$\Delta\lambda = \lambda_2 - \lambda_1 = \frac{h}{m_0 c}(1 - \cos\phi) \qquad (1)$$

Here, λ_1 is the wavelength of the incident radiation, λ_2 is the wavelength of the radiation scattered at the angle ϕ, h is Planck's constant, m_0 is the rest mass of the electron, c is the speed of light, and ϕ is the angle by which the scattered radiation deviates from the direction of the incident radiation.

The quantity $h/m_0c = 2.426310 \times 10^{-12}$ m is called the Compton wavelength of the electron. The Compton wavelengths of other particles are defined in terms of their rest masses in an analogous manner. Thus, for example, the Compton wavelength of the proton is 1.321410×10^{-15} m.

There is a near consensus that the Compton effect provides the most persuasive evidence from any physical phenomenon in support of the photon description of electromagnetic radiation. The evidence provided by the angular dependence of the wavelength shift is not in itself sufficient to establish the reality of photons. However, when supplemented by the experimental evidence that a single scattering electron suffices to conserve both energy and momentum in a binary collision with a photon, it provides compelling support for the photon picture.

A. H. Compton's measurements, carried out in the era of the old quantum theory, challenged the validity of J. J. Thomson's theory of coherent scattering by electrons, which was based on the Maxwell equations of electromagnetism and the wavelike nature of x-rays. The wavelike properties of x-rays were established by the use of crystalline solids as diffraction gratings, leading to the development of wavelength-dispersive x-ray spectrometry. Compton's mastery of this new technology led him to the proof that x-rays also display particlelike properties. *See* MAXWELL'S EQUATIONS; X-RAY DIFFRACTION; X-RAY SPECTROMETRY.

The modern picture of coherent scattering differs from that of Thomson. His calculated differential cross section for unpolarized radiation is given by Eq. (2). Here $d\Omega$ is the solid scattering angle, and r_e is

$$d\sigma = \frac{r_e^2}{2}(1 + \cos^2\phi)d\Omega \qquad (2)$$

the classical electron radius, equal to e^2/m_0c^2, where e is the charge on the electron. This result must be multiplied by the square of an atomic form factor, $f(\phi)$, because the electrons in an atom scatter in a cooperative manner. The resulting Rayleigh cross section depends very strongly on both the atomic number Z and the energy E. Data from low-Z targets such as graphite have the simple form that leads to the Compton analysis. Higher-Z targets such as iron or copper produce data dominated by Rayleigh scattering, showing little shift in wavelength. For example, markedly different energy spectra are obtained when

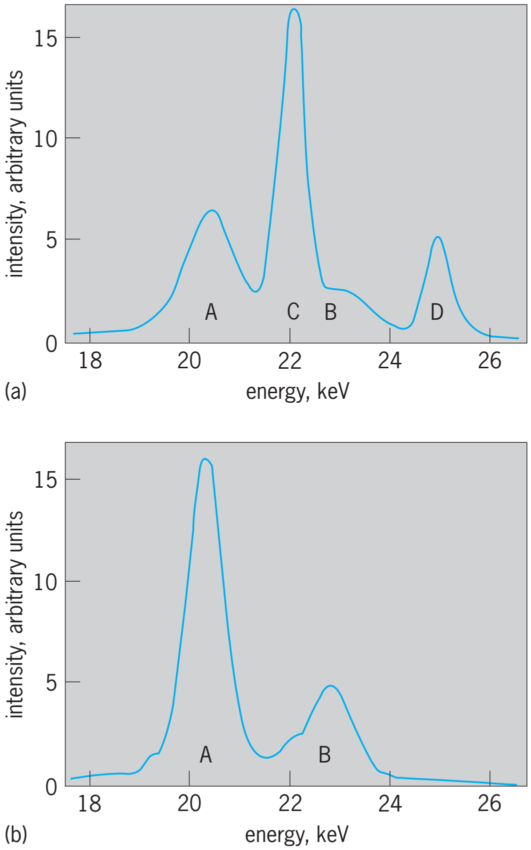


Fig. 1. Energy spectra of K x-rays of silver after scattering at about 170° from targets of (*a*) copper and (*b*) polyethylene (CH_2). The peaks labeled A and B are from Compton scattering; those labeled C and D are from Rayleigh scattering.

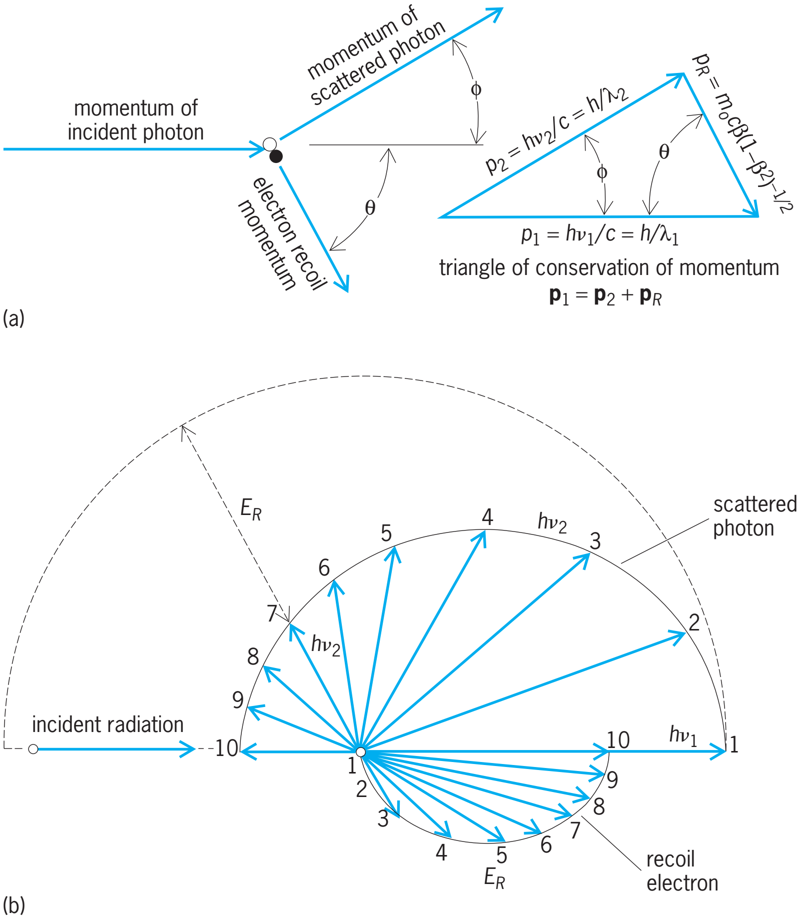


Fig. 2. Geometry of Compton scattering. (*a*) Diagrams for applying energy and momentum conservation to the collision of a photon with an electron, initially at rest. Symbols defined in text. (*b*) Relation of energy and direction of scattered photon, $h\nu_2$, and of recoil electron, E_R, in the special case that initial photon energy, $h\nu_1 = m_0c^2$. Photon and electron energy and direction are plotted for 10 photon scattering angles varying from 0 to 180°. Paired arrows mean, for example, that when the secondary photon goes in direction 5 in the upper half of the diagram, recoil electron follows arrow 5 in the lower half. (*After B. R. Wheaton, The Tiger and the Shark, Cambridge University Press, 1983*)

the K x-rays of silver (with energy of 22.1 keV) are backscattered from polyethylene (CH_2) and copper (**Fig. 1**). These spectral differences, easily revealed by a modern germanium detector, are hidden and unsuspected causes of inconsistency if a detector of low resolving power is used. *See* SCATTERING OF ELECTROMAGNETIC RADIATION.

Theory. The essential break with a classical theory of scattering is to adopt a model pioneered by A. Einstein, in which photons of frequency ν travel as discrete quanta with energy hν and linear momentum hν/c. Compton's analysis applies the photon concept to a collision with an unbound electron at rest. The photon transfers some energy and momentum to the electron so the scattered photon must have less energy, $h\nu_2$, than the primary, $h\nu_1$. Since $\nu = c/\lambda$ for a wave of speed c, the wavelength of the scattered photon, λ_2, must exceed the initial wavelength λ_1. *See* PHOTOEMISSION; PHOTON; QUANTUM MECHANICS.

In an elastic collision, both the energy and the linear momentum must be conserved. Application of these two principles to determine the wavelength shift expected for a given scattering angle leads to what is now known as the Compton equation, Eq. (1). *See* COLLISION (PHYSICS); CONSERVATION LAWS (PHYSICS); CONSERVATION OF ENERGY; CONSERVATION OF MOMENTUM.

Scattering process. Compton's analysis applies to the scattering process for a collision between an incident photon of linear momentum p_1 and wavelength λ_1 and a resting, unbound electron (**Fig. 2***a*). After the collision, the scattered photon moves at an angle ϕ and the electron recoils at an angle θ, both angles being with respect to the direction of the incident photon.

Compton's decisive x-ray data were produced at such low energies that the recoil electron traveled at nonrelativistic speeds, but both Compton and P. Debye treated the problem generally. The principle of conservation of energy yields Eq. (3), where β is

$$h\nu_1 = h\nu_2 + m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) \qquad (3)$$

V/c and V is the speed of the recoil electron. Conservation of linear momentum yields two equations, Eq. (4), for the horizontal component and Eq. (5)

$$\frac{h\nu_1}{c} = \frac{h\nu_2}{c}\cos\phi + \frac{m_0V}{\sqrt{1-\beta^2}}\cos\theta \qquad (4)$$

$$0 = \frac{h\nu_2}{c}\sin\phi - \frac{m_0V}{\sqrt{1-\beta^2}}\sin\theta \qquad (5)$$

for the vertical component. By squaring these equations and substituting $\nu = c/\lambda$, the electron velocity can be eliminated and Eq. (1) is obtained for the shift in wavelength. *See* RELATIVITY.

Many tests of the theory, particularly those using modern energy-dispersive detectors, are checked by reverting to frequency. Equation (1) can be rewritten to give the energy of the scattered photon, and can be recombined with Eq. (3) to obtain an expression for the recoil energy of the initially stationary electron. Following Debye, the nature of these solutions can be illustrated compactly for the important special case that $h\nu_1 = m_0c^2$ by plotting the energy and direction of both the scattered photon and the recoil electron for various scattering angles (Fig. 2*b*). The resulting diagram emphasizes that while the photons may scatter backward as well as forward, the recoil electron is always projected forward in a much narrower cone.

Compton profile. The assumption that the scattering electron is at rest in the laboratory frame of reference is not consistent with the real situation in experiments. The photons are scattered by electrons whose speeds are typically 1% of the speed of light for valence electrons and 10% for core electrons, causing substantial Doppler shifts. Analysis shows that a second term should be added to the right-hand side of Eq. (1) for the wavelength shift. This second term is proportional to the projection of the electron's initial momentum on the scattering vector. Accurate measurement of the complete

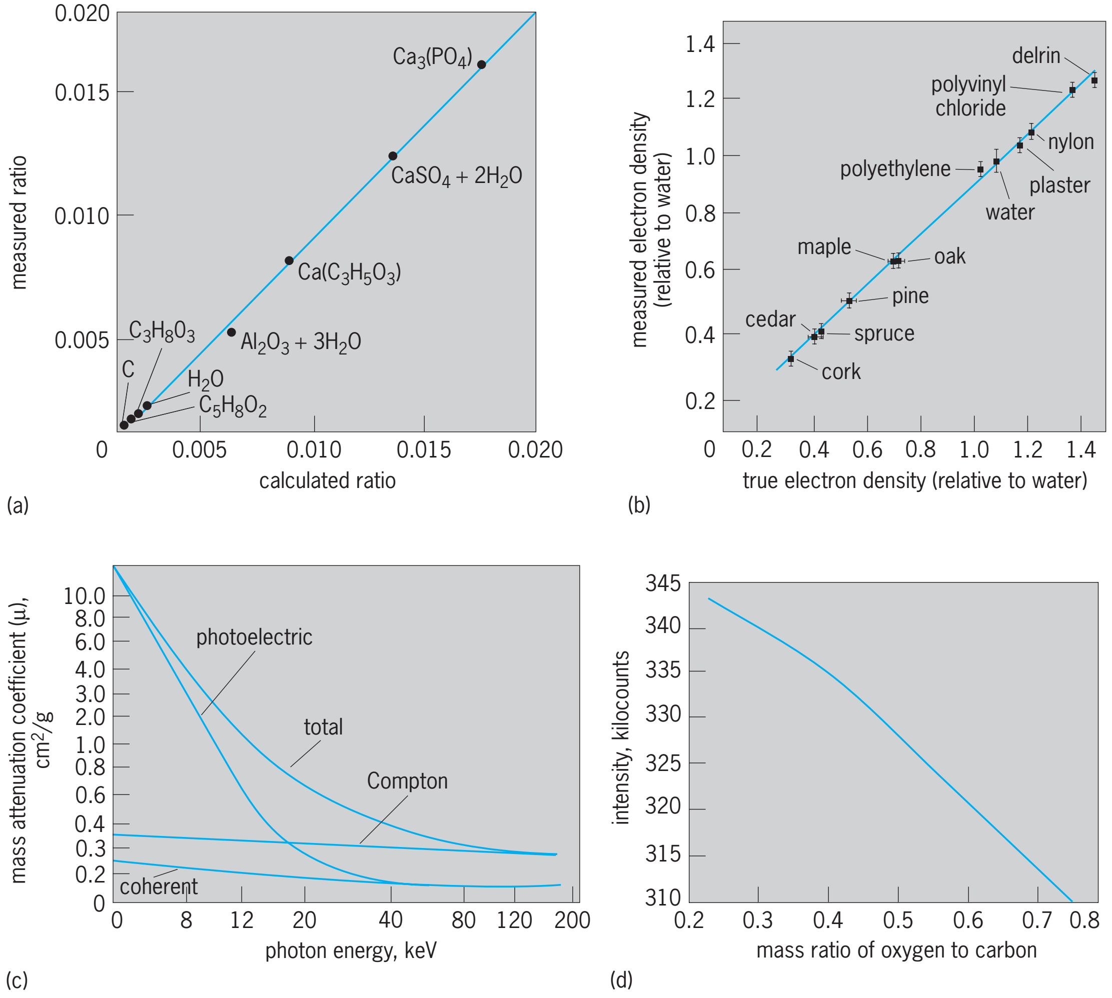


Fig. 3. Examples of nondestructive analysis of low-*Z* compounds using Compton scattering. (*a*) Comparison of measured and calculated Rayleigh-Compton ratios at an energy of 60 keV. Calculated ratio is based on assigning an effective atomic number to the compound. Diagonal line represents equality of measured and calculated ratios. (*b*) Comparison of Compton-measured electron density and true electron density of compounds for energies (662 keV) where Compton effect is totally dominant. Diagonal line represents equality of measured and true densities. (*c*) Energy dependence of the linear attenuation coefficient for the main interactions in soft tissue. Coefficients for total attenuation and components due to photoelectric effect, Compton effect, and coherent scattering are shown. (*d*) Dependence of backscatter intensity on the carbon-oxygen ratio in methanol-water mixtures (which simulate proportions of fat and lean meat) for the L x-rays of neptunium (∼ 17 keV). This dependence results from competition of Compton scattering with photoelectric absorption. (*Parts a, b, c after R. Cesareo, ed., Nuclear Analytical Techniques in Medicine, Elsevier Science, 1988*)

spectrum of scattered wavelengths gives a distribution of one cartesian component of the velocity of the scattering electrons. With a beryllium target, this technique was used to demonstrate that electrons follow Fermi-Dirac rather than Boltzmann statistics. If the incident radiation in this method is provided by ordinary x-ray generators, then the intensity of the scattered radiation is so low as to make most experiments impractical, because of the need to define the scattering angle by collimators. However, the advent of highly luminous synchrotron x-ray sources has made this an active research area. It permits accurate determination of directional variations of velocity spectra in single-crystal specimens and opens new research opportunities in the study of molecular bonds. *See* DOPPLER EFFECT; FERMI-DIRAC STATISTICS; SYNCHROTRON RADIATION.

Intensity distribution. Thomson's theory of x-ray scattering by electrons makes predictions not only of the wavelength shift but also of the intensity as a function of scattering angle. However, his expression depends on the distance of the photon from the scatterer, and Compton's model makes no prediction of this distance. That prediction requires the use of quantum mechanics in its relativistic form, due to P. A. M. Dirac. The result, known as the Klein-Nishina formula, contains the Thomson expression as a first term but goes on to include large frequency- and angle-dependent corrections. *See* RELATIVISTIC QUANTUM THEORY.

Applications. The Compton effect often plays a major nuisance role, producing most of the background in x-ray diffraction and in the field of gamma-ray spectroscopy, where interest focuses on producing energy spectra with narrow lines whose intensity and mean energy can be estimated accurately. Compton scattering of x-rays by materials of low atomic number is so dominant that it forces the versatile technique of x-ray fluorescence to employ extremely thin targets, thus removing it from the list of nondestructive analytical techniques. However, the development of high-resolution silicon and germanium semiconductor radiation detectors in the 1960s opened new areas for applications of Compton scattering. Those related to the measurement of Compton profiles are discussed above. *See* JUNCTION DETECTOR; X-RAY FLUORESCENCE ANALYSIS.

Noninvasive analysis. Semiconductor detectors make it possible to measure the separate probabilities for Rayleigh and Compton scattering. An effective atomic number has been assigned to compounds that appears to successfully correlate theory with Rayleigh-Compton ratios (**Fig. 3***a*).

Average density can be measured by moving to higher energies where Compton scattering does not have to compete with Rayleigh scattering. At these energies, Compton scattering intensity has been successfully correlated with mass density (Fig. 3*b*). An appropriate application is the measurement of lung density in living organisms.

At low energies and low atomic numbers, the main competition for photon attenuation is between Compton scattering and photoelectric absorption (Fig. 3*c*). This competition can be used to analyze very low Z mixtures such as fat-lean ratios (Fig. 3*d*). *See* NONDESTRUCTIVE EVALUATION.

Gamma-ray astronomy. The ability to put large detectors in orbit above the Earth's atmosphere has created the field of gamma-ray astronomy. This field is now based largely on the data from the Compton Gamma-Ray Observatory, all of whose detectors make use of the Compton effect (although not exclusively). The information produced by this observatory on gamma-ray bursters may change the estimated age of the universe by a factor of 2. *See* GAMMA-RAY ASTRONOMY; GAMMA-RAY DETECTORS; GAMMA RAYS; X-RAYS.

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Computational chemistry

A branch of theoretical chemistry that uses a digital computer to model systems of chemical interest. In this discipline, the essential physics that determines molecular behavior is captured in mathematical models and programmed for digital computers. The models are imperfect but have proven remarkably useful.

The domain of computational chemistry is vast. In principle, almost any quantity that can be measured can be computed. In practice, programs are available that calculate properties of individual molecules, including geometries, charge distributions, and modes of vibration for both ground and excited electronic states. Changes in those properties can also be calculated as the computer transforms compounds from reactants to products during the simulation of a chemical reaction. Properties, such as absorption and emission spectra which involve the interaction of molecules with electromagnetic radiation, can also be computed. Where possible, computational procedures are validated by comparison with experiment, and the confidence gained from such comparisons often encourages application to properties that are at or beyond what can be measured experimentally. Computations can thus provide information about the geometries of short-lived high-energy species or molecules that may be only a glimmer in the eye of a creative chemist.

In addition to estimates of important quantities, computations also provide deep insight into the reasons that chemicals behave as they do. For example, electronic structure calculations provide information about bonding electrons that can explain structural preferences and foretell chemical reactivity. In favorable cases, this information can be used proactively to design molecules to user specifications or aid in the design of catalysts that promote the production of a desired compound.

Because of the increasing power of computers and the simultaneous development of well-tested and reliable theoretical methods, computational chemistry and experimental chemistry are becoming interdependent partners. In addition to the more traditional use of computational chemistry as a tool to explain experimental outcomes, computations are increasingly used to develop plausible hypotheses that are then tested in the laboratory. Hypothetical molecules conceived by a molecular designer are often synthesized and evaluated in the computer long before they are ready to be tested in the laboratory.

The practice of computational chemistry can involve either the application of existing computational tools to new molecules or the development of new computational methods. New software developments are constantly pushing back the frontiers of what is computable. Breakthroughs may involve the incorporation of better physics into the underlying mathematical models, the implementation of algorithms that better utilize computing resources, or the use of time-saving approximations. Popular approximate methods include semiempirical methods that rely partially on experiment to estimate model parameters, and methods that partition a large complex system into two parts, with one part being the focus of the calculation that is treated rigorously and the other being the surroundings that is treated with less rigor. Such approaches coupled with improvements in hardware have made it possible to perform calculations, which required supercomputing capabilities just a few years ago, on a desktop workstation or even a personal computer. *See* ALGORITHM.

Before a computational study is begun, an effective method must first be identified that balances the computational cost against a combination of factors, including accuracy, scalability, interpretability, response speed, and ease of implementation and use.

While keeping this balance in mind, a practitioner's first decision is often between two fundamentally different mechanical treatments of molecules: quantum mechanics and molecular mechanics.

Quantum mechanics. One active area of computational chemistry involves the calculation of molecular properties based on Schrödinger's wave equation

$$H\Psi = E\Psi$$

where H is the Hamiltonian operator for a molecule's electrons as they move in the field of the fixed nuclei, Ψ is a function of the electron coordinates, and E is a constant identified as the electronic energy of the molecule. H typically includes operations that evaluate the kinetic energy of the electrons in terms of the curvature of Ψ, and multiplication operations that account for potential energy. In order for a function Ψ to be a suitable wavefunction, the Hamiltonian operations when applied to Ψ must return Ψ multiplied by the constant E. Solutions of the Schrödinger equation exist for only certain quantized values of E, the lowest of which corresponds to the ground electronic state of the molecule. This energy will change as the positions of the nuclei are moved, and most electronic structure programs feature gradient methods to locate nuclear configurations that correspond to minima in the energy E. The wavefunction Ψ has no physical meaning, but its square is interpreted as the electron density and indicates where the electrons are likely to be found in a molecule. Electron density plays a profound role in determining the physical and chemical properties of a molecule. *See* QUANTUM MECHANICS; SCHRÖDINGER'S WAVE EQUATION.

Regrettably, the Schrödinger equation cannot be solved exactly for any but the simplest molecular systems. Fortunately, useful approximations abound. One popular and successful approximation is to partition Ψ into factors known as molecular orbitals (MOs). Each MO is expressed as a linear combination of atom-centered basis functions known as atomic orbitals (AOs). The coefficients of the AOs in the MOs are determined by an energy minimization process that attributes an orbital energy to each of the MOs and assigns electrons usually in pairs to those MOs that have the lowest energy. *See* MOLECULAR ORBITAL THEORY.

Molecular orbital calculations can take from a few seconds of computer time to many hours, depending on the level of approximation. Computing time is also a steep function of molecular size, increasing roughly as the fourth or fifth power of the number of basis functions (atomic orbitals) used to express the MOs. High-level ab initio calculations can rival the accuracy of experiment in determining ground- and excited-state molecular geometries, electronic-transition frequencies, vibration frequencies, and heats of formation.

Density functional theory is another quantum-mechanical method that has been applied to molecules. Originally developed for problems in solid-state physics, these calculations express the total energy of the system as a function of the ground-state electron density rather than of the molecular wave function. Since the computer time increases only as the cube of the number of basis functions, density functional methods can be used for larger molecules than molecular orbital methods, while often maintaining comparable accuracy. *See* QUANTUM CHEMISTRY.

Electronic structure calculations have been used productively in many chemical disciplines. In the life sciences, electronic structure calculations provide plausible explanations for the biological activity of known molecules, and guidance for the design of new molecules with desired properties. For example, calculated charge distributions for the transition state of an essential biochemical transformation can serve as a template for the design of drugs which act by inhibiting the enzyme responsible for catalyzing this transformation in a pathogenic organism.

Molecular mechanics. The molecular-mechanics model treats the atoms and bonds in a molecule much like a collection of balls joined by springs. Because of its relative simplicity, it can be applied to proteins and other large molecules, where quantum-mechanical methods are impractical. Molecular-mechanics programs can adjust the molecular structure until a conformation of minimum energy is determined. The spring force constants and atomic sphere parameters that define a force field are typically preadjusted by developers so that their programs produce results that nearly agree with a "training set" of experimentally measured or reliably calculated quantities. These parameter values are often assumed to be valid for other molecules and molecular conformations that are outside of the training set. *See* BOND ANGLE AND DISTANCE; CHEMICAL BONDING; MOLECULAR MECHANICS.

Force fields differ mainly by the inclusion of additional terms for interactions such as hydrogen bonding or coupling between the springs. Some force fields have been customized for families of compounds such as proteins and nucleic acids. At one time or another, missing or inappropriate force-field parameters are the bane of every practitioner of molecular mechanics, especially when treating molecules and conformations that are far different from those represented in the training set used to fix the parameters of the force field. In spite of limitations, satisfactory accuracy for many applications and modest computer demands have made molecular mechanics–based methods popular, especially for large molecules.

Gradient techniques used in either molecular or quantum mechanics assure that a low-energy structure at the bottom of an energy well containing the starting point will be found. If the energy surface is complex, other lower-energy structures are likely to exist at remote locations and may not be found unless algorithms that promote broader exploration are exercised. One technique used for broader sampling of potential-energy surfaces is molecular dynamics. *See* CHEMICAL DYNAMICS.

Molecular-dynamics calculations simulate atomic motion by integration of Newton's equations.

Acceleration is directed by the negative gradient of the potential energy, which is calculated with the underlying molecular-mechanics model. The method requires large amounts of computer time just to simulate a few hundred picoseconds to nanoseconds of atomic motion. Various approximations have been developed to decrease the amount of computer time required, while maintaining the accuracy of the calculations. Large systems may be simulated by the imposition of periodic boundary conditions. This means that the box containing the particles is considered to be replicated in all three dimensions, similar in the manner by which strips of wallpaper continue a pattern around a room. The influence of explicit molecules can be replaced by a solvation function whose magnitude depends on the type and fractional exposure of solute atoms to the solvent. In Monte Carlo methods, each particle movement is determined randomly and selectively accepted, based on certain energy criteria. In Langevin dynamics methods, forces between nearby particles are treated exactly, and those due to remote particles, including solvent, are treated stochastically. Software is available for computer simulations of small molecules moving in a variety of solvents, of solutes permeating through lipid membranes, and for various motions of proteins and nucleic acids. *See* MONTE CARLO METHOD; STOCHASTIC PROCESS.

Many important structural and thermodynamic quantities may be computed from simulations of sufficient length by averaging over the ensemble of molecular conformations, which are sampled during the simulation. In order to evaluate the free-energy change associated with a chemical reaction, advantage is often taken of the principle that free energy is a function of state. Consequently in a reaction, changes in free energy F are independent of the path taken to get from the reactants to the products. This principle enables the calculation of the free-energy change of a reaction from the known change for a closely related reference reaction. For example, if the free-energy change ΔF_3 for binding ligand B to a protein receptor R has been measured experimentally (see **illustration**), the free energy change for binding ligand A to the same receptor (ΔF_1) can be estimated as $\Delta F_1 = \Delta F_2 + \Delta F_3 + \Delta F_4$. Molecular simulations can be used to calculate the free-energy changes associated with the kind of structural morphing involved in steps 2 and 4. These transformations, which are an alchemist's dream come true, may be impossible in the laboratory, but are readily simulated in a computer using advanced algorithms based on thermodynamic perturbation or integration theories. In the hands of experienced computational chemists, simulations of this type can be used to find analogs of a reference compound that alter receptor-binding characteristics in a desired fashion. *See* FREE ENERGY; SIMULATION.

$$\begin{tikzcd}
R + A \arrow[r, "\Delta F_1"] \arrow[d, "\Delta F_2"'] & RA \\
R + B \arrow[r, "\Delta F_3"'] & RB \arrow[u, "\Delta F_4"']
\end{tikzcd}$$

Thermodynamic cycle to calculate free energy of binding of ligand A to a receptor based on a known value for binding ligand B.

Interactive computer graphics. Graphical methods are not necessarily based on a mechanical model, but are often used in conjunction with the mechanical methods described above. Interactive graphics has become so prevalent in the chemical community that it is almost impossible to conceive of calculations without associated molecular manipulation and visualization. Here a picture is worth millions of numbers. When seated at a molecular graphics terminal, the chemist is essentially working with a sophisticated set of molecular models that are stored in the computer memory and displayed on a screen. Molecular orbitals, electron densities, and normal-mode vibrations can be viewed from a variety of perspectives. The sequence of conformations from computer simulations, displayed one frame after another, in effect creates a movie of the thermal motion of the molecules. Moving a mouse or turning a dial moves atoms about the screen as easily as tangible models can be moved physically.

Seeing in three dimensions is often essential for understanding the behavior of a molecule. A sense of depth is produced when a pair of computer-generated left- and right-eye images is seen through one of several types of viewers that aid in merging the images. Stereoscopic viewing is most useful when comparing the structures of two molecules or when studying interactions between them. Structural comparisons in three dimensions enable the user to discern similarities and differences between molecules that might escape a reader of the printed page. Unlike physical models, these graphical renderings of molecules can be easily overlaid in order to further enhance comparisons. Computer graphics can also be used to dock models of small guest molecules into cavities within larger host molecules. This is particularly important for drug designers. For example, when the structure of a target protein is available, computer graphics can be used to study the fit of a drug candidate into potential binding sites in the protein and to anticipate the influence of such binding on the protein's function. Alterations can then be made on the small molecule with the goal of improving the fit to the binding site. The potential of this technology continues to increase as the number of available crystal structures of important enzymes or receptors rises. *See* COMPUTER GRAPHICS; CONFORMATIONAL ANALYSIS; STEREOCHEMISTRY.

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Computational fluid dynamics

The numerical approximation to the solution of mathematical models of fluid flow and heat transfer. Computational fluid dynamics is one of the tools (in addition to experimental and theoretical methods) available to solve fluid-dynamic problems. With the advent of modern computers, computational fluid dynamics evolved from potential-flow and boundary-layer methods and is now used in many diverse fields, including engineering, physics, chemistry, meteorology, and geology.

Computational methods. The fundamental model of fluid flow, known as the Navier-Stokes equations, is derived from the conservation of mass, momentum, and energy. For example, if the fluid is incompressible, the Navier-Stokes equations can be written as Eqs. (1) and (2), where u, v, and w are the cartesian

$$\text{Continuity}: \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \tag{1}$$

Momentum :

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} + w\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial x} + \frac{1}{\mu}\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) \tag{2a}$$

$$\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y} + w\frac{\partial v}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial y} + \frac{1}{\mu}\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2}\right) \tag{2b}$$

$$\frac{\partial w}{\partial t} + u\frac{\partial w}{\partial x} + v\frac{\partial w}{\partial y} + w\frac{\partial w}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \frac{1}{\mu}\left(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2}\right) \tag{2c}$$

components of velocity, ρ the fluid density, p the pressure, and μ the fluid viscosity. The compressible form of the Navier-Stokes equations, which is of slightly different form because of the variable fluid properties, additionally contains the energy equation, which couples the temperature, velocity, and pressure fields. The complete formulation requires initial and boundary conditions and thermodynamic relations for fluid properties. Numerical solution of this set of nonlinear coupled partial differential equations presents many difficulties, including application of boundary conditions, particularly for free and moving surfaces; grid generation for complex geometries; turbulence modeling; pressure-velocity coupling for incompressible flows; and resolution of shock waves in supersonic flows. A hierarchy of approaches is available for simplifying Eqs. (1) and (2) [see **table**]. *See* DIFFERENTIAL EQUATION; NAVIER-STOKES EQUATION.

Computational fluid dynamics is associated with field-equation solutions of the Euler and Navier-Stokes equations instead of other computational techniques such as boundary-element methods for inviscid flows and momentum-integral methods for boundary-layer flows. The crucial elements of computational fluid dynamics are discretization, grid generation and coordinate transformation, solution of the coupled algebraic equations, turbulence modeling, and visualization.

Discretization. Numerical solution of partial differential equations requires representing the continuous nature of the equations in a discrete form. Discretization of the equations consists of a process where the domain is subdivided into cells or elements (that is, grid generation) and the equations are expressed in discrete form at each point in the grid by using finite difference, finite volume, or finite element methods. The finite difference method requires a structured grid arrangement (that is, an organized set of points formed by the intersections of the lines of a boundary-conforming curvilinear coordinate system), while the finite element and finite volume methods are more flexible and can be formulated to use both structured and unstructured grids

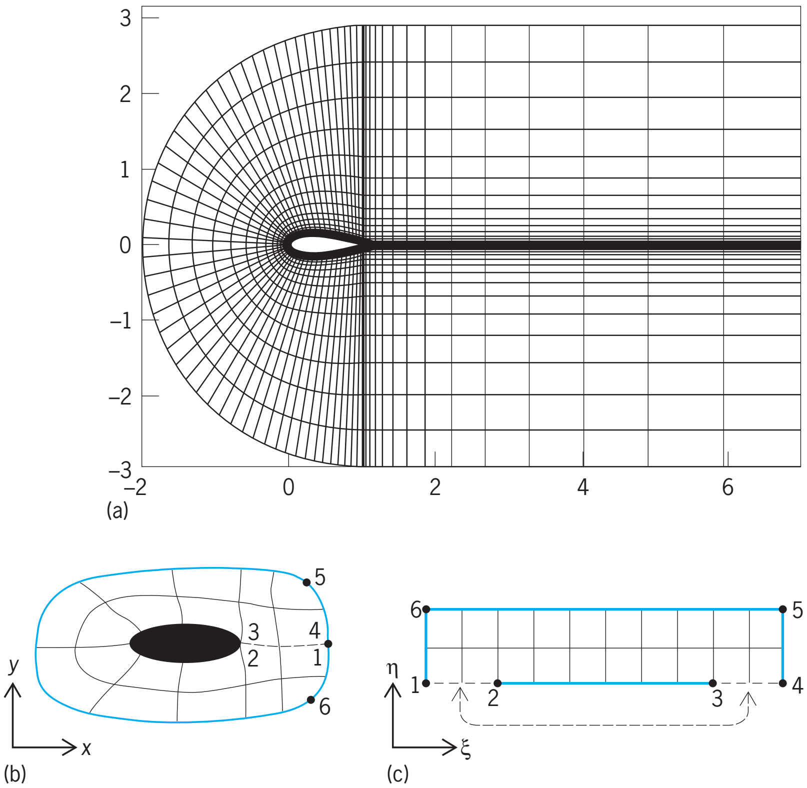

Fig. 1. **Computational grid for numerical analysis of flow about a hydrofoil. (*a*) Structured grid. (*b*) Schematic of physical domain. (*c*) Schematic of computational domain.**

Hierarchy of approaches to fluid-flow problems*

Mathematical basis	Type of partial differential equation	Physical problems
Laplace equation	Elliptic	Inviscid and irrotational flow
Euler equation	Hyperbolic	Inviscid flow
Boundary-layer equations	Parabolic	Thin viscous layer
Navier-Stokes equations	Mixed	Laminar flow
Reynolds-averaged Navier-Stokes (RaNS) equations + turbulence model	Mixed	Turbulent flow
Large-eddy simulation (Navier-Stokes equations + subgrid model)	Mixed	Turbulent flow
Direct numerical solution (Navier-Stokes equations + grid resolving all length scales)	Mixed	Turbulent flow

*Listed in order of increasing complexity of numerical solution.

(that is, a collection of triangular elements or a random distribution of points). Complex shapes necessitate nonuniform, boundary-conforming grids with grid points concentrated in regions of high gradients, such as inside boundary layers or near shock waves. Structured grids are usually generated by using algebraic interpolation functions or elliptic partial differential equations. For finite difference methods, the equations are rewritten in generalized nonorthogonal coordinates and evaluated on a so-called computational domain, which is defined by the transformation between the boundary-conforming curvilinear-coordinate system in the so-called physical domain and an orthogonal grid with uniform spacing (**Fig. 1**). *See* FINITE ELEMENT METHOD.

Finite difference discretization of Eqs. (1) and (2) is based on the algebraic representation of derivatives by using Taylor-series expansions. For example, the temporal derivative in Eq. (2*a*) expressed as a first-order backward difference is Eq. (3), where (i, j, k) is

$$\frac{\partial u}{\partial t} = \frac{u^{n}_{i,j,k} - u^{n-1}_{i,j,k}}{\Delta t} + \vartheta\,[(\Delta t)] \tag{3}$$

the location of the grid point, (n) is the current time level, $(n-1)$ is the previous time level, Δt is the time step between (n) and $(n-1)$, and $\vartheta(t)$ represents the truncated terms in the Taylor-series approximation of the partial derivative $\partial u/\partial t$. (Dropping these terms introduces a source of error, known as a truncation error, which is of an order of magnitude equal to that of the time step Δt.) Due to advantageous stability characteristics, in comparison to central differencing, an upstream-backward difference is typically used for the convective terms. Assuming that the grid is uniform and orthogonal, the first-order upstream difference for the x-component convective term of Eq. (2*a*) is given by Eq. (4), where Δx or the

$$u\frac{\partial u}{\partial x} = u^{n-1}_{i,j,k}\,\frac{u^{n}_{i,j,k} - u^{n}_{i-1,j,k}}{\Delta x} + \vartheta\,[(\Delta x)] \tag{4}$$

grid spacing, and the grid point locations (i,j,k), are given by a numerical molecule (**Fig. 2**). Usually, the viscous terms in the momentum equations are evaluated by using a central difference. For example, the second-order central difference of the second partial derivative of u in the x direction [from Eq. (2*a*)] is given by Eq. (5).

$$\frac{\partial^2 u}{\partial x^2} = \frac{u^{n}_{i+1,j,k} - 2u^{n}_{i,j,k} + u^{n}_{i-1,j,k}}{(\Delta x)^2} + \vartheta\,[(\Delta x)^2] \tag{5}$$

Solution of equations. The assembly of the finite difference equations for each grid point results in a large implicit system of algebraic equations for each of the velocity components (u, v, w). For example, the equation for the u component of velocity at the point (i, j, k) is Eq. (6), where A is a matrix of co-

$$\begin{aligned} &A_{i,j,k}u^{n}_{i,j,k} + A_{i+1,j,k}u^{n}_{i+1,j,k} + A_{i-1,j,k}u^{n}_{i-1,j,k} \\ &\quad + A_{i,j+1,k}u^{n}_{i,j+1,k} + A_{i,j-1,k}u^{n}_{i,j-1,k} \\ &\quad + A_{i,j,k+1}u^{n}_{i,j,k+1} + A_{i,j,k-1}u^{n}_{i,j,k-1} = C^{n-1} \end{aligned} \tag{6}$$

efficients related to the grid and the transformation relations (between the physical and computational domains) and C is a known column vector including pressure, body-force, and velocity terms from the previous time step. Equation (6) is usually solved by iterative schemes, such as the alternating direction implicit (ADI) method, which is based upon splitting Eq. (6) into three tridiagonal systems that correspond to sweeps along each of the index (i,j,k) directions. If Eq. (4) and Eq. (5) are evaluated at time level $(n-1)$ instead of (n), the system of finite difference equations is explicit and the solution at each point can be directly evaluated. However, explicit formulations have restrictions on the ratio of the time step to the grid spacing, which are significant for viscous flows

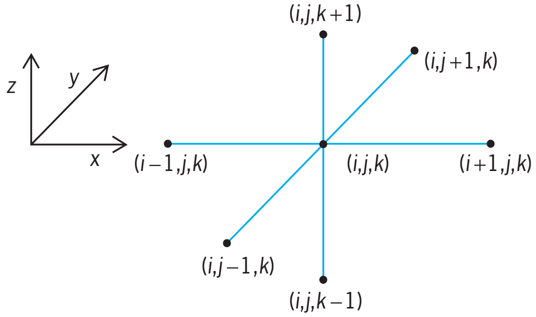

Fig. 2. Numerical molecule, showing nomenclature for neighboring grid points in finite difference discretization.

because of the fine near-wall grid spacing required to resolve the boundary layer. *See* MATRIX THEORY.

For either implicit or explicit approaches, efficient use of computers is required. Current-generation supercomputers are based on vector processors, which are most efficient with large arrays (vectors) of numbers. Optimizing a program, or vectorization, is accomplished by following programming rules so that the compiler can translate the code into vector instructions. *See* SUPERCOMPUTER.

Complete solution of the Navier-Stokes equations requires, for compressible flow, an equation of state such as the ideal gas equation, which relates temperature and density. In contrast, the solution of the incompressible equations presents the problem that the system of equations is lacking an equation for the direct solution of the pressure field. Typically, an equation for pressure is derived which satisfies continuity, and an algorithm must be incorporated which iteratively couples the pressure and velocity fields.

Turbulence modeling. There are a variety of approaches for resolving the phenomena of fluid turbulence. The Reynolds-averaged Navier-Stokes (RANS) equations, which are derived by decomposing the velocity into mean and fluctuating components, contain additional turbulent Reynolds-stress terms which are unknown. Closure of the RANS equations can be accomplished by using the Boussinesq assumption, which relates the Reynolds stresses to the mean rate of strain or the Reynolds-stress equations, which can be solved directly with additional modeling assumptions. An alternative to the RANS equations is large-eddy simulation, which solves the Navier-Stokes equations in conjunction with a subgrid turbulence model. The most direct approach to solving turbulent flows is direct numerical simulation, which solves the Navier-Stokes equations on a mesh that is fine enough to resolve all length scales in the turbulent flow. Unfortunately, direct numerical simulation is limited to simple geometries and low-Reynolds-number flows because of the limited capacity of even the most sophisticated supercomputers. *See* TURBULENT FLOW.

Visualization. The final step is to visualize the results of the simulation. Powerful graphics workstations and visualization software permit generation of velocity vectors, pressure and velocity contours, streamline generation, calculation of secondary quantities (such as vorticity), and animation of unsteady calculations. Despite the sophisticated hardware, visualization of three-dimensional and unsteady flows is still particularly difficult. Moreover, many advanced visualization techniques tend to be qualitative, and the most valuable visualization often consists of simple x-y plots comparing the numerical solution to theory or experimental data. *See* COMPUTER GRAPHICS.

Applications. Computational fluid dynamics has wide applicability in such areas as aerodynamics, hydraulics, and geophysical flows, with length and time scales of the physical processes ranging from millimeters (fractions of an inch) and seconds to kilometers (miles) and years.

Vehicle aerodynamics and hydrodyamics, which have provided much of the impetus in the development of computational fluid dynamics, are primarily concerned with the flow around aircraft, automobiles, and ships where the goal is the determination of the lift and drag forces and the moments resulting from these forces. Furthermore, computational fluid dynamics is being applied to explicate basic physics and to examine complete vehicle configurations. *See* AERODYNAMIC FORCE; AERODYNAMICS; HYDRODYNAMICS.

Hydraulics and environmental fluid dynamics also find many applications of computational fluid dynamics. The prediction of pollutant dispersion in rivers, lakes, and estuaries and riverine morphology, including river-bed formation and sediment deposition, have been studied by using computational fluid dynamics. Detailed analysis of hydraulic structures by using computational fluid dynamics can provide data which are useful in new designs and in the modernization of aging facilities. *See* HYDRAULICS; RIVER ENGINEERING; WATER POLLUTION.

The study of atmospheric and oceanic dynamics finds prolific use of computational fluid dynamics. Although long-term prediction of weather is not possible, because of its random nature and the multiplicity of length and time scales, the study of smaller problems (such as thunderstorms and ocean circulation) and low-resolution global-scale phenomena (for example, global climate models) is possible. *See* CLIMATE MODELING; DYNAMIC METEOROLOGY; FLUID FLOW; FLUID-FLOW PRINCIPLES; NUMERICAL ANALYSIS; OCEAN CIRCULATION; SIMULATION; WEATHER FORECASTING AND PREDICTION.

Eric Paterson; Fred Stern

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Computational intelligence

An approach to designing intelligent systems using mathematical algorithms. It consists of the fields of neural networks, evolutionary computation, and fuzzy sets. The term was first used as an alternative to artificial intelligence in the 1980s. The current popular use of the term as defined above results from an effort by James Bezdek in the early 1990s to differentiate the fields of neural networks, evolutionary computation, and fuzzy sets from classical artificial intelligence (AI). There is significant continuing research in the area of computational intelligence, as well as a number of examples of practical, everyday systems that make use of computational intelligence approaches.

Computational intelligence has been used to enable a car to autonomously navigate from Washington, DC, to San Diego with a human driver intervening only a few times; to support automatic transmissions and antilock braking systems; and to determine whether one might grant credit card purchase requests. One of the best checkers-playing computer programs developed so far uses a computational intelligence approach.

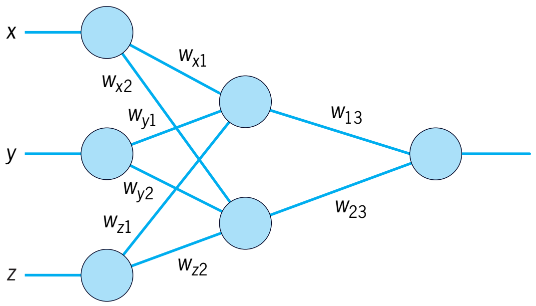
In the classical approach to intelligent systems, known as artificial intelligence, all reasoning may be done using high-level symbols. For example, one can use rules such as: if it is raining, bring an umbrella. These types of rules (called heuristic rules) may also be used in fuzzy systems with the difference being that approximate matches are allowed. So one might still bring an umbrella on a cloudy overcast day where it was not quite raining at the moment. *See* ARTIFICIAL INTELLIGENCE.

Systems that are described by the term "computational intelligence" make use of lower-level computational features even when they may have a high-level interpretation. For example, in the case of fuzzy systems, which may be expressed as heuristic rules, there will be an underlying mathematical description of sets as well as conjunction, disjunction, and inference operators. Fuzzy rules have been successfully used in the control of antilock brakes.

Fuzzy systems. A fuzzy system is one that makes use of approximate reasoning using the mathematical basis of fuzzy logic. The concept of fuzzy logic is concerned with membership in the classes of true or false. For example, a person with some bald spots might be said to be balding. However, he would completely belong neither to the class of bald people nor to the class of people with hair.

To see how this differs from probability, consider that you have the opportunity to acquire one of two lottery tickets after the winning tickets from the lottery have been chosen. The first is described as having a 90% chance of having won a lot of money, and the second one is described as having a 0.9 membership in the class of tickets which have won a lot of money. In the first case you have a 90% chance of winning a lot of money and a 10% chance of winning nothing. In the second case, you will have approximately won a lot of money. This is likely to translate into something between a lot of money and a fair amount of money. If you had to put a probability distribution on the likely winnings in the second case, you might have a probability of 0 of winning no money and a probability of 0 of winning the entire lottery, but a probability of 80% of being runner-up, 10% of being second runner-up, and 10% of being third runner-up. Most people would choose the ticket with the 0.9 membership in the class of tickets which have won a lot of money because they would be guaranteed a good sum of money. Of course, some gamblers would choose the all-or-nothing route. *See* FUZZY SETS AND SYSTEMS.

Neural networks. Perhaps the most widely used technology within the computational intelligence approaches is that of neural networks. Neural networks are inspired by the underlying processing done in the human brain. There are nodes which correspond (loosely) to neurons in the brain and have interconnections which correspond (loosely) to the synapses that connect neurons in the brain. A simple three-layer neural network is shown in the **illustration**.



Feedforward neural network with three inputs, one output, and one hidden layer of two nodes. The connection weights are denoted by w_{ij}.

A neural network learns from a set of labeled examples to produce intelligent responses. Neural networks are also used to intelligently group unlabeled data into clusters. Thus, a neural network is one attempt to mimic the underlying learning processes of the human brain. Clearly, a system that can learn to improve its performance will be quite valuable. There are many approaches to training a neural network. Many of them rely on the feedforward–backpropagation approach which was popularized in the mid-1980s. In this approach, examples are presented to the neural network, and the connection weights between nodes are updated to make the outputs of the network closer to those of the examples. The connection weights loosely correspond to the synaptic strengths of connections between neurons in the human brain.

Neural networks have a powerful property of universal approximation. This means that they can arbitrarily closely approximate any function, in theory. This has been proven mathematically. In practice, the theorems do not show how to configure the network, what type of functions should exist within a node to determine its output or, perhaps most importantly, do not guarantee that the appropriate weights can be learned. So it is known that there is a neural network that arbitrarily closely approximates a particular function, but it is not known if this network can ever be discovered.

Consider the function that emulates a person who decides whether a credit card transaction should be allowed. Given what is known about neural networks, it would be possible to develop one that was as good as any human expert if we knew how to do so. It is unknown if this can actually be done, but in practice systems for making such decisions (with capabilities that do not necessarily match those of a human) have been built. The function to be approximated is the binary human decision of whether to grant credit or not grant credit. A highly accurate system will, clearly, save money for the credit card company, and it will have the side effect of preventing people from getting in too much debt.

Fuzzy systems and neural networks have been combined to produce neuro-fuzzy systems. Under certain conditions they have been shown to be universal approximators, also. Typically, a set of fuzzy rules can be extracted from a neuro-fuzzy system which may provide an explanation capability that is lacking in a typical neural network where all information is stored as a set of weights. The extent of the explanation capability will depend on the complexity of the fuzzy rules. There is, typically, a trade-off between complexity and accuracy. So more understandable but less complex rules will be less accurate than the more complex rules in the usual case. *See* NEURAL NETWORK.

Evolutionary computation. Evolutionary computation embodies a set of methods to evolve solutions to problems. Evolutionary computation has typically been applied to optimization problems. For example, excellent solutions to the classical traveling salesman problem have been evolved. This problem is to minimize the distance traveled by a salesperson who has to make calls in a set of cities.

Evolutionary computation considers potential solutions to a problem as members of a population. Mimicking how natural evolution is considered to work, members of the population can be chosen to mate. They then produce offspring, typically with the use of a crossover operator in which parts of each solution become a part of the offspring. After crossover, a mutation operator is often applied to the child which may randomly change some of its characteristics. The offspring compete for survival to the next generation based upon a fitness function. Those that are more fit survive.

There are at least three major paradigms within evolutionary computation. Genetic algorithms, which merge parts of solutions to form new solutions and then apply random mutation to them, can be applied to both binary bit strings and real-valued solutions. Evolutionary strategies make heavy use of the mutation operator. There is also genetic programming in which computer programs are evolved, typically in the Lisp language. The latter approach provides a computer-executable solution to a problem. *See* GENETIC ALGORITHMS.

Evolutionary computation has been used to evolve the weights, and sometimes the structure, of neural networks. It has also been used to evolve fuzzy systems and fuzzy neural networks. Thus, these approaches are complementary. An interesting application of evolutionary computation was in evolving an expert checkers-playing program that did not require any human knowledge. The system evolved weights for a neural network which served as a board evaluation function. After evolution, it was able to beat an expert-level checkers player. *See* EVOLUTIONARY COMPUTATION.

In summary, all the computational intelligence approaches discussed here can be used alone or together to produce systems that exhibit human expertise or intelligence. Lawrence O. Hall

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Computer

A device that receives, processes, and presents information. The two basic types of computers are analog and digital. Although generally not regarded as such, the most prevalent computer is the simple mechanical analog computer, in which gears, levers, ratchets, and pawls perform mathematical operations—for example, the speedometer and the watt-hour meter (used to measure accumulated electrical usage). The general public has become much more aware of the digital computer with the rapid proliferation of the hand-held calculator and a large variety of intelligent devices, ranging from typewriters to washing machines, and especially with exposure to the Internet and the World Wide Web. *See* CALCULATORS; INTERNET; WORLD WIDE WEB.

In the 1950s and 1960s the definition of "computer" included only the provision of input and output, and the ability to process the input to produce the output. Since then, the common understanding of the term (in particular, for digital computers) has come to include storage, and even the ability to store the program of instructions, allowing decision making based on previously computed results. *See* COMPUTER PROGRAMMING; COMPUTER STORAGE TECHNOLOGY.

Analog computer. An analog computer uses inputs that are proportional to the instantaneous value of variable quantities, combines these inputs in a predetermined way, and produces outputs that are a continuously varying function of the inputs and the processing. These outputs are then displayed or connected to another device to cause action, as in the case of a speed governor or other control device. *See* CONTROL SYSTEMS.

Small electronic analog computers are frequently used as components in control systems. Inputs come from sensing devices which output an electrical signal (transducers). These electrical signals are presented to the analog computer, which processes them and provides a series of electronic outputs that are then displayed on a meter for observation by a human operator or connected to an electrical action device to ring a bell, flash a light, or adjust a remotely controlled valve to change the flow in a pipeline system. If the analog computer is built solely for one purpose, it is termed a special-purpose electronic analog computer.

In any analog computer the key concepts involve special versus general-purpose computer designs, and the technology utilized to construct the computer itself, mechanical or electronic. An analog computer is often combined with a digital computer to form a hybrid computer. *See* ANALOG COMPUTER.

Digital computer. In contrast, a digital computer uses symbolic representations of its variables. The arithmetic unit is constructed to follow the rules of one (or more) number systems. Further, the digital computer uses individual discrete states to represent the digits of the number system chosen.

Electronic versus mechanical computers. The most prevalent special-purpose mechanical digital computers used to be the supermarket cash register, the office adding machine, and the desk calculator. Each of these has been universally replaced by electronic devices allowing much greater logical decision making and greatly increased speed. For example, most products now carry a bar code, the Universal Product Code (UPC). The code is scanned by a light-sensitive device, bringing information about each product into the point-of-sale (POS) terminal that has replaced the mechanical cash register. The POS terminal then computes total charges and provides a receipt for the customer. It may also communicate with a centralized computer system that controls inventory, accounts payable, salaries and commissions, and so on. While a mechanical cash register could carry out only a small number of operations each minute, and some electromechanical devices might handle several hundred operations per second, even a small general-purpose electronic computer can carry out its computations at millions of operations per second.

Stored program operation. A digital computer works with a symbolic representation of variables; consequently, it can easily store and manipulate numbers, letters, images, sounds, or graphical information represented by a symbolic code. Typically, a general-purpose electronic digital computer operates on numbers by using both decimal and binary number systems, and on symbolic data expressed in an alphabet. It contains both an arithmetic unit and a storage unit. As the digital computer processes its input, it proceeds through a series of discrete steps called a program. The storage unit serves to retain both the values of the variables and the program to process those variables. The arithmetic unit may operate on either variables or coded program instructions interchangeably, since both are usually retained in the storage unit in the same form. Thus, the digital computer has the capability to be adaptive, because processing can be determined by the previously prepared program, by the data values supplied as input to the computation, and by the values generated during the course of the computation. Through the use of the stored program, the digital computer achieves a degree of flexibility unequaled by any other computing or data-processing device.

Applications. In the past, most digital computers were confined to standard applications, such as bookkeeping, accounting, engineering design, and test data reduction. However, the advent of the relatively inexpensive and readily available personal computer, and the combination of the computer and communications, such as by the use of networks, have dramatically altered that pattern. The most common application now is probably text and word processing, followed by electronic mail. *See* ELECTRONIC MAIL; LOCAL-AREA NETWORKS; MICROCOMPUTER; WORD PROCESSING.

Ready access to national networks has fostered the growth of communities of computer users who communicate easily and effectively on the World Wide Web, including an explosion of commerce via online communications. The convergence of computers and network communications also has encouraged the development of network computers, smaller and simpler computers that depend on the availability of software and data from around the world arriving via networks in order to accomplish their tasks.

The ability of even modest computer systems to store, organize, and retrieve very large amounts of information has brought about radical changes in the very nature of many business offices. Indeed, many industrial, academic, and governmental processes have been irrevocably changed by the computer. It is often said that the Manhattan Project, although managed by paper and pencil in the 1940s, simply could not have been accomplished at all today without using computers. That is, there has been a change in the very thought processes that people use to accomplish tasks, in order to accommodate computer-based solutions for those tasks.

Personal workstations, used in engineering design and other applications requiring intense computation and sophisticated graphics, have become more powerful than earlier, very large computer systems. This has moved computation, and even the storage of many large data files, directly onto each person's desk, and in many cases, into handheld computers. In addition, applications that were once considered esoteric have led to industrial applications, such as the use of robots on manufacturing assembly lines. Many of the heuristic techniques employed by these robots are based on algorithms developed in such artificial-intelligence applications as virtual reality. *See* ARTIFICIAL INTELLIGENCE; COMPUTER-AIDED DESIGN AND MANUFACTURING; COMPUTER-AIDED ENGINEERING; COMPUTER GRAPHICS; ROBOTICS; VIRTUAL REALITY.

Computers have begun to meet the barrier imposed by the speed of light in achieving higher speeds. This has led to research and development in the areas of parallel computers (in order to accomplish more in parallel rather than by serial computation) and distributed computers (taking advantage of network connections to spread the work around, thus achieving more parallelism). Continuing demand for more processing power has led to significant changes in computer hardware and software architectures, both to increase the speed of basic operations and to reduce the overall processing time. *See* COMPUTER ARCHITECTURE; CONCURRENT PROCESSING; DISTRIBUTED SYSTEMS (COMPUTERS); MULTIPROCESSING; SUPERCOMPUTER.

In the hardware domain, clock rates approaching gigahertz speed have led to ever smaller computers, since electronic pulses cannot travel further than 1 ft (0.3 m) per nanosecond; instruction and video caches have been enlarged for faster processing and display; and central processing units are continually being redesigned to enable more parallelism (and to avoid the "von Neumann bottleneck" inherent in a serial architecture). In the software domain, parallelism is being achieved both locally via multithreading and multiprocessor operating systems, and globally via distributed computation. *See* COMPUTER PERIPHERAL DEVICES; DATABASE MANAGEMENT SYSTEM; DIGITAL COMPUTER; HUMAN-COMPUTER INTERACTION. Bernard A. Galler; John H. Sayler

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Computer-aided circuit design

The application of specialized computer software to the design, simulation, and physical layout of electronic circuits on semiconductor chips and circuit boards. *See* INTEGRATED CIRCUITS; PRINTED CIRCUIT.

Designing integrated circuits is extremely challenging because of the large amount of detailed technical data associated with circuits containing many transistors and their interconnections. Competition in the integrated circuit marketplace requires that integrated circuit products be optimal in some respect to be profitable. Thus, the integrated circuit design task is necessarily coupled with an optimization task. Readily available transistors make many alternative circuit implementations possible, and optimization means choosing the circuit that maximizes (or minimizes) an objective function of interest, such as performance, power consumption, area, or ease of testing. Because of this complexity, computer-aided design software has evolved into the principal tool used by most designers of high-performance analog and digital electronic devices and systems. Only computer programs can choose optimal designs, can evaluate these designs before prototypes are built, and can simulate circuit performance under realistic component tolerances and environmental conditions.

Classical "breadboarding" and bench testing of design prototypes are infeasible when circuits containing anywhere from hundreds to millions of transistors are involved. Even for circuits containing few components, conventional breadboarding techniques may not evaluate circuit performance adequately. Component positioning on the circuit board, component interconnect routing, and board material properties all can have a significant effect on circuit performance, and if the breadboard does not faithfully replicate all of these final product physical characteristics, its results may be of little use. *See* BREADBOARDING.

Once an analog or digital circuit design has been completed and extensive simulation has shown its performance to be satisfactory, the myriad details required to prepare the device or electronic system for manufacture must be conveyed to the appropriate fabrication facility. Comprehensive computer-aided design systems contain software to generate computer files that describe the physical structure and layout of the circuit components and the routing of their interconnections. *See* COMPUTER-AIDED DESIGN AND MANUFACTURING.

In semiconductor manufacturing, these files are used to create integrated circuit mask sets. Microelectronic circuits are manufactured using a photolithographic process, by which patterns corresponding to transistors and connection wires are transferred onto a silicon wafer, which is then customized by local physical or chemical reactions. These patterns are contained in a mask set, a detailed draft of the geometries of the transistors and wires on several layers.

In circuit board fabrication, data files are used to generate conductor path-etching masks and to provide positioning data for drilling via and component mounting holes. This software also can generate circuit schematic drawings and prepare component parts lists. Philip V. Lopresti

Design of Digital Circuits

Most digital electronic products employ very large scale integration (VLSI) circuits, often called microelectronic circuits. Such circuits may have over 1 million transistors. This large scale of integration is made possible by advances in semiconductor technologies that allow the manufacture of transistors and wires with dimensions much smaller than 1 micrometer. Raising the scale of circuit integration is advantageous, because increasingly complex functions can be realized on a single integrated circuit, with a corresponding increase in reliability and decrease in overall cost.

There are four stages in the creation of a digital integrated circuit: design, fabrication, testing, and packaging (**Fig. 1**). Design is the refinement of a functional specification into the geometries needed for fabrication. Fabrication means manufacturing semiconductor dies, that is, the unpackaged circuits. Testing means checking for manufacturing defects that may lead to erroneous operation. Working dies are placed into ceramic or plastic packages. Computer-aided-design tools support design and testing, while computer-aided-manufacturing tools support the remaining stages.

Major design tasks. Circuit design can be split into three major tasks: conceptualization and modeling, synthesis and optimization, and validation. Conceptualization consists of casting an idea into a model that captures the function the circuit will perform. Synthesis consists of refining the model from an abstract one to a detailed one with all the features required for fabrication. Validation consists of verifying the consistency of the models used during design, as well as some properties of the original model.

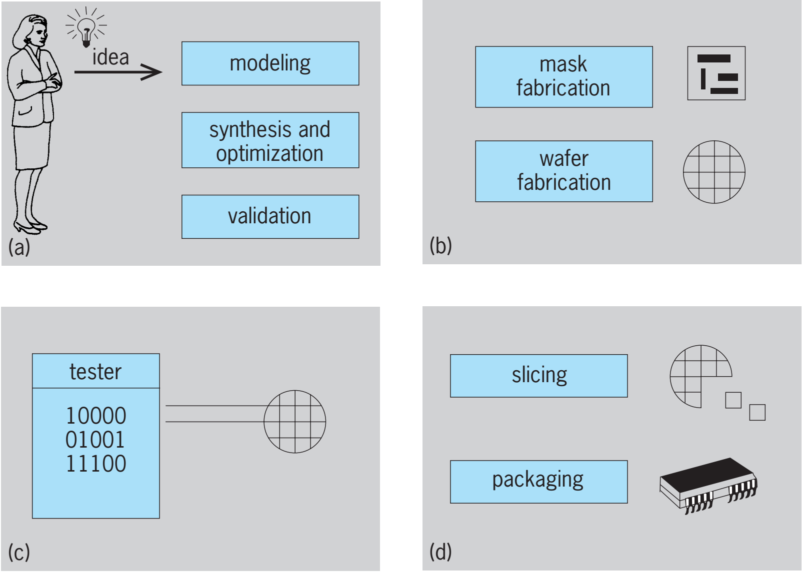


Fig. 1. Four phases in creating a microelectronic chip. (*a*) Design. (*b*) Fabrication. (*c*) Testing. (*d*) Packaging. (*After G. De Micheli, Synthesis and Optimization of Digital Circuits, McGraw-Hill, 1994*)

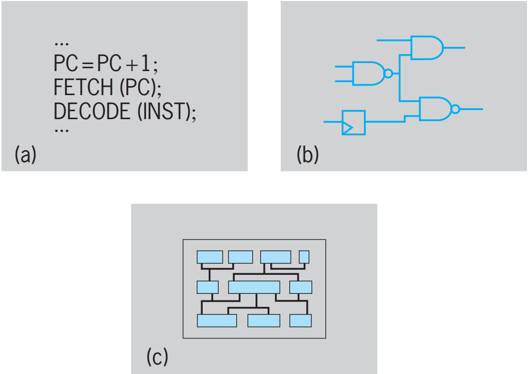
Modeling. Circuit modeling plays a major role in microelectronic design, because it represents the vehicle used to convey information. Modeling must be rigorous as well as general, transparent to the designer, and machine-readable. Most modeling is now done using hardware description languages (HDLs). Graphic models are sometimes used, such as flow and schematic diagrams. The very large scale nature of the problem forces the modeling style, both textual and graphical, to support hierarchy and abstractions, allowing a designer to concentrate on a particular portion of the model at any given time.

Synthesis. The overall goal of circuit synthesis is to generate a detailed model of a circuit, such as a geometric layout, that can be used to fabricate the chip. This objective is achieved through a stepwise refinement process, during which the original abstract model provided by the designer is iteratively detailed. As synthesis proceeds in refining the model, more information is needed regarding the technology and the desired design implementation style. A functional model of a circuit may be fairly independent from the implementation details, while a geometric layout model must incorporate all technology-dependent specifics, such as wire widths.

Circuit synthesis is usually layered in three stages, related to the modeling abstraction level involved: high-level synthesis, logic-level synthesis, and physical design (**Fig. 2**). High-level synthesis, also called architectural-level synthesis, consists of generating the macroscopic structure of a circuit. This activity corresponds to determining an assignment of the circuit functions to operators, called resources, as well as their interconnection and the timing of their execution. Logic-level synthesis is the task of generating the gate-level structure of a circuit. It entails the manipulation of logic specifications to create logic models as interconnections of logic primitives. Logic design is often eased by the use of libraries of logic gates. The task of transforming a logic model into an interconnection of instances of library cells, that is, the back end of logic synthesis, is often referred to as library binding or technology mapping. Physical design consists of creating the geometric layout of the circuit. It entails the specification of all geometric patterns defining the physical layout of the chip, as well as their position on the die.

Circuit optimization is often combined with synthesis. It entails the selection of some particular choices in a given model, with the goal of raising one or more figures of merit of the design. The role of optimization is to enhance the overall quality of the circuit. Most designers equate quality with circuit performance. Performance involves the time required to process some information, as well as the amount of information that can be processed in a given time period. Circuit performance is essential to competitive products in many application domains. Power consumption is an important quality measure for microelectronic circuits to be used for portable applications, where the autonomous operation time depends on the battery capacity and discharge rate. Another measure of circuit quality is the overall circuit area. An objective of circuit design is to minimize the area, for three main reasons: (1) smaller circuits allow more dies to be placed on each wafer, and therefore enable lower manufacturing costs to be achieved; (2) the manufacturing yield decreases with an increase in chip area; and (3) large chips are more expensive to package. The circuit quality also involves the circuit testability, that is, the ease of testing the chip after manufacturing. Testable chips are clearly desirable because earlier detection of malfunctions in electronic systems enables overall costs to be lowered. *See* OPTIMIZATION.

Validation. Circuit validation consists of acquiring a reasonable certainty level that a circuit will function correctly, under the assumption that no manufacturing fault is present. Circuit validation is motivated by the need to remove all possible design errors before proceeding to expensive chip manufacturing. It can be performed by simulation and by verification



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...
PC=PC+1;
FETCH (PC);
DECODE (INST);
...
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Fig. 2. Three abstraction levels of a circuit representation. (*a*) Architectural level. (*b*) Logic level. (*c*) Geometrical level. (*After G. De Micheli, Synthesis and Optimization of Digital Circuits, McGraw-Hill, 1994*)

methods. Digital circuit simulation consists in analyzing the circuit variables over an interval of time for one specific set (or more sets) of input patterns. Simulation can be applied at different levels, corresponding to the model under consideration. Simulated output patterns must then conform to the expected ones. Even though simulation is the most commonly used way of validating circuits, it is often ineffective for large circuits except for detecting major design flaws. Indeed, the number of relevant input pattern sequences needed to analyze a circuit grows with the circuit size, and designers must be satisfied with monitoring a small subset. Verification methods, often called formal verification methods, consist of comparing two circuit models and detecting their consistency. Another facet of circuit verification is checking some properties of a circuit model, such as whether there are deadlock conditions. *See* SIMULATION.

Testing. Microelectronic circuits are tested after manufacturing to screen fabrication errors. Thus, testing is the verification of correct manufacturing. Since impurities are unavoidable in the air of manufacturing plants, particles from the air can cause defects in random positions on some circuits. There are several testing techniques, and their relation to design is important. In particular, circuits may be designed with a self-testing feature. After manufacturing, the circuit can be set in testing mode, where it will generate, apply, and analyze testing patterns to check proper operation.

Design for testability means addressing the ease of testing during the design stage. Circuit testability affects the circuit quality. A circuit that is not fully testable is less valuable than another one that is, because faulty units may be released on the market. Enhancing testability can be done by appropriate logic and architectural synthesis techniques.

Hardware/software codesign. Digital microelectronic circuits may contain complex building blocks, such as processors, controllers, and memories. Processors and controllers may be designed to execute specific programs stored in memory, which are referred to as embedded software. For integrated circuits containing programmable components executing software, hardware/software codesign techniques are needed to exploit the synergism between hardware and software to achieve the design objectives. Computer-aided codesign tools support a variety of tasks, including performance analysis of hardware/software systems, support for deciding on the hardware/software implementation of system functions, and support for developing software compilers that are retargetable to various processor architectures. Giovanni De Micheli

Design of Analog and Radio-Frequency Circuits

To meet the challenges of delivering high performance at low power, and to avoid the high cost of multiple design prototyping, designers of analog and radio-frequency circuits utilize very specialized simulation and extraction tools that equate physical design to electrical performance. Mixed analog, radio-frequency, and digital circuit design needs detailed process-dependent active device and passive interconnect characterization data as well as robust circuit simulation tools to accurately predict proper circuit operation under all operating conditions.

Integrated-circuit design process. The analog-integrated circuit design process may be broken down into four principal areas involving multiple design and design support teams. The first area is dedicated to model development and computer-aided design or electronic design automation (EDA) tool support. Team activity focuses on active device model parameter extraction (usually through measurement on actual devices), passive component model extraction (usually through electromagnetic simulation), and component library development and maintenance, including the implementation of parametrized layout structures or “cells.” A second design area is dedicated to system-level architectural design and block partitioning. At this high level, designers are responsible for meeting overall system requirements (both digital and analog) and specifying the requirements for individual functional blocks or subcircuits. The third principal design activity is devoted to detailed circuit design and to follow-on system integration. This group uses the electrical models and associated layout information provided by the modeling group. The fourth design team is involved in design testing and verification. This area concerns itself with validating the actual hardware, accounting for physical measurements, test fixturing, and electrical packaging. Sophisticated tool infrastructure and model databases are required to tie together the data flowing among these four design teams.

At high frequencies, component material and geometric attributes play a strong role in electrical performance. Therefore, reliable schematic-to-layout modeling is critical to successful design. Sophisticated design environments that provide a user interface for synchronized schematic and layout capture are fully integrated within several modern analog and radio-frequency simulators. Many of these environments also support parameter tuning, optimization, statistical analysis, and result generation.

Behavioral versus circuit models. In early design phases involving definition of the system architecture and block partitioning, a top-down approach using a high-level behavior model representation is common, since behavior model simulation requires much less computational effort than is needed for transistor-level circuit simulation. Computer models for various function blocks, such as low-noise amplifiers, mixers, voltage-controlled oscillators, or in-phase and quadrature demodulators, typically are used to support early system development.

Behavior model parameters will supply performance simulation accuracy to only a second order of parameter analysis and simulation accuracy within the radio-frequency system. Modern systems are complex and behavioral models may not predict the integrated circuit behavior sufficiently accurately under a wide range of specified operating conditions.

Some of the lost critical circuit detail includes the device terminal impedances, bias and temperature dependencies, transient response times, and signal feedback conditions.

Working with more detailed circuit information can overcome these deficiencies, but doing so comes at the cost of increased characterization effort. Proven existing netlist-based circuit models are an alternative to behavioral models, but circuit-level modeling requires a simulator that can analyze circuits containing a very large number of transistors. These simulators also need to contain libraries of commercial components and manufacturer's device models for standard transistors, diodes, resistors, capacitors, and inductors. The simulator also should be able to support cosimulation with functional blocks described by other circuit or behavioral models, and should include utilities to speed the process of transmission-line design, matching network extraction, and filter synthesis for both lumped and distributed radio-frequency designs.

To address characterization of a wide range of on-chip or packaged physical, analog and radio-frequency/microwave circuit designers rely heavily on a variety of electromagnetic simulation technologies. These tools are used to extract electrical behavior from the structure in the form of transmission-line parameters or equivalent SPICE (Simulation Program with Integrated Circuit Emphasis) models. The resulting extracted electrical models are then inserted into the complete network for cosimulation with transistor-level circuits or high-level behavioral models.

Linear circuit simulation. Linear analysis is used to compute the frequency response of passive circuits or circuits which operate under small-signal conditions. In active circuits operating under small signal conditions, signal level and termination values do not influence the operation of circuit components and the superposition principle holds true. Most high-frequency circuit designers rely on linear analysis to develop circuits to (1) match impedances between cascaded components to ensure optimum power transfer, (2) suppress unwanted signal transmission at specific frequencies, and (3) deliver optimum load terminations for active devices.

Linear simulation results are offered in a wide range of representations including scattering, impedance, and admittance (S,Z,Y) network parameters at specific excitation frequencies. For two-port (terminal) networks, linear analysis also can determine stability, voltage and power gain, noise, and matching element parameters. If there are nonlinear devices in the circuit, a bias-point analysis must first be performed, in which case each device is linearized at its bias point, and linear analysis in the frequency domain proceeds.

Extended linear analysis results may include group delay (delay of the propagation of energy at a given frequency), or even steady-state time-domain responses for impulse, step, and modulated pulses, and nodal voltages at internal circuit nodes. In this case the frequency-domain results from linear-network analysis are transformed into the time domain via the fast Fourier transform (FFT), which presents steady-state (periodic) information about network parameters in the time domain. *See* FOURIER SERIES AND TRANSFORMS.

Harmonic balance analysis (HBA). Harmonic balance analysis supports the large-signal simulation of nonlinear devices and is performed using a spectrum of harmonically related frequencies, similar to measured signals on a spectrum analyzer. This analysis type involves the periodic steady-state response of a fixed circuit to a given predetermined set of fundamental tones. This analysis is limited to periodic responses because the basis set chosen to represent the physical signals in the circuit are sinusoids, which are periodic. *See* SPECTRUM ANALYZER.

In harmonic balance, the circuit is usually divided into two subcircuits connected by wires forming multiports. One subcircuit contains the linear components of the circuit and the other contains the nonlinear device models. The linear subcircuit response is calculated in the frequency domain at each harmonic component and is represented by a multiport Y (admittance) matrix. This is the function performed by linear analysis. The nonlinear subcircuit contains the active devices whose models compute the voltages and currents at the intrinsic ports of the device. (Parasitic elements are linear and absorbed by the linear subnetwork.)

For circuits operating under large signal conditions, device nonlinearity will generate harmonically related signals. Analysis parameters, such as the number of harmonics, specify which combinations of these harmonically related signals will be considered and set the fundamental frequencies used in the analysis of the network. Harmonic balance analysis is often used to examine the compression characteristics and spurious output of radio-frequency circuits such as amplifiers, mixers, and frequency converters.

Since harmonic balance analysis supports frequency domain linear models such as transmission lines as well as nonlinear device models such as transistors, it is well suited to simulate high-frequency networks operating under steady-state conditions.

Transient analysis. Many of today's communication devices, however, as a result of fast switching and on/off states, operate under non-steady-state conditions. Transient circuit analysis is required to understand circuit behavior under nonperiodic conditions. Radio designers, for example, often use transient analysis to investigate the transient performance of oscillators and phase-locked-loop synthesizers.

Transient analysis discretizes time and uses numerical integration methods to solve the circuit equations over each time increment. The equations are derived from the circuit interconnections and circuit device models. The analysis begins with vectors of initial values for the node voltages and branch currents. At the beginning of each iteration, the simulator linearizes the circuit around the solution calculated in the previous iteration, and calculates the matrix associated with the linearization point. The simulator then uses a matrix solver to calculate a new vector of unknowns. At the end of each iteration, the analysis updates the solution and checks to see if the new solution satisfies the specified tolerances. If the result is within tolerance, the loop terminates. Otherwise, the loop uses the new result to start the next iteration.

Time-domain simulators have waveform sampling requirements that can lead to excessively long run times for certain applications or that can introduce simulation errors. For a device operating under multitone excitation, a time-domain simulator must have a sample rate twice the highest frequency rate, yet must take enough samples to capture the lowest frequency of interest. High sampling rates continuing for a long sampling period result in a lengthy simulation. Capturing the intermodulation products of a radio-frequency circuit under multitone drive, for example, can require prohibitive simulation run times. It also has been shown that the black-box S-parameter and SPICE models used in these simulators has inadequately modeled high-frequency time-domain effects in a number of cases.

High-frequency passive modeling. One of the most fundamental impairments in a radio-frequency circuit or a high-speed channel is the attenuation of the transmitted signal across the printed circuit board caused by transmission line loss. Printed circuit boards with dielectric substrates composed of FR4 (Flame Retardant 4, a fiber glass-epoxyresin combination that is widely used in printed circuit boards) were not originally intended to support signals at multigigabit speeds, and their dielectric loss is very pronounced at high frequency. Typical microstrip differential transmission lines on FR4 exhibit an insertion loss of roughly 0.5 dB/in. at 5 GHz and 0.9 dB/in. at 10 GHz. This loss effectively performs a low-pass filtering on transmitted radio-frequency or digital signals and hence severely limits the distance that they can propagate on printed circuit board transmission lines.

Passive models for integrated circuit components (spiral inductors, for example) and interconnects (transmission lines, vias, and packages) are having increasing impact on the circuit performance of many high-frequency designs. Circuit designers can employ models for these passive components ranging from simple single lumped elements to rigorous measurement or electromagnetic-based broadband response representations.

Electromagnetic simulation is a cost-effective alternative to physical prototyping and is therefore used throughout the high-frequency modeling community. It is employed to both extract electrical behavior and optimize component performance through optimization. Parametric optimization is often used to reduce the electrical losses associated with silicon-based designs.

Various types of electromagnetic simulation such as finite-element (for full-wave three-dimensional extraction), method of moments (for two-dimensional surface currents), and quasistatic solvers (for lower frequencies) are available to characterize the parasitic effects of transmission media operating at various frequencies. The outputs of these solvers are extracted RLGC (resistance, inductance, conductance, capacitance) models (limited bandwidth), w-elements, or S-parameters. (The w-elements are a set of physical parameters needed for the electromagnetic field analysis of circuit conductors. S-parameters essentially provide the expected broadband transmission and reflection properties of the signal propagating through the given structure.) The outputs are represented by data tables with terminal nodes defining the connection points for input/output signals.

Convolution. Properly addressing linear frequency domain models such as transmission lines and S-parameters in transient time-domain simulations requires a time-domain representation of the linear components or network. One method involves a technique known as convolution.

Direct convolution is a relatively slow mathematical process, even at today's computational speeds. Theoretically, in order for the convolution technique to obtain correct results, the sampling range should be set to infinity. However, this is not practical simulation. A finite sampling range will also lead to excessive computation times. For example, if convolution analysis will calculate the spectral components of the impulse response to be at a bandwidth of 0–200 GHz with a resolution of 100 MHz, the number of frequency sampling points is 2000 and the number of time sampling points is 4000 (0–10 ns with a step of 2.5 ps).

Therefore, an alternate method that does not have the computational burden of direct convolution is desired. Such an alternative mathematical method must still recognize the physical behavior of the frequency-dependent losses that the simulator is attempting to model. One option is to select a "state space" representation for the frequency-dependent model in the time domain, in which a set of rational polynomial functions in the time domain provide a least-squares fit to the frequency-domain behavior after a Fourier transform. Thus, performance of the transient simulation does not call upon convolution. The same technique can be applied for obtaining a usable model from frequency-dependent S-parameter inputs, to avoid demanding convolution during the transient simulation to follow.

One challenge for representing frequency-based models in the time domain is preserving causality. Causality requires that "effects" happen after "causes," which means the impulse response for time $t < 0$ must be zero. Beyond proper handling of losses to conform to causality, a state-space conversion of a transmission-line model can become just as numerically intense as direct convolution if not handled properly. For instance, a given transmission-line model might contain a large number of signal conductors to account for the behavior of each line and the crosstalk between them. Computing state-space models for such transmission matrices without extracting out consistent behavior between like terms would be exceedingly wasteful. This means first capturing the modal delay or propagation delay from the line behavior, before generating the polynomials that represent the loss behavior.

Validation. As the number and complexity of integrated circuit performance metrics continue to proliferate, accurate design verification becomes a greater challenge and is further complicated by the effects of high-density input-output packaging. System metrics such as bit error rate (BER), error vector magnitude (EVM), or intersymbol interference (ISI) must be characterized by exact standards and specifications: Design details of the integrated circuit, the advanced package, or both must now be incorporated in a simulation. For integrated circuit verification, a high-level system test bench environment is often employed to define complex excitations and derive these figures of merit. In such system test benches, complex modulated communication waveforms may be applied directly to the circuit design. Additionally, package effects and test fixture contributions may also be included, either through electromagnetic simulation or direct measurement of existing hardware. David Vye

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Computer-aided design and manufacturing

The application of digital computers in engineering design and production. Computer-aided design (CAD) refers to the use of computers in converting the initial idea for a product into a detailed engineering design. The evolution of a design typically involves the creation of geometric models of the product, which can be manipulated, analyzed, and refined. In CAD, computer models and graphics replace the sketches and engineering drawings traditionally used to visualize products and communicate design information.

Engineers also use computer programs to estimate the performance and cost of design prototypes and to calculate the optimal values for design parameters. These programs supplement and extend traditional hand calculations and physical tests. When combined with CAD, these automated analysis and optimization capabilities are called computer-aided engineering (CAE). *See* COMPUTER-AIDED ENGINEERING; OPTIMIZATION.

Computer-aided manufacturing (CAM) refers to the use of computers in converting engineering designs into finished products. Production requires the creation of process plans and production schedules, which describe how the product will be made, what resources will be required, and when and where these resources will be deployed. Production also requires the control and coordination of the necessary physical processes, materials, equipment, and labor. In CAM, computers assist managers, manufacturing engineers, and production workers by automating many production tasks. Computers are used to develop process plans, order and track materials, and monitor production schedules. They also control the machines, industrial robots, test equipment, and systems that move and store materials in the factory.

Advantages of automation. CAD/CAM can improve productivity, product quality, and profitability. Computers can eliminate redundant design and production tasks; improve the efficiency of workers; increase the utilization of equipment; reduce inventories, waste, and scrap; decrease the time required to design and make a product; and improve the ability of a factory to produce different products. Today most manufacturers employ CAD/CAM to varying degrees. *See* AUTOMATION; PRODUCTIVITY.

Several factors account for the rapid development of CAD/CAM technology since the 1960s. First, advances in computer technology produced faster, more capable, smaller, and less expensive machines. Together with improved techniques for software engineering, this makes CAD/CAM increasingly cost-effective even for small companies. Second, world markets for manufactured goods are more competitive. CAD/CAM has become an essential tool for economic success. Third, the design life cycle of many products has been compressed. New products must be developed quickly and brought to market at high levels of quality, reliability, and safety. *See* SOFTWARE ENGINEERING.

Computer-integrated manufacturing. The deployment of CAD/CAM in the manufacturing industry has led to new ideas about organization and production. Traditionally, manufacturing companies, especially large companies, have been organized into functional units such as marketing, design, engineering, quality, and production. These departments were coordinated by a higher level of management, often without a great deal of direct communication among the units themselves.

The fact that CAD, CAE, and CAM work best together has led to the breakdown of many of the traditional barriers between functional and manufacturing units. The goal of computer-integrated manufacturing (CIM) is a database, created and maintained on a factory-wide computer network, that will be used for design, analysis, optimization, process planning, production scheduling, robot programming, materials handling, inventory control, maintenance, quality assurance and control, and marketing. Although many technical and managerial obstacles must be overcome, computer-integrated manufacturing appears to be the future of CAD/CAM. *See* COMPUTER-INTEGRATED MANUFACTURING; DATABASE MANAGEMENT SYSTEM.

Developing disciplines in CAD/CAM integration include concurrent engineering, design for manufacture and assembly (DFM/A), and factory modeling. In concurrent engineering, interdisciplinary product development teams consider all phases of a product life cycle during the design process. DFM/A software allows a design team to assess the effort and costs involved in the production of a part or assembly and to consider ways to redesign the product for ease of production. Discrete event simulation programs have been developed to model and optimize the processes, equipment, and layout of the factories in which the design will be produced. *See* SIMULATION.

CAD technology. Initially, CAD workstations were terminals connected to a mainframe computer. They allowed graphic displays of the product model and included devices (mouse, joystick, trackball, light pen, and stylus and tablet) for interacting with both the model and its display. Today a CAD workstation can be a personal computer or a graphics workstation (**Fig. 1**), and may be stand-alone or a link on a network. Large machines (mainframes or supercomputers) are often necessary for creating, manipulating, and analyzing complex models and assemblies. Raster graphics (cathode-ray tubes) permit displays of models in full color, immediate updates as the model is changed, sophisticated rendering, and even animation. Interactive devices include the mouse and keyboard, but for manipulating a three-dimensional (3D) model in all its degrees of freedom, a spaceball or other 3D input device is helpful. Virtual reality and gaming environments have led to useful 3D interactive devices (such as data gloves, body suits, control sticks, and steering wheels). Output devices, such as printers, plotters, and various media and storage devices, can also be linked to the computer. *See* COMPUTER PERIPHERAL DEVICES; MICROCOMPUTER; SUPERCOMPUTER; VIRTUAL REALITY.

The CAD system allows the designer to create a geometric model of the product design, display different views of the model, modify it as desired, save different models in a database for later recall, and make printed copies of design notes, engineering drawings, and rendered images as needed.

The appropriate computer model depends on the type of product. In the design of printed wiring assemblies, for example, two-dimensional models are used to lay out circuits and electronic components on the face of a circuit board. In mechanical and civil engineering design, three-dimensional, geometric models represent parts, devices, assemblies, and structures.

Several types of geometric models are possible, including solid models, wire-frame (line) drawings, and surface representations, such as planes, patches, or sculptured drawings. Solids modeling is the basis for most current CAD systems, because the information in the model database represents a distinct solid object, completely and unambiguously. There are several modeling schemes for producing complete solid models: boundary representation (b-rep), constructive solid geometry (CSG), cell decomposition, spatial enumeration (octrees), and primitive instancing. Boundary representations define an object in terms of its bounding faces, edges, and vertices, and their relationships. Constructive solid geometry builds complicated solid models by adding or subtracting simpler geometric shapes (cubes, slabs, cylinders, spheres, and cones), called primitives. In cell decomposition, a solid model is composed of a collection of nonoverlapping geometric entities called hyperpatches. Spatial enumeration maps an object into a defined spatial grid and represents whether elements in the grid are filled or empty. Primitive instancing involves parametrized shapes that can be transformed into particular instances. Most commercially available CAD systems are based on boundary representation and constructive solid geometry schemes. Newer solid modelers incorporate design by features, parametric and variational modeling, and constraint-based systems.

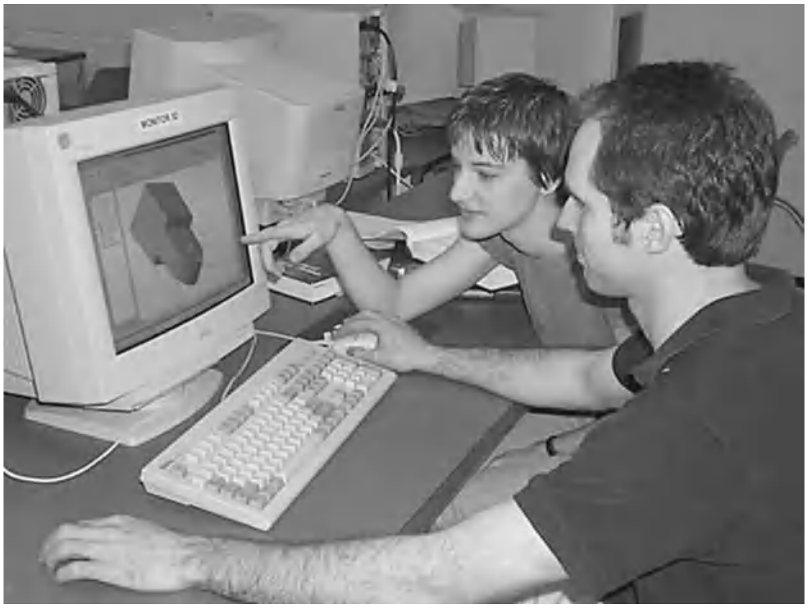
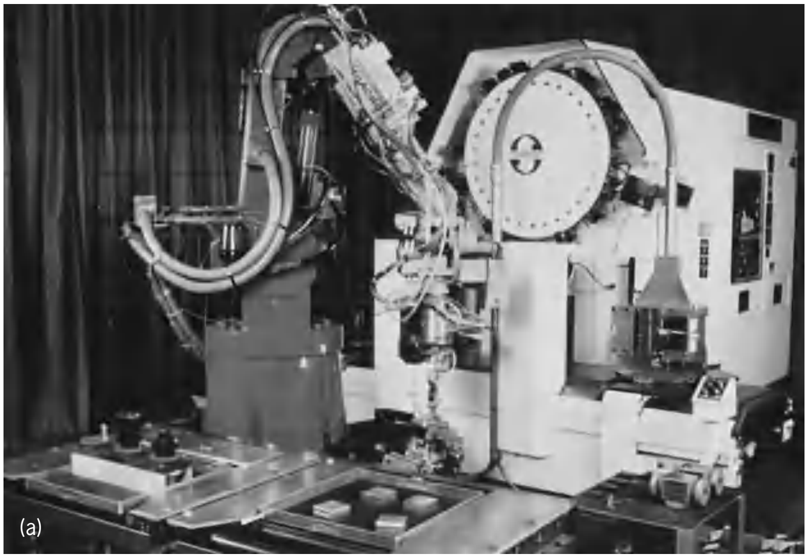


Fig. 1. Computer-aided design workstation where the designer creates and refines a geometric model of a product. (*Center for Computer-Aided Engineering*, *University of Virginia*)

Many CAD systems are still used as electronic drafting devices. Although this has many time- and labor-saving advantages, the true benefits of CAD arise from 3D modeling systems. In the traditional drafting environment, several views of a single object must be drawn to capture its geometry, whereas with 3D CAD a single solid model is created from which any particular view can be derived automatically. As the design evolves, each change does not require an entirely new model. In the future, as CAD, CAE, and CAM are integrated in CIM, the CAD model will become part of a common database for the entire design and manufacturing cycle. *See* COMPUTER GRAPHICS; DRAFTING; ENGINEERING DRAWING.

Analysis programs. A CAD model can be coupled with various analysis programs to predict the behavior of an object or assembly in its operating environment. Finite element analysis (FEA) determines the internal response of an object to applied loads or forces; computational fluid dynamics (CFD) is concerned with flow analysis and visualization; mechanical dynamics programs simulate the behavior of multibody systems (mechanical assemblies) over time; and ergonomic and human factors models assess how people interact with vehicles, machines, and structures. *See* COMPUTATIONAL FLUID DYNAMICS; FINITE ELEMENT METHOD; HUMAN-FACTORS ENGINEERING.



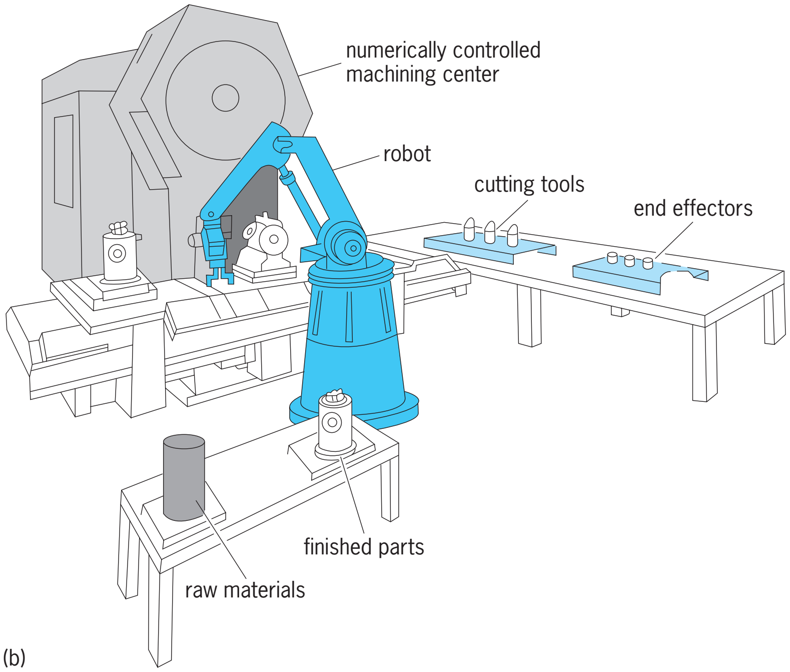


Fig. 2. Horizontal machining workstation. (*a*) Workstation with an industrial robot that loads and unloads parts processed on a numerically controlled machining center. (*b*) Computer simulation display used to verify the robot and part programs which control the workstation. (*Automated Manufacturing Research Facility*, *National Institute of Standards and Technology*)

CAM and numerically controlled machines. The origin of automated manufacturing predates CAM and is usually associated with the introduction of numerically controlled machine tools in the mid-1950s. Machine tools, such as drills, lathes, saws, and milling machines, are used to cut and shape parts from stock. Numerically controlled machine tools use precoded information to operate the machine, rather than a human machinist.

The precoded information, called a program of instructions, contains a detailed set of directions, in symbolic form, that instructs the machine which operations to perform. The program may be punched on paper tape, recorded on magnetic tape, or manually input to the controller unit by a human operator. The more sophisticated numerically controlled systems used in CAM employ direct numerical control, where the program is transmitted electronically to the controller unit over a direct link with the computer.

The numerical controller unit reads the program, interprets the symbols, and sends the appropriate control signals to servomotors and other physical controls on the machine itself. Various sensors send information back to the controller unit. The purpose of this closed-loop or feedback system is to ensure that the actual process is following the program. Most modern numerical control systems are computer–numerically controlled, and the control unit is based on a microprocessor. Microprocessors are also used to monitor and control other types of equipment and processes. The microprocessor control units are called programmable controllers. *See* MICROPROCESSOR; PROGRAMMABLE CONTROLLERS.

Machining centers and cells. Numerically controlled machines vary in complexity from simple, open-loop, tape-controlled drill presses to versatile, multifunction machining centers. A horizontal numerical control machining center is shown in **Fig. 2**, as one component of a still more complex and versatile group of automated machines called a machining workstation or cell. The machining center can perform a variety of functions, such as drilling, boring, reaming, tapping, and milling. The tools required for these operations are stored in a circular tool drum. When the controller calls for a new tool, an automated tool changer removes the current tool from the spindle chuck and returns it to the drum. The drum rotates the new tool to the position in front of the changer, and the changer inserts the new tool in the chuck. The machining center also controls the position and orientation of the part being made, so that it can be machined on all sides.

Automated part programming. Preparing numerically controlled programs is called part programming. Manual part programming is tedious and difficult, because the programmer must calculate and record a long list of the relative positions of tools and parts for each movement along the tool path. Computer-assisted part programming simplifies this task. The

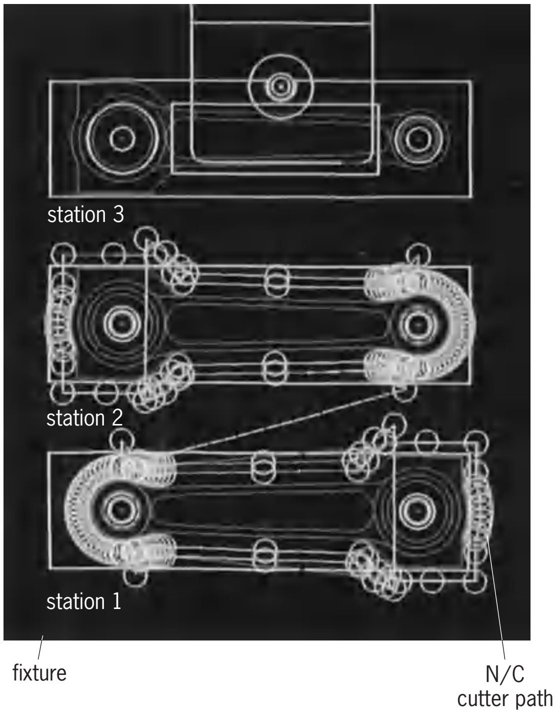


Fig. 3. Computer-aided design and manufacturing display on a system that allows the part programmer to create a cutter location file and preview the cutter path before machining. (*Control Data Corp.*)

programmer specifies the part geometry and machining information (tool sizes, speed, feed rates, and tolerances) in a high-level programming language. The module creates the part program. **Figure 3** shows the display of a numerically controlled machine tool creating a part program for a connecting rod; **Fig. 4** shows this rod being cut out of stock. Automation significantly reduces the time required for part programming and program verification, especially for complex parts with many machining steps. In integrated CAD/CAM systems, the part geometry is specified in the CAD database and does not need to be reentered during programming.

Advances in manufacturing. The development of CAD software for creating true solid models caused designers and manufacturing engineers to think about product models in new ways. They now recognize three approaches to the production of parts: subtractive, additive, and net shape production. Traditional manufacturing relies largely on processes that shape and remove material. Parts are created by subtracting material from stock. Rapid prototyping involves a set of manufacturing techniques based on additive processes; the techniques build up to the desired shape. Several distinct rapid prototyping methods have been developed into commercial systems, including stereolithography (**Fig. 5***a*), selective laser sintering, laminated object manufacturing, ballistic particle manufacturing, fused deposition modeling, (Fig. 5*b*), and 3D printing (Fig. 5*c*). These systems create physical models of parts directly from a CAD database. Such models (prototypes) may be used for presentation, communication, and understanding; as masters for the production of secondary tooling; or for making actual production-quality parts.

The first rapid prototyping system was developed in 1986. The stereolithography apparatus (Fig. 5*a*) uses a CAD driven laser beam to draw individual layers of a part by transforming liquid polymer into solid material using ultraviolet light. It defines the industry standard for rapid prototyping.

Net shape manufacturing techniques produce engineering materials to finish or near-finish dimensions from the start. Working from the CAD model, the goal is to produce a part as close as possible to the final version on the first pass. A variety of fabrication techniques are available: melt processing, shaping from powder, and forming from sheets or billets. Net shape production conserves resources and can reduce costs.

Robotics. Industrial robots are general-purpose, programmable manipulators that perform a variety of production tasks. Robots can move material, load and unload parts on other machines, assemble components, spray paint, and spot-weld. The first industrial robot was installed in a United States automotive diecasting facility in 1961. Figure 2 shows a type of robot that loads and unloads parts and changes tools in a tool drum at a machining center. To spare humans the tasks, robots can do unpleasant, boring, fatiguing, or dangerous jobs, such as working in areas contaminated by fumes, acid, or radiation.

Robots can be reprogrammed for different tasks as needed. In walk-through and lead-through training, the robot arm and end effector (hand or specialized tool) are moved through the desired sequence, and that sequence is recorded in the robot's memory. With a more sophisticated technique, the robot program is created on an off-line computer using a high-level programming language, and then loaded into the robot memory when needed. This eliminates the loss of production time during robot training, and

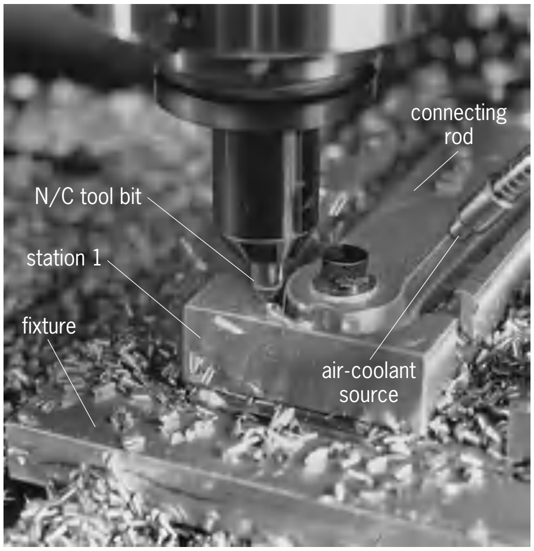


Fig. 4. Numerically controlled machine tool in profiling operation using data from the part program. (*Control Data Corp.*)

Fig. 5. Rapid prototyping systems. (*a*) Stereolithography apparatus, which uses a CAD-driven laser beam to draw individual layers of an object by transforming a photosensitive epoxy plastic into a solid material (*3D Systems*). (*b*) Fused deposition modeling system, which extrudes thermoplastic material from a temperature-controlled head to produce a physical 3D prototype of the CAD model displayed on the graphics monitor (*Stratasys, Inc.*). (*c*) Thermojet 3D printer, whose jets spray a thermoplastic material that builds up in layers to create an object (*3D Systems*).

allows a repertoire of programs to be stored and used interchangeably.

Robots also can be equipped with humanlike senses (vision, touch, and hearing) to perform more complicated tasks. For example, a video camera and a computer equipped with image-processing hardware and software are used for robot vision. This allows the robot to discern objects in the camera field and recognize the position and orientation of familiar objects. In this way the robot can retrieve randomly oriented parts, recognize specific parts in the presence of other objects, perform visual inspections, and assemble products requiring precise alignment. Similarly, touch, force (stress), and proximity sensors let the robot sense contact with another object, gage and control the force of contact (for example, its grip strength), and sense the presence of nearby objects it has not touched. *See* COMPUTER VISION; ROBOTICS.

Automated materials handling. Materials handling refers to the movement, storage, retrieval, and tracking of raw materials, work in process, and completed products. Conveyor belts, hand trucks, fork lifts, and cranes are familiar equipment used to move materials. Shelves, bins, pallets, and silos are used for storage. Inventory sheets, traveler cards, parts lists, and fixed storage locations aid in tracking and retrieving materials.

In CAM, the goal is to automate all materials handling under computer control. Mobile robots, called automated guided vehicles, follow routes on the factory floor defined by wires or tape. Combined with automated pickup and delivery stands, automated guided vehicles move bins or trays of material without human intervention. A typical automated storage and retrieval system uses conveyors and lifts to move bins into and out of specialized inventory shelving. The computer automatically assigns entering bins to empty shelf locations, recording the bin number and shelf location for future retrieval. The bins are labeled with bar codes and can be identified automatically by optical scanners. Large-scale software systems, such as manufacturing resource planning, assist managers in determining what raw materials and components will be required during the current production period. These systems also help the managers to decide when materials and components must be ordered or manufactured to maintain production schedules. *See* MATERIALS HANDLING.

Flexible manufacturing systems. Flexible manufacturing systems are a form of computer-integrated manufacturing used to make small to moderate-sized batches of parts. A typical flexible manufacturing system comprises a cluster of numerical control machine tools, served by an automated materials-handling system and controlled by a central computer. A typical flexible manufacturing system can make from 4 to 100 different kinds of parts in volumes of 40–2000 parts per year, all with minimal human intervention. Such a system is efficient because it is highly automated and requires little downtime for changeovers for making batches of different parts. The flexible manufacturing system is in contrast to the familiar assembly line, which depends for its efficiency on making a single product in very large numbers. *See* FLEXIBLE MANUFACTURING SYSTEM.

Globally distributed manufacturing. With the evolution of the Internet and the World Wide Web, globally distributed manufacturing is possible. Virtual corporations can be established involving participants from around the world. Design, production, and assembly can occur wherever is most convenient and cost-effective for the enterprise. Developments in CAD/CAM, including advances in product data models and international standards, have made this possible. *See* COMPUTER PROGRAMMING; DIGITAL COMPUTER; ENGINEERING DESIGN; INTERNET; WORLD WIDE WEB.

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Computer-aided engineering

Any use of computer software to solve engineering problems. With the improvement of graphics displays, engineering workstations, and graphics standards, computer-aided engineering (CAE) has come to mean the computer solution of engineering problems with the assistance of interactive computer graphics. *See* COMPUTER GRAPHICS.

CAE software is used on various types of computers, such as mainframes and superminis, grid-based computers, engineering workstations, and even personal computers. The choice of a computer system is frequently dictated by the computing power required for the CAE application or the desired level and speed of graphics interaction. The trend is toward more use of engineering workstations. *See* DIGITAL COMPUTER; MICROCOMPUTER.

Design engineers use a variety of CAE tools, including large, general-purpose commercial programs and many specialized programs written in-house or elsewhere in the industry. Solution of a single engineering problem frequently requires the application of several CAE tools. *See* ENGINEERING DESIGN.

A typical CAE program is made up of a number of mathematical models encoded by algorithms written in a programming language. The natural phenomena being analyzed are represented by an engineering model. The physical configuration is described by a geometric model. The results, together with the geometry, are made visible via a user interface on the display device and a rendering model (graphics image). *See* ALGORITHM; COMPUTER PROGRAMMING; MODEL THEORY; PROGRAMMING LANGUAGES.

CAE allows for many more iterations of the analysis-design cycle than was possible by hand computation, especially when the CAE is coupled with optimization systems that drive this cycle automatically. The benefits are translated into improved productivity and quality of design.

Program structure. A CAE program usually consists of a series of mathematical models and a data structure. **Figure 1** illustrates a simplified view of a typical CAE program operating in an engineering workstation environment. First, a mathematical description of the physical phenomena being analyzed is written. This engineering model may consist of equations such as Newton's second law to describe the dynamics of a system or the Navier-Stokes equations to analyze a fluid flow field. Next, a model of the physical configuration is created. This geometric model may consist of two- or three-dimensional (2D or 3D) curves, surfaces, faceted approximations to surfaces, or solid elements. The results of the engineering analysis are frequently displayed on the geometric model by color fringing to show the variation of a scalar parameter. Large amounts of data are created during this modeling phase, and the need for a data structure to store and retrieve them is greater than for the engineering model. *See* DATA STRUCTURE.

Although the engineering and the geometry are fully described, they cannot be viewed on the display until a model for rendering has been formulated and coded. A mathematical description of the lighting conditions, the approximate intensities of

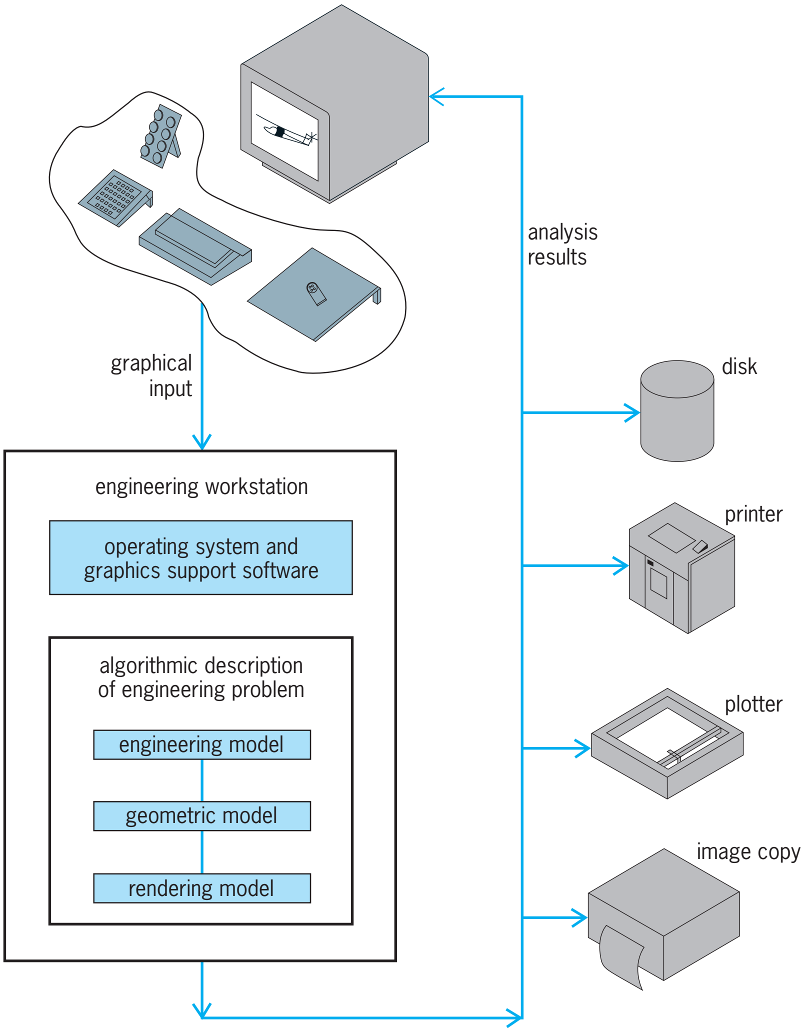

Fig. 1. CAE program in an engineering workstation environment.

light reflected by the nodes of the geometric model, and the corresponding shades of color provide the graphics data necessary for the model to be realistically shaded. Before viewing, the graphics data are transformed from geometric model coordinates to a normalized coordinate system. Parameters are set for an orthographic or perspective projection from 3D model coordinates to 2D coordinates for final transformation to the display screen in device coordinates. The CAE applications programmer accomplishes most of these tasks with the help of precoded algorithms provided by graphics-support software. Interactive communication with the graphics image and the geometric and engineering models occurs through a user interface written with the assistance of the graphics software or windowing software provided with the workstation.

In the past, CAE programs have been predominantly coded in the FORTRAN programming language. The present trend is toward the C, C++, and Java programming languages together with the UNIX and Windows operating systems. *See* OPERATING SYSTEM.

Graphics standards. Portability, the ability to move programs easily from one computer to another, is important for CAE software. Although it has long been possible to make a computational program code portable by using standard programming languages, this was not previously possible for CAE software because of the lack of graphics standards. A proposed 3D graphics standard (CORE), introduced to the American National Standards Institute (ANSI), was superseded by the adoption in 1985 of the 2D Graphical Kernel System (GKS) as an international standard by the International Organization for Standardization (ISO).

A new 3D device-independent graphics standard, the Programmer's Hierarchical Interactive Graphics System (PHIGS), was proposed by ANSI in 1985 and adopted as an international standard by ISO in 1988. Where possible, the concepts and nomenclature of GKS have been used in PHIGS.

The principal limitation to CAE software portability has been the wide variety of graphics hardware and the direct dependence of CAE software on this hardware. Both GKS and PHIGS give the programmer device-independent graphics primitives and coordinate systems as well as a set of logical graphics input devices to replace the wide variety of input hardware. For example, the pick action (selection of a graphics entity on the screen) could be physically accomplished by a light pen, a cursor and tablet, or a mouse. Using graphics standards, the CAE programmer will always specify a logical pick device regardless of the physical device used to achieve the pick.

PHIGS has several important advantages over GKS for CAE software. It is a full 3D system for viewing and modeling transformations, and allows both graphics and nongraphics data to be stored in its data structure. The data structure can invoke other structures and store transformations as attributes. The result is a hierarchical graphics data structure well suited for animation and representation of entities with multiple components. A number of extensions to PHIGS, called PHIGS PLUS (PHIGS+), were adopted as a separate international standard in 1990. PHIGS+ provides support for most of the rendering model and some of the geometric model in a CAE program. PHIGS+ routines address lighting, shading, hidden surface elimination, transparency, nonuniform rational B-spline (NURBS) curves and surfaces, and improved user interaction and control. PHIGS and PHIGS+ were merged into a single international standard, PHIGS, in 1997.

The emergence of PHIGS+ was in response to dramatically improved computer graphics hardware capabilities in the late 1980s and early 1990s, and that were rapidly being incorporated into the new breed of CAE workstations. Vendors did not wait for international committees to address these new capabilities in their standards, but deployed their own proposed extensions in the interim. While this made these new capabilities available to the CAE software developers, it also prevented the CAE software from easily being ported from one hardware platform to another, which is the main purpose of a standard.

Taking advantage of this noncompliance to the adopted international standard and the slow rate at which new technologies and capabilities were addressed by these standards, an industry consortium was established in 1992 to support a new graphics standard known as OpenGL. The aim of OpenGL is to provide a timely integration of new technologies and capabilities as they emerge and to avoid the problem of partial conformance to the standard. GKS, PHIGS, and other standards have been plagued by partially conforming deployments, which makes portability between platforms difficult and defeats a key purpose of standards. The OpenGL Architecture Review Board, which draws its membership from nine leading computer graphics hardware vendors, avoids this problem by permitting only the term OpenGL to be applied to products that conform completely to the OpenGL standard. OpenGL is today the most widely used and supported 2D and 3D graphics application programming interface (API).

Hardware. Computer systems ranging from workstations to mainframe computers are used for CAE software. For example, the aerospace and automotive industries make wide use of very large mainframe computers and large grid-based computer systems to support computer-intensive CAE software such as finite element analysis and computational fluid dynamics. These large computational resources are connected by high-speed data transmission lines to file servers holding the model and resulting data. The precomputation model description and the postcomputation interrogation of the results, and frequently the computations themselves, are usually performed on ultra-high-end workstations capable of managing these vast amounts of data. These workstations are typically 64-bit multiprocessor systems, with 12 to 24 gigabytes (GB) of shared memory

(RAM) and a UNIX operating system, which are connected to the file servers via one or more 1- or 10-gigabit/second network connections. Ultra-high-end workstations are necessary when working with large, complex models and datasets, such as the solid modeling of a complete automobile or aircraft.

For less complex models and datasets, or for subsets of the larger models and datasets, it is typical to use high-end engineering workstations. These workstations are typically 32-bit single- or dual-processor systems with up to 4 GB RAM running a Windows or UNIX operating system, the former being more common. These engineering workstations distinguish themselves from personal computers by having more RAM and faster central processing units (CPU), graphical processing units (GPU), hard disks, network connections, and internal interconnects and data transfer rates. These high-end engineering workstations cost two or three times more than a typical personal computer and are commonly used by engineers. In contrast, ultra-high-end workstations typically cost three to five times more than a high-end engineering workstation, and consequently are less used.

Computer-intensive engineering problems are frequently distributed across multiple CPUs. These CPUs can be connected in a grid structure where each CPU has its own RAM and where communications between these CPUs and their RAM takes place over a computer network. Occasionally these grids are composed of regular personal computers and engineering workstations that are accessed whenever they are idle, such as during nighttime hours. The bottlenecks of such systems are the limited bandwidth between the CPUs and the personnel time required to configure and manage these grids. Grid systems tend to be most successful when the computations can be easily parallelized and when there is minimal need to communicate and move data between the CPUs. Computational problems that do not fall into this category are best performed on large multiprocessor, shared-memory systems with high-speed, high-bandwidth interconnects between the CPUs. Examples of such systems include mainframes and the ultra-high-end workstations described earlier. The advantages of these systems include the flexibility of how data can be accessed simultaneously by multiple CPUs without having to be moved across a network, and the reduced need for manually managing the distribution of the computational resources within the system. *See* MICROPROCESSOR; MULTIACCESS COMPUTER; MULTIPROCESSING; SUPERCOMPUTER.

These large centralized computational resources are often connected to networks of from 10 to 100 client workstations that act as display terminals with local controllers (**Fig. 2**). When a large number of CAE users invoke computer-intensive programs, a significant delay in response usually occurs. For this reason, as well as initial cost considerations, most companies today deploy high-end engineering workstations on a two- or three-year upgrade cycle. Though many small CAE applications programs are written for personal computers, of which most engineering companies have a wide array, most large, commercial CAE programs do not perform effectively or at all on personal computers. Engineering workstations, on the other hand, have the necessary computer power and local resources, and usually run only one CAE program at a time and serve only one user. As a result of this independence, a demanding CAE code at one workstation node in a computer network will not affect the response time for other users. *See* DISTRIBUTED SYSTEMS (COMPUTERS); LOCAL-AREA NETWORKS.

Fig. 2. Solid modeling and simulation on a mainframe via a CAE workstation.

The personal-computer gaming industry has been instrumental to the recent widespread availability of affordable, high-quality graphical processing units that are capable of supporting the heavy demands of CAE graphics processing. These graphical processing units contain a number of specialized high-speed, parallel graphics engines, display list memory, image memory, buffer memory, and alpha memory to permit the real-time generation of color-shaded images desired for CAE applications. The graphics engines perform graphics modeling and viewing transformations, lighting and shading computations, and scan conversion of models for raster-scan display. Display list memory retains the rendering model structure. The z-buffer provides fast hardware support for hidden surface elimination, whereas alpha memory allows fast hardware-assisted transparency computations. The final rasterized image is stored in one of two image memories for fast transmission to the display screen. Most graphical processing units support the OpenGL graphics standard by performing its operations directly in hardware as opposed to computing them in software. *See* COMPUTER ARCHITECTURE.

The graphical processing unit used in a typical personal computer accounts for approximately 2–4% of the personal computer cost. In contrast, in a high-end engineering workstation, the graphical processing unit typically accounts for 20% of the hardware cost. Where ultra-high-end workstations are also used for graphics processing and visualization, it is increasingly common to use multiple high-end graphical processing units working in parallel, with each unit capable of computing 750 million triangles per second or 8 billion pixels per second.

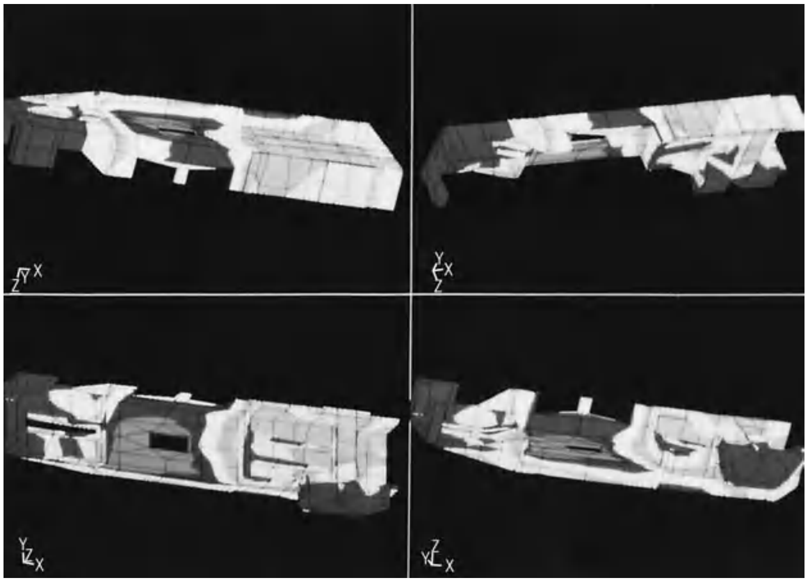

Fig. 3. Finite-element stress analysis using commercial CAE software.

A wide variety of output devices are available for CAE images. The most popular are ink-jet and laser printers for color images and line drawings on paper and Mylar. Others include wall projection and stereovision display systems, often combined with positional and orientation input from the observer. Many types of graphics input devices are available for workstations and mainframe displays. Cursor and tablet, mouse, joystick, ball, glove, function key box, and dial box are the most widely used. Light pens are generally in use on older-technology displays. *See* COMPUTER PERIPHERAL DEVICES.

Commercial CAE software. Most companies use a combination of a few commercial CAE programs and a number of smaller, specialized CAE applications programs typically written in-house or elsewhere in the industry. There are several classes of commercial CAE software. The first large commercial programs used for CAE were dynamic simulation systems, which usually had no graphical output or at best a printer-plotter output of graphs. They required the engineer to give input in the form of ordinary differential equations or building-block elements to describe the dynamic behavior of a real system, in many ways similar to the patching (programming) of analog computers. These systems numerically integrate the set of coupled differential equations, thereby simulating the dynamic behavior of the particular system. Simulation systems are still widely used, and although the graphics output has improved considerably, the description of the input has not changed greatly. *See* ANALOG COMPUTER; NUMERICAL ANALYSIS; SIMULATION.

A need to solve detailed problems, such as stress or deformation analysis, for components of systems led to the development of the finite-element method or finite-element analysis. In this method, a complex object is broken down into simpler elements. With these, a set of equations is formulated which, when solved, predict the behavior of the object as modeled by the set of elements. The modeling of the object is known as finite-element preprocessing, and the validity of the solution is largely dependent on the skill of the modeling engineer. Although very advanced methods of interactive graphics are used in finite-element preprocessing, it is still a very tedious and expensive operation. The solution of the equations is highly computer-intensive. Finite-element methods are applicable for a wide variety of physical phenomena, including mechanical stress and strain, fluid flow, acoustics, heat transfer, and electrical fields. **Figure 3** illustrates the solution of a finite-element stress analysis problem with a commercial CAE code running on a mainframe computer. *See* FINITE ELEMENT METHOD.

Computer-aided design and manufacturing. CAD/CAM systems were created by the aerospace industry in the early 1960s to assist with the massive design and documentation tasks associated with producing airplanes. By the late 1970s, these codes were being distributed to other industries. CAD/CAM systems have been used primarily for detail design and drafting along with the generation of numerical control instructions for manufacturing. Gradually, more CAE functions are being added to CAD/CAM systems. A trend toward open architecture with flexible geometry interfaces is stimulating the addition of more analysis and manufacturing functions. Modeling with CAD/CAM systems has become fairly sophisticated. Most popular commercial systems support 2D and 3D wireframe, surface models, and solid models. Rendered surface models differ from solid models in that the latter have full information about the interior of the object. For solid models, a combination of three types of representation is commonly used: constructive solid geometry, boundary representation, and sweep representation. Complex systems require significant amounts of processing power, primary memory space, and disk space. *See* COMPUTER-AIDED DESIGN AND MANUFACTURING.

Integration of CAE software. Frequently, all of these CAE tools are needed together with specialized CAE applications programs to solve a single engineering problem. The integration of these tools or the communication of data between them is a challenging problem. To successfully integrate these programs, a centralized database is necessary. Data from the various CAE tools are processed into and retrieved from this database through a database management system. If the CAE software is proprietary and the data structure not easily accessible, the proprietary programming interfaces may be used or, sacrificing of functionality and interactivity, a data interchange standard may be used. *See* DATABASE MANAGEMENT SYSTEM.

The Initial Graphics Exchange Specification (IGES) was developed under the leadership of the National Bureau of Standards (today known as the National Institute of Science and Technology) and was accepted as a standard by ANSI in 1981 (Y14.26M-1981). The goal of IGES is to allow the transfer of geometric data between dissimilar CAD systems. IGES is widely available and is generally capable of providing the translation of a snapshot of the model in one CAD system into a static model that cannot be edited in another CAD system.

The standard for exchange of product model data (STEP) has been adopted as an international standard by the International Organization for Standardization (ISO 10303). The aim of STEP is to provide a neutral, computer-interpretable representation and description of product data throughout the life cycle of a product that is independent from any particular system. It can be used for both data exchange and for archiving data over time. The latter is an important issue when the product life cycle exceeds the life span of the software and hardware that created the product data. Given this extremely broad objective, ISO 10303 is not a single standard but a collection of interrelated documents that form a multipart standard. A number of these documents have been adopted as an international standard, while many others are still in development. The **table** lists of some of the documents that have been adopted as part of ISO 10303.

The software industry's support for adopted ISO 10303 documents has been significantly slower than was the case for PHIGS (graphics standards). In the case of STEP, the software vendors have been hesitant to support the standard, both because of the high up-front cost associated with complying with the complexity of the standard, and because of their desire to provide a comprehensive yet proprietary solution for the customer in which the customer's data is locked into. Thus far, it is primarily the large mechanical CAD/CAM/CAE vendors serving the automotive industry that have given into customer pressure and competition to provide support for STEP (AP 203, AP 214). Recently it appears that AP 210 and AP 212 have also started to receive some initial vendor support.

Adopted ISO 10303 documents

Document number	Title
STEP AP 201	Explicit Draughting
STEP AP 202	Associated Draughting
STEP AP 203	Configuration Controlled Design
STEP AP 204	Mechanical Design using Boundary Representation
STEP AP 207	Sheet Metal Die Planning & Design
STEP AP 209	Composite and Metallic Structural Analysis and Related Design
STEP AP 210	Electronic Assembly, Interconnection and Packaging Design
STEP AP 212	Electrotechnical Design and Installation
STEP AP 214	Core Data For Automotive Mechanical Design Processes
STEP AP 215	Ship Arrangement
STEP AP 216	Ship Moulded Forms
STEP AP 218	Ship Structures
STEP AP 224	Process Planning Using Machining Features
STEP AP 225	Building Elements Using Shape Rep
STEP AP 227	Plant Spatial Configuration
STEP AP 232	Technical Data Packaging: Core Info & Exch.

Applications. The CAE methods for electrical and electronics engineering are well developed. The geometry is generally two-dimensional, and the problems are primarily linear or can be linearized with sufficient accuracy. Chemical engineering makes extensive use of CAE with process simulation and control software. The fields of civil, architectural, and construction engineering have CAE interests similar to mechanical CAE with emphasis on structures. Aerospace, mechanical, industrial, and manufacturing engineering all make use of mechanical CAE software together with specialized software.

An example of CAE is the design of an aircraft landing-gear mechanism. The first step is definition of the problem and creation of a set of performance specifications. Next, the conceptual design phase may be aided by specialized programs to determine a size estimate of the landing gear based on specified loads and deflections. Commercial CAE programs are available for kinematic synthesis of mechanisms based on specified motion requirements, but this landing-gear mechanism will be designed with an in-house program written for the purpose. *See* LANDING GEAR.

The next phase is preliminary design. An applications program is used to analyze the deflection and response of a shock-absorbing, energy-dissipating strut. Dynamic analysis of the guiding mechanism and complete assembly is determined by a commercial code. When the dynamic loads are determined, a finite-element stress analysis of each link of the mechanism is done by using commercial finite-element-method software. Following the stress analysis, some links are changed in size and the dynamic analysis repeated to determine new loads. Using the new loading, another iteration of the finite-element-method software is made to verify that the stresses fall below the strength limits.

The next phase is the final design. All components of the assembly are drawn in 2D on a CAD/CAM system and detailed, giving dimensions, material specifications, and other instructions. An assembly drawing is created from the components, and mating of components are verified. An alternative approach is to create a solid model of each component, assemble the solid components, and run an automatic interference-clearance check; 2D drop-offs are then automatically made of each component and manually detailed (at the workstation) by a drafter. From the final part geometry, instructions for numerically controlled machine tools are generated to produce the part. Some systems may support tooling design and process planning. Finally, a design release is made to the manufacturing department.

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Computer architecture

The art or practice of designing computer systems. Just as the architecture of a building describes its overall structural concept and principal features, the architecture of a computer system consists of a description of the overall layout and major features of a computer system. In both cases, we are concerned with how the object, whose architecture we are describing, appears to the user. In computer architecture, the user is not the final user of the system, but the person who writes computer programs to be run on the system. Compared to the architecture of buildings, which is largely an issue of esthetics, the architecture of a computer system is principally about efficiency and economy of operation. There may be an esthetic dimension to computer architecture, but when present it is distinctly lower in importance.

At present, computer architecture is the highest level of the closely related field of computer design. The field has evolved from being the top level of the design process used by the early developers of computers into a separate area of specialization within the overall hierarchy of computer designers and engineers. Underneath computer architecture are the fields of computer organization and implementation, and computer engineering. *See* COMPUTER; DIGITAL COMPUTER.

Computer organization and implementation. Closely related to the field of computer architecture is a subsidiary discipline known as computer organization and implementation. It is difficult to define precisely where computer architecture stops and computer organization and implementation begins. In general, computer architecture is concerned with the principal design parameters, while computer organization and implementation is concerned with the subsidiary points of design of the system, including the composition of the logic circuits that make up each structural component of the system and the implementation of each of those logic circuits as an arrangement of specific electrical circuits of some particular type or types. Computer organization focuses on issues such as whether an adder circuit will be implemented as a ripple-carry adder or as a carry-lookahead adder and whether the underlying electrical circuits will be implemented in TTL (transistor-transistor logic), bipolar transistors, CMOS (complementary metal-oxide semiconductors), or gallium arsenide (GaAs). *See* INTEGRATED CIRCUITS; LOGIC CIRCUITS.

Major issues. There are several major issues in the design of a computer system covering all or nearly all of the architectural considerations. *See* MICROCOMPUTER.

Instruction-set architecture. Traditionally, the instruction-set architecture—the detailed design of the set of machine instructions implemented in the processor—has been the core issue in defining the architecture of a computer system. For example, how many machine instructions will there be, will the instructions be of uniform length or variable in length, and how many fields will the machine instruction contain. *See* MICROPROCESSOR.

Registers. The typical central processor contains several special-purpose registers (storage units), including an instruction register, a program counter or instruction pointer, a processor status register, perhaps one or more separate index registers, segment (base) registers, one or more general-purpose registers to hold integer or fixed-point data (integer registers), and either the same or a distinct set of registers to hold floating-point data. Although integer registers, a single instruction register, and the program counter or instruction pointer have traditionally been of the same width (number of bits), there is no law requiring such. Floating-point registers may or may not be of different width from integer registers. *See* COMPUTER STORAGE TECHNOLOGY.

Native data types. These are the data types that will be separately and distinctly represented and recognized by the computer hardware. Some computers may natively represent and carry out arithmetic on decimal integers via an underlying binary representation. Floating-point representation may or may not be present. *See* NUMBERING SYSTEMS.

Word size. The most commonly encountered number of bits contained in a single word of memory (word width) are 32 and 64. *See* SEMICONDUCTOR MEMORIES.

Memory addressing scheme. There are two principal issues under the topic of memory addressing scheme. The first is the smallest unit of addressable memory, which is usually the byte, although there are several machines of major significance that are not byte-addressable but word-addressable. The second issue is the order in which the bytes are stored for the several bytes that constitute a single word. In the scheme known as big-endian, the leftmost byte (that is, the byte with the numerically smallest address) contains the most-significant bits of the word content, while the byte containing the bits of least significance possesses the numerically highest address. The opposite arrangement is known as little-endian.

Maximum size of memory. A major issue for the modern computer architect is how large the memory address space should be, since memory has been getting cheaper at a prodigious rate. For every doubling of size of the memory address space, the width of an address increases by one bit. Therefore, the designer is not free to increase the memory address space by an arbitrary amount, as every increase in address width has much wider implications for instruction set architecture, as well as imposing requirements affecting lower levels of computer organization and implementation. On the other hand, insufficiency of memory address space has been one of the principal factors causing an architecture to become outmoded.

Number of buses and their relationship. A modern computer typically has a frontside bus and a backside bus, as well as one or more subsidiary busses. The backside bus connects the registers in the central processing unit (CPU) with the main memory and with the various levels of cache memory. The frontside bus constitutes the main conduit between the CPU and peripheral devices, and one or more subsidiary buses interconnect various groups of peripheral devices. Each subsidiary bus is designed to accommodate the needs of peripheral devices within a particular speed range. A simpler and therefore cheaper computer uses a smaller number of subsidiary buses, and each such bus may operate at a lower efficiency while it is communicating with a peripheral device that is considerably slower than the maximum speed that the bus is capable of. *See* COMPUTER PERIPHERAL DEVICES.

Datapath width. This is the number of bits involved in a single transfer of data within or between units within the central processor, such as its internal registers.

CISC versus RISC. Historically, the mainstream of computer architecture was monopolized by complex instruction-set computers (CISC). During the evolution of CISC machines, a lot of the ingenuity of the designer lay in coming up with a larger repertoire of machine instructions, of which the more recently developed tended to be instructions of ever-greater capability and complexity. However, there is a price to pay for the existence of the extra, more powerful instructions. A more elaborate decoding circuitry is required in the central processing unit to interpret these instructions, or there must be a distinctly longer and wider within-processor special-purpose memory to represent the microprograms for all of the instructions contained in the machine's instruction set architecture (ISA).

During the early 1960s, research carried out at IBM suggested that an alternative approach in which the size of the instruction set was actually diminished to a central core of frequently used instructions might be more efficient. In a reduced instruction-set computer (RISC), the area of the processor chip that is saved by omitting either the extra decoding circuitry or the extra length and width of the microprogramming store necessitated by the presence of the omitted more complex instructions is used instead to increase the number of registers. As a result, there are two forms of time savings involved in the execution of the remaining instructions. First, the smaller size and simplified circuitry of the arithmetic logic unit (ALU) enables this component to significantly faster execute the remaining instructions. Second, the presence of a much larger number of registers enables intermediate data to be retained in a register for significantly longer periods of time, reducing both the number of write operations from registers to memory and read operations from memory to registers, compared to the numbers of such operations that must be performed in a CISC processor because of the need temporarily to vacate a register to enable it to do something else. In fact, a great part of the savings in processing time for the RISC processor is due to the substantial reduction in transfers to and from main memory that is occasioned by the much larger number of registers present in the RISC processor. Among the CISC instructions that are omitted in the RISC processor are those that operate directly upon or that write out their results directly to memory. Instead, there are only two instructions provided to accomplish memory transfer operations: a LOAD instruction and a STORE instruction. For this reason, a RISC processor is sometimes referred to as a Load/Store processor. As with any other design decision, a price must be paid performance-wise in exchange for the gain in execution speed. The remaining, "core" instructions that are still present in the RISC processor are executed with a dramatically improved speed. However, the omitted instructions, when they otherwise would have been called for by the source program, must each be emulated by the compiler by means of a series of shorter instructions. As a result, the execution time for one of these instructions omitted from the processor's instruction set will be dramatically longer than it otherwise would have been. For some source code programs, such as those that used very few of the omitted instructions, and those relatively rarely, there will be a net time savings. But for other source code programs, such as those that used relatively heavily and frequently the instructions that have been omitted, the performance will be slower. *See* COMPUTER PROGRAMMING.

RISC remained largely out of the mainstream of computer architecture until the 1990s, when it began to compete seriously with CISC computers. Some of the pioneers in this area include the IBM RS/6000 and the Digital Equipment Corporation Alpha, followed by a number of other products by these and other vendors. Currently, the CISC and RISC streams of processor development have shown some convergence, with microprocessors of predominantly one or the other design incorporating some features previously associated with the other stream.

It should be noted that the earliest supercomputers designed by the famous computer architect and designer Seymour Cray used some of the same principles of design that we know today as RISC. *See* SUPERCOMPUTER.

Pipelining. Pipelining is a design approach to increase the rate of instruction execution. The traditional operation of a computer processor was described as the fetch-execute cycle or more precisely as the fetch-decode-execute cycle. In the first or fetch portion of the cycle, the instruction pointed to by the instruction pointer is copied into the instruction register. Once it has been copied, electronic circuitry within the processor decodes the instruction, that is, determines what sequence of steps must be performed in order to execute the instruction. An example of such a sequence is to (1) copy the contents of memory location A to register temp01, (2) copy the contents of memory location B to register temp02, (3) add the contents of temp01 and temp02 and write the result to register temp02, and

(4) copy the contents of register temp02 to memory location C. Once the sequence of actions has been identified, it must be carried out. This is the execute portion of fetch-decode-execute. In a pipeline machine, these three phases of executing a machine instruction can be done on three or more instructions in parallel. That is, while the first instruction of a sequence of machine instructions is being executed after having first been fetched and decoded, the second instruction, having previously been fetched, is simultaneously undergoing decoding, while the third instruction in the sequence is being fetched. In addition, the execution of a single instruction usually involves several component steps, and therefore a pipeline can be constructed with more than three stages, thus making it possible for more than three instructions to be present simultaneously in the pipeline at various stages of processing. This last technique is known as super-pipelined architecture.

Other techniques for increasing the processing speed. In addition to instruction pipelining, several techniques can be used to increase the processor speed, principally by increasing the extent to which different machine instructions are executed in parallel. These include branch prediction, speculative execution, and superscalar architecture.

Multiprocessor core. In the competition for higher processor speeds, one of the more recent design techniques is to include within the processor more than one core unit capable of carrying out arithmetic-logic operations in parallel. A substantial speedup is possible, even though the presence of other structures within the overall framework of the processor might not allow the various cores each to operate at full speed, making one or more of the processor cores have to wait for some commonly used resource to become available. *See* CONCURRENT PROCESSING; MULTIPROCESSING.

Compiler as adjunct to processor. All of the techniques that are used for increasing the parallelism of instruction execution possess a common restriction on their application; that is, they can succeed in producing an improvement in performance only with the active cooperation of the compiler to define precisely where in the program each of them can be applied. For example, pipelined processing is successful in increasing processor speed only for those parts of the program where the precise order of instruction execution is certain. When it happens, as on occasion it must, that an unexpected branch of program execution must occur, then many of the instructions already in the pipeline, some of which might have already been partially executed, must all be flushed from the pipeline, and the pipeline must be reloaded from the point to which the program has unexpectedly branched. In fact, in some number of instances it might even be necessary for already executed instructions or parts of instructions to be undone. Thus, there are distinct limits to the extent to which parallel processing can be successfully deployed to increase processor throughput. As the degree of parallelism within the processor has increased with the development of more advanced architectural techniques, the role of the compiler in using the additional opportunities for parallelism has become ever more important. Thus, the modern computer architect must be knowledgeable in the design and construction of compilers as well as of computer hardware.

Economics. What drives computer design more than any other factor is economics. It is always possible to make improvements in the design of a computer. But the main factor that architects and designers must consider is the importance of being able to build a machine for a price that will return a reasonable profit in the market for which it is targeted.

Historically significant computer architects. There have been many computer architects of distinction. John Vincent Atanasoff invented the stored-program computer in something akin to its current form. Even so, the computer architecture he originated is often referred to as the "von Neumann" architecture. J. Prosper Eckert and John W. Mauchly were the designers of the electronic integrator and computer (ENIAC) built at Aberdeen, Maryland, in 1946. They also designed the binary automatic computer (BINAC), the first machine to use magnetic tape instead of punched cards; and the first model of the universal automatic computer (UNIVAC), which was the first machine able to handle both characters and numeric information. Seymour Cray was the inventor of an entire genre, the supercomputer, and was certainly one of the most prolific computer architects of all time. Gene M. Amdahl, in addition to having originated the law of computer architecture that bears his name, was the principal architect for the IBM Series 360 series of mainframes, which to date is the longest-lived computer architecture. The first machines of this series were introduced in 1963, were extended to become the System 370 and the System 390, and are still being produced. Gordon Bell was the principal architect of many members of the PDP series at Digital Equipment Corporation and oversaw the development of its VAX series of machines.

Charles Abzug

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Computer-based systems

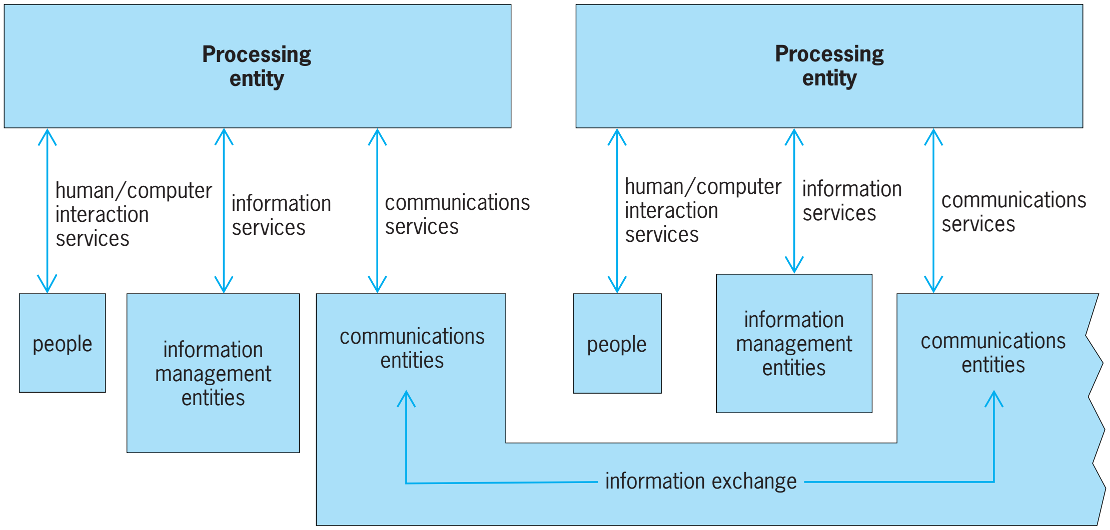
Complex systems in which computers play a major role. While complex physical systems and sophisticated software systems can help people to lead healthier and more enjoyable lives, reliance on these systems can also result in loss of money, time, and life when these systems fail. Much of the complexity of these systems is due to integration of information technology into physical and human activities. Such integration dramatically increases the interdependencies among components, people, and processes, and generates complex dynamics not taken into account in systems of previous generations. Engineers with detailed understanding of the application domain and computer electronics, software, human factors, and communication are needed to provide a holistic approach to system development so that disasters do not occur.

Complex computer-based systems can contain distributed processing and databases, internal communication systems, heterogeneous processing components, and sophisticated human-machine interfaces. Processing components by themselves can constitute a system, or they may be embedded in a physical system such as an automobile, aircraft, or medical diagnostic system. Both the encompassing system and the processing system are known as computer-based systems. *See* DISTRIBUTED SYSTEMS (COMPUTERS); EMBEDDED SYSTEMS; HUMAN-COMPUTER INTERACTION.

Such systems are normally built by people from diverse disciplines. Each discipline uses terminology, problem structuring, and techniques specific to its field, which prevents information from being shared, increases integration difficulties, and makes interdisciplinary optimization extremely difficult. The lack of communication and interdisciplinary understanding makes it more difficult to keep the parts and interfaces consistent, and to analyze system-level aspects such as security, performance, and safety. In real-time systems, meeting performance requirements is as important as meeting functional requirements. Delayed timing can cause catastrophic results in control systems such as digital flight systems or nuclear power plants.

Engineering activities. The computer-based systems engineer develops a system within a system; the properties of the former have pervasive effects throughout the larger system. The computer-based system consists of all components necessary to capture, process, transfer, store, display, and manage information. Components include software, processors, networks, buses, firmware, application-specific integrated circuits, storage devices, and humans (who also process information). Embedded computer-based systems interact with the physical environment through sensors and actuators, and also interact with external computer-based systems (see **illus.**). The computer-based systems engineer must have a thorough understanding of the system in which the computer-based system is embedded, for example an automobile, medical diagnostic system, or stock exchange.

Computer-based systems engineering is analogous to traditional systems engineering, but the focus and necessary skills are different. To better understand the differences, it is useful to look at how these disciplines work together to develop a sophisticated vehicle. The systems engineer has primary responsibility for specifying and allocating requirements for the vehicle. The computer-based systems engineer works with the systems engineer on system-level requirements that relate to the distributed processing system. One such requirement is "the vehicle operator shall be able to navigate." The systems engineer and the computer-based systems engineer make decisions concerning the system boundary; for example, they decide which navigation functions the system automates and which navigation functions the vehicle operator performs. They also make design decisions; for example, they might decide that the system will include maps and that a global positioning system will provide location coordinates. To architect the



Model of a distributed computer-based system.

computer-based system, the computer-based systems engineer must understand the global positioning system and how the operator will use it, together with the maps, to navigate the vehicle.

The computer-based systems engineer must also determine what is done in software, hardware, and firmware, and make decisions with respect to resources and allocation. These decisions determine the types of processors, communication links, and storage devices that are needed, such as a signal processor for processing data from the proximity sensor and a CD-ROM (compact disk–read-only memory) for storing the map database. Based on dependability needs, the computer-based systems engineer chooses fault tolerance features such as dual buses, standby processors, fault-tolerant operating systems, and software recovery blocks. The computer-based systems engineer also optimizes both the number of standard parts in the computer-based system (commonality) and the system's affordability. Standard software and hardware parts and standard interfaces reduce development and maintenance costs. *See* FAULT-TOLERANT SYSTEMS.

After considering various trade-offs, including those involving processing allocation, the systems engineer and computer-based systems engineer define the subsystems and interfaces. Interfaces should be minimal for ease of change and good maintainability. Software engineers work with computer-based systems engineers to define software requirements and allocate them to processing resources. In the example, some software will be allocated to the signal processor, and other software will be allocated to data processors. Such allocation decisions can be difficult to make and can seriously affect performance. Tools that simulate software functionality running dynamically on different hardware configurations support these trade-offs. *See* SOFTWARE ENGINEERING; SYSTEMS ENGINEERING.

Model-based development. Models are necessary in systems engineering as they support interdisciplinary communication, formalize system definition, improve analysis of trade-offs and decision making, and support optimization and integration. The use of models can reduce the number of errors in the design and thus the system, reduce engineering effort, and preserve knowledge for future efforts. Maintaining models with up-to-date knowledge is a major problem as most systems are not generated from models, although this should be an industry goal. During the later stages of system development and testing, significant schedule pressure makes it difficult to keep the models and manually developed software consistent.

Model types are numerous, and include domain models, process models, data models, system dynamics models, dependability models, and communication models. Integrating diverse models is a major issue in systems engineering science. The Unified Modeling Language (UML) attempts to address this problem. This language is object-oriented and integrates scenario models, state models, and information models. Scenario models describe interactions between the system and its environment, including people who use the system. State models describe system dynamics, changes that occur in the system because of events that occur externally or internally. Information models define the data in the system. *See* OBJECT-ORIENTED PROGRAMMING.

Integrated design environments support tool integration, and are a necessity for integrating the tools that support diverse models. Although integrated design environments are in their infancy, standards such as Computer-Aided Systems and Software Engineering Data Interchange Format (CDIF) are contributing to their development. Stephanie M. White

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Computer graphics

A branch of computer science that deals with the theory and techniques of computer image synthesis. Computers produce images by analyzing a collection of dots, or pixels (picture elements). Computer graphics is a mature discipline with a growing range of applications. It is used to enhance the transfer and understanding of information in science, engineering, medicine, education, and business by facilitating the generation, production, and display of synthetic images of natural objects with authentic realism almost indistinguishable from photographs. Computer graphics facilitates the production of images that range in complexity from simple line drawings to three-dimensional reconstructions of data obtained from computerized axial tomography (CAT) scans in medical applications. Images of three-dimensional anatomical surfaces can be constructed from the two-dimensional slices generated by computerized tomography or magnetic resonance imaging. These images help physicians to understand the complex anatomy present in the slices, and to evaluate and plan the treatment and even surgery of complex anatomical abnormalities (**Fig. 1**). *See* COMPUTERIZED TOMOGRAPHY; MEDICAL IMAGING.

Scientific data visualization combines computer graphics and data analysis techniques to allow visualization and analysis of large data sets in scientific and engineering computations and thus offer insights that would be difficult or impossible to extract from numerical results. The creation and interaction that is afforded by computer graphics has become an indispensable tool in automobile, aircraft, and architectural design. New products can be simulated from conception to testing, thereby bypassing several steps and weeks of the traditional design and test cycle. Molecular modeling (**Fig. 2**) and user interaction facilitates and speeds the design of new drugs.

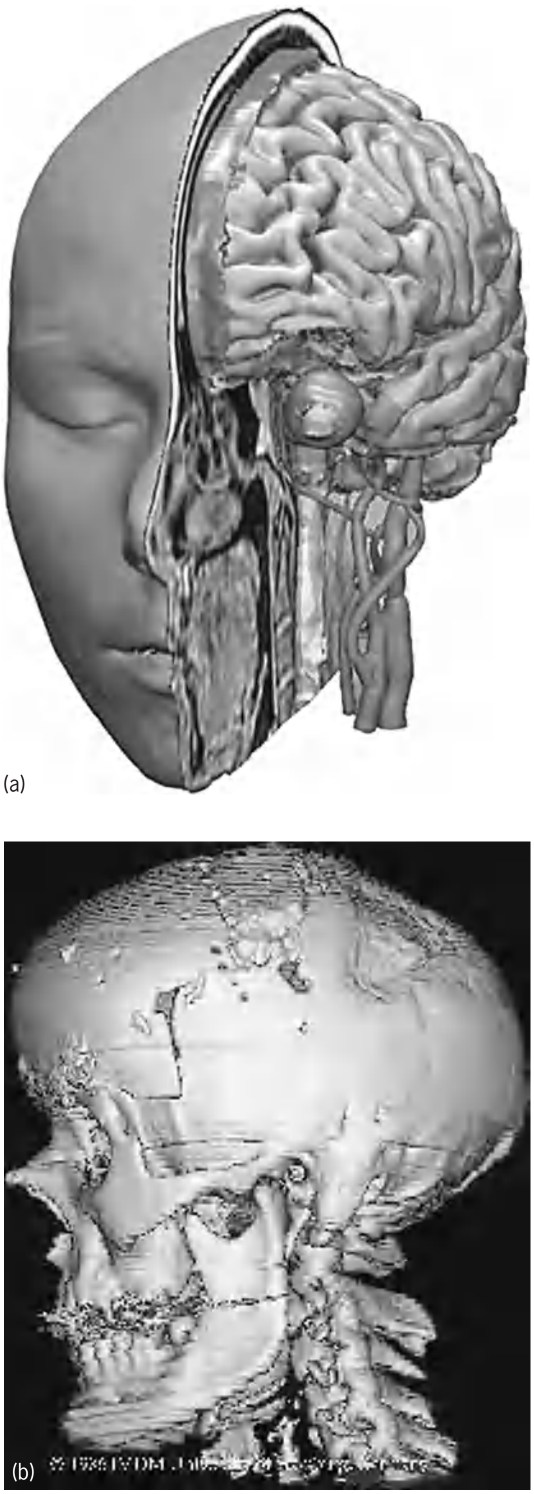

Fig. 1. Volume visualizations of medical image data from computerized tomography and magnetic resonance imaging. Such anatomical images of living subjects are used to create interactive atlases. (*a*) Visualization of brain and skull utilizing the VOXEL-MAN system. (*b*) Post-operative computerized tomography study. (*IMDM, University of Hamburg*)

User interaction can be increased through animation, which conveys large amounts of information by seemingly bringing to life multiple related images. Animation is widely used in entertainment, education, industry, flight simulators, scientific research, and heads-up displays (devices which allow users to interact with a virtual world). Virtual-reality applications permit users to interact with a three-dimensional world, for example, by "grabbing" objects and manipulating objects in the world.

Digital image processing is a companion field to computer graphics, which also deals with images. However, image processing, unlike computer graphics, generally begins with some image in image space, and performs operations on the components (pixels) to produce new images that exhibit some desired feature. *See* IMAGE PROCESSING.

Image presentation and display hardware. Computers are equipped with special hardware to display images. Several types of image presentation or output devices convert digitally represented images into visually perceptible pictures. They include pen-and-ink plotters, dot-matrix plotters, electrostatic or laser-printer plotters, storage tubes, liquid-crystal displays (LCDs), active matrix panels, plasma panels, and cathode-ray-tube (CRT) displays. Images can be displayed by a computer on a cathode-ray tube in two different ways: raster scan and random (vector) scan. *See* CATHODE-RAY TUBE; COMPUTER PERIPHERAL DEVICES.

Liquid-crystal and plasma displays. Liquid-crystal and plasma panel displays are frequently employed in laptop computers. Plasma panels comprise an array of tiny neon bulbs which emit orange light ("in the on" or "intensified" state) under an applied voltage. It remains in this state until it is changed, and thus does not need to be refreshed. Plasma panels typically have about 50–125 cells per inch (20–50 per centimeter) and employ raster technology. The screens are flat, flicker-free, and rugged, making them ideal for military and industrial applications.

A liquid-crystal display is made up of six layers sandwiched together to form a thin panel. The front layer is a vertical polarizer plate. Next is a layer with thin vertical grid wires electrodeposited on the surface adjoining the crystal. This is followed by the thin liquid-crystal layer, a layer of horizontal grid wires, and a horizontal polarizer. The final layer is a reflective layer.

Active matrix panels are liquid-crystal-display panels that have transistors at each grid point. The transistors are used to make the crystals change their state quickly and to control the degree to which the state has been changed. These properties make active-matrix panels attractive display devices for miniature television sets with continuous-tone images. The crystal can also be dyed to provide color. *See* FLAT-PANEL DISPLAY DEVICE; LIQUID CRYSTALS.

Fig. 2. Arrangements of hydrophobic and hydrophilic atoms which give rise to distinctive properties of living cells. Hydrophobic carbon atoms are white; hydrophilic atoms are various shades of gray. (*a*) Plant enzyme dihydrofolate reductase. (*b*) Double strand of deoxyribonucleic acid (DNA). (*From D. S. Goodsell, Machinery of Life, Springer-Verlag, 1993*)

Vector displays. In the 1960s, random scan (vector) displays became a popular technique for generating graphics on a screen without using large amounts of computer memory. Vector images are specified as a series of lines maintained in a list. The lines are specified by the coordinates of their end points. These are stored in a display buffer, a contiguous memory containing all of the information required to draw the picture on a cathode-ray-tube screen. The computer cycles through the list, redrawing each line 30 times a second to maintain a flicker-free picture on the screen. One drawback of most random scan displays is that they do not allow for patterned shading except when it is defined as a series of lines.

Raster-scan displays. The most common display for raster scan images is the cathode-ray tube. The raster scan is very similar to a television set. The beam in this system traces a regular pattern on the screen. It usually starts at the upper left corner of the screen and is directed across the screen in the horizontal direction. After completing one pass across the screen, it moves down and traces the next line. Each line is referred to as a scan line. Images are composed of continuous shaded rows and columns of discrete pixels. Thus horizontal and vertical line segments are represented as a group of adjacent pixels in a row or column. The area of computer graphics that is responsible for converting a continuous figure such as a line segment into its discrete representation is called scan conversion.

Raster-scan systems normally refresh the entire screen with the display pattern 30–60 times a second, recreating a pattern that is stored as a bit map in a special high-speed video memory. Every pixel in the display corresponds to one or more bits of memory. The total number of pixels in an image is a function of the size of the image and the number of pixels per unit length; the latter number is referred to as the resolution of the image. A 2 by 1 in. (5 by 2.5 cm) image at a resolution of 300 pixels per inch (120 pixels per centimeter) would have a total of 180,000 pixels.

The quality of an image is determined by its spatial and contrast resolution. The spatial resolution (sharpness) is determined by the number of rows and columns of pixels. For example, a high-resolution image might consist of about 1000 by 1000 pixels. The contrast resolution is the number of different shades of gray in a monochromatic display or the number of possible colors in a color display. The control over the intensity or color of each pixel is obtained by storing multiple bits for each pixel. For example, three bits will yield eight intensity levels. These bits are then used to control not only intensity but color. Higher-resolution images require more data to represent the image and more solid-state memory to store the image. For color images, three times as many bits are needed, one for each of the three additive primary colors from which the image is made; for example, 8 bits for each of the colors red, blue, and green (yield a total of 24 bits in a so-called full-color system. Systems with 24 bits per pixel of color provide for up to 2^{24} or 16,777,216 different colors to produce the smooth shades required of realistic images.

A need for only a small number of colors in a given image is often coupled with a need to change colors from image to image. A look-up table can be employed in such situations. This display device facilitates reductions in storage requirements that never the less satisfy the need to support a sufficient number of simultaneous colors. The look-up table has as many entries as there are pixel values. A pixel's value is not used to control the beam intensity directly but rather as an index into the look-up table. The entry in the table is then used to control the beam's intensity or the color of the screen. For example, a pixel value of, say, 92 is used to access entry number 92 in the table, and the value stored in that entry is then used to control the beam.

Color displays use a shadow-mask cathode-ray tube, which is similar to the television picture tube. Here, the inside of the tube's viewing surface is covered with closely spaced groups of red, blue, and green phosphor dots. The dot groups, arranged in a triad, are so small that light emanating from the individual dots is perceived as a mixture of the three colors. Very high resolution displays require masks to be fine spaced. The triads are placed on about 0.20-mm centers, whereas home television sets are placed on about 0.60-mm centers. This distance is called the pitch of the tube. *See* ELECTRONIC DISPLAY; PICTURE TUBE.

Interactive techniques. Interaction with the object takes place via devices attached to the computer, starting with the keyboard and the mouse. Each type of device can be programmed to deliver various types of functionality. The area of computer graphics that deals with effective use of interactive devices and the protocols that facilitate computer-human interaction is called interactive techniques.

The quality and ease of use of the user interface often determines whether users enjoy a system and whether the system is successful. In critical applications such as air-traffic control and command/control or in "situation display" problems, a poorly designed user interface can contribute to accidents.

Interactive graphics aids the user in the creation and modification of graphical objects and the response to these objects in real-time. The most commonly used input device is the mouse. It is a small hand-held device whose relative motion across a surface can be measured. The roller ball on the underside of the mechanical mouse is converted into digital values that determines its movement in two orthogonal (x, y) directions. The mouse typically specifies locations in image space. Here, the cursor is often displayed as visual feedback to allow the user to see the locations being specified. It could also be used to select an item in a pull-down or pop-up menu. Often in this case the item selected is highlighted or framed in a filled rectangle, since the location of the cursor becomes irrelevant.

Other kinds of interaction devices include the joystick, trackball, light pen, and data tablet. The trackball is often described as an upside-down mouse. The user operates the trackball by dragging the palm across it. The motion of the ball rotating freely within a housing is measured by potentiometers or shaft encoders. Mice are "relative" devices that have no absolute origin—only changes from previous positions are reported—and thus they can be moved, lifted, and moved again. However, the joystick is homed in a center position from which it can be moved left, right, backward, or forward. Here again potentiometers sense the movements. *See* POTENTIOMETER.

A data tablet is a flat surface, from 6 by 6 in. (15 by 15 cm) to 4 by 6 ft. (1.2 by 1.8 m) or larger in size, which is capable of detecting the position of a movable stylus held by the user. Most tablets use magnetic signals generated by electrical pulses applied to a patterned grid which is embedded in the tablet to sense the position of the stylus. The tablet is an absolute device as there is a frame of reference or origin to which the position of the stylus is referred. Through this device, the physical movement of a user's hand can be converted into the movement of a cursor of an object on the display screen.

Voice recognition systems, which free the user's hands for other activities, provide other means of interaction. They analyze the waveforms created when users speak. These systems must, however, be trained to recognize the waveform of a speaker.

Some of these two-dimensional (2D) devices can be modified to extend to three dimensions (3D). The space ball (**Fig. 3**), an example of a three-dimensional device, is a rigid sphere containing strain gages. The user can pull or push the space ball in any direction

Fig. 3. Space ball motion-control input device, which resolves fingertip pressure into translation in three dimensions and rotation, providing six-degrees-of-freedom control. (*Labtec, Inc.*)

to provide three-dimensional translation and orientation. The data glove is a device capable of recording hand movements. It records both the position of the hand and its orientation as well as finger movements. The data glove is capable of a simple gesture recognition and general tracking of hand orientation.

Computer graphics and image processing complement each other. Remarkable visual effects can be achieved by using a combination of these technologies.

Image representation. The representation and description of objects requires the creation of geometric models. Geometric objects have important characteristics such as size, shape, and orientation and certain spatial relationships to each other.

The surfaces of objects in an image can be described as a collection of polygons or patches that are stitched together to make up the scene. This method is called geometric or shape modeling. Polygons work reasonably well for objects that have flat surfaces, like buildings. When surfaces are highly curved, it is generally necessary to cover the surface with many small polygons, which require increases in storage and in execution time. Patches are very efficient at representing surfaces of objects to a given accuracy. Often fewer patches are required, but the equations require more computation than those used for polygons.

The production of a computer-generated image requires additional steps. The designer has to specify the objects in the image and their shapes, positions, orientations, and surface colors or textures. Further, the viewer's position and direction of view (camera orientation) must be specified. The software should calculate the parts of all objects that can be seen by the viewer (camera). Only the visible portions of the objects should be displayed (captured on the film). (This requirement is referred to as the hidden-surface problem.) The rendering software is then applied to compute the amount and color of light reaching the viewer eye (film) at any point in the image, and then to display that point. Some modern graphics work stations have special hardware to implement projections, hidden-surface elimination, and direct illumination. Everything else in image generation is done in software.

Solid modeling is a technique used to represent three-dimensional shapes in a computer. The importance of solid modeling in computer-aided design and manufacturing (CAD/CAM) systems has been increasing. Engineering applications ranging from drafting to the numerical control of machine tools increasingly rely on solid modeling techniques. Solid modeling uses three-dimensional solid primitives (the cube, sphere, cone, cylinder, and ellipsoid) to represent three-dimensional objects. Complex objects can be constructed by combining the primitives. *See* COMPUTER-AIDED DESIGN AND MANUFACTURING; COMPUTER-AIDED ENGINEERING.

Color models. Color specification using the RGB (red, green, and blue) color model is an additive process. The appropriate primary color component is added to black to yield a desired color. This method matches closely the working principles of the display monitor. The complementary color model, called the CMY (cyan, magenta, and yellow) model, defines colors using a subtractive process. This model matches the working principles of the printer. It begins with white, and the appropriate color is subtracted to yield the desired color. *See* COLOR.

Image synthesis. The creation of images by simulating a model of light propagation is often called image synthesis. The goal of image synthesis is often stated as photorealism, that is, the criterion that the image look as good as a photograph. Rendering is a term used for methods or techniques that are used to display realistic-looking three-dimensional images on a two-dimensional medium such as the cathode-ray-tube screen. A three-dimensional image has to be projected before it is displayed on a two-dimensional display medium. The display of a wire-frame image (**Fig.** 4*a*) is one way of rendering the object. The most common method of rendering is shading. Generally, rendering includes addition of texture, shadows, and the color of light that reaches the observer's eye from any point in the image. The specification of this color (as determined by each of the red, green, and blue color components) is computed by the rendering software that is used to generate the image.

The concept is somewhat related to operation of a camera that is used to photograph an object that is illuminated by a light source, albeit simplified in the

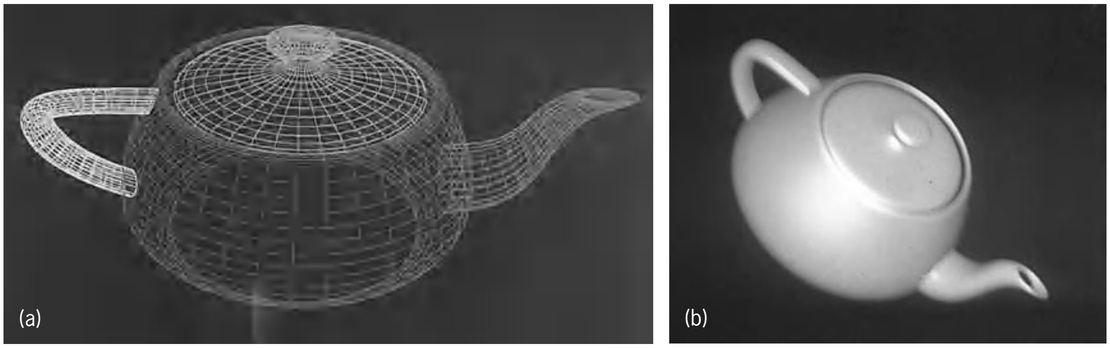

Fig. 4. Renderings of a teapot. (*a*) Wire-frame model with 512 polygons. (*b*) Smooth shading (non-shiny). (*A. Tokuta, Technical Report, Department of Computer Science and Engineering, University of South Florida*)

Fig. 5. Animation frame showing both reflections from and refraction through Geri's eyeglasses in Pixar's Geri's Game. (*Pixar Animation Studios*)

model. Light energy emanating from the source interacts with the physical environment, is reflected off the surface of the object through the camera lens, and is registered on the film, forming an image of the object. The parts of the object closer to the light source should appear brighter, while the parts farther away or directed away from the light source should appear darker. The mathematical model that is used for these types of optical phenomena is called a local illumination model. It tracks the light energy coming directly from the light source to a particular object surface but does not fully account for the energy arriving at the surface. Light energy is also reflected from other objects in the environment, and energy can pass through transparent and translucent objects in the environment (**Fig. 5**). Models of computation that strive to account for the accurate transportation of light are referred to as global illumination models.

Producing realistic images involves both physics and psychology. The psychology of visual perception is extensively documented. The amount of light propagation can be computed by the rendering software, based on simple models. Shading techniques (constant, Gourad, or Phong) can be applied to evaluate the illumination model at various locations. In constant shading, a single color is computed for an entire polygon, based on the position of the light source. This method of shading tends to produce poor results because the human visual system exaggerates changes in intensities that may exist between adjacent polygons that may have different shading.

Consequently, some form of interpolation is often used. For the Gourad shading, the evaluation of the model is done once for each vertex. The intensities are then interpolated across the polygon. The direction of the normal to the surface must be taken into account in the calculation of the intensities; here, the vertex normal that is used is the computed average of the adjacent surface normals. In the case of Phong shading (Fig. 4*b*), the evaluation of intensity is done once for each pixel. The normal vector that is used in the evaluation is computed, however, as the interpolated values of normals at the vertices. This has the added advantage of preserving specular highlights.

The character of the light that is reflected from a surface of an object depends on the composition, direction, and geometry of the source, the orientation of the surface, and the surface properties of the object. It is also characterized as either diffusely or specularly reflected. An ideal mirror reflects light that strikes it, and each ray that hits a point on the surface is reflected in one direction. An observer who happens to be located in that direction, and is looking at the point, should see a reflection of the light source in its original color and not the surface itself. This ideal reflection is called specular. Specular reflection is directional; that is, it depends on the angle of incident light. An ideal dull surface reflects light in all directions because the microfacets constituting the surface are considered to be pointing in different directions. Thus an observer perceives the same light, intensity to be reflected from a given point regardless of the observer's position. This type of reflection is called diffuse. Each point on a surface is thus considered to emit three types of light: diffuse light, specularly reflected light, and transmitted or refracted light. Each ray leaving a surface comprises the sum of these three contributions. Modeling of shadows, requires additional computation. *See* ILLUMINATION; REFLECTION OF ELECTROMAGNETIC RADIATION.

Ray tracing is a technique that is used to produce realistic images but is view-dependent. This means that the entire computation must be repeated when the observer's position is changed. This method, however, interleaves the determination of visibility, illumination, and shading at each pixel. The basic idea is to trace the paths of rays, from the viewpoint of an observer looking through each pixel in the screen into the image. If the ray hits a surface, reflected and possibly refracted rays are spawned, which in turn are traced to see if they intersect any other surfaces. The final color and intensity of each pixel are determined as the summation of the contributions from each spawned ray.

The radiosity method is view-independent. The radiosity of a surface is the rate at which energy leaves the surface, and is the sum of the rates at which the surface emits energy and reflects or transmits it from that surface. Given an image, the calculations are done only once, even before the visible-surface determination is performed from a desired viewpoint of the observer. Once the global illumination has been determined, it is easy to move the observer to different viewpoints and thus create a series of images. This method uses the principle of conservation of energy (by modeling energy equilibrium in a system of surfaces) to compute the light intensity for each surface in the image, and assumes ideal diffuse surfaces composed as either light sources or reflecting surfaces. *See* CONSERVATION OF ENERGY.

Natural and synthetic objects. Computer-generated images are used extensively in the entertainment world and other areas. Realistic images have become essential tools in research and education. Conveying realism in these images may depend on the convincing generation of natural phenomena. A fundamental difficulty is the complexity of the real world. Existing models are based on physical or biological concepts.

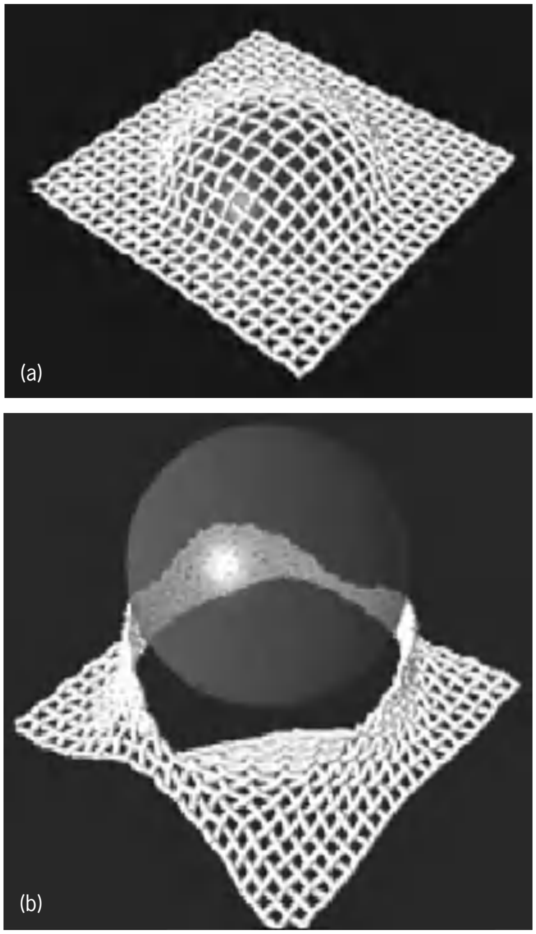

Fig. 6. Example of realistic images based on physical properties. (*a*) Net falling over a physical obstacle. (*b*) Fracture developing in the net. (*D. Terzopoulos and K. Fleischer, Schlumberger Palo Alto Research*)

The behavior of objects can be determined by physical properties or chemical and microphysical properties. (**Fig. 6**).

Many natural phenomena are not efficiently represented by geometric or solid models. Procedural models, fractals, grammar-based models, and particle systems have been used to model a variety of things. Procedural models describe objects that can be modeled from a procedure and a parameter set. The appearances of textured surfaces from wood to marble, and woven material to fur, have been simulated by use of procedural texturing techniques.

Clouds and mountain terrain are examples of objects that have been modeled using fractals. The term "fractal" was introduced by Benoit Mandelbrot to describe a particular attribute of certain natural phenomena. For example, an aerial view of a coastline tends to exhibit a so-called recurrent pattern that is not dependent on the scale of the image. *See* FRACTALS.

Grammar-based models can describe the structure of certain plants and trees. Work in this area is based on a parallel graph grammar called L-system. This system specifies the construction of a plant or tree as a sentence in the language that the grammar generates.

Particle systems have been used to model fuzzy objects such as fire and clouds. An object is represented by a set of particles that evolve over time—each is born, evolves in space, and dies or is extinguished, all at different times.

Volume rendering. Volume rendering combined with animation is a major tool used in visualization. Visualization offers a method to see the unseen. It enables researchers to observe their simulations and computations, thus enriching the process of scientific discovery. A major application of this area is medical imaging (Fig. 1), where volume data are available from positron emission tomography (PET) scanners, for example. *See* SIMULATION.

Alade O. Tokuta

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Computer-integrated manufacturing

A system in which individual engineering, production, and marketing and support functions of a manufacturing enterprise are organized into a computer-integrated system. Functional areas such as design, analysis, planning, purchasing, cost accounting, inventory control, and distribution are linked through the computer with factory floor functions such as materials handling and management, providing direct control and monitoring of all process operations.

Computer-integrated manufacturing (CIM) may be viewed as the successor technology which links computer-aided design (CAD), computer-aided manufacturing (CAM), robotics, numerically controlled machine tools (NCMT), automatic storage and retrieval systems (AS/RS), flexible manufacturing systems (FMS), and other computer-based manufacturing technology. Computer-integrated manufacturing is also known as integrated computer-aided manufacturing (ICAM). Autofacturing includes computer-integrated manufacturing, but also includes conventional machinery, human operators, and their relationships within a total system. *See* COMPUTER-AIDED DESIGN AND MANUFACTURING; FLEXIBLE MANUFACTURING SYSTEM; ROBOTICS.

Agile manufacturing and lean manufacturing. Flexible manufacturing has been subsumed by the concept of agile manufacturing, which presumes that all operations can be virtually instantly reconfigured to satisfy a changing market demand. For example, only cars with certain options are selling, but the marketing department has directed the manufacturing department to gear up to produce models with other options. Agile manufacturing could efficiently reconfigure operations to satisfy the new requirement, or it could create a virtual manufacturing facility by electronically combining the operations of many different locations into the optimum configuration required to meet new market demands.

Lean manufacturing reorganizes and reduces operations to the minimum required to produce certain parts or products at the absolutely lowest cost. Lean manufacturing typically focuses on either market-niche-type products or seeks a virtual monopoly on large-volume low-variability products.

Modern manufacturing enterprise. The CIM factory integrates the traditional hard or process-based technology factory (departments) with software of systems-based technology (nondepartments).

Effectiveness, efficiency, and economy. Manufacturing companies seek the optimal combination of effectiveness, efficiency, and economy. Efficiency is most often associated with transfer-line or assembly-line technology. The best-known developer of this technology was Henry Ford. His Model T factory could produce cars at an unprecedented rate for that time, but the consumer had no choice at all about the specifications of the product. Flexibility is most often associated with robotics and other reprogrammable automation. Effectiveness is usually associated with the soft technology and organizational support structure of the enterprise.

Optimization of the CIM factory is based on specific criteria. By considering efficiency, flexibility, and effectiveness, the CIM factory enables economy of scope. In economy of scope, flexibility is at least as important as efficiency, because the factory is seen to be an ever-changing dynamic environment which must always respond quickly to the needs of the marketplace, if not actually lead the need. The traditional factory with both rigid transfer-line technology and a rigid organizational structure cannot satisfy this objective; it strives for maximum volume of each product. In the ideal case, the CIM factory provides for profit with an order quantity of one, that is, when no two products are identical. Within the manufacturing enterprise, the CIM factory combines agility during manufacturing planning and leanness during production.

Organization. The CIM factory concept includes both soft and hard technology. Soft technology can be thought of as the intellect or brains of the factory, and hard technology as the muscles of the factory. The type of hard technology employed depends upon the products or family of products made by the factory. For metalworking, typical processes would include milling, turning, forming, casting, grinding, forging, drilling, routing, inspecting, coating, moving, positioning, assembling, and packaging. For semiconductor device fabrication, typical processes would include layout, etching, lithography, striping, lapping, polishing, and cleaning, as well as moving, positioning, assembling, and packaging. More important than the list of processes is their organization.

Whatever the products, the CIM factory is made up of a part fabrication center, a component assembly center, and a product assembly center. Centers are subdivided into work cells, cells into stations, and stations into processes. Processes comprise the basic transformations of raw materials into parts which will be assembled into products. In order for the factory to achieve maximum efficiency, raw material must come into the factory at the left end and move smoothly and continuously through the factory to emerge as a product at the right end. No part must ever be standing; each part is either being worked on or is on its way to the next workstation.

In the part fabrication center, raw material is transformed into piece parts. Some piece parts move by robot carrier or automatic guided vehicle (AGV) to the component fabrication center. Other piece parts (excess capacity) move out of the factory to sister factories for assembly. There is no storage of work in process and no warehousing in the CIM factory. To accomplish this objective, part movement is handled by robots or conveyors of various types. These materials handlers serve as the focus or controlling element of work cells and workstations (**Fig. 1**). Each work cell contains a number of workstations. The station is where the piece part transformation occurs from a raw material to a part, after being worked on by a particular process.

Components, also known as subassemblies, are created in the component assembly center. Here materials handlers of various types, and other reprogrammable automation, put piece parts together. Components may then be transferred to the product assembly center, or out of the factory (excess capacity) to sister factories for final assembly operations there. Parts from other factories may come into the component assembly center of this factory, and components from other factories may come into the product assembly center of this factory. The final product moves out of the product assembly center to the product distribution center or in some cases directly to the end user. *See* AUTOMATION.

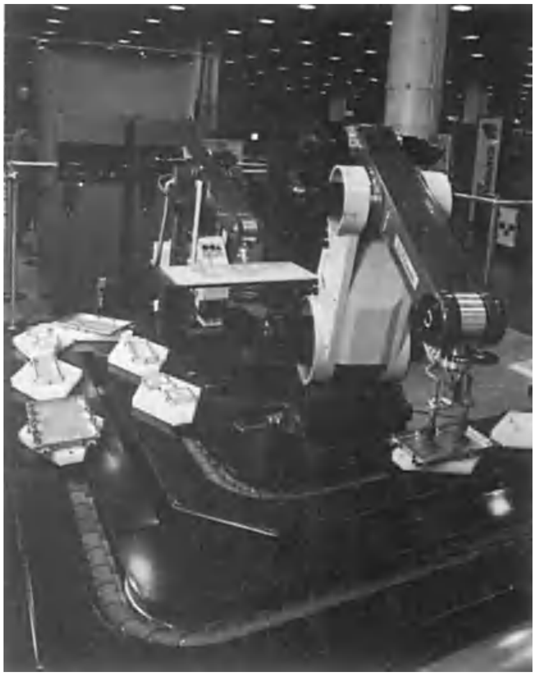

Fig. 1. Typical CIM workstation.

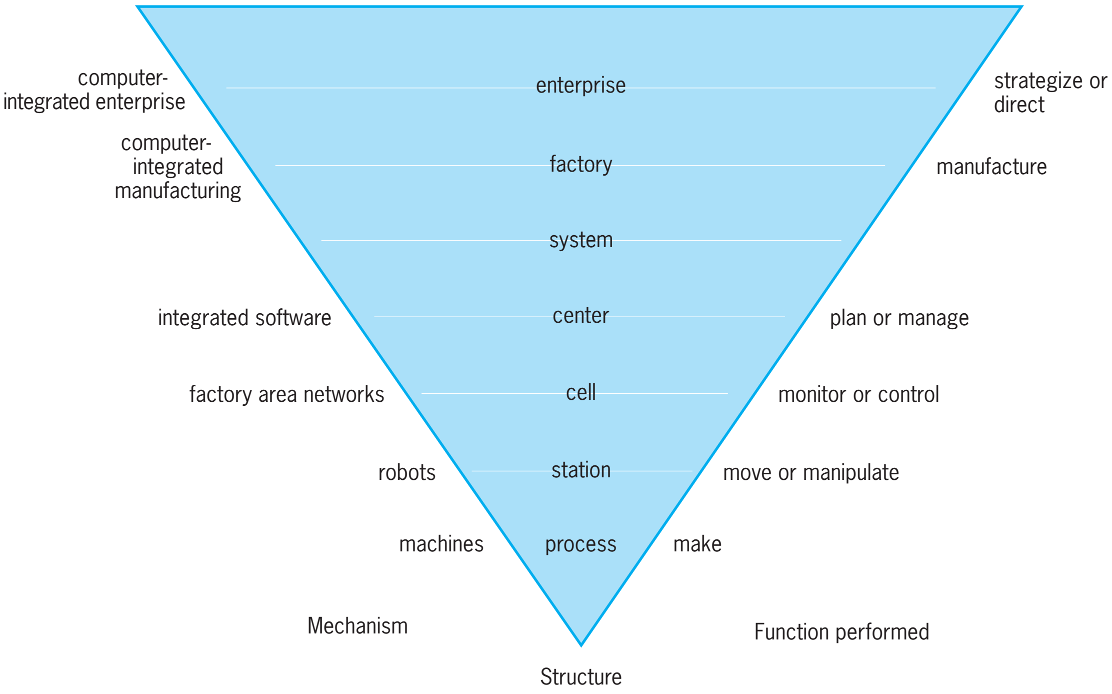

Fig. 2. Diagram of the architecture of manufacturing.

Integration. The premise of CIM is that a network is created in which every part of the enterprise works for the maximum benefit of the whole enterprise. Independent of the degree of automation employed, for example, whether it is robotic or not, the optimal organization of computer hardware and software is essential. The particular processes employed by the factory are specific to the product being made, but the functions performed can be virtually unchanged in the CIM factory no matter what the product. These typical functions include forecasting, designing, predicting, controlling, inventorying, grouping, monitoring, releasing, planning, scheduling, ordering, changing, communicating, and analyzing.

It must be recognized that independent, optimum performance of the individual functions is not as important as their integration with one another, or their integration with the factory floor itself. This integration is brought about in two ways. The first is through an architecture of manufacturing which specifies precisely how and when each function is integrated with the other (**Fig. 2**). The second is through a controller and networks.

For example, a cell controller ensures integration of data between each machine, robot, automatic guided vehicle, and so forth, of the cell. The cell network (**Fig. 3**) actually performs this communication within the cell, and connects cells together into centers. In the cell network, communication is possible between each machine of the network and between different networks. The cell controller itself serves to perform such tasks as downloading part programs or recipes from the CAD system or planning system to each machine in the cell, monitoring actual performance of each machine and comparing this performance to the plan, selecting alternate routing for a part if a machine is not operable, notifying operators of pending out-of-tolerance conditions, archiving historical performance of the cell, and transmitting to the center level on an exception basis the cell performance compared to plan. Typically, the human interface with factory floor operations and intermachine communications is accomplished through networked programmable controllers, personal computers running soft logic, machine and robot controllers, display devices, and programmable logic controllers (PLCs) communicating through Wireless Application Protocol (WAP) devices. These interactions are managed through personal computer–based technology integrated in real time through various communications protocol standards. *See* PROGRAMMABLE CONTROLLERS.

The center level of the CIM factory is all of the policies and procedures that run the factory. These are embodied in computer software, which is in turn based upon an overall integration plan or CIM architecture.

The purpose for the architecture is to provide a blueprint for employing CIM. While there are as many variations of the details of the architecture of the CIM factory as there are factories, the structure of the architecture is generic. The focus is the agile manufacturing system (AMS), which is made up of cells, stations, and processes. The information to be fed back to functions where decisions are made is as important as the product itself. In this example, the functions are defined very broadly and are used only to illustrate the absolute necessity for interaction between functions if the CIM factory is to be made to work efficiently, flexibly, and effectively.

In CIM, as decisions are made, they are tested on a computerized model of the CIM architecture to

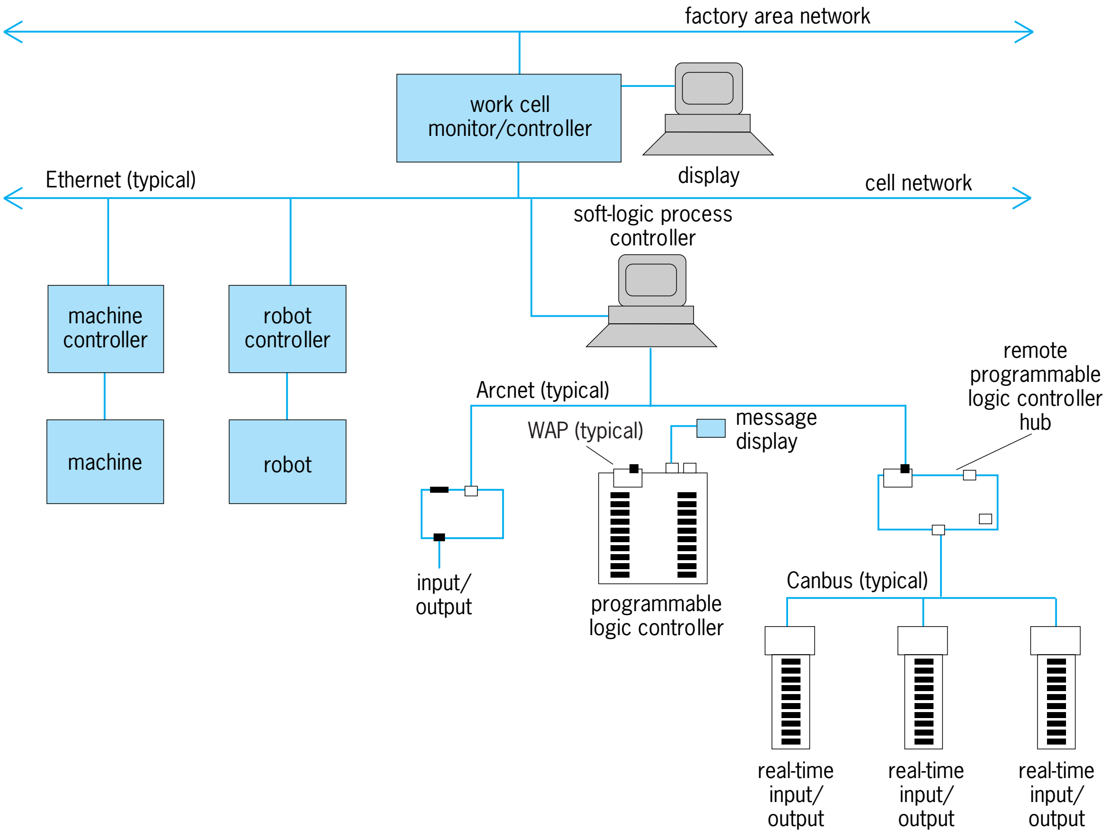

Fig. 3. Organization of a production cell network for computer-integrated manufacturing. Ethernet, Arcnet, Wireless Application Protocol (WAP), and Canbus are international standards for communication.

determine feasibility. Thereby, mistakes are discovered in the computer, not in production in the factory. Simulation and emulation software is used for this purpose. Computer aided software engineering (CASE) software is used to convert the CIM models for decision making into software for operating the CIM factory. Interchangeable and reusable software programs, known as objects, are manipulated by CIM engineers to accomplish this objective. *See* SOFTWARE ENGINEERING. Dennis E. Wisnosky

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Computer numerical control

The method of controlling machines by the application of digital electronic computers and circuitry. Machine movements that are controlled by cams, gears, levers, or screws in conventional machines are directed by computers and digital circuitry in computer numerical control (CNC) machines.

Computer numerical control provides very flexible and versatile control over machine tools. Most machining operations require that a cutting tool be fed at some speed against a workpiece. In a conventional machine such as a turret lathe, the turning tool is mounted on a slide with hand-operated infeed and crossfeed slides. The operator manually turns a crank that feeds the cutting tool into the workpiece (infeed) to the desired diameter. Another crank then moves the turning tool along the longitudinal axis of the machine and produces a cylindrical cut along the workpiece. The feed rate of the turning tool is sometimes controlled by selecting feed gears. These gears move the axis slide at the desired feed. A CNC machine replaces the hand cranks and feed gears with servomotor systems. *See* SERVOMECHANISM.

Computer numerical controls allow the desired cut depths and feed rates to be “dialed in” rather than controlled by cranks, cams, and gears. This provides precise, repeatable machine movements that can be programmed for optimal speeds, feeds, and machine cycles. All cutting-tool applications, whether on a lathe, drill press, or machining center, have optimum speeds and feeds, which are determined by carefully weighing the economics of tool life, required production rates, and operator attentiveness. With computer numerical control these parameters are set once, and then they are repeated precisely for each subsequent machine cycle.

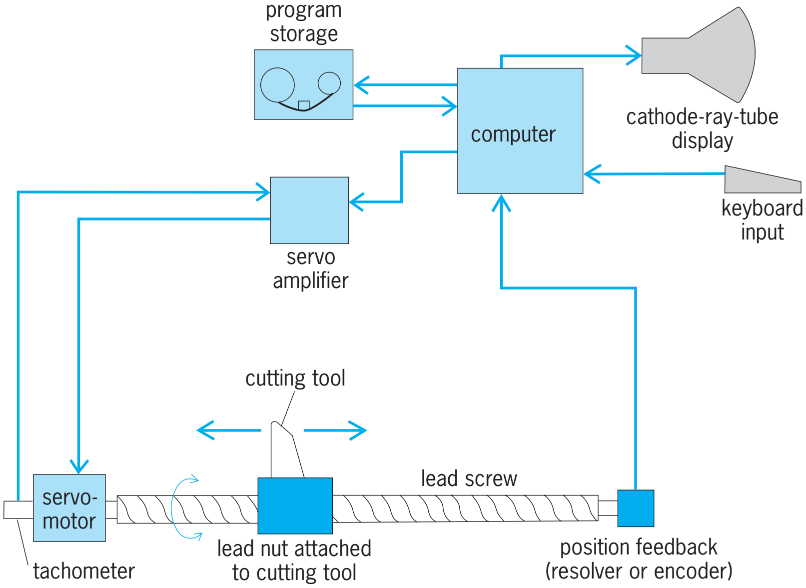

Fig. 1. Schematic diagram of a servo system.

The decision to purchase a CNC machine instead of a conventional machine is a complex one. The CNC machines are usually more complex than conventional machines, which adds to their cost and puts greater burdens on maintenance and support personnel. This added cost is often worthwhile, because of the flexibility and sophistication of the machine. The total cost of purchasing and operating a CNC machine must be weighed against the total cost of purchasing and operating a conventional machine. Complexity of the parts, programming and maintenance costs, and the availability of skilled labor are some of the factors to be considered.

History. Machines with numerical control (NC) became possible in the 1960s, when the development of the transistor made electronic servosystems practical. Earlier NC cutting tools were programmed with punched tape. This technique, while an impressive and productive technology, lacked the sophistication and flexibility that have become available with the development of more advanced systems. Numerical control programs had to be written by hand. Punched tape tended to rip and tear in the hostile environment of the shop floor. Once punched, the programs could not be modified without punching an entirely new tape. Punched tape was also bulky, and if many programs were required, a great deal of space was needed to store the tapes. *See* COMPUTER; TRANSISTOR.

Computer numerical control advanced further with the advent of inexpensive computers in the early 1980s. Instead of being programmed to move to discrete, precalculated locations, the machines can be programmed to perform complex mathematical calculations that determine the locations of the machine's axes. With computer numerical control, milling cutters can be programmed to move in a sinusoidal pattern, for example, by programming a simple sine function into a loop. Previously, each point would have to be explicitly programmed. Programs for computer numerical control can be written parametrically; that is, the same basic motions to be programmed for many different sizes of parts can be controlled with the same program. Programming has become simpler, more powerful, and more user-friendly. It has even become possible to program machine tools graphically at the machine while machining is taking place. *See* PROGRAMMABLE CONTROLLERS.

System components. Machine systems designed for computer numerical control use servosystems to control the position of cutting tools. A typical servosystem (**Fig. 1**) is composed of six parts: a lead screw (ball screw) and lead nut, an electric servomotor, a servoamplifier, a position-feedback device, a velocity-feedback device, and a computer.

Lead screws are precision-ground screws. To prevent any backlash in the screw system, a special lead nut utilizing hundreds of ball bearings tracks the screw. The many ball bearings help equalize and distribute the load forces on the screw. This improves the accuracy, while minimizing friction between the nut and the screw.

Servomotors are specially constructed electric motors. They are designed to operate at very low angular velocities. Although they sometimes drive the lead screw through a gear reduction system, they are usually directly coupled to the lead screw. This direct coupling minimizes any backlash or positioning errors introduced by gears. The motor is required to provide full torque at low, or zero, rpm. Traditionally, servomotors have been direct-current (dc) types. Such motors provide excellent torque at low speeds and have relatively simple electrical requirements, but they have brushes, which are a source of wear and are subject to contamination. The electrical requirements for alternating-current motors are more complex than for dc motors, but the motors themselves are more reliable, especially in hostile environments. *See* ALTERNATING-CURRENT MOTOR; DIRECT-CURRENT MOTOR; GEAR.

The servoamplifier powers the servomotor. Servomotors require precise control of the electrical voltage and current supplied to them. Voltage and current are varied by the servoamplifier. High power is required to accelerate the machine's axes. Moderate power is required to keep them moving. High power (of opposite polarity) is required to decelerate them at the end of a programmed move. Additionally, if the servosystem encounters a physical resistance (such as the load for a heavy cut on a lathe), the servoamplifier must compensate with additional power to keep the lead screw turning at the desired rpm.

The servoamplifier receives a signal voltage from the computer that indicates the desired machine axis direction and speed. A tachometer is mounted on the servomotor and measures the motor's rpm. The output of the tachometer is fed into the servoamplifier, which examines the rpm of the servomotor and varies the voltage and current supplied to the motor to keep it turning at the desired rate. *See* TACHOMETER.

Position feedbacks are provided by resolvers or encoders. These allow the computer to know where the machine's axes are at any time, and to calculate how far the axes must move to reach their programmed positions. Resolvers, and to a lesser extent encoders, are precision devices that must be protected against shock and impact. If not subject to abuse, they generally are very reliable. They are usually directly coupled to the lead screw so that they measure every minute movement of the screw, without the slight backlash that gearing could introduce.

The computer provides overall control of the entire system. It examines the part program, determines the desired positions of the machine axes, then provides special signals to the servoamplifiers to move the servomotors and thereby move the machine's axes. The computer monitors the position feedback provided by the resolvers or encoders. In addition, the computer handles various so-called housekeeping tasks such as displaying the axes' locations on the cathode-ray-tube (CRT). The computer also monitors the program to ensure that dangerous functions, such as opening the chuck in the middle of a cut, have not been programmed.

The speed and computing power of the computer directly affects the quality of the finished workpiece. The computer must examine the axes' locations and velocities, compare their current locations to their programmed locations, and update command signals to the servoamplifiers hundreds or thousands of times each second. Generally, the more often the computer can update in this manner, the smoother and more precise the machine's motions will be. Advances in computing power have led to the construction of CNC machines that can smoothly move six or seven axes simultaneously. This can be accomplished while the computer is still updating the CRT display and checking for errors.

Machine axis layout. Each servo-controlled axis can move either forward or backward in a straight line. The machine tool builder assigns numerical reference (home) locations to each axis. The location of each axis is then determined as a linear measurement from the home position. The home location is usually considered to be 0.0000. A point 2 in. from home would therefore have the coordinate of 2.0000. Programming the machine axis consists of instructing the axis to move to some numerical coordinate.

Most machines require cutting tools to move in at least two directions. On a lathe, this corresponds to the longitudinal and infeed axes (usually labeled Z and X, respectively). Since each axis can move in only one direction, the axes are compounded by being built one on top of the other. In this way, the X axis is mounted on top of the Z axis. A cutting tool mounted to the X axis is therefore also controlled by the Z axis, and has two directions of movement (**Fig. 2**).

Programming. Programming for computer numerical control, at its most basic level, consists of indicating a series of numerical coordinate locations to which the axes will move under program control. Various parameters, such as velocity, are programmed along with the locations of the axes. Ancillary operations, such as turning on both the spindles and the coolant, and specifying the spindle rpm, are also programmed.

Most part programs are broken into lines known as blocks, each of which is a specific program step, executed at one time by the computer. A block may consist of one or more axis locations and a feed rate, a miscellaneous command, or some combination of these. Generally, the execution of each block is completed before the next one is begun.

There are several major classes of part program codes. Although each machine or computer manufacturer is free to define the meaning of each code word, there are several conventions that have been nearly universally adopted.

The block number is coded with an N followed by a number having one to four digits. On older CNC controls, block numbers were necessary, but more modern controls may not require them. Most programmers still use them to assist in reading previously written programs. Block numbers are very useful when part programs must be edited, since they allow specific blocks to be referenced.

The G codes specify how the machine's movements will be made. One of the most common G codes is G01, which activates the linear interpolation mode. In this mode, all the axes move from their current locations to their programmed locations at controlled feed rates, so that they all arrive at the same time. A cutting tool, mounted to both axes, moves in a straight line at the programmed feed rate. If each axis has different distances to traverse in order to reach its programmed location, the one with the longer distance moves faster, so that both axes arrive at the same time. Most part programming consists of moving the axes in coordinated straight lines, and so this function is very common.

A G90 code activates the so-called absolute programming mode. For example, the block N45 G90 X − 2.500 Z − 1.000 will move the X axis to the absolute axis location of −2.500 in., and the Z axis to the absolute axis location of −1.000 in. These

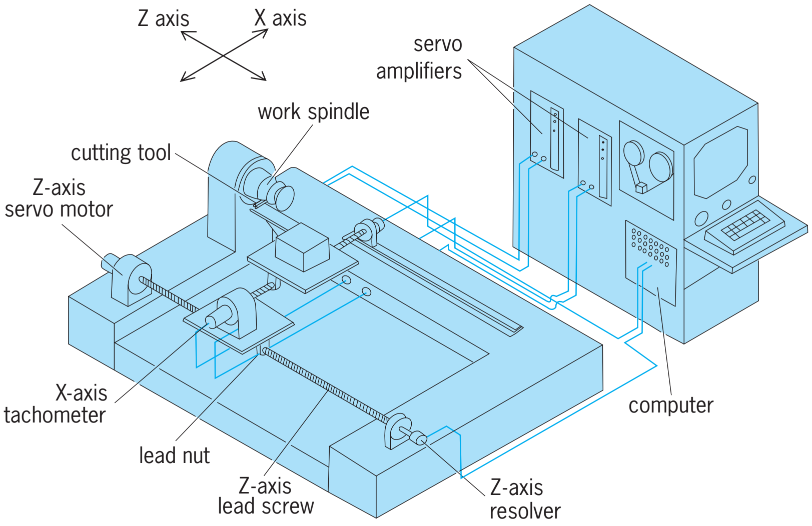

Fig. 2. Diagram of a two-axis computer numerical control lathe.

positions will be reached, regardless of where each axis was before the command was issued.

A G91 code activates the incremental programming mode. In this mode the programmed move is coded as a distance to move from the current location. For example the block N45 G91 X − 2.500 Z − 1.000 will move the X axis 2.500 in. in the negative direction from its current location. The Z axis will move 1.000 in. in the negative direction from its current location. The final locations of the axes will be determined by both their initial locations and the incremental movements programmed.

Just as it is possible to specify the linear interpolation mode, the circular interpolation mode can be specified. This mode causes the axes to move in a controlled circular motion. The programmer merely specifies the radius of the cut and the final location. The computer will automatically calculate the minuscule discrete movements required to move two axes in a coordinated circular fashion.

Parametric programming is the method of programming movements of the axes in terms of computer variables known as parameters. Instead of programming explicit X and Z axes locations in the part program, the programmer indicates that the axes are to move to locations according to specific parameters. Then, by loading the parameter variables with specific values, the computer will move the axes to those locations. This has the advantage of allowing programmers to write programs known as family of parts; these programs have the same basic movements but have differing locations of the axes. The family-of-parts program is logically identical from part to part, but the locations of specific axes may be different.

An example of a parametric program is a program to turn three different truck axle shafts that are identical except for their diameters. A single parametric part program could be written for these three shafts. Instead of specifying the infeed axis locations that correspond to the diameters explicitly, the programmer could have the infeed axis move to the location specified in a parameter variable. By changing the value of the parameter, a shaft with a different diameter can be machined on the lathe with the same program.

In some cases, it is desirable to have all the programs stored in a central computer. The process of direct numerical control can then be used to download the part programs from the central computer to the CNC machine by way of a communication wire. This process eliminates the paper-tape or floppy-disk program storage at the machine. Sophisticated multimachine production lines frequently use this technique to help integrate and automate several machining steps. *See* COMPUTER STORAGE TECHNOLOGY.

In computer-aided manufacturing (CAM), computers are used to assist in programming CNC machines. In sophisticated CNC manufacturing operations, machined parts are first designed on computer-aided-design (CAD) equipment. The same electronic drawing is then used to create the CNC part program automatically. A less advanced version of CAM is the use of high-level part programming languages to write part programs. Special computer programming languages, such as APT and COMPACT II, allow programmers to write complex part programs easily and quickly. For example, indexing a CNC lathe turret may take five or six blocks of a part program. This action can typically be accomplished in just one line of APT or COMPACT II program code. *See* COMPUTER-AIDED DESIGN AND MANUFACTURING.

Typical applications. Computer numerical control machines are used mainly when flexibility is required or variable and complex part geometries must be created. They are used to produce parts in lot sizes of a few pieces to several thousand. Extremely large manufacturing lot sizes frequently call for more product-specific machines, which can be optimized for large production runs.

Complex forms such as pockets, steps, or large radii can be programmed easily on CNC machines. On conventional machines, these features require either special fixturing and tooling or a great deal of operator skill. Often several discrete machining steps can be combined on CNC machines. This saves machine setups and simplifies production processes within a manufacturing plant.

Although CNC machines can help set optimum cutting-tool parameters, the individual cuts made by a CNC machine are usually no faster than those possible on conventional machines of good quality. In fact, sometimes conventional machines can be faster.

Although CNC machines are often simpler to operate than conventional machines, they can sometimes be more difficult. Those CNC machines that allow simultaneous performance of multiple operations require operators who are knowledgable about several production steps. The operator must be able to set up and check more complex parts.

Operators of CNC machines must be able to think numerically. To adjust a machined diameter, the operator usually adds or subtracts a desired amount from the machine's offsets. With conventional machines the operator may only have to turn a crank a few graduations. A CNC machine will require the person to look up an offset on the CRT display, add or subtract the desired diameter change, then type in the new offset. Many people are not adept at such rapid mental arithmetic. In addition, some people find computers intimidating and are not comfortable working with them.

It is often assumed that a machine controlled by a computer is inherently more accurate than an equivalent manual machine, this is not necessarily true. In fact, CNC machines are sometimes less accurate than manual machines. The CNC machines rely on precision-ground slides and screws to position accurately, and normal machine wear can degrade this accuracy. The computer is usually unable to detect or compensate for this wear, while a skilled mechanist can.

Traditionally, CNC machines were mostly lathes and machining centers. Lathes turned axle shafts, drill-bit shanks, or any other multisurfaced cylindrical parts, and machining centers machined engine

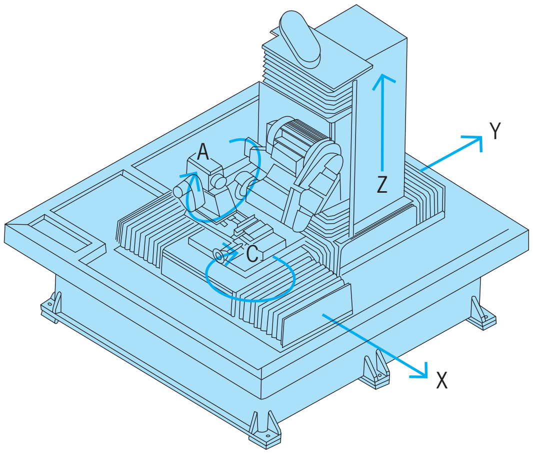

Fig. 3. Five-axis computer numerical control grinder. (*S. E. Huffman Corp.*)

blocks and aircraft rib spars. Now there are complex multiaxis grinders (**Fig. 3**), laser cutters, benders, and many more machines with computer control. Parts such as end mills, airfoils, and universal ball joints can be economically and accurately machined on CNC machines. *See* CONTROL SYSTEMS.

J. R. Casey Bralla

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Computer peripheral devices

Any device connected internally or externally to a computer and used in the transfer of data to or from a computer. A personal computer (PC) or workstation processes information. Data (unprocessed information) must get into the computer, and the processed information must get out. Information is entered and displayed on a wide variety of accessory devices called peripherals, which are also known as input/output (I/O) devices. Some peripherals (such as keyboards) are only input devices, others (such as most printers) are only output devices, and some are both. Peripherals may be located inside or outside a computer's case (called an internal or external device, respectively). The I/O bus is the collection of circuits where an internal device is attached. An I/O port (such as parallel or serial port) is a connector where an external device is connected (plugged in). *See* DIGITAL COMPUTER; MICROCOMPUTER.

Monitor. The monitor is the device on which images or text produced by the computer operator or generated by the program are displayed on a cathode-ray tube (CRT) or a liquid-crystal display (LCD). Electron guns in a CRT (one in a monochrome monitor, three in a color monitor) irradiate phosphors on the inside of the vacuum tube, causing them to glow. Aside from the presence or absence of color, monitors are mainly distinguished by the size of the screen and the sharpness of resolution. Screens generally range from about 7 in. (18 cm), measured diagonally, for small portable computers to 21 in. (54 cm) for graphic-intensive work. Sharpness is determined by the number of shades of gray, if any, or colors that the monitor, in conjunction with the computer's circuits and memory, can display; the number of pixels (picture elements) per inch; and the dot pitch, the size of the individual phosphorescent dots.

The flat-panel displays on most portable (notebook, laptop, or tablet) computers are known as liquid-crystal displays. LCD flat-panel monitors are superior to CRTs as computer monitors for desktops for a variety of reasons, among them being that CRTs contain hazardous materials (such as phosphors and lead), consume more power, generate more heat, and are more bulky. In place of the vacuum tube coated with phosphors, LCDs use two polarizing filters with liquid crystals between them to produce the image.

A monitor can be connected to an analog or digital video interface. Some flat-panel LCD monitors can be connected as both an analog monitor to one computer and a digital monitor to another and include a "toggle" switch to connect to either. *See* CATHODE-RAY TUBE; ELECTRONIC DISPLAY; LIQUID CRYSTALS.

Keyboard. The computer keyboard, based on the typewriter keyboard, contains keys for entering letters (usually in the familiar QWERTY arrangement), numbers, and punctuation marks, as well as keys to change the meaning of other keys. For example, pressing the "s" key on any keyboard produces a lowercase s, and pressing the "shift" and "s" keys produces an uppercase S. But pressing the "control" and "s" keys on computers running some programs saves a copy of the file being worked on to the disk or diskette, whereas this function is accomplished by pressing the "command" and "s" keys on other systems' keyboards. Other special keys or combinations of keys move the section of the file being viewed, such as "page up," move the cursor (pointer); or perform other tasks, such as "print screen." The function keys, usually a row across the top or along the left side of the keyboard and numbered F1 through F10 or F12, perform tasks that vary from program to program. In some programs, for example, the F1 key brings a "help" file to the screen. Keyboards generally are physically connected to a computer via one of three interfaces: specialized keyboard interface, a serial port, or a universal serial bus (USB). Keyboards also can connect through a wireless IR (infrared) port or Bluetooth (2.4 GHz) port.

Mouse. A mouse is a device that is rolled on the desktop to move the cursor on the screen. The mouse has one to three buttons. In the syntax of computers, the cursor is moved to select the object on which an action is performed, and then one or more buttons are pressed to perform the action. A ball on the bottom of the mouse translates the device's movements to sensors within the mouse and then through the connecting port to the computer. There are also mice that substitute optical devices for mechanical balls, and mice that use wireless infrared or Bluetooth technology. Many mouse actions can be accomplished with a keyboard using substitute keystroke sequences.

Trackball. A trackball is essentially an upside-down mouse, with the ball located on the top rather than on the bottom. Since a trackball is attached and therefore does not require an area in which to be moved, it requires less working space than a mouse (although most trackballs occupy more standing space than a stationary mouse).

Touchpad. A touchpad is a device that senses both a user's finger movement and downward pressure exerted on the device (for example, tapping). The movement of the user's finger on the pad results in a corresponding cursor movement on the monitor in a manner corresponding to the movement of a mouse.

Pointing stick. A pointing stick (for example, the IBM TrackPoint™) is a small eraserlike device that is located in the center (between the "g", "h," and "b" keys) of a keyboard. A user applies pressure on this device to the point in the direction desired for the movement of the cursor.

Joystick. A joystick is a pointing device with a vertical handle that is used principally for games. Moving the handle moves the cursor or other simulated object on the screen; pressing the button or buttons on the base or vertical piece performs an action that depends on the software program.

Touch-enabled device. Touch-enabled devices allow an individual to experience a sense of touch. Such a device typically works with a user's computer screen to create a sense that one is actually touching what appears on the screen.

Light pen. A light pen performs the same functions as a mouse or trackball, but it is held up to the screen, where its sensors detect the presence of pixels and send a signal through a cable to the computer. Light pens seem to be a more natural transition from paper and pencil to computers than mice or trackballs, but they have proven to be tiring to use.

Graphic tablet. A graphics, or digitizing, tablet is a pad with electronics beneath the surface on which one can write or draw using a pointed device, called a stylus. The shapes drawn appear on the device's screen. For any but the simplest projects, it is easier to draw with a stylus and tablet than with a mouse or trackball. Tablets are used on PDAs (personal digital assistant) and tablet PCs (a form of notebook computer).

Microphone. A microphone, sometimes called a mic (pronounced "mike"), is a transducer that converts sound into an electrical signal. Microphones are used as input devices in many applications where speech recognition is involved.

Disk drive. The term disk drive has taken on new meanings in recent years. Originally, disk drives were magnetic media devices. Now, there are many devices that connect via a universal serial bus (USB) port and look like a disk drive to the operating system; however, they are devices with no moving parts that use flash memory.

Magnetic media (hard drives and diskettes). The most common input/output, or storage, device in personal computers or workstations is a hard disk drive, a stack of magnetized platters on which information is stored by heads generating an electrical current to represent either 1 or 0 in the binary number system. The device is called hard because the platters are inflexible, and is called a drive because it spins at 3600 revolutions or more a minute, within a sealed case. The heads are only a few millionths of an inch from the platters. Storage capacity of hard disk drives has grown from a few megabytes of data (1 megabyte $= 10^6$ characters or bytes) to 40 or more gigabytes (10^9 characters). Diskettes, made of flexible plastic (usually polyester) film like that used in recording tape, are stored within a hard shell and are spun by their drives at about 360 revolutions per minute. Their capacity is quite limited, commonly about 1.1 megabytes (3.5-in. diskette), although both smaller and larger ones are available. Since they are removable, they are useful for transporting data.

Bernoulli boxes, zip drives, and jazz drives are similar to a hard drive in storing larger amounts of information and similar to a diskette drive because they can be removed and replaced.

A disk drive as described above is an output device when writing information to the device. When stored programs and data are needed again, it is an input device, reversing the storage procedure to transfer the instructions or information to the computer's working memory for use or further processing. *See* COMPUTER STORAGE TECHNOLOGY.

USB drive. A USB drive, also called a jump drive or flash drive, is a device smaller than a key (it often is placed on a keychain and hence is called a keychain drive) that connects to a computer via the universal serial bus port. USB drives range in size from 16 megabytes to multiple gigabytes of information. They are preferred to floppy disks and zip drives because of their size and capacity. Other devices that connect to a USB through a special adapter and look like a disk drive include compact flash cards and memory sticks. *See* SEMICONDUCTOR MEMORIES.

Optical drives. Most programs and data are stored on magnetic media, including diskettes, hard disks, and tapes. But data can also be stored and retrieved with light, the light of a laser beam reading a pattern of pits on a so-called optical disk.

CD-ROM drive. The most familiar type of optical disk is the CD-ROM (compact disk read-only memory). It is called a compact disk because it is almost identical to audio compact disks; it is read-only because the data can be viewed or heard on the computer but not altered or added to. CD-ROMs have moved from such specialized uses as storing vast amounts of information for businesses and government agencies to consumer products offering software, especially games and reference works, enhanced with video clips, animation, and music and sound effects. CD-R (write) drives are write-only devices, while CD-RW (rewritable) drives can be rewritten numerous times. The capacity of a standard CD-ROM is 650–700 megabytes.

DVD drive. A DVD (digital videodisc) drive is similar to a CD-ROM drive and is backward-compatible in that the can read CD-ROMs. Standard DVDs have a minimum capacity of 4.7 GB of data. There are a number of different formats for DVDs (such as DVD-R, DVD+R, DVD-RW, and DVD+RW). DVD+RW and DVD-RW drives are rewritable. DVDs are excellent backup devices for personal computers. *See* COMPACT DISK; OPTICAL RECORDING; VIDEO DISK.

Tape drives. The early personal computers of the 1970s stored programs and data on tape cassettes in recorders similar or identical to those of audio tape recorders. The drawback with tape storage is that it is sequential; that is, the tape must be gone through from the beginning until the desired data are reached. Disks, whether floppy or hard, are random-access, which means they can go directly to the data. Because of their greater efficiency and speed, disk drives have quickly replaced tape drives as the primary means of data and program storage. Tape drives are still in use for backup storage, copying the contents of a hard disk as insurance against mechanical failure or human error. The relative slowness of tape drives does not matter when they are used for backup because the recording can be scheduled to begin at the end of the workday or work week, and the recovery of the data may never be necessary. Usually, the entire hard disk is backed up in the first session. In later sessions, only files that have changed are recorded (incremental backup). Tape capacity has grown from tens of megabytes of data to more than 100 gigabytes of data, depending on the format and how much data compression is used. *See* MAGNETIC RECORDING.

Camera. A digital camera can be connected to a computer through a USB port. It essentially looks like a USB drive to the computer system. Hence, photos can be moved to and from the camera with simple copy commands or automatically uploaded to the computer via special software supplied with the camera.

A PC or Web camera provides video input to a computer. Such cameras can be used for a variety of applications, including security monitoring. A common use of such cameras is for online "chatting" in which participants can see each other as well hear each other. Such a use requires broadband connections for high-speed transmission and receiving of data.

Scanner. A scanner converts a hard-copy image, such as text, a drawing, or a photograph, into a digital image and sends into the computer for display or further processing. Hand-held scanners are rolled over the image, while flatbed scanners hold the image on a sheet of glass. The image is viewed as a graphics image, not a text image, so it can be altered with a graphics program but not edited with a word-processing program unless the scanner is part of an optical character-recognition (OCR) system. To digitize photographs, a scanner may dither the image (put the dots a varying amount of space apart), or use the tagged image file format (TIFF), storing the image in 16 gray values. Some scanners can use standard video cameras to capture images for the computer. *See* CHARACTER RECOGNITION; IMAGE PROCESSING.

Bar-code reader. Bar-code readers are specialized scanners. A bar-code reader is able to scan and interpret bar codes, the most common of which is a UPC (universal product code) stored as a one-dimensional bar code, where each digit is represented by the ratio of the widths of adjacent stripes and white areas. Such bar-code readers are found on products in grocery stores and other establishments. Two-dimensional bar-code readers are able to read bar-codes that store information along the height as well as the length of the code. Common examples of such bar codes are those printed on income tax forms by tax software.

RFID reader. An RFID (radio-frequency identification) reader is used to poll an RFID tag with radio signals sent via its antenna. The tag in turn responds with identification information sent to the reader. Hence, RFID readers are technically input/output devices.

Printer. This device puts text or other images produced with a computer on paper or other surfaces. In the early days of personal computers, it was widely believed that computers would lead to the paperless office. But because of the convenience of paper copies and the ease of duplicating them, the personal computer and printer have resulted in a great increase in paper documents. Printers are either impact or nonimpact devices.

Impact printers. A daisy-wheel or thimble printer is so called from the shape of the elements bearing raised images of the characters that strike the paper through an inked or carbon ribbon. They produce printouts similar to those from a typewriter. The quality of the printouts is high, but they are limited to the characters contained on the printing element, and their speed, perhaps 30 characters per second, which is considered too slow.

Dot-matrix printers produce their images by striking a series of wire pins, typically 9, 18, or 24, through a ribbon in the pattern necessary to form the letter, number, line, or other character. The quality of the printout varies. A matrix with a small number of pins will produce characters in which the individual dots can be distinguished; one with a large number of pins can produce characters of a crispness that rivals the quality of daisy-wheel or laser printers. Some dot-matrix printers can strike a line a second time, with the dots slightly offset to produce more solid characters but with a penalty of reduced speed.

A thermal printer uses heated pins against heat-sensitive paper. The disadvantage of this type of printer is that it cannot print on standard paper. Many store receipts are printed on small thermal printers.

Line printers generally print a line at a time. There are two types of line printers: drum printers and chain (or "train") printer. Chain printers use a chain with a print "slug" for each character that can be printed. As the chain moves across the printer, a print hammer strikes the slug against a ribbon from the back of the paper resulting in the struck character being printed in that position. A drum printer uses a similar method of hammers behind the paper striking against a rotating drum. Chain and drum printers can operate at speeds of thousands of lines per minute.

Nonimpact printers. Laser printers are similar to photocopying machines. A laser beam is directed by a rotating mirror to draw the image on a drum, where it is changed to an electrostatic charge that attracts a fine powder, called toner. The paper, also charged, rolls on the drum and attracts the toner's image, which is then fused to the paper by heat. The image can be formed, with a sharpness of 300 dpi (dots per inch) or more, at a speed of four pages or more per minute. The quality of laser printer output is the highest generally available. However, laser printers cannot print through multipart forms or, usually, on wider paper, so dot-matrix and even daisy-wheel printers have not been totally abandoned. *See* PHOTOCOPYING PROCESSES.

Ink-jet printers carry their ink in a well, where it is turned into a mist by heat or vibration and sprayed through tiny holes to form the pattern of the character on paper, much as a dot-matrix printer does by direct impact with the ribbon. The quality of the printout rivals that of laser printers, although ink-jet printers can suffer problems with clogging, smearing, and speed.

Color printers. Printers designed to print images in one color or a full range of colors may use similar technologies to black-and-white printers. Most color printers use ink-jet and laser technology. Some color printers are thermal-transfer printers, in which heat melts colored wax onto the paper. Many color printers also provide for photo printing of digital photos. *See* PRINTING.

Modem. A modem (modulator demodulator) connects one computer to another, ordinarily through the telephone lines, to exchange information. A modem sending data modulates the digital information from the computer into tones, the analog signals that can be transmitted over a telephone line. A modem receiving data demodulates the tones coming from a telephone line back into digital information for its computer. The speed of a modem is measured in bits per second (bps), and the speed for most dial-up modems is 28 to 56 kbps (kilobits per second). [The baud is occasionally and incorrectly used as a synonym for bps.] Higher speeds are preferable not only for convenience but also for reducing telephone charges. The communicating modems operate at the highest speed that they have in common, or the highest speed that the quality of the telephone connection permits. Most modems also send and receive facsimile images. A cable modem operates over a coaxial or fiber-optic cable. The speed of cable modems is over 1 Mbps (megabits per second). *See* MODEM.

Multifunction devices. While printers are typically considered output devices, some are multifunction devices that include a scanner, a laser or color ink-jet printer, and a fax modem. Because the multifunction nature of these devices, they can also operate as a standalone fax machine, a copier, or a color copier (if the printer is a color printer). *See* FACSIMILE.

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Computer programming

Designing and writing computer programs, or sequences of instructions to be executed by a computer. A computer is able to perform useful tasks only by executing computer programs. A programming language or a computer language is a specialized language for expressing the instructions in a computer program. A person engaged in computer programming is commonly called a programmer. Two major stages can be identified in a typical process to develop a computer program: problem solving and implementation.

Problem solving. In this stage the programmer gains a full understanding of the problem that the computer program under development is supposed to solve, and devises a step-by step procedure (an algorithm) that, when followed, will solve the problem. Such a procedure is then expressed in a fairly precise yet readily understandable notation such as pseudo code, which outlines the essentials of a computer program using English statements and programming language–like key words and structures. *See* ALGORITHM.

A useful example concerns the problem of finding the greatest common divisor (gcd) of two given positive integers. After an analysis of the problem, a programmer may choose to solve the problem by the procedure described by the following pseudo code. (In the pseudo code, the modulus operator produces the remainder that results from the division of one integer by another; for example, 15 modulus 6 yields 3.)

```
1) Let x and y be the two given integers
2) As long an x and y are greater than 0,
   repeat lines 3–5
3)     if x is greater than y
4)         then replace x by the value of x
           modulus y
5)         else replace y by the value of y
           modulus x
6) If x is 0
7)     then y is the gcd
8)     else x is the gcd
```

See NUMBER THEORY.

Lines 3–5 and 6–8 are examples of the selection control structure, which specifies alternative instructions and enables a computer to choose one alternative for execution and ignore the other. Lines 2–5 form a repetitive control structure (commonly called a loop), which causes the computer to execute certain instructions (lines 3–5) repeatedly.

Programmers indent to show the structural relationship among the statements and to enhance the readability of the program. In the example, indentation makes it clear that lines 4 and 5 are part of the selection structure beginning at line 3, that lines 3–5 are part of the loop that begins at line 2, and that lines 7 and 8 are part of the selection structure that begins at line 6.

An algorithm developed to solve a given problem should be verified to ensure that it will function correctly. The following list shows how the above procedure derives the gcd of 48 and 18 by successively modifying the values of x and y.

x	y
48	18 (Let x be equal to 48 and y equal to 18)
48	18 (48 modulus 18 is 12, which replaces 48)
12	18 (18 modulus 12 is 6, which replaces 18)
12	6 (12 modulus 6 is 0, which replaces 12)
0	6 (since x is 0, the loop ends and 6 is the gcd)

Implementation. In this stage the pseudo-code procedure developed in the problem-solving stage will be expressed in a programming language. There are numerous programming languages, in two broad classes: low-level languages, which are difficult for human programmers to understand and use but can be readily recognized by a physical computer; and high-level languages, which are easier for human programmers to use but cannot be directly recognized by a physical computer. Nowadays most computer programs are first written in a high-level language and then translated into an equivalent program in a low-level language so that a physical computer can recognize and obey the instructions in the program. The translator itself is usually a sophisticated computer program called a compiler. *See* PROGRAMMING LANGUAGES.

Shown below is the gcd-finding procedure written in a widely used high-level language called C++.

```
/*********************************************************
 * The function findgcd computes the greatest   *
 * common divisor of two int parameters, and    *
 * returns the result as an int value           *
 *********************************************************/
 int findgcd (int x, int y)
 {  while (x > 0 && y < 0)
          if (x > y)
                  x = x % y;
          else    y = y % x;
    if (x == 0)
                  return y;
          else    return x;
 } .
```

The text beginning with /∗ and ending with ∗/ (the first five lines above) is a program comment. Program comments are not executable instructions and do not affect the functioning of a computer program in any way, but are intended as a way to document a computer program. Appropriate program comments enhance program readability and are considered an important part of a computer program. A more readable program is usually easier to enhance or modify when such needs arise later. The rest of the above text is C++ code (instructions in the language C++) to compute the gcd of two given integers. Indentation in C++ code serves the same purpose as in pseudo code. It is obvious that the above C++ code closely parallels the pseudo code developed previously, as they both express the same abstract procedure.

Syntax errors and logic errors. When a program in a high-level language is being compiled (translated) into machine-executable instructions, the compiler is usually able to detect syntax errors in the program. Syntax errors reflect the incorrect use of a programming language and must be corrected before a program can be successfully compiled. However, error-free compilation of a program does not guarantee that the program will function correctly when it is executed by a computer. Execution of such a program on a computer may not yield the desired result if there is a logic error in the program. Logic errors often require more skill to correct than syntax errors. In order to identify the source of an error in program logic, a programmer may need to revisit both the problem-solving and the implementation stages in the program development process.

Top-down design. Seldom is a large computer program constructed as a single, monolithic entity. The problem that a program is intended to solve can usually be divided into subproblems, each of which can often be further divided into even smaller subproblems. The process can be repeated until all subproblems are sufficiently small and easy to solve. Known as top-down design or stepwise refinement, such repeated decomposition of a large, complex task into smaller, more manageable ones is a widely accepted principle for designing large, complex computer programs.

Object-oriented programming. Object-oriented programming is a way to structure a computer program. The object-oriented paradigm has gained widespread acceptance in recent years and is supported by such widely used languages as C++ and Java. An object includes relevant data and operations on the data as a self-contained entity. Interaction with an object can be made by invoking the object's operations. Each object is an instance of an object class. Object classes may be related by inheritance; one class may be a subclass (specialization) of another class. At the center of an object-oriented program design is a collection of objects that represent entities in the application domain. Identifying the objects and object classes, the relationship among the object classes, and the interactions among the objects is a major issue in designing an object-oriented program. *See* OBJECT-ORIENTED PROGRAMMING.

Language processors. Although many widely used programming languages are processed by compilation into machine-executable instructions, some programming languages (for example, LISP and Prolog) are usually interpreted instead of being compiled. When a computer program is interpreted, it is directly executed by another program called an interpreter without being translated into low-level, machine-executable instructions. Some other languages are processed by a hybrid approach. For example, a program in the language Java is first compiled into an equivalent program in an intermediate-level language, which is executed by an interpreter. *See* COMPUTER; DIGITAL COMPUTER. Samuel C. Hsieh

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Computer security

The process of protecting against threats to computing systems. A threat is an event that can cause harm to computers, data or programs, or computations. A failure of computer security occurs because of a vulnerability or weakness in a computing system. A threat agent—person, event, or circumstance—exploits a vulnerability. Computer security involves protecting against failures of availability, integrity or correctness, and confidentiality or privacy.

A failure of availability is also known as denial of service. Partial denial of service is lack of capacity or unacceptable responsiveness. Computer users expect programs and data to be available on demand to meet computing needs. Applications such as power generation, stock trading, and even airplane cockpit navigation and aspects of medical care have become so dependent on computing that loss of availability becomes a serious threat to life or society. Even on a less dramatic level, people have become dependent on computers in aspects of everyday life, and so maintaining expected availability of computers is probably the most important of the three goals of computer security.

Integrity means different things in context: sometimes it means that data or programs should be returned exactly as they were when they were recorded, or that modifications to data or programs should be made only by authorized persons, or by authorized programs, or in certain ways, or that the quality of data should be maintained. Data and programs should meet the demands of the way in which they are to be used.

The third category of failure is loss of confidentiality or privacy or inappropriate disclosure. Privacy of personal information or of data about individuals is a significant concern, as is that of sensitive corporate data (such as trade secrets and proprietary information) and government classified data.

The categories of security failures relate to authorized or acceptable behavior. In order for actions to be authorized or acceptable, a security policy must define who is allowed what access to what resources, what is to be protected, against what threats, to achieve what goals.

Computer users explicitly or implicitly perform a risk analysis by assessing the threats to computing, the likelihoods of these threats, and the harm that could occur from actualization of these threats. Risk must be balanced against the value of computing. Users select controls that prevent exploitation of one or more vulnerabilities as a means of lowering risk. Controls can be physical (such as a lock on a door), procedural (such as a policy that only supervisors can modify critical data items), or technical (such as a program control that blocks access to the password file). Controls can alter the balance among the three categories of failure: a high degree of confidentiality can reduce the availability of a system. *See* RISK ASSESSMENT AND MANAGEMENT.

Technical Controls

Technical controls can be a part of a computing system or application, or they can be added separately. If controls are added to an existing system, they must be integrated properly so that they function as expected.

Security enforcement mechanisms. A computing system must first be able to determine with high assurance the identity of the person who is seeking access (a process called identification and authentication), and the system must then verify that this person's proposed access is consistent with the security policy (a process called access control).

Identification and authentication. Identification is typically performed by logging in or entering a username. But after entering a name, a user may be asked to prove it, so that the system can be certain that one user is not trying to impersonate another. A user can authenticate an identity based on (1) what the user knows, such as a password, (2) who the user is, such as a physical characteristic (for example, a fingerprint), or (3) what the user possesses, such as a token. An authenticator must be something that cannot be easily forged, lost, forgotten, or guessed, while still making it easy for the legitimate owner to use. Techniques can use two or more approaches.

User passwords are commonly employed. Password guessing attacks use computers and actual dictionaries or large word lists to try likely passwords. Brute force attacks generate and try all possible passwords. To block these attacks, users should choose strong passwords.

Physical characteristics can be determined by biometric devices. In addition to fingerprints, voice recognition, retina patterns, and pictures are used. Although biometric authentication devices can be expensive, they are less susceptible to forgery and guessing than other methods, and they tend to be easy for users to adopt. *See* FINGERPRINT.

Tokens are widely used. Identity cards containing magnetic stripes or other elements that can be sensed combine computer access control with physical access control. Some identity cards contain small processors; these cards, called smart cards, can perform computation to guard against forgery. Another form of token resembles a pocket calculator; it is used for challenge-response, in which the user is given a challenge, a problem to solve, to which the calculator provides part of the answer. Each time the user seeks authentication, a different challenge is set, with a different corresponding answer. Challenge-response is especially desirable with computer network authentication because, even if someone intercepts the challenge and response, the interceptor cannot later reuse the response for impersonation because the challenge will be different.

Access control. The system uses a validated user identity to limit the actions the user can perform. An access control policy is a series of acceptable triples (user, object, action), such as (system administrator, password file, modify), meaning that the user "system administrator" is allowed to perform the action "modify" on the object "password file." An access control list (ACL) is a set of these triples. Access control lists can be represented as a two-dimensional matrix, as a set of rules, or in other ways.

Before permission to access an object is allowed, a reference monitor (also known as a reference validation mechanism or access control mechanism) checks that the access is allowable. A reference monitor must be complete (invoked to validate every reference permission), correct (made to implement the intended access control policy exactly), and tamperproof (unable to be disabled).

Reference monitors can simply process a representation of the access control policy in list or table form. Alternatively, they can process capabilities, which are prevalidated access "tickets." The access control system gives a user a capability to perform a certain access on a particular object, and the user later presents the capability to a reference monitor, which will inspect the capability and allow the access. Capabilities are useful in networked and distributed systems, in which access control may be done at one point and actions on objects may be done elsewhere. The Kerberos system is a popular distributed access control system based on capabilities.

Cryptography. A valuable tool in computer security is cryptography or encryption. Encryption is the process of transforming data so that the data are not readily understandable to unauthorized users; consequently unauthorized people cannot modify encrypted data in a knowledgeable way. Encryption is an important tool in computer security because it provides concealment and immunity to modification, so that it can be used to protect integrity and confidentiality. Cryptography alone is not a security control; it is a technology upon which controls can be based.

Encryption is a transformation function. Data to be encrypted are called plaintext, and the encrypted form is called ciphertext. The encryption function E is denoted $C = E(P)$, where P is a body of plaintext and C is its resulting ciphertext. There may also be a decryption function D that reverses the effect of encryption, so that $P = D(C) = D(E(P))$.

Encryption is a means by which two people can share a secret: one encrypts the secret and the other decrypts it. To facilitate sharing secrets using encryption, people use keyed encryption. A key is an additional parameter that tailors the encryption function, in the same way that a key tailors a basic lock so that it can be opened only by someone possessing the key. The key must be supplied to encrypt or decrypt, and so a single algorithm can represent many different encryptions with different keys.

Key management—arranging the distribution, revocation, and replacement of cryptographic keys—is very difficult, especially in a situation with many users who have no common basis for trust, as is true in many computing systems. The implementation of encryption must be secure in order for the encrypted results to protect the data adequately. *See* CRYPTOGRAPHY.

Security of Programs

Computer programs are both part of the protection and part of the things protected in computer security. Programs implement access controls and other technical security controls. But those same programs must be protected against accesses that would modify or disable their ability to protect. And those programs must be implemented correctly.

Correctness, completeness, and exactness. A computer program is correct if it meets the requirements for which it was designed. A program is complete if it meets all requirements. Finally, a program is exact if it performs only those operations specified by requirements. Computer security requires correct, complete, and exact programs, and nothing more. A program has inevitable side effects. For example, a program inevitably assigns values to internal variables, uses computing time, and causes entries to be generated in audit logs. Although side effects seem benign, they can be used maliciously to leak information. The exactness requirement really concerns only those significant operations specified by requirements, but in security almost any side effect can be significant. Determining which additional actions are security-relevant is difficult, if not impossible.

Correctness and completeness can be determined to some degree by careful testing, although with large or complex systems it may be infeasible to test all possible situations. It is difficult to test security systems appropriately, because they can be large and complex, and because it is hard to simulate all the environments and approaches by which systems can be attacked.

Malicious code. Computing is so fast and complex that users cannot know everything a program is doing. Programs can be modified or replaced by hostile forms, with the replacements seeming outwardly the same as the originals. The general term "malicious code" covers Trojan horses, viruses, worms, and trapdoors. Malicious code has been present in computing systems since the 1960s, and it is increasingly prevalent and serious in impact. Unfortunately, there are no known complete forms of protection against malicious code.

A Trojan horse is a program that has an undocumented function in addition to an apparent function.

For example, a program may ostensibly format and display electronic mail messages while also covertly transmitting sensitive data.

A virus is a program that replicates and transfers itself to another computing system. When executed, each copy can also replicate, so that the infection spreads at a geometric rate. A virus typically inserts its replicated copy into another executable program so that when the other program is executed, so is the copy of the virus. Viruses often perform covert malicious actions.

A worm is a program that, like a virus, seeks to replicate and spread. However, the goal of the worm is only to spread and consume resources. The malicious effect of the worm is denial of service by exhaustion of resources.

A trapdoor is an undocumented entry point into a program. The trapdoor is inserted by a programmer to allow discreet access to a program, possibly with exceptional privileges. A user who had legitimate access at one time might have installed the trapdoor as a means of obtaining access in the future.

All these forms of malicious code are serious security threats for several reasons. First, malicious code can be relatively small, so that it is not readily detected. Second, its actions can be concealed: If a program fails to perform as it did, the change is evident, but an attacker can cause the change to be subtle, delayed, or sporadic, making it very difficult to detect, let alone diagnose and correct. The covert effect of malicious code can be almost anything: It can delete files, transmit messages or files, modify documents or data files, and block a user from accessing a computer system. The attack can be transmitted in pieces that activate only when the entire attack has been delivered. Finally, protecting against malicious code is difficult: The only known totally effective countermeasure is not to accept any executable items from anyone else, a solution that is scarcely acceptable for current networking and information-sharing environments.

Security of code. It is infeasible for a user to determine that a program is secure. The user has little evidence on which to base an opinion, an insecure program may intentionally hide its weaknesses, and many users have little control even over the sources from which programs are derived. Even well-intentioned programmers can fail. Beyond principles of good software engineering, the security field uses rigorous independent evaluation and penetration testing to add confidence that a program is secure. *See* COMPUTER PROGRAMMING; SOFTWARE ENGINEERING.

Independent evaluation. Users need an independent quality assessment, both that the programs meet their stated requirements and that they have no obvious security requirements. An international effort has led to the publication of the *Common Criteria for Information Technology Security Evaluation* (CC). The successor to the U.S. *Trusted Computer System Evaluation Criteria* (TCSEC or "Orange Book") and the European *Information Technology Security Evaluation Criteria* (ITSEC), the CC specifies a structure for defining security and functionality requirements (a protection profile) and a description of a product meeting those requirements (a security target) so that the security target can be evaluated objectively against the protection profile. The evaluation then serves as a seal of approval that, with a stated degree of confidence on the part of the evaluators, the product has met the requirements. The CC scheme has been applied to operating systems, firewalls, intrusion detection systems, cryptographic systems, database management systems, and networking products.

Penetration testing. Because programs intended to enforce security must be robust enough to enforce it rigorously, a special form of security testing is sometimes performed. Ordinary testing is directed toward verifying that the program does what it is expected to do; penetration testing is intended to determine if there is a way to make the program not do what it is expected to do. Penetration testers use known flaw types, common actual (and well-known) attacks, and intuition to study the system, hypothesize flaws that would prevent it from enforcing security, and conduct experiments to confirm or refute the flaws hypothesized.

Security of Operating Systems

Operating systems are the basis of security enforcement in a computing system because the operating system has control over the system resources: the file system, printers, shared buffers, memory, time, and shared programs. The original purpose of an operating system was to promote efficient and equitable sharing of computing resources, which led swiftly and naturally to security enforcement.

Operating system security functions. Operating systems are the first contact of a user with a computing system. Thus, the operating system performs user identification and authentication, as a basis for controlling resource usage and providing each user with a unique computing environment. Operating systems control access to primitive resources, such as files, devices, network connections, programs, and computing time. Most operating systems generate an audit log of what security-relevant events have occurred to the resources they control.

Operating system design for security. Operating systems are the point of fundamental security enforcement. Consequently, for strong security enforcement, security cannot be added successfully to an operating system after the design is partially completed. The reference monitor is the gate that controls access to all security-relevant objects. Several examples of secure operating systems have been implemented based on the reference monitor concept. These examples have involved thoughtful design followed by intense analysis of the design and its implementation. *See* OPERATING SYSTEM.

Database Security

A database is a collection of records containing fields, organized in such a way that a single user can be allowed access to none, some, or all of the data.

Typically the data are shared among several users, although not every user will have access to every item of data. A database is accessed by a database management system that performs the user interface to the database.

Integrity is a much more encompassing issue for databases than for general applications programs, because of the shared nature of the data. Integrity has many interpretations, such as assurance that data are not inadvertently overwritten, lost, or scrambled; that data are changed only by authorized individuals; that when authorized individuals change data, they do so correctly; that if several people access data at a time, their uses will not conflict (for example, two people cannot write a single data item at the same time); and that if data are somehow damaged, they can be recovered.

A database management system is an application program that does not necessarily have a reliable interface to the operating system, and the operating system cannot necessarily be highly trusted. Therefore, a database management system typically maintains its own lists of users and their permitted actions, and the database management system may perform its own identification and authentication of users, quite independent from that performed by the operating system.

Inference and aggregation. Database systems are especially prone to inference and aggregation. Through inference, a user may be able to derive a sensitive or prohibited piece of information by deduction from nonsensitive results without accessing the sensitive information itself. For example, knowledge of any individual's salary may be restricted, but statistical measures (such as mean, median, maximum, and minimum) of the general salary pool may be freely released. If a user can formulate a database query that selects exactly one record (for example, "select all employees who are 6′2″ tall and live in Glenwood, Maryland"), the user can then determine a single individual's salary by asking for the mean salary for the select set (of one employee). Various statistical methods make it very difficult to prevent inference.

A related problem is aggregation, the ability of two or more separate data items to be more (or less) sensitive together than separately. For example, neither the longitude nor the latitude of the location of a secret gold mine is sensitive by itself, but these two values together pinpoint the mine. It is infeasible to release one value to some people and the second value to others (even though no single person is told both) because two people could pool their knowledge. Aggregation is extremely difficult to prevent, since users can access great volumes of data from a database over long periods of time and then correlate the data independently.

Database controls. Encryption is sometimes used in database management systems for both confidentiality and integrity. A device called an integrity lock is used to ensure that the contents of a field are not modified. The field may be stored in plaintext, but a cryptographic checksum of the field, the integrity lock, is also stored. Each time an authorized change to the field is made, a new integrity lock is computed and stored; each time the contents of the field are retrieved (in response to a query), a lock is computed on the value of the field and compared with the stored lock. If the two values do not match, the field has been modified without authorization. To guard against swapping data and their locks, the encrypted data may comprise the actual data of the field together with the record identifier and the name of the field. *See* DATABASE MANAGEMENT SYSTEM.

Network Security

Enforcing security across a network has all the problems of local enforcement, coupled with problems brought on by distance and transmission. Identification and authentication, for example, requires not just verifying the identity of a requesting user but also identifying the system to the user. A user does not want to supply a password (or a credit card number or other sensitive information) to the wrong system. Even if the user is assured initially that the remote system is authentic, the user may need assurance continuously throughout a transaction that the remote system has not been commandeered by an attacker or that the communication has not been diverted to a hostile system.

In a network, the same considerations apply as with nonnetworked systems: identification and authentication, access control, and auditing. The two additional areas of concern are the communications link between the local user and the remote system, and the physical and technical security of the remote system. (In fact, the remote system may be multiple systems, with the user's communication passing from one to another without the user's knowledge.)

Communications security. It is necessary to protect the communications lines by which users communicate with remote systems. Lines are subject to interception, redirection, falsification, and interruption, and the attacks range from very crude (simply cutting a wire) to very sophisticated (intercepting a message, modifying portions of it, and retransmitting the modified message).

Strong encryption is very effective in protecting against interception and modification. It is useful to consider a communication from A, through intermediate points X and Y, and ultimately to B. With end-to-end encryption, the message is encrypted at A and travels in encrypted form all the way to B. End-to-end encryption can be applied from an application to a corresponding application, so that the message is protected even as it is stored temporarily on a file system or as it passes through the operating system. This approach requires that part of the message, the routing and destination information, not be encrypted, so that along the way X and Y, which do not share the encryption between A and B, are able to move the message toward its destination.

An alternative is link encryption, in which a message is encrypted just along one path, say from A to X. At X the message is decrypted and reencrypted for the link from X to Y, and so forth. Link encryption can be applied at the physical link from A to X, so that all communications along that path are protected. Key management may be simpler than with end-to-end encryption because the encryptor needs to have keys only for its neighbors, the next points to which it sends communications. The individual user does not have to apply the encryption, manage cryptographic keys, or even understand encryption. However, a message is exposed at X and Y and also within the source and destination computing systems up to the application that handles the message.

Virtual private networks. Organizations can benefit from sharing access to computing systems that are not all located together. To do this, organizations have established virtual private networks (VPNs). These networks approach the security of a private network at costs closer to those of shared public resources. The primary security technique used is encryption. A virtual private network involves a set of known participants since an organization knows which systems will form a part of its network. Thus, cryptographic key management is reasonably straightforward: By some secured means, such as postal mail or a telephone conversation, a seed or master cryptographic key is distributed to all the systems that will participate in the private network. One party of the virtual private network then generates a new key, sometimes called a session key, that will be used for communications with that system or for a specific period of time. The session key is encrypted under the master key to be passed on to the other VPN partners.

Internet security. The Internet, or any similar public network, is subject to threats to its availability, integrity, and confidentiality. A complicating feature is that there is effectively no control on transmissions over the Internet. Consequently, a system connected to the Internet is exposed to any malicious attack that any other Internet user wants to launch.

Availability threats. Availability or denial of service threats range from disabling the connection of a system to flooding or saturating the system. The main cause of this type of threat is natural: loss of power, equipment failure, or a failed communications link. Disabling the physical connection requires access to the target system, but disabling the logical connection does not require physical access, and so it is a more likely choice for a malicious outside attacker. It requires only changing the routing information of the Internet so that the target host's address is no longer recognized. Fortunately, the Internet routing information is very well protected, so that this type of attack seldom succeeds.

A flooding attack is fairly common and difficult to protect against. The attacker either transmits (automatically) a vast amount of data to the target host, overwhelming its ability to handle legitimate communication, or the attacker exploits a flaw in the network communications protocols to cause the target host to generate its own massive volume of traffic to itself. A crafty attacker will falsify the source address of malicious communications, so that it is difficult to trace back to the attacker, making it infeasible to block or disregard communications from the malicious source.

Integrity threats. Threats to integrity include unauthorized changes to the data or programs of the target computing system. Integrity attacks seek to modify the data or programs at a target host. Malicious programs can be introduced by commandeering the target host, delivering the malicious program as if it were from a reliable source, or conveying the malicious program through a Trojan horse attack. Additionally, data can be modified by an attacker at any point on the communications link between the source and destination.

Again, encryption becomes a significant tool to control integrity. However, an advantage of the Internet is that it connects millions of sites, but the disadvantage is that there may be no shared encryption between all pairs of those sites. The difficulty is for two previously unknown entities (representing hosts or users) to authenticate each other. A certificate can be used to establish shared encryption with some degree of trust. A certificate contains an identification, an encryption key, and an encrypted field, called a digital signature, from a third party, attesting to the authenticity of the identity. Certificates can be countersigned by trustworthy third parties to add to their credibility. The encryption key in a certificate provides a basis for two unknown entities to establish a shared encryption.

Confidentiality threats. Confidentiality threats in a distributed environment are closely related to integrity threats. With minor modification, integrity attacks can be made to expose the sensitive data at the remote site or in transit. Several network protocols, such as secure http (shttp) or secure socket layer (ssl), use encryption to protect both confidentiality and integrity of communications on the Internet. *See* INTERNET; WORLD WIDE WEB.

Security perimeter. A security perimeter is a logical boundary surrounding all resources that are controlled and protected. The protected resources are called a domain (or enclave or protected subnetwork). There may be overlapping domains of varying protection, so that the most sensitive resources are in the innermost domain, which is the best protected. Protecting the security perimeter may be physical controls, identification and authentication, encryption, and other forms of access control. Two controls that relate especially to the security perimeter are network vulnerability scanning and firewalls.

Scanning. A network vulnerability scan is the process of determining the connectivity of the subnetwork within a security perimeter, and then testing the strength of protection at all the access points to the subnetwork. With a network domain, if a forgotten access point is not secured, its weakness can undermine the protection of the rest of the domain. A network scanner maps the connectivity of a domain, typically by probing from outside the domain, to determine what resources are visible from the outside. Once all outside connections are identified, each is tested with a range of attacks to determine the vulnerabilities to which it is susceptible and from which it needs to be better protected.

Firewall. It is infeasible to seal off a domain completely against outside access, because a purpose of the domain is to support communication with the outside. For example, a web site may be intended for broad public access. A firewall is a host that functions as a secured gateway between a protected enclave and the outside. The firewall controls all traffic according to a predefined access policy. For example, many firewalls are configured to allow unhindered communication outbound (from the protected domain to a destination outside the domain) but to allow only certain kinds of inbound communication. A firewall can be a separate computer, or firewall functionality can be built into the communications switch connecting the enclave to the external network.

Some firewalls hide internal resources from being visible outside the enclave. An enclave may have registered only the address of the firewall; internal hosts are not registered as part of the Internet or external network, and therefore outsiders have no way to communicate directly with them, only through the firewall. The firewall can be configured to allow only certain types of communications, for example, electronic mail, while blocking communications that could affect the status or integrity or confidentiality of an internal host, such as network management commands. Proxy firewalls simulate the effects of complex interactions across a security perimeter, filtering undesirable information flows.

Unprotected hosts. Hosts that must be accessible to the general public are often situated outside the protected domain, so that they are readily accessible to users without exposing any of the resources inside the domain. An unprotected host is acknowledged to be exposed. Unchanging content of the host can be sealed with integrity checks to detect modification, and if the content is modified, either maliciously or accidentally, the content can be restored readily from a protected copy inside the domain. Data gathered at the open site are moved inside the protected domain for more secure storage.

Intrusion detection. It is most effective to eliminate vulnerabilities, but if that is not possible, it is then desirable to recognize that an attack is occurring or has occurred, and take action to prevent future attacks or limit the damage from the current one. Anti-intrusion technologies are the different ways in which an attack can be detected and countered. Anti-intrusion technologies are prevention, to block an attack; deterrence, to make an attack sufficiently difficult to discourage the attacker; detection, to detect the existence of an attack; deflection, to encourage the attacker to direct the attack elsewhere; and diminution, to limit the negative effect of an attack. Such technologies are often collectively referred to as intrusion detection systems.

Intrusion detection can be either anomaly detection, which seeks to identify an attack by behavior that is out of the norm, or misuse detection, to identify an attack by its attempted effect on sensitive resources. Intrusion detection systems monitor a computing system in order to warn of an attack that is imminent, is under way, or has occurred.

Incident response. When an attack has occurred, the affected organization will generally study the attack in order to learn what has occurred, how to prevent a recurrence, and what is the extent of the damage. The science of computer forensics is the study of evidence from an attack. Computer forensics is much like any other investigative science in that it involves assembling potentially significant pieces of evidence and using insight, experience, and intuition to suggest connections among the pieces.

In order to assemble the knowledge about attacks and their countermeasures, organizations and countries staff computer emergency response teams (CERTs). These teams collect information about significant vulnerabilities and attack patterns and provide warnings and possible countermeasures. *See* LOCAL-AREA NETWORKS; WIDE-AREA NETWORKS.

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Computer storage technology

The techniques, equipment, and organization for providing the memory capability required by computers in order to store instructions and data for processing at high electronic speeds. In early computer systems, memory technology was very limited in speed and high in cost. Since the mid-1970s, the advent of high-density, high-speed random-access memory (RAM) chips has reduced the cost of computer main memory by more than two orders of magnitude. Chips are no larger than $^1/_4$ in. (6 mm) square and contain all the essential electronics to store tens to hundreds of thousands of bits of data or instructions. An analogous increase in magnetic recording density has increased the capacity and reduced the cost per bit of secondary memory. Traditionally, computer storage has consisted of a hierarchy of three or more types of memory storage devices (for example, RAM chips, disks, and magnetic tape units). *See* BIT.

Memory Hierarchy

Memory hierarchy refers to the different types of memory devices and equipment configured into an operational computer system to provide the necessary attributes of storage capacity, speed, access time, and cost to make a cost-effective practical system. The fastest-access memory in any hierarchy is

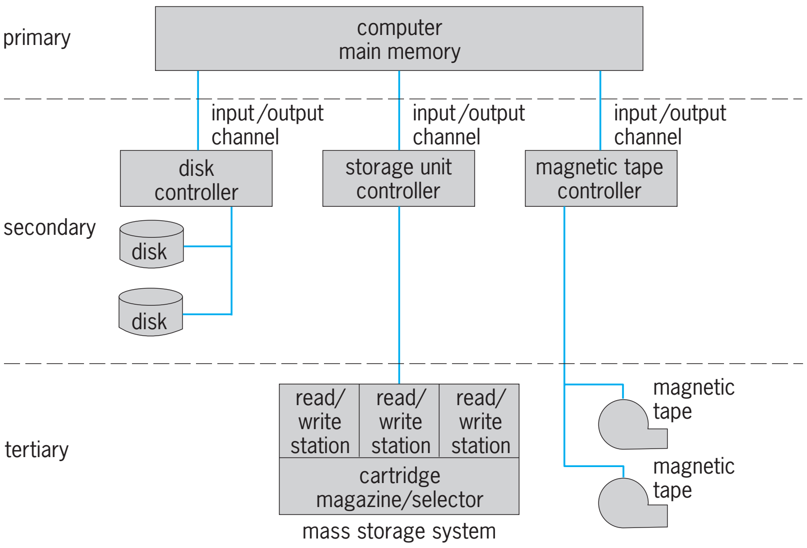

Fig. 1. Memory hierarchy levels and equipment types.

the main memory in the computer. In most computers manufactured after the late 1970s, RAM chips are used because of their high speed and low cost. Magnetic core memories were the predominant main-memory technology in the 1960s and early 1970s prior to the RAM chip. The secondary storage in the hierarchy usually consists of disks. Significant density improvements have been achieved in disk technology, so that disk capacity has doubled every 3 to 4 years. Between main-memory and secondary-memory hierarchy levels, however, there has always been the "memory gap."

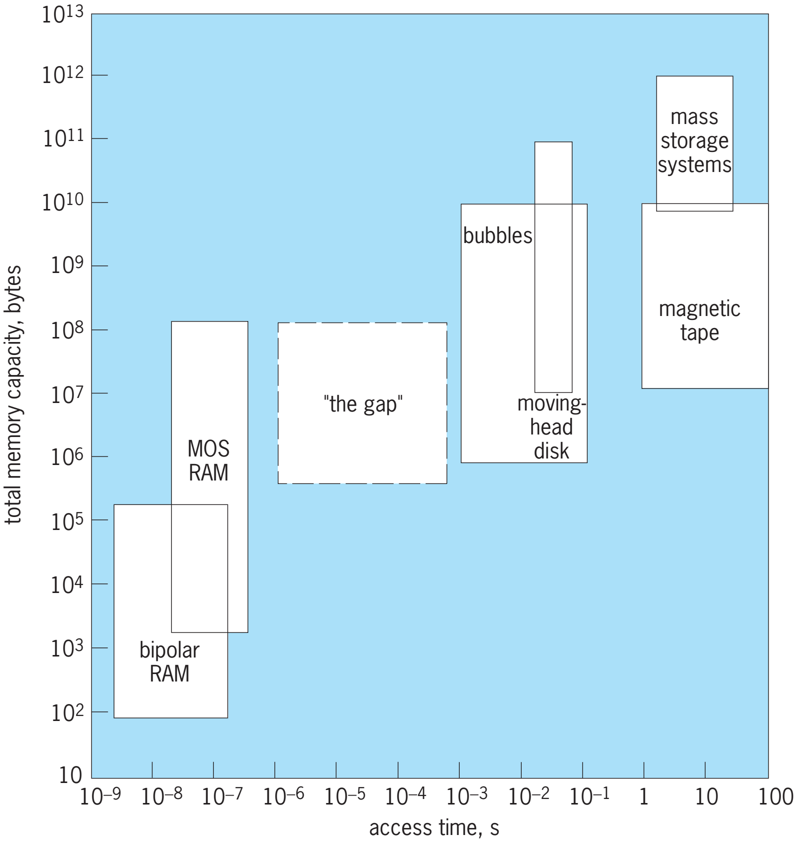

Fig. 2. Memory capacity versus access time for various storage technologies.

The memory gap, noted in the 1940s, still presents a problem for the data-processing system designer. The memory gap for access time is bounded on one side by a 60-nanosecond typical computer main memory cycle time and on the other by the 10-millisecond typical disk-drive access time. Capacity is bounded on the one side by a typical mainframe memory capacity of 256 megabytes and on the other by multiple disks, each with a capacity of from 100 megabytes to over 1 gigabyte.

The last, or bottom, level (sometimes called the tertiary level) of storage hierarchy is made up of magnetic tape transports and mass-storage tape systems (**Fig. 1**). Performance (**Fig. 2**) is usually measured by two parameters: capacity and access time. (Speed or data rate is a third parameter, but it is not so much a function of the device itself as of the overall memory design.) Capacity refers to the maximum on-line user capacity of a single connectable memory unit. Access time is the time required to obtain the first byte of a randomly located set of data.

Memory Organization

The efficient combination of memory devices from the various hierarchy levels must be integrated with the central processor and input/output equipment, making this the real challenge to successful computer design. The resulting system should operate at the speed of the fastest element, provide the bulk of its capacity at the cost of its least expensive element, and provide sufficiently short access time to retain these attributes in its application environment. Another key ingredient of a successful computer system is an operating system (that is, software) that allows the user to execute jobs on the hardware efficiently. Operating systems are available which achieve this objective reasonably well. *See* COMPUTER ARCHITECTURE.

The computer system hardware and the operating system software must work integrally as one resource. In many computer systems, the manufacturer provides a virtual memory system. It gives each programmer automatic access to the total capacity of the memory hierarchy without specifically moving data up and down the hierarchy and to and from the central processing unit (CPU). During the early years of computing, each programmer had to incorporate storage allocation procedures by determining at each moment of time how information would be distributed among the different hierarchic levels of memory, whenever the totality of information was expected to exceed the size of main memory. These procedures involved dividing the program into segments which would overlay one another in main memory. The programmer was intimately familiar with both the details of the machine and the application algorithms of the program. This all changed in the 1970s and improved significantly after 1980, when sophisticated higher-level program languages and database management software became well established, to provide significantly greater problem-solving capability. Thus manufacturer-supported operating systems evolved, with complete built-in virtual memory support capabilities, which made it possible for the user to ignore the details of memory hierarchy internal software and hardware operations. *See* COMPUTER PROGRAMMING; DATABASE MANAGEMENT SYSTEM; OPERATING SYSTEM; PROGRAMMING LANGUAGES.

In the area of memory organization, two types of memory augmentation have been employed in the more widely used computers to enhance the overall computer performance capabilities. These two memory organization techniques are the cache memory, which speeds up the flow of instructions and data into the central processing unit from main memory, and an intelligent disk controller memory that is used as a staging buffer memory to queue up instructions and data for more rapid access into main memory.

Cache memory. A cache memory is a small, fast buffer located between the processor and the main system memory. Data and instructions in current use are moved into cache, producing two benefits. First, the average access time for the processor's memory requests is reduced, increasing the processor's throughput. Second, the processor's utilization of the available memory bandwidth is thereby reduced, allowing other devices on the system bus to use the memory without interfering with the processor. Cache memory is thus used to speed up the flow of instructions and data into the central processing unit from main memory. This cache function is important because the main memory cycle time is typically slower than the central processing unit clocking rates. To achieve this rapid data transfer, cache memories are usually built from the faster bipolar RAM devices rather than the slower metal oxide semiconductor (MOS) RAM devices.

Performance of mainframe systems is very dependent upon achieving a high percentage of accesses from the cache rather than main memory. In typical systems 80–95% of accesses are to cache memory, with a typical cache size of 256K bytes. (1K bytes is equal to 1024 bytes.) Since the cache contents are a duplicate copy of information in main memory, writes (instructions to enter data) to the cache must eventually be made to the same data in main memory. This is done in two ways: write-through cache, in which write is made to the corresponding data in both cache and main memory; and write-back cache, in which main memory is not updated until the cache page is returned to main memory, at which time main memory is overwritten.

Intelligent disk controller memory. This is used as a cache memory between disk and main memories. Typically it consists of MOS RAM chips which overlap the disk operations, with their longer access time, to mask out the disk access delays so that main memory can execute subsequent tasks more rapidly and efficiently. Intelligent disk controllers provide the latest techniques to fill the memory gap with the best practical memory organization techniques for high performance. Microprocessors are also an integral part of intelligent disk controllers, and carry out many central processing unit operating system functions necessary for disk operations. This off-loads the mainframe computer from doing this kind of overhead processing to a large extent. *See* MICROPROCESSOR.

Main Semiconductor Memory

The rapid growth in high-density very large-scale integrated (VLSI) circuits has advanced to a point where only a few applications require the tens to hundreds of thousands of transistors that can now be placed on a chip. One obvious exception is computer main memory, in which there is a continual demand for higher and higher capacity at lower cost. *See* INTEGRATED CIRCUITS.

In the 1960s and early 1970s, magnetic core memories dominated computer main-memory technology, but these have been completely replaced by semiconductor RAM chip devices of ever-increasing density. This transition started with the introduction of the first MOS 1K-bit RAM memory in 1971. This was followed with the 4K-bit RAM chip in 1973, the 16K-bit chip in 1976, the 64K-bit chip in 1979, the 256K-bit chip in 1982, the 1M-bit chip in 1985, and the 4M-bit chip in the 1990s. (A 1M-bit chip has 1024 × 1024 or 1,048,576 bits.) The progression of RAM chips (**Fig. 3**) has followed the "rule of four," according to which the cost of development of a new RAM device generation can be justified only by a factor-of-four increase in capacity. *See* SEMICONDUCTOR MEMORIES.

4M-bit RAM chips. The 4M-bit MOS RAM has continued to push photolithographic fabrication techniques with feature sizes of 1 micrometer or less. For RAM chip densities of 1M bits or more per device, the integrated circuit industry has had to make a twofold improvement to maintain volume production and device reliability: better means, such as x-ray step-and-repeat equipment, to achieve features under 1 μm; and plasma-etching or reactive-ion-etching machines to achieve vertical profiles needed as horizontal dimensions decrease. Considerable progress has been made in the use of both x-ray and electron-beam techniques to achieve the submicrometer-size features needed to make even higher-density RAM chips. Most 4M-bit RAMs are dynamic RAMs. The production techniques for dynamic and static RAM chips are identical. Therefore, the cost per unit quickly becomes the cost for mass-producing one chip. Since building costs per chip are about the same whether they store 4K bits or 4M bits, higher densities lead to lower costs per bit.

RAM chip types and technologies. RAM chips come in a wide variety of organizations and types (**Table 1**). Computer main memories are organized into random addressable words in which the word length is fixed to some power-of-2 bits (for example, 4, 8, 16, 32, or 64 bits). But there are exceptions, such as 12-, 18-, 24-, 48-, and 60-bit word-length machines. Usually RAMs contain NK · 1 (for example, 64K · 1) bits, so the main memory design consists of

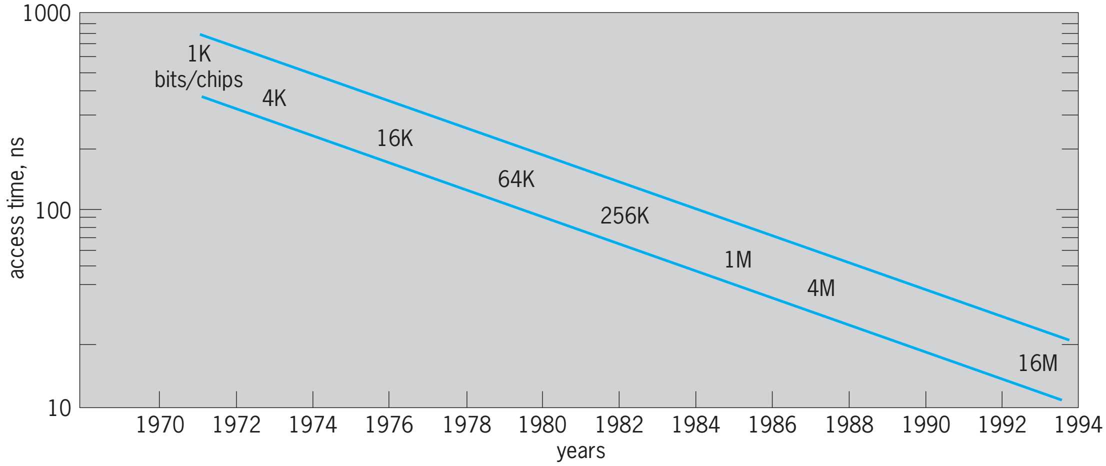

Fig. 3. Trends in performance and density (in bits per chip) of dynamic RAM chips. 1K = 1024 bits; 1M = 1024 × 1024 bits = 1,048,576 bits.

a stack of chips in parallel with the number of chips corresponding to that machine's word length. There are two basic types of RAMs, static and dynamic. The differences are significant. Dynamic RAMs are those which require their contents to be refreshed periodically. They require supplementary circuits on-chip to do the refreshing and to assure that conflicts do not occur between refreshing and normal read-write operations. Even with those extra circuits, dynamic RAMs still require fewer on-chip components per bit than do static RAMs (which do not require refreshing).

Static RAMs are easier to design, and compete well in applications in which less memory is to be provided, since their higher cost then becomes less important. They are often chosen for minicomputer memory, or especially for microcomputers. Because they require more components per chip, making higher bit densities more difficult to achieve, the introduction of static RAMs of any given density occurs behind that of dynamic versions.

There is another trade-off to be made with semiconductor RAMs in addition to the choice between static and dynamic types, namely that between MOS and bipolar chips. Biopolar devices are faster, but have not yet achieved the higher densities (and hence the lower costs) of MOS. Within each basic technology, MOS and bipolar, there are several methods of constructing devices, and these variations achieve a variety of memory speeds and access times, as well as power consumption and price differences. Within the basic MOS technologies there are several types, such as the *n*-channel MOS referred to as NMOS and the complementary MOS solid-state structure referred to as CMOS. For bipolar there are several types such as transistor-to-transistor logic (TTL) and the emitter-coupled logic (ECL). *See* LOGIC CIRCUITS.

Memory cycle and access times. The RAM memory cycle time in a computer is defined as that time interval required to read or write one word of data. Access time is defined as the time interval in which the data are available after the initiation of the read cycle. From the user's point of view, cycle time is also an important characteristic because it has more impact on overall computational speed of the system. A new data read-write cycle does not begin until the previous read cycle is completed. The specified timing, signal overlap, and tolerances allowed vary with each RAM main memory system.

Error checking and correction. Most computer main memories have a memory fault control consisting of a memory controller and a fault control subsystem which automatically corrects all single-bit errors and detects and reports all double-bit or three-bit errors. Each bit in a word is read from a separate RAM

TABLE 1. Summary of characteristics of various memory chip types

Characteristics	Dynamic RAMs	Static RAMs	Static RAMs	ROMs	PROMs	PROMs	EPROMs	EEPROMs (EAROMs)
Chip technology	NMOS CMOS	NMOS CMOS	Bipolar (ECL)	CMOS	Bipolar	CMOS	MOS (UVPROMs)	MOS
Speed (access time)	60–100 ns	50–100 ns	1–5 ns	50–100 ns	5–100 ns	50–200 ns	50–300 ns	50–300 ns
Volatility	Volatile	Volatile	Volatile	Nonvolatile	Nonvolatile	Nonvolatile	Nonvolatile	Nonvolatile
Programmability	Easy	Easy	Easy	During manufacture	Once only	Once only	Many times, long procedure	Many times, easier and faster than EPROMs
Power dissipation	Low	Low	High	Low	High	Low	Medium	Medium
Chip density of currently available devices	4M	1M	4K, 16K, 64K	256K, 1M	16K, 64K	16K, 64K	256K, 1M	64K, 256K, 1M

device. The fault control permits computer operation to continue even if a memory module is malfunctioning, and thus the computer will operate even if a memory chip is removed from the board. Failures are pinpointed to the specific chip by fault-indicating light-emitting diodes built into each array board. *See* LIGHT-EMITTING DIODE.

FIFO and LIFO chips. As memory chips increased in storage density and designers attempted to minimize interconnection circuitry, specialty memory function organizations such as first-in first-out (FIFO) buffers and last-in first-out (LIFO) buffers became available as chips. These kinds of chips are readily used in memory buffering applications to accommodate varying data rates between one element and another. The other complementary feature of FIFO and LIFO chips is the dual data paths (called ports) to allow simultaneous transfer of data into and out of these memory buffer chips. These chip types are commonly used on microcomputer boards and in the computer's peripheral interface and controller electronics.

Gallium arsenide memory chips. All the memory chips discussed above are based on the predominant silicon technology. Reliable gallium arsenide (GaAs) integrated circuits have been produced: 16K-bit and 64K-bit static RAM (SRAM) devices with 1-nanosecond access times. Development of 4M-bit SRAMs has been undertaken for military applications. Considering the need for and emphasis on increasingly rapid computers, there is definite potential for high-speed gallium arsenide logic and memory devices. *See* GALLIUM.

ROMs, PROMs, and EPROMs. Microcomputers have evolved their own special set of semiconductor memory chips (Table 1) to suit their application needs. Whereas large, medium-size, and minicomputers primarily use only RAMs that have read-write capability, microcomputers have found significant use for read-only memory (ROM) chips and programmable read-only memory (PROM) chips. Data and program storage in most microcomputer applications is separately allocated between RAMs and ROMs. ROMs provide protection, since the contents are fixed or hardwired and the chips are completely nonvolatile. During microcomputer program development, PROMs are typically used. A PROM can be written only once and involves the irreversible process of blowing polysilicon fuse links. These PROMs are neither erasable nor reprogrammable. Another kind of device, called an erasable PROM (EPROM), is cleared or rewritten by putting the EPROM chip under an ultraviolet light to zero out its contents and then using a PROM programmer to write in the new bit pattern for the modified program. After the microcomputer application program has completed final tests and acceptance, the final bit pattern in the EPROM can be put into ROMs or PROMs (using a chip mask) to facilitate quantity production. *See* MICROCOMPUTER.

EEPROMs. There are also memory chip devices called electrically erasable programmable read-only memories (EEPROMs). They have an internal switch on the chip to permit a user to electrically rewrite new contents into them. This means EEPROMs do not have to be removed from the circuit in order to clear their contents to put in the new or modified bit pattern representing another program of instructions. Thus EEPROMs have met the need in microcomputer systems for a nonvolatile in-circuit reprogrammable random word access memory device.

EEPROMs use two distinctively different technologies. The more mature technology is metal nitride oxide semiconductor (MNOS), which is a very different gate insulator process technology from that used for MOS. The MNOS technology previously used the generic acronym EAROM (electrically alterable read-only memories) until EEPROMs became common in usage for both technologies. The other technology is floating-gate MOS (also called FAMOS). FAMOS technology was used for ultraviolet erasable EPROMs (UVPROMs) and was subsequently refined to provide an electrically erasable technology. Both technologies rely on Fowler-Nordheim tunneling to move the charge to be stored from the substrate to the gate. FAMOS stores the charge on the gate itself, whereas MNOS devices trap the charge in the nitride layer under the gate.

Secondary Memory

High-capacity, slower-speed memory consists of two major functional types: random-access, which has been provided primarily by disk drives, and sequential-access, which has been provided primarily by tape drives. Since tape drives provide removability of the medium from the computer, tape is used for the majority of off-line, archival storage, although some disks are removable also. The on-line random-access disk devices are classed as secondary, and tape-based systems are classed as tertiary.

Over the history of electronic computers, while the technology for processors and main memory has been evolving from vacuum tubes to transistors to very large-scale integration (VLSI) chips, the predominant technology for secondary memory has continued to be magnetic recording on tape and disk. This has not been due so much to the absence of competing alternatives as to the continuous and rapid progression in magnetic recording capability (**Figs. 4** and **5**).

The current magnetic-disk technology will be discussed, and also the potential of new magnetic recording techniques such as thin-film, vertical recording, and bubble-memory devices; and a nonmagnetic technology, optical recording.

Magnetic disk storage. Conventional magnetic-disk memories consist of units which vary in capacity from the small 360-kilobyte floppy disks (used with microcomputers) to 1-gigabyte disk drives used with large-scale computers. Hard-disk memories are characterized by access times in the 20–80-ms region (versus access times of tens to hundreds of nanoseconds for RAMs). Figure 5 shows the historical progression in several performance factors: capacity, transfer rate, and access time.

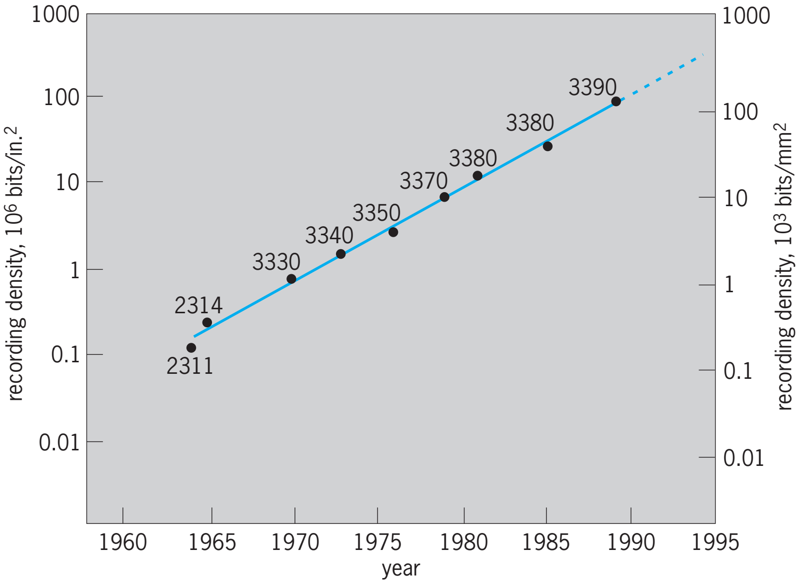

Fig. 4. Increase in recording density on magnetic disk storage. Data points represent IBM models, and model numbers are indicated. Since vertical scale is logarithmic, the straight line represents an exponential increase.

Capacity. The major area of development in disks has been the progressive and even spectacular increases in capacity per drive, particularly in terms of price per byte. There is a substantial economy of scale in storage capacity, in that the cost per byte goes down as the drive capacity goes up. Between small disks and top-end drives, the differences in access time and transfer rate may be only a factor of two to five, while the capacity difference is a factor of as much as 2000, that is, from 20 megabytes to several gigabytes.

Transfer rate. The rotation rate of the disk platter, like the action of the head actuators, is limited by considerations of physical dynamics. Increases in transfer rate will come from greater linear bit density around the track. In an absolute sense, transfer rates are not as often a system performance bottleneck as is access time.

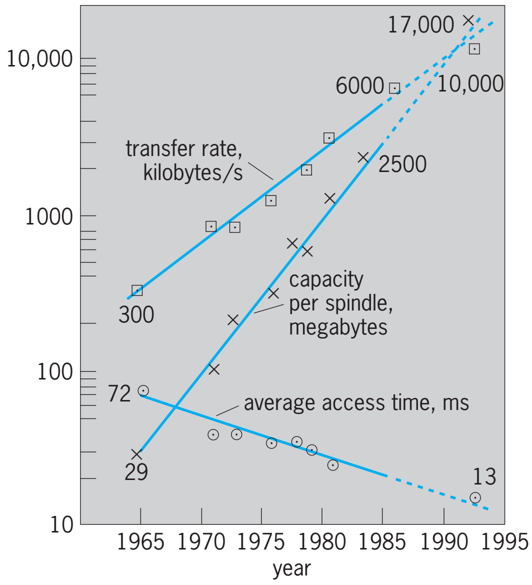

Fig. 5. Development of magnetic disk performance factors.

Average access time. Since the arm supporting the read-write head is one of the few moving mechanical parts in a computer system, it has not shown the multiple-orders-of-magnitude performance improvement over time that the electronic technologies have. Also, average access times for the highest-priced and lowest-prices disks do not vary by an enormous factor, being in the range of 10 to 80 ms for a typical microcomputer hard (as opposed to floppy) disk, and 10 to 30 ms for large disks on mainframe computers. There is nothing which indicates a breakthrough in the technology governing access time, even though greater capacities and transfer rates are still coming. Therefore, for random-access bottlenecks, the solution in the future will be the same as it is now: multiple smaller drives to allow overlapped seeks instead of a single large-capacity drive.

Basic disk technology. Many significant advances in the capabilities of commercially available disk memory technology were made during the late 1970s. One of the major trends was toward larger-capacity disks, progressing from 100 megabytes to several gigabytes per disk drive. The majority of technology improvements to provide higher capacities, lower costs, and better reliabilities resulted from the Winchester technology. Prior to this technology, removable disk packs established themselves as the most advanced technology for large-capacity disks. The Winchester technology is characterized by nonremovable, sealed disk packs, which inherently provide more reliability due to less handling and make more stringent alignment tolerances practical.

The head, or read-write transducer, has undergone substantial refinement. Central to the advance in increasing disk-packing density was the reduction in the flying height of the read-write head. Because flux spreads with distance, reduced separation between the read-write head and the magnetic surface will decrease the area occupied by an information bit. This obviously limits the number of bits that can be defined along an inch of track and increases the minimum spacing between tracks. The ideal would be a direct contact between head and surface, which is the case with magnetic tape. But this is not possible with a rigid aluminum disk whose surface is traveling at rates that can exceed 100 mi/h (45 m/s). By applying a load on the head assembly, proper spacing is maintained. All movable media memories utilize an air-bearing mechanism known as the slider or flying head to space the transducer in proximity to the relatively moving media. The slider, when forced toward the moving surface of the medium, rests on a wedge of air formed between it and the medium by virtue of their relative motion. The thickness of the wedge can be controlled by the applied force, and the wedge in effect is an extremely stiff pneumatic spring. Head-to-medium spacings were well under 10 μin. (0.25 μm) in 1982. *See* TRANSDUCER.

Some standards have been developed for interfaces between the drive and the controller, to permit compatibility among drives of various capacities and manufacturers. Among these are the storage module device (SMD) interface, enhanced small device interface (ESDI), small computer system interface (SCSI), intelligent peripheral interface (IPI), and high performance parallel interface (HPPI).

SMD drives can run at 3 megabytes per second. ESDI drives can also attain that rate. The IPI Level II drives can operate at 10 megabytes per second. The transfer rates of SCSI vary. As an intelligent interface between peripherals and computer systems, SCSI allows system designers to avoid device-level idiosyncrasies that make quick integration of new peripherals difficult. It is suitable for use on small personal computers with standard asynchronous transfer rates of 1.5 megabytes per second. It can also be used with supermicrocomputers and minicomputers with an optional synchronous transfer rate of 4 megabytes per second. Work has been done toward raising the transfer rate to 8 megabytes per second by tightening the timing specifications of the SCSI interface. Although initial versions of SCSI were designed for small computers, SCSI can meet the high-performance and high-capacity requirements of larger computers. For example, a single SCSI bus can support six SCSI-to-ESDI controllers with 24 disks, providing 7.2 gigabytes of storage, in addition to tape drives and other devices.

The HPPI was intended for interprocessor memory communication and as a data path for high-speed display monitors. It is a half-duplex point-to-point channel and can transmit data at 800 or 1600 megabytes per second. By using HPPI, it is possible to set up a high-performance high-capacity storage system of 256 gigabytes (or more) for supercomputer applications.

In addition to fixed Winchester-type disk units of various capacities, disk storage is used in several removable forms.

Cartridge disks. Removable storage cartridges containing single-disk packs are used extensively with minicomputer systems. The cartridge disk-drive unit has capacities ranging from 1 to 10 megabytes, depending on the recording density. Average access times range from 35 to 75 ms, and data transfer rates from 200 to 300 kilobytes per second. Physically, these plastic-encased cartridges are either top-loaded or front-loaded units. These units, besides having a removable disk, also have a fixed disk. The performance features of cartridge disks compete favorably with the larger-capacity disk pack storage equipment. A disadvantage of removable disk cartridges or disk packs is reduced reliability compared to fixed units.

Floppy disks. Floppy disks have become the widely used random-access secondary memory for microcomputer systems. The floppy disk was originally developed by IBM in 1965 for internal use on its large 370 computers. The disk was designed to be a permanent nonvolatile memory storage device, written at the factory. However, large numbers of new and varied applications evolved for these relatively small, compact disk systems. Floppy disks derive their name from the recording medium, an oxide-coated flexible disk (similar to, but more flexible than, plastic 45-rpm music records) enclosed within a protective plastic envelope. The Mylar flexible disk is $7^3/_4$ in. (195 mm) in diameter, 0.003 in. (0.075 mm) thick, and records 3200 bits per inch (125 bits per millimeter) and 48 tracks per inch (1.9 tracks per millimeter). The disk is permanently enclosed in a protective envelope. The common reference to the size of this disk is 8-in. (200-mm). The protective envelope contains alignment holes for spindle loading, head contact, sector-index detection, and write-protect detection. The capacity of this easily transportable medium is 8 megabits, commonly laid out on 77 tracks, each divided into 26 sectors.

The flexible-disk drive subassembly consists of the metal base frame, the disk-drive motor that rotates the spindle (360 rpm for 8-in. or 200-mm, 300 rpm for $5^1/_4$-in. or 133-mm) through a belt drive, and a stepping motor with an integral lead screw to form the head-positioning actuator. The read-write head is mounted on a carriage that the lead screw moves. Head load is achieved by moving a load pad against the disk and restraining the disk between the head and the load pad to accomplish the head-to-disk compliance.

The removable floppy disk, called a diskette, was originally 8 in. (200 mm), in both single and double densities, and single- and double-sided. A variety of incompatible formats exist, particularly in double density, as the majority of suppliers use a common (IBM) format in single density. The most conspicuous format difference is in sector boundaries, hard-sector referring to boundaries of physical holes in the diskette, and soft-sector to boundaries that are software-formatted. As recording density increased and packaging considerations for microcomputers became important, a smaller, $5^1/_4$-in. (133-mm) diskette was introduced in 1976 with a similar proliferation of formats as in 8-in. (200-mm). Many systems use yet smaller sizes such as 3, $3^1/_4$, and $3^1/_3$ in. (75, 83, and 90 mm). Standard storage capacities range from 720 kilobytes to 1.44 megabytes. The dominant format is the $3^1/_2$-in. (90-mm) high-density (1.44-megabyte) floppy diskette. Floppy diskettes (and drives) with density higher than 1.44 megabytes are available. However, floppy diskettes are often replaced with CD-ROM disks.

Thin-film and vertical recording. Several technologies are in development for disk storage.

The recording technology for conventional magnetic disk recording has been based upon ferrite heads and a recording surface consisting of a coating embedded with ferrous oxide particles. One of the limiting factors is the thickness of the recording layer, which is 20–50 μin. (0.5–1.25 μm). With current products pushing the limits of recording density achievable with that approach, a successor technology has been developed, called thin-film.

The thin-film technique uses a continuous magnetic film of cobalt or nickel, applied by electroplating to a controlled thickness of as little as 1 μin.

(25 nanometers). Either the head or the recording surface or both can use thin-film technology. Most of the major conventional large disks use thin-film heads and an oxide recording surface. Advanced models are designed to use a thin-film recording surface. Thin-film technology is the source for current progress in disk capacity and transfer rate. It was first introduced in small disks, partly due to greater ability to withstand the more portable environment of the small computer. The hardness of the medium which provides this resiliency also reduces both the likelihood and consequences of head crashes.

Another magnetic recording technique is vertical, or perpendicular, recording. In this approach the miniature magnets which are formed in the recording media are oriented downward into the surface rather than longitudinally along the surface. This allows closer packing of the magnetized spots, not just because of spatial compression, but also because of improved magnetic interaction between adjacent spots. The adjacent spots repel each other in the longitudinal case but attract in the vertical case. This technique offers the potential for significantly extending recording density and the accompanying performance parameters.

Recording density is the product of the bit density along the recording track, in bits per inch (or bits per millimeter), and the number of tracks per inch (or tracks per millimeter) across the recording surface (**Table 2**). For a given rotation rate of the disk, the bit density along the track determines the transfer rate.

The point at which vertical recording becomes attractive to develop into commercial products depends in part upon the level of capability which can ultimately be achieved with thin-film technology. The density level achieved by vertical recording technology may represent a limit for magnetic recording. If so, one possible answer to the question of how further levels of performance can be obtained is optical recording.

Optical recording. Optical recording is a nonmagnetic disk technology that uses a laser beam to burn pits in the recording medium to represent the bits of information, and a lower-power laser to sense the presence or absence of pits for reading. This technology has the potential for higher ultimate recording density than magnetic recording. The medium is removable and relatively inexpensive. The removability is significant in light of the nonremovability of most current and projected high-capacity magnetic disks. The recording density increase is apparent when it is noted that 4-gigabyte capacity is achieved on a single disk, whereas current-model large-capacity (2.5-gigabyte) magnetic drives typically consist of a cabinet containing two disk assemblies, each assembly having 16 platters.

One of the first optical disk mass-storage devices has 4 gigabytes on a removable, nonerasable, 14-in. (350-mm) disk. The transfer rate of 1.5 megabytes per second buffered or 3.0 megabytes streaming is similar to that of conventional magnetic disks (3.0 for the IBM 3380). The average access time is slower than that of high-performance magnetic disks at 84.7 ms, versus the 3380's 24 ms, but track-to-track access is a comparatively fast 1.0 millisecond. The corrected bit error rate is 1 in 10^{13}, which is compatible with magnetic disk standards.

In addition to the 14-in. (356-mm) disk for large-capacity systems, 12-in. (300-mm) optical disk systems in the 1-gigabyte capacity range have been produced for use with 16- or 32-bit microcomputer and minicomputer systems.

Disadvantages. Optical technology has several disadvantages. First, the medium is not inherently erasable, although systems which can erase and rewrite are also in development. The primary problem in producing a commercial optical disk system has been getting the bit error rate down to an acceptable level, with sufficient recording density to be competitive with magnetic recording. To be competitive with magnetic tape, a bit error rate, after error detect and correct, of 1 in 10^{10} to 10^{11} is needed, and to compete with magnetic disk, 1 in 10^{13} to 10^{14}. Through error detect and correct techniques, the 1 in 10^{13} level has been attained.

The bit error rate problem is far less critical for storage of documents and images, since bit dropout is seldom noticeable, in contrast with financial information, where it could be disastrous. This is the reason that optical disk recording was first used successfully in consumer and industrial systems for videotape image information, and for document storage and retrieval systems. *See* VIDEO DISK.

Applications. The nonerasability of the technology can be an advantage for some applications. Examples are data which must be kept for historical or audit-trail purposes, and applications where large amounts of data must be shipped among different locations.

When this technology matures, it will be an event of major significance, being a removable, large-capacity, random-access device using a recording technology with large potential for further growth. The potential for development of yet higher

TABLE 2. Storage densities for various recording technologies

	Bit density per track		Track density	
Technology	Bits/in.	Bits/mm	Tracks/in.	Tracks/mm
(Magneto) optical	20,500	800	15,000	600
Magnetic (floppy)	17,500	700	135	5
Magnetic (hard disk)	24,000	960	1,000	40
Floptical (optical floppy)	24,000	960	1,250	50

recording densities is perhaps the most significant factor, but in addition, having large capacity on a removable platter would allow some other kinds of system development. One possible system, referred to as a jukebox, would store on the order of 100 disks in an automatic retrieval and mounting device, so that a given disk could be fetched and accessed in around 5 seconds giving an on-line storage in the range of 500 gigabytes. Previous systems for very large online storage which have been delivered in significant quantity are the cartridge tape systems from IBM and CDC and automated tape libraries discussed below. The cartridge tape systems have capacities to 50 megabytes (IBM) and 8 megabytes (CDC) per cartridge; hence the optical system would provide a great improvement in the capacity available on the basic storage unit, and the automated tape libraries of course have the limitation of sequential data access.

CD-ROM and WORM. CD-ROM (compact disk–read-only memory) and WORM (write once, read many) are special types of optical disks. CD-ROM resembles the related audio compact disk technology in that users of CD-ROM can read only prerecorded data on the disk. A 5-in. (125-mm) CD-ROM can hold 500 to 600 megabytes, which is equivalent to 1400 to 1700 (360-kilobyte) diskettes. For example, the text of a 20-volume encyclopedia could be easily stored on a CD-ROM disk. CD-ROM has become an add-on peripheral device for some personal computers and workstations.

The CD-ROM disk and its drive are physically similar to the audio compact disk and its player, but there are several key differences: (1) A CD-ROM drive does not have a digital-to-analog converter. (2) It does have more powerful error correction than the audio system, because computer data requires a lower error rate, typically one error every 10^{15} bits, while the ratio of one error in 10^8 is acceptable in an audio compact-disk system. (3) The CD-ROM drives employ data scrambling to protect the servo control circuits from harmful dc components.

In CD-ROM, data are stored digitally on the surface of the substrate as a series of pits and lands of variable lengths. A land is the surface of the substrate between pits. Instead of using pits and lands to represent ones and zeros, the data in CD-ROM are represented in terms of the transitions from a pit to a land and vice versa (ones) and by the lack of such transitions (zeros). This arrangement, together with a modulation scheme, enhances the resolution with which data are read off the disk from about 1 μm—the diameter of the laser beam—to about 0.6 μm. The result is a 60% increase in the density of the data on the disk.

The pits on the disk surface can be arranged in either concentric circles, like tracks on magnetic disks, or in a spiral track, as on vinyl phonograph records. One common data format uses concentric tracks with the disk rotating at a constant angular speed. This simplifies the servomechanism but wastes space on the outer part of the disk because the bits in the outer tracks are separated from each other by more space than that necessary for adequate resolution. With the spiral track, the disk can be rotated so that the track passes the read head at a constant linear speed. This means that the disk must rotate more slowly when the laser beam is focused on the outer tracks and more quickly when the beam is on the inner tracks. Whether the tracks are concentric or spiral, the intertrack distance is about 1.6 μm, and the width of the pits is about 0.6 μm.

The average access time for CD-ROM drives ranges from 320 ms (for double-speed drives) to 160 ms (for quadruple-speed drives). The average data transfer rates vary from 300 kilobytes per second for double-speed drives to 450 kilobytes per second for triple-speed drives and 600 kilobytes per second for quadruple-speed drives.

While CD-ROM technology is fairly well established, the lack of established standards for WORM technology could delay its acceptance. WORM drives come in different sizes: $3^1/_2$, $5^1/_4$, 8, 12, and 14 (90, 133, 200, 300, and 350 mm). Capacities of $5^1/_4$-in. (133-mm) WORM drives range from 200 megabytes to over 1 gigabyte, while 12-in. (300-mm) WORM drives are in the 2–10-gigabyte range. *See* COMPACT DISK.

Bubble memory devices. Bubble memories are chips rather than disks, but are different from semiconductor memories in that they are magnetic devices, in which the absence or presence of a magnetic domain is the basis for a binary 1 to 0. The performance characteristics of these devices makes them competitive as small-capacity secondary storage. A magnetic bubble is in reality a cylindrical magnetic domain with a polarization opposite to that of the magnetic film in which it is contained. These cylinders appear under a microscope as small circles (which give them their name) with diameters from 80 to 800 μin. (2 to 20 μm). The size of a bubble is determined by the material characteristics and thickness of the magnetic film.

Bubbles are moved or circulated by establishing a magnetic field through a separate conductor mounted adjacent to the bubble chip. A large portion of the bubble chip must be given over to circuitry for generating, detecting, and annihilating the bubbles. Magnetic-domain bubble devices typically operate in an endless serial loop fashion or in an organization with serial minor loops feeding major loop registers. Bubble memories are particularly well suited to applications such as portable recorders because of their physical advantages (low power requirements and light weight) and speed advantage over electromechanical devices such as cassettes and floppy disks. Like their electromechanical counterparts, bubble devices are nonvolatile; that is, they retain their contents when the power goes off.

The controller is central to any bubble memory system, which it serves as the interface between the bubble chip and the system bus. It generates all of the system timing and control functions and supervises the handshaking operations required to access and transfer data between the system bus and the bubble memory module. Usually a controller can operate more than one bubble chip module, in most cases up to eight modules. The function-driver integrated circuit produces the control currents required to generate and input or ouput tracks on the chip. The sense-amplifier integrated circuit converts the analog out-put signals produced by the bubble detector into a transmittable data stream that passes to the controller. The coil-driver integrated circuits excite the x and y coils of the bubble chip package with out-of-phase signals to produce the rotating field that moves the bubbles.

Several companies are producing 1-megabit and 4-megabit bubble memory chips, and 16-megabit bubble memory chips are in the development stages. Under a cross-license and alternate source agreement, these companies have agreed to jointly adopt a low-height leaded package for complete component level interchangeability. Each company developed its peripheral chip set for the 4-megabit magnetic bubble module that will be compatible with the 1-megabit units.

For portable and other special applications, bubbles have definite advantages such as nonvolatility, low power, and high compactness. Performance capabilities relative to floppy disks are 100 kilobits per second for bubbles versus 200–250 kilobits per second for floppies, and 40 milliseconds average access time for bubbles versus 200–250 milliseconds for floppies.

Magnetic Tape Units

In magnetic tape units, the tape maintains physical contact with the fixed head while in motion, allowing high-density recording. The long access times to find user data on the tape are strictly due to the fact that all intervening data have to be searched until the desired data are found. This is not true of rotating disk memories or RAM word-addressable main memories. The primary use of tape storage is for seldom-used data files and as back-up storage for disk data files.

Half-inch tapes. Half-inch (12.5-mm) tape has been the industry standard since it was first used commercially in 1953. Half-inch magnetic tape drive transports are reel-to-reel recorders with extremely high tape speeds (up to 200 in. or 5 m per second), and fast start, stop (on the order of 1 millisecond), reverse, and rewind times.

Performance and data capacity of magnetic tape have improved by orders of magnitude (**Table 3**). Just prior to the 1970s came the single-capstan tape drive, which improved access times to a few milliseconds. These vacuum-column tape drives have such features as automatic hub engagement and disengagement, cartridge loading, and automatic thread operation. There are two primary recording techniques, namely, nonreturn-to-zero-inverted (NRZI) and phase-encoded (PE), used with packing densities of 800 and 1600 bytes per inch (31 and 63 bytes per millimeter). These typically use a 0.6-in. (15-mm) interrecord gap. In phase encoding, a logical “one” is defined as the transition from one magnetic polarity to another positioned at the center of the bit cell. “Zero” is defined as the transition in the opposite direction also at the center of the bit cell, whereas NRZI would involve only one polarity. The advantage of the phase-encoding scheme over NRZI is that there is always one or more transitions per bit cell, which gives phase encoding a self-clocking capability, alleviating the need for an external clock. The disadvantage of phase encoding over NRZI is that at certain bit patterns the system must be able to record at twice the transition density of NRZI.

Computer-compatible magnetic tape units are available with tape drives of 6250 bytes per inch (246 bytes per millimeter). They have nine tracks, where eight bits are data and one bit is parity. Each track is recorded by a technique called group-coded record (GCR), which uses a 0.3-in. (7.5-mm) record gap. Every eighth byte in conjunction with the parity track is used for detection and correction of all single-bit errors. Thus, GCR offers inherently greater reliability because of its coding scheme and error-correction capability. It does, however, involve much more complex circuitry.

The on-line capacity is strictly a function of the number of tape drives that one controller can handle (eight is typical). A 2400-ft (730-m) nine-track magnetic tape at 6250 bytes per inch (246 bytes per millimeter) provides a capacity of approximately 10^9 bits, depending on record and block sizes.

Quarter-inch tapes. The installation of $^1/_4$-in. (6-mm) streaming tape drives has increased very rapidly. There are several recording-format standards for $^1/_4$-in. (6-mm) tape drives; the most common one is called QIC (quarter-inch compatibility)-24, which connotes a full-size cartridge class with formatted storage capacity of 60 megabytes on nine tracks, using 600 ft (183 m) of tape. The device interface for a QIC-24 drive is either an intelligent interface

TABLE 3. Standard recording densities for magnetic tape

		Bit density along track		Area density	
Year	Number of tracks	bits/in.	bits/mm	bits/in.^{2}	bits/mm^2
1953	7	100	4	1,400	2
1955	7	200	8	2,800	4
1959	7	556	22	7,784	12
1962	7	800	32	11,200	17
1963	9	800	32	14,400	22
1965	9	1600	63	28,800	45
1973	9	6250	246	112,500	174
1990	9	43,200	1,864	35,280,000	50,400

such as QIC-02; the SCSI; or a basic drive interface, QIC-36. Another recording format, QIC-120, provides 125 megabytes on 15 tracks. The recording format QIC-1350 provides 1.35 gigabytes.

Cassettes and cartridges. The most frequently used magnetic tape memory devices for microcomputer systems are cassette and cartridge tape units. Both provide very low-cost storage, although their access times are long and their overall throughput performance is not as great as that of floppy disks. Cassette and cartridge units both use $^1/_4$-in. (6-mm) magnetic tape.

The digital cassette transport was orginally an outgrowth of an audio cassette unit. Unfortunately, the very low-cost audio-designed transport did not meet the endurance needs of true digital computer applications. There are two basic design approaches to digital cassette transports: capstan drive and reel-to-reel drive. Capstan tape drives are better for maintaining long-term and short-term tape-speed accuracy, while reel-to-reel transports have better mechanical reliability.

During the 1960s the first true digital tape cartridge was developed. With the cassette, a capstan must penetrate the plastic case containing the tape in order to make contact. There is no such penetration system with the cartridge because the transport capstan simply drives an elastomer belt by pressing against the rim of the belt's drive wheel. This simplicity eliminates a major source of tape damage and oxide flaking.

Cassettes have undergone evolution as a digital medium, and capacity has increased to 1 gigabyte, at a density of 61,000 bits per inch (2400 bits per millimeter). Transfer rates are 30 kilobytes per second at 30 in. (0.76 m) per second, or 100 kilobytes per second at 90 in. (2.29 m) per second. Some cassettes can transfer data at 400 kilobytes per second. The $^1/_4$-in. (6-mm) streaming tape cartridge has a typical capacity range of 100 to 300 megabytes, with some available with over 1 gigabyte. Transfer rates are 30 to 90 kilobytes per second, at densities of from 6400 to 10,000 bits per inch (252 to 394 bits per millimeter).

A typical mainframe tape cartridge can store data at 38,000 bits per inch (1496 bits per millimeter). At typical blocking factors, a 550-ft (168-m) tape cartridge contains about the same amount of data as a 2400-ft (730-m) reel of tape at 6250 bits per inch (246 bits per millimeter), but it requires less storage space. The data transfer rate between the tape cartridge drive and the process is 4.5 megabytes per second.

Half-inch (12.5-mm) tape is also used for back-up for microcomputer hard disk systems. Configured to standard microcomputer packaging sizes, these give 50-megabyte capacity in $5^1/_4$-in. (133-mm) form, and 300 megabytes in 8-in. (200-mm) form.

Mass Storage Tape Systems

With the gradual acceptance of virtual memory and sophisticated operating systems, a significant operational problem arose with computer systems, particularly the large-scale installations. The expense and attendant delays and errors of humans storing, mounting, and demounting tape reels at the command of the operating system began to become a problem. Cartridge storage facilities are designed to alleviate this problem.

Their common attributes are: capacity large enough to accommodate a very large database on-line; access times between those of movable-head disks and tapes; and operability, without human intervention, under the strict control of the operating system. The cartridge storage facility is included within the virtual address range. All such configurations mechanically extract from a bin, mount on some sort of tape transport, and replace in a bin, following reading or writing, a reel or cartridge of magnetic tape.

Cartridge storage systems are hardware devices that need operating system and database software in order to produce a truly integrated, practical hardware-software system. Users require fast access to their files, and thus there is a definite need to queue up (stage) files from the cartridge storage device onto the disks. The database software must function efficiently to make this happen. In general, users base their storage device selection on the file sizes involved and the number of accesses per month. Magnetic tape units are used for very large files accessed seldom or infrequently. Mass-storage devices are for intermediate file sizes and access frequencies. Disk units are used for small files or those which are accessed often.

In practice, most users have been satisfied with tapes and disks, and have not chosen to install mass storage systems. During the 1970s, two basic kinds were delivered, although some others were built and installed in the earlier years. In different ways, these units combine the low cost of tape as a storage medium with the operating advantages of on-line access. One is a mechanical selection and mounting unit to load and unload tape reels onto and off standard magnetic tape units; another is a mechanical selection and accessing unit to operate with special honeycomb short-tape units. The first type (sometimes called automated tape libraries) eliminated manual tape-mounting operations. The main objective of the short-tape honeycomb cartridge system is to improve access time. The shorter tape (770 in. or 20 m, versus 2400 ft or 730 m) results in better access time. Operationally, the honeycomb cartridge tape system and the mechanical standard tape-mounting units are capable of handling 100 to 300 cartridge or tape loads per hour.

The first type of fully automated tape library uses standard magnetic tape $^1/_2$ in. or 12.5 mm wide). Under computer control, this equipment automatically brings the tapes from storage, mounts them on tape drives, dismounts the tapes when the job is completed, and returns them to storage. Accessing up to 150 reels per hour, this unit can store up to 7000 standard tapes or 8000 thin-line reels in a lockable self-contained library that can service up to 32 tape drives and that can interface with up to four computers.

The honeycomb cartridge storage system uses a storage component called a data cartridge. Housed in honeycomb storage compartments, these 2 × 4 in. (24 × 50 mm) plastic cartridges can each hold up to 50,000,000 bytes of information on 770 in. (20 m) of magnetic tape approximately 3 in. (75 mm) wide. Whenever information from a cartridge is needed by the computer, a mechanism selects the desired cartridge and transports it to one of up to eight reading stations. There the data are read out and transferred to the staging disk drives. *See* COMPUTER; DIGITAL COMPUTER.

Peter P. Chen; Michael Plesset; Douglas Theis

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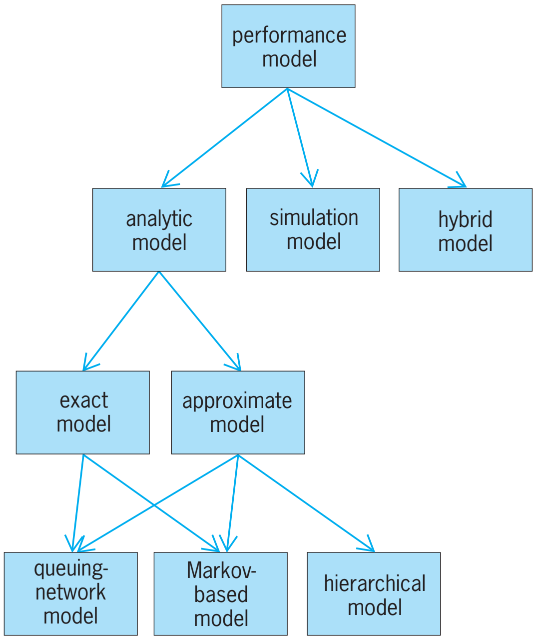
Computer-system evaluation

The evaluation of performance, from the perspectives of both developers and users, of complex systems of hardware and software. Modern computer-based information systems have become increasingly complex because of networking, distributed computing, distributed and heterogeneous databases, and the need to store large quantities of data. People are relying increasingly on computer systems to support daily activities. When these systems fail, significant breakdowns may ensue. *See* DISTRIBUTED SYSTEMS (COMPUTERS); LOCAL-AREA NETWORKS.

A computer system can fail in two major ways. First, functional failure occurs when the system fails to generate the correct results for a set of inputs. For example, if an information system fails to retrieve records that match a set of keywords, or if an air-missile tracking system fails to distinguish between a friendly and enemy missile, a functional failure has occurred. Second, performance failure occurs when the system operates correctly but fails to deliver the results in a timely fashion. For example, if an information system takes a longer time than users are willing to wait for the records they requested, the system is said to fail performancewise even though it may eventually retrieve the correct set of records. Also, if the air-missile tracking system fails to detect an enemy missile in sufficient time to launch a counterattack, the system manifests performance failure.

Therefore, in designing a computer system it is necessary to guarantee that the end product will display neither functional nor performance failure. It is then necessary to predict the performance of computer systems when they are under design and development, as well as to predict the impact of changes in configurations of existing systems. This requires the use of predictive performance models.

Performance models. The input parameters of performance models include workload intensity parameters, hardware and system parameters, and resource demand parameters. The outputs generated by performance models include response times, throughputs, utilization of devices, and queue lengths. There are analytic, simulation, and hybrid performance models (see **illus.**). Analytic models are composed of a set of equations, or computational algorithms, used to compute the outputs from the input parameters. Simulation models are based on computer programs that emulate the behavior of a system by generating arrivals of so-called customers through a probabilistic process and by simulating their flow through the system. As these simulated entities visit the various system elements, they accumulate individual and system statistics. Hybrid models combine both analytic and simulation approaches by, for example, replacing an entire subsystem in an analytic model by an equivalent device whose input–output behavior is obtained by simulating the subsystem. Analytic models can be exact or approximate. *See* SIMULATION.



Taxonomy of performance models.

Approximations are needed either when there is no known mathematically tractable exact solution or when the computation of an exact solution is very complex. Modern computer systems are very complex because of ubiquitous networking, distributed processing using client–server architectures, multiprocessing, and sophisticated input–output subsystems using network-attached storage devices. For this reason, most computer system performance models are approximate models. *See* CLIENT-SERVER SYSTEM; MULTIPROCESSING.

Exact performance models. Exact models may be further classified into queuing-network and Markov-chain-based models. Queuing-network models represent a computer system by a network of devices (also called queues) through which customers (for example, transactions, processes, and server requests) flow. Queues may form at each device because of the finite service rate of the device. Solving a queuing network amounts to finding the probability that the network is found in each of the possible states, or at least finding the performance metrics (for example, response times, throughputs, and queue lengths) associated with the queuing network. The solution to a class of queuing networks, called product-form queuing networks, can be obtained through very efficient computational algorithms such as convolution and mean-value analysis.

In Markov-based models, the system is modeled by a Markov chain, which represents the set of all possible states of the system with the possible transitions between these states. Each state gives rise to a linear flow-equilibrium equation. Solving the Markov chain amounts to solving the resulting system of linear equations, called the global balance equations. The unknowns in the global equations are the probabilities of finding the system at each of the possible states. In some cases, the Markov chain is not explicitly generated from an analysis of the system, but is derived from a higher-level model used to represent the dynamic and temporal behavior of the system. Examples of these higher-level models include generalized stochastic Petri nets (GSPNs), which are timed stochastic extensions to Petri nets. Algorithms exist that generate the Markov chain automatically from the generalized stochastic Petri net. *See* PROBABILITY; STOCHASTIC PROCESS.

Approximate performance models. Product-form queuing networks (PFQNs) cannot model many features of modern computer systems because the conditions for a queuing network to have a product-form (efficient) solution are violated in most cases of interest. For instance, priority-based scheduling disciplines for the devices in the computer system, such as those implemented by many operating systems for scheduling of central processing units, cannot be modeled directly by product-form queuing networks.

Product-form conditions are also violated in a queuing network that exhibits simultaneous resource possession, that is, a situation where a customer is allowed to hold more than one resource at the same time. This occurs when a file is being transferred from a network-attached tape drive to a disk through a HIPPI (High Performance Parallel Interface) switch. In this case, the tape drive is held by the customer simultaneously with the HIPPI switch or the disk during the transfer. Another example of simultaneous resource possession occurs in shared-memory multiprocessors. In this case, a request to access shared memory needs to hold the processor, the bus, and the shared memory bank during the memory access at the same time.

Queuing networks also do not satisfy product-form conditions when fork-and-join synchronization is present. This situation is characterized by a customer being split into more than one customer at the fork point. These customers follow independent paths within the system and are reassembled into a single customer at the join point when all of them arrive. An example of fork-and-join synchronization occurs in the modeling of a RAID-5 disk (a Redundant Array of Inexpensive Disks, with five disks in the array). Here, a read or write request to a RAID-5 disk is split into five requests to the physical disks that compose the RAID-5 disk. *See* COMPUTER STORAGE TECHNOLOGY.

Another case of violation of the product-form conditions occurs when the routing of customers in a queuing network is a function of the number of customers at other parts of the network. This may occur in the modeling of computer network routing algorithms which decide on the next link to which a packet should be sent based on the level of congestion at the set of possible links in the path to the destination.

Finally, another case where product-form conditions do not hold is when there is a constraint on the maximum number of customers in a part of the queuing network. An example occurs in the modeling of multiprogrammed computer systems where there is a maximum degree of multiprogramming.

Many approximate models have been developed to deal with queuing networks with non-product-form solutions. Some of these approximations are based on modifying the equations of the mean value analysis algorithm. Other approximations are based on formulating the problem as a fixed-point equation and solving it iteratively.

Even queuing networks with product-form solutions may be more efficiently solved with the use of approximate algorithms. The reason is that the computational complexity of solving a queuing network is proportional to the product of the number of devices in the computer system times the number of different classes of customers multiplied by the number of customers in each class. This may render models of moderately large computer systems unmanageable. Several approximations have been developed that drastically cut down the number of operations and memory requirements of the algorithms to solve product-form queuing networks. The most widely used approximation technique in this category is the Schweitzer approximation that can be used to derive an efficient iterative algorithm to solve product-form queuing networks.

Approximation techniques are also used when solving large Markov chains with an extremely large number of states. These techniques are aimed at cutting down the number of states without significant loss of accuracy. Finally, an important category of approximate models comprises hierarchical models. In this case, the complete model is decomposed into a hierarchy of models, $M_1, \ldots, M_n$. The output of the model at level i is used as input to the model at level $i + 1$. In some cases, a dependency between models M_n and M_1 is established requiring an iterative fixed-point procedure to solve the series of models. The modeling techniques used at each level may vary. It is possible to use queuing networks at one level and Markov-based models at another level of the hierarchy. Hierarchical models are very useful when dealing with client–server systems.

Performance of software systems. The design and development of complex software systems is a time-consuming and expensive task. Performance modeling techniques must be integrated into the software development methodology. This integrated approach is called software performance engineering. One goal is to estimate the resource consumption of software under development so that performance models can be used to influence the architecture of the software under development. Better estimates on the resource consumption are obtained as the software development process evolves. *See* INFORMATION SYSTEMS ENGINEERING; SOFTWARE ENGINEERING. Daniel A. Menascé

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Computer vision

The technology concerned with computational understanding and use of the information present in visual images. In part, computer vision is analogous to the transformation of visual sensation into visual perception in biological vision. For this reason the motivation, objectives, formulation, and methodology of computer vision frequently intersect with knowledge about their counterparts in biological vision. However, the goal of computer vision is primarily to enable engineering systems to model and manipulate the environment by using visual sensing. *See* VISION.

Sensing and image formation. Computer vision begins with the acquisition of images. A camera produces a grid of samples of the light received from different directions in the scene. The position within the grid where a scene point is imaged is determined by the perspective transformation. The amount of light recorded by the sensor from a certain scene point depends upon the type of lighting, the reflection characteristics and orientation of the surface being imaged, and the location and spectral sensitivity of the sensor.

Image segmentation. The objective of this early stage is to compress the huge amount of image detail by identifying and representing those aspects of image structure which are salient for later stages of interpretation. Typically, this is accomplished by detecting homogeneous regions in the image or, equivalently, their edges. It must be done for all degrees of regional homogeneity and sizes, yielding a multiscale segmentation. Further, small regions may group together to form a larger structure seen as a homogeneous texture, which may define another basis for characterizing the homogeneity of a segment. The result of segmentation is a partitioning of the image such that each part is homogeneous in some salient property relative to its surroundings.

Three-dimensional interpretation. One central objective of image interpretation is to infer the three-dimensional (3D) structure of the scene from images that are only two-dimensional (2D). The missing third dimension necessitates that assumptions be made about the scene so that the image information can be extrapolated into a three-dimensional description. The presence in the image of a variety of three-dimensional cues is exploited. These cues may occur in a single image taken by a camera at a single time instant, a sequence of images acquired by one camera over a time interval, a set of images taken by multiple cameras from different positions or angles at a single time instant, or a time sequence of images taken by multiple cameras. In each case, the main task is to devise algorithms that can estimate three-dimensional structural parameters from image-based measurements. Some examples of such cues will now be discussed.

Image curves. The boundaries of image regions, or the curves composing a line-drawing image, reveal scene characteristics such as the extent and shape of an object and the occlusion between objects.

Shading. The nature of gradual spatial variation of image values within a region is related to surface shape characteristics such as convex or concave, and planar or curved.

Texture gradient. Variation in the coarseness of image texture is indicative of how the corresponding texture surface is oriented in the scene. For example, the distant flowers in an image of a large field of flowers are packed more densely together than the closer ones.

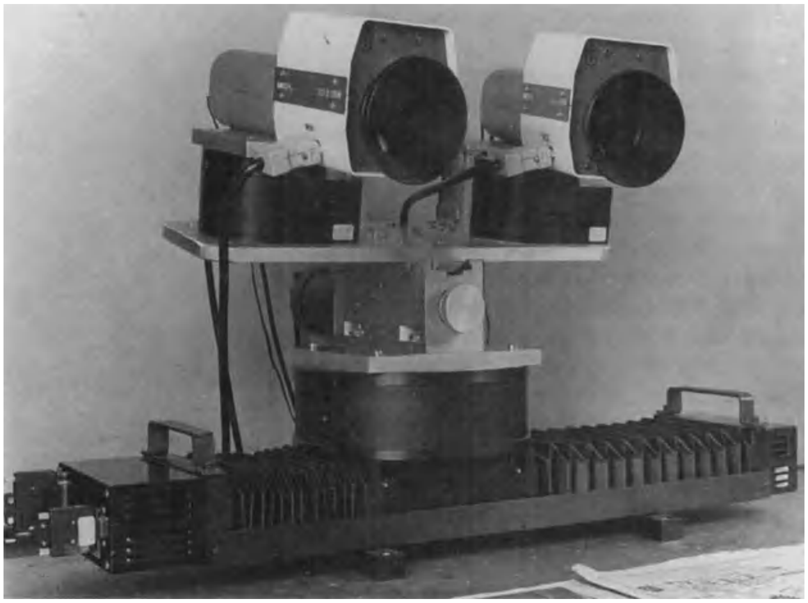
Stereo. If two cameras are placed at different locations and orientations (like the human eyes), then the coordinates at which a given scene projects within the two images are different, and their disparity is trigonometrically related to the three-dimensional position of the scene point. The disparity variation within an image can be used to estimate the three-dimensional configuration of surfaces in the scene. Three or more cameras can also be used.

Dynamic cues. If there is relative motion between the scene and the camera, the image data consists of a dynamic image sequence. Each of the above-mentioned cues then provides added information since observations about the temporal behavior of the cue are available, in addition to its spatial properties. For example, the temporal variation in image values, called optical flow, can be used to estimate the relative motion, surface shape, and layout of the objects. A moving object gives rise to a decreasing amount of flow as its distance from the camera increases. Similarly, moving image curves, such as those corresponding to orientation discontinuities on an object surface or the silhouette of a rotating object, yield a wealth of information about the shape of an object as well as about its motion. Sequences may be taken by multiple cameras simultaneously, making surface estimation easier because a larger amount of data is available, that is, the spatial disparity as well its variation over time.

Active image acquisition. If the cameras maintain a single, fixed geometry or optical configuration, the amount of additional information extracted from successive images depends on the changes occurring in the scene, due, for example, to relative motion. It is possible to maximize the increment in scene information obtained from successive images by dynamically reconfiguring the cameras so that the cues in the new images are most informative. Thus, a partial interpretation of the scene is used to dynamically control the sensing parameters so that each stage of image acquisition adds the most to the interpretation. For example, if a scene is too bright, the aperture size may be reduced; if the object is not in sharp focus, the focus setting may be changed; and if the object is not well placed with respect to both cameras in stereo analysis, the cameras may be verged to fixate on the object, all of these actions happening simultaneously (see **illus.**). As a certain part of the scene is satisfactorily interpreted, the results of the interpretation may be used to determine where to point the cameras next, and even to suggest how to analyze these new parts so as to obtain the best final interpretation in the minimum time.

Representation. The two-dimensional structure of an image or the three-dimensional structure of a scene must be represented so that the structural properties required for various tasks are easily accessible. For example, the hierarchical two-dimensional structure of an image may be represented through a pyramid data structure which records the recursive embedding of the image regions at different scales. Each region's shape and homogeneity characteristics may themselves be suitably coded. Alternatively, the image may be recursively split into parts in some fixed way (for example, into quadrants) until each part is homogeneous. This approach leads to a tree data structure. Analogous to two dimensions, the three-dimensional structures estimated from the imaged-based cues may be used to define three-dimensional representations. The shape of a three-dimensional volume or object may be represented by its three-dimensional axis and the manner in which the cross section about the axis changes along the axis. Analogous to the two-dimensional case, the three-dimensional space may also be recursively divided into octants to obtain a tree description of the occupancy of space by objects.

Recognition. A second central objective of image interpretation is to recognize the scene contents. Recognition involves identifying an object based on a variety of criteria. It may involve identifying a certain object in the image as one seen before. A simple example is where the object appearance, such as its color and shape, is compared with that of the known, previously seen objects. A more complex example is where the identity of the object depends on whether it can serve a certain function, for example, drinking (to be recognized as a cup) or sitting (to be recognized as a chair). This requires reasoning from the various image attributes and the derivative three-dimensional characteristics to assess if a given object meets the criteria of being a cup or a chair. Recognition, therefore, may require extensive amounts of knowledge representation, reasoning, and information retrieval.



Active camera system that can dynamically vary the part of the scene it has under view, focus on it, adjust the zoom, and open the aperture as necessary. Performing such changes under computer control and on the basis of the contents of the scene allows autonomous visual exploration.

Visual learning. Visual learning is aimed at identifying relationships between the image characteristics and a result based thereupon, such as recognition or a motor action. For example, the essentials of the visual appearance of a person may be learned so that whenever the person reappears in the scene his or her identity will be recognized despite changes such as in lighting and observer's viewpoint. Alternatively, continuous use of visual feedback to perform a task may be learned. For example, a person trying to pick up a suitcase moves his or her hands toward it while continuously using vision to control and correct the hand configuration and motion to reach the desired location and grip.

Applications. Vision is the predominant sense in humans, and it can play a correspondingly central role in computer-aided systems. In manufacturing, vision-based sensing and interpretation systems help in automatic inspection, such as identification of cracks, holes, and surface roughness; counting of objects; and alignment of parts. Computer vision helps in proper manipulation of an object, for example, in automatic assembly, automatic painting of a car, and automatic welding. Autonomous navigation, used, for example, in delivering material on a cluttered factory floor, has much to gain from vision to improve on the fixed, rigid paths taken by vehicles which follow magnetic tracks prelaid on the floor. Recognition of symptoms, for example, in a chest x-ray, is important for medical diagnosis. Classification of satellite pictures of the Earth's surface to identify vegetation, water, and crop types, is an important function. Automatic visual detection of storm formations and movements of weather patterns is crucial for analyzing the huge amounts of global weather data that constantly pour in from sensors. *See* ARTIFICIAL INTELLIGENCE; CHARACTER RECOGNITION; COMPUTER GRAPHICS; INTELLIGENT MACHINE; ROBOTICS. Narendra Ahuja

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Computerized tomography

An imaging technique which uses an array of detectors to collect information from a beam that has passed through an object (for example, a portion of the human body). The information collected is then used by a computer to reconstruct the internal structures, and the resulting image can be displayed—for example, on a television screen.

Technique. Wave phenomena can penetrate into regions where it is impossible or undesirable to introduce ordinary probes—regions as diverse as the ocean, the human body, and the deep interior of the Earth. Since wave attenuation and velocity are affected by material properties, such as temperature and density, information concerning these properties is accumulated by a wave packet as it travels along its path. Thus, the intensities and travel times of such pulses measured at a receiver represent such accumulations. Although a single such datum does not allow point-to-point variation to be inferred, when many rays crisscross a region the corresponding interrelated data contain constraints that allow an inversion to determine interior structures. Considerable computational power and mathematical sophistication are needed in dealing with indirect, incomplete, and imperfect measurements. The relevant branch of mathematics is called inverse theory. The term computerized tomography for this type of remote sensing arose in medicine, where x-ray attenuation data along many straight paths confined to a plane were used to obtain a map of density structure in a body section. The term tomography refers to methods that display only thin slices or sections through an object or a human body. *See* INVERSE SCATTERING THEORY.

Examining a person or object in the laboratory requires the use of a gantry, composed of an x-ray tube, an array of detectors opposite the tube, and a central aperture in which the person or object is placed. The rigid gantry maintains the proper alignment between the x-ray tube and the detectors.

Earlier computerized tomography scanners had a conventional x-ray tube with a rotating anode and small focal spot. X-rays generated in short bursts, usually lasting 2–3 ms, were picked up by detectors after passing through a section of the body (for example, the abdomen). Invisible images picked up by the detectors were fed to the computer, which reconstructed the image. The thickness of the section to be examined varied from 1 to 10 mm and was determined by collimating the x-ray beam.

Less sophisticated scanners used linear and rotational motions of both x-ray tube and detector. One employs a pencil-shaped x-ray beam and a single detector. The time needed for a single slice or scan was 4.5–5 min. A fan-shaped beam with an array of detectors (as many as 30) and a greater rotation increment (30○ instead of 1○) made possible a time interval of 10–90 s.

Sophisticated electronic technology eliminates the need for mechanical movement. An electron beam is used, which is focused on stationary anode rings located in the gantry surrounding the patient, making it possible to generate considerable x-ray output within a very short time and to acquire images while the patient is advancing through the gantry. Up to 34 scans or slices can be obtained within 1 s; a single slice can be obtained in only 50 ms. Some computerized tomography scanners use as many as 1536 measuring channels constituted by xenon detectors with extremely high efficiency. *See* IONIZATION CHAMBER; SCINTILLATION COUNTER.

The computer reconstructs the image from the information collected by the detectors in the following way. The cross section of the object to be reconstructed is divided into tiny blocks, called voxels, giving a square matrix. Matrices can be constructed having voxels of different sizes; for example, 80 × 80, 160 × 160, 320 × 320, 512 × 512, and 1024 × 1024 voxels. In the 320 × 320 matrix, the voxels are simply one-fourth of the volume of those of an 80 × 80 matrix, and therefore the resolution is greater. The computer assigns each voxel a number proportional to the degree that the voxel has attenuated the beam passing through it. Once the voxel has received a computer number, it is called a pixel (picture element). The linear attenuation coefficient (a measure of the quantity of radiation attenuated by each centimeter of absorber) is used to quantify the attenuation of the beam. Each voxel is "examined" by the beam incident from several positions, generating many "positional" equations. The computer must solve many thousands of equations to determine the linear attenuation coefficient for a single voxel. In order to obtain enough information to calculate one image, at least 90,000 readings (300 pulses and 300 detectors) are needed.

Applications. The ability of computerized tomography to explore the internal structure of objects has made it a valuable tool in medicine and geophysics.

Medical tomography. In medicine, computerized tomography represents a noninvasive way of seeing internal structures. In the brain, for example, computerized tomography can readily locate tumors and hemorrhages, thereby providing immediate information for evaluating neurological emergencies. Equally important is the fact that, in a great majority of cases, computerized tomography offers an alternative approach to the more problematic invasive procedures.

Reductions in scanning time have made it possible to do whole-body scans, and many abdominal tumors, hemorrhages, and infections can now be detected without the need for exploratory surgery. Tumors deep in the body can be biopsied easily with fine needles by using computerized tomography guidance, thereby alleviating the need for surgery. Another advantage of computerized tomography is three-dimensional reconstruction. It is most useful in cases of fracture of the hip or facial bones, helping the surgeon to do reconstructive surgery. Other medical imaging techniques that make use of computerized tomographic methods include magnetic resonance imaging, positron emission tomography, and single-photon emission tomography. *See* MEDICAL IMAGING; RADIOGRAPHY. Nicole-Fr. Bolender

Geophysical tomography. After the success of computerized tomography in medicine, its possibilities in other fields were quickly realized. In the earth, atmospheric, and ocean sciences it has supplemented, but by no means replaced, older methods of remote sensing. Seismic tomography is now an important tool for investigating the deep structure of the Earth, testing theories such as plate tectonics, and exploring for oil. Ocean acoustic tomography is applied to physical oceanography, climatology, and antisubmarine warfare. Atmospheric tomography finds applications to weather, climate, and the environment.

1. *Seismic tomography.* The data for tomographic analysis are the earthquake signal arrival times monitored by the global network of seismic stations. These signals are propagated as elastodynamic waves that can be classified as compressional or shear and as body or surface waves. Compressional waves such as acoustic waves consist of alternating compressions and rarefactions caused by the oscillations of material particles in the direction of wave propagation. Shear waves are of a different (slower) type in which the motion of material particles is at right angles to the wave motion. Surface waves are guided by the Earth's surface; they travel along great circle paths and penetrate the upper mantle, but not deeper. However, body waves are not confined to the surface and can penetrate deeply, even reaching the Earth's core. They can be of the compressional or shear type. There are also two kinds of surface waves: Rayleigh waves, composed of a vertical shear component and a compressional component, and Love waves, which are pure horizontal shear waves. *See* SEISMOLOGY.

The diversity of wave phenomena allows various physical variables to be computed from wave velocities. Temperature, density, and crystalline structure of rock are the most important of these. Body-wave ray paths are not straight as in medical tomography but are curved by refraction in the vertical due to variation in the Earth's mechanical properties. Body and surface ray paths and travel times are calculated from arrival time data at many stations by means of a standard spherically symmetric reference model of the Earth. The travel time associated with thousands of crossing paths are treated as tomographic data and used to draw maps of wave velocity anomalies (deviations from the reference model). These maps reveal much about internal structure and dynamics of the Earth. Since velocity decreases as temperature increases, an anomalously slow velocity may point, for example, to upwelling hot material from the mantle toward the surface. An opposite anomaly may represent subduction of cool surface matter as one tectonic plate is thrust beneath another. Large anomalies near the core have revealed a previously unknown aspherical (bumpy) structure. *See* PLATE TECTONICS.

Smaller-scale seismic tomography serves as a tool for oil exploration. In cross-borehole tomography a seismic source such as a small explosive or impact device creates a mechanical disturbance at a number of different depths in a shaft. A linear array of receivers in a second borehole measures signal arrival times. The propagation paths connecting each source position with each receiver form a tomographic network. Maps of propagation velocity in the region between boreholes are used to detect changes in rock strata. *See* SEISMIC EXPLORATION FOR OIL AND GAS.

2. *Ocean acoustic tomography.* A tomographic array in the ocean consists of a number of acoustic sources and receivers that span an ocean region of interest. Each source transmits a pulse that is detected at each receiver. Because of refraction due to temperature variations and other (smaller) effects, the pulses follow curved paths, which usually reverse direction in the vertical at a number of upper and lower turning points. These paths are determined mainly by the temperature stratification of the ocean and tend to be restricted to a vertical plane because of strong vertical stratification. The elements of each source-receiver pair are connected by many acoustic paths (called multipaths). Since a system typically contains many source-receiver pairs, the ocean volume within the tomographic array is penetrated by hundreds of acoustic paths. Pulse travel times along these paths are the measured data. They are determined by the variation of sound speed and currents along the respective paths. To the first order, sound speed in the ocean is determined by temperature, and the effect of currents is negligible. Thus, the information contained in the data is related mainly to the temperature variation in the ocean, and the monitoring of this distribution has been the primary objective in the development of this technology. However, monitoring of currents is also possible by the use of reciprocal (two-way) transmissions. By subtracting reciprocal travel times, temperature effects are canceled out and the effect of currents becomes dominant.

The operation of a system begins with initialization of the array, referring to the fact that a knowledge of the distribution of ocean variables (mainly temperature) is required at the initial moment of operation in order to identify the acoustic paths that connect sources and receivers. Thereafter, as these paths change position, they can be tracked by the system. In early experiments the necessary initial information was supplied by ship surveys of vertical temperature profiles.

It is not possible in the ocean environment to achieve the extremely fine spatial resolution obtained in medical scanning; a prohibitively large number of sources and receivers would be required.

However, future ocean monitoring systems will include satellite observations, providing global coverage of the ocean surface with excellent horizontal resolution but no significant vertical penetration. Acoustic tomography provides vertical penetration but poorer resolution. These two techniques can play complementary roles in ocean monitoring. *See* OCEANOGRAPHY; UNDERWATER SOUND.

3. *Atmospheric tomography.* Electromagnetic waves interact with the atmosphere in two ways useful for remote sensing. Parts of the atmosphere can reflect incident radiation directly to a detector or can absorb energy and reradiate it. Lidar, a form of radar that uses laser beams, is a suitable source for active tomographic systems because it confines incident energy to narrow beams and because optical frequencies interact strongly with the atmosphere. Alternatively, a system can be based on passive detection of emitted energy from the atmosphere by means of the radiometer, an instrument that measures the intensity of waves arriving from a particular direction. For active systems, measured data are the attenuation of lidar pulses along straight path segments from source to point of reflection to receiving telescope. For passive systems, a measured datum is the total intensity of radiation emitted toward the radiometer by all sources on its line of sight. *See* LIDAR.

A simple example of a configuration that provides the network of crossing paths required for tomography consists of two radiometers in fan beam mode: Each instrument moves its line of sight up and down, forming a fan of receiving beams. The intersection of the two fans forms a network of paths for tomography; this configuration has been used to map the liquid water content of clouds. Other tomographic configurations have been obtained from instruments mounted on satellites, aircraft, surface vehicles, and the ground. *See* AIRGLOW.

As a characteristic tomography, the data represent not the value of physical variables at a point but the integration of variables along a line. Point-to-point mapping is accomplished by inversion algorithms similar to those used in other fields. Although attenuation and emissivity are often of interest in themselves, they can also be related to other physical variables of interest. Thus, atmospheric applications also include mapping of visible airglow, temperature, and properties of aerosols. **Thomas J. Eisler; Ronald New**

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Concentration scales

Numerical systems defining the quantitative relations of the components of mixtures. In solutions the concentration is expressed as the mass, volume, or number of moles of solute present in proportion to the amount of solvent or of total solution. Each scale of concentration has significant features of experimental simplicity or of theoretically significant relationship.

Percentage. The simplest scale to measure is percentage; hence it is often used for medicinal or household solutions. Weight percent is the number of parts of weight of solute per hundred parts of weight of solution (total). For example, a 10% saline solution contains 10 g of salt in 90 g of water, that is, 100 g total weight. Gaseous mixtures, being difficult to weigh, are often expressed as volume percent. Thus, air is said to contain 78% nitrogen by volume. Solutions of liquids in liquids (say, alcohol in water) may also be expressed in volume percent.

Molarity. To the chemist, the number of moles of solute is of more significance than the number of grams. In SI units the concentration would be given in moles per cubic meter (mol m^{-3}). The molarity (abbreviated M) is the number of moles of solute per liter of total solution. Thus, 12 M HCl means that the solution contains 12 formula weights (12×36.5), or 438 g, of hydrochloric acid per liter (or, in SI units, mol dm^{-3}). Concentration is an intensive, rather than an extensive, property of solutions. Thus, 0.5 liter of the acid just mentioned is still 12 M, although it contains only 6 moles of solute. As used here, the mole is an amount of substance whose weight in grams is numerically the same as the molecular weight. Chemical engineers sometimes use a mole which is a pound-molecular weight.

Molality. Certain solution properties, for example, the lowering of the freezing point of water by addition of salt, require the use of a concentration scale which relates the number of moles of solute to the weight of solvent rather than to the volume of solution. This scale, called molality (abbreviated m), indicates the number of moles of solute per 1000 g of solvent. Thus 34.2 g of sucrose ($C_{12}H_{22}O_{11}$, mol wt 342), if dissolved in 200 g of water, has the concentration of 0.5 mole of sucrose per 1000 g of water, and hence is 0.5 m. For dilute aqueous solutions, the molality is essentially identical with the molarity. In solutions with densities other than unity, the two scales differ. Molality may be computed from molarity, as shown in the equation below, by first subtracting from the weight of 1 liter ($1000 \times$ density d)

$$m = M\left(\frac{1000}{1000d - M \times \text{mol wt}}\right)$$

the weight of solute, and then scaling the result by proportion to the number of moles per 1000 g, where the molecular weight is that of the solute.

Normality. Molarity does not represent reactive capacity for solutes which possess more than one active unit per molecule. Since sulfuric acid (H_2SO_4) molecules yield twice as many hydrogen ions (H^+) as do those of hydrochloric acid, a liter of 0.1 *M* sulfuric acid will neutralize twice as much base as will a liter of 0.1 *M* hydrochloric acid. When it is important to know the reactive capacities of reagents, as in volumetric analysis, the normality scale is used. Normality (abbreviated *N*) is found by multiplying molarity by the number of active units in the formula.

In methathesis (double decomposition) reactions, normality may be an ambiguous concept unless referred to a specific reaction. Phosphoric acid (H_3PO_4) may be reacted with sodium hydroxide (NaOH) to yield NaH_2PO_4, Na_2HPO_4, or Na_3PO_4; thus, phosphoric acid may have three normalities, depending on whether the reaction involves replacing one, two, or three hydrogen atoms. In oxidation-reduction reactions, there is a change in oxidation number, and normality must be calculated on the basis of this change. *See* OXIDATION-REDUCTION.

For reaction in a solution, the product of normality times the volume is the same for both reactants; for a solution of normality N_1, determined by titrating a volume V_1, with volume V_2 of a known solution of normality N_2, this equivalence can be expressed as $V_2N_2 = N_1V_1$. If the volume is expressed in milliliters, the products are in milliequivalents; if in liters, in equivalents.

Formality. The molarity scale is ambiguous when applied to ionic reactions. For example, 1 mole of Na_2HPO_4 in a liter of solution can yield 2 moles of sodium ion (Na^+), 1 mole of H^+, and 1 mole of phosphate ion (PO_4^{3-}), leaving zero mole of undissociated Na_2HPO_4. What the proper molarity is may not be clear. To obviate the confusion, it is possible to disregard moles and to use instead the number of formula weights of solute per liter of solution. This scale is designated the formality scale. In the example given, the solution would be 1 *F* Na_2HPO_4. This identifies the amount of total solute per liter and removes ambiguity in making up a solution; the reactive capability of the solution under various conditions is not considered.

Other scales. For very dilute solutions, for example, hard water, it is useful to express concentration in parts per million (ppm). Parts per billion are given in nanograms (10^{-9} g) per liter. With modern analytical techniques, quantities can be expressed in picogram (10^{-12} g) and femtogram (10^{-15} g) ranges. Particular applications often require special scales; for example, radon concentration in the atmosphere is given in units of picocuries per liter.

Mole percent (mole fraction). Many properties of solutions (for example, vapor pressure of one component) are dependent on the ratio of the number of moles of solute to the number of moles of solvent, rather than on the ratios of respective volumes or masses. The mole fraction (abbreviated N_A or X_A for component *A*) is the ratio of the number of moles of solute to the total number of moles of all components. Thus for 16 g of methanol (0.5 mole) dissolved in 18 g of water (1 mole), the mole fraction of methanol is 0.5/1.5, or 1/3; the mole percent is 33.3. For gases the mole percent is identical with the volume percent. *See* GRAM-MOLECULAR WEIGHT; SOLUTION; STOICHIOMETRY; TITRATION. Allen L. Hanson

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Concrete

A composite material that consists essentially of a binding medium, such as a mixture of portland cement and water, within which are embedded particles or fragments of aggregate, usually a combination of fine and coarse aggregate.

Concrete is by far the most versatile and most widely used construction material worldwide. It can be engineered to satisfy a wide range of performance specifications, unlike other building materials, such as natural stone or steel, which generally have to be used as they are. Because the tensile strength of concrete is much lower than its compressive strength, it is typically reinforced with steel bars, in which case it is known as reinforced concrete. *See* REINFORCED CONCRETE.

Materials. A composite material is made up of various constituents. The properties and characteristics of the composite are functions of the constituent materials' properties as well as the various mix proportions. Before discussing the properties of the composite, it is necessary to discuss those of the individual constituents as well as the effects of the mix proportions and methods of production. *See* COMPOSITE MATERIAL.

Cement. There are many different kinds of cements. In concrete, the most commonly used is portland cement, a hydraulic cement which sets and hardens by chemical reaction with water and is capable of doing so under water. Cement is the "glue" that binds the concrete ingredients together and is instrumental for the strength of the composite. Although cements and concrete have been around for thousands of years, modern portland cement was invented in 1824 by Joseph Aspdin of Leeds, England. The name derives from its resemblance of the natural building stone quarried in Portland, England. *See* CEMENT.

Portland cement is made up primarily of four mineral components (tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite), each of which has its own hydration characteristics. By changing the relative proportions of these components, cement manufacturers can control the properties of the product.

The primary product of cement hydration is a complex and poorly crystalline calcium-silicate-hydroxide gel (or CSH). A secondary product of hydration is calcium hydroxide, a highly crystalline material. A category of siliceous materials known as pozzolans have little or no cementitious value, but in finely divided form and in the presence of moisture will react chemically with calcium hydroxide to form additional CSH. This secondary hydration process has a generally beneficial effect on the final concrete properties. Examples of pozzolans are fly ash, ground granulated blast-furnace slag, and microsilica or silica fume.

The American Society for Testing and Materials (ASTM) defines five types of cement, specifying for each the mineral composition and chemical and physical characteristics such as fineness. The most common cement is Type I. Type III cement is used if more rapid strength development is required. The other types are characterized by either lower heat of hydration or better sulfate resistance than that of Type I cement.

Aggregate. The aggregate is a granular material, such as sand, gravel, crushed stone, or iron-blast furnace slag. It is graded by passing it through a set of sieves with progressively smaller mesh sizes. All material that passes through sieve #4 [0.187 in. (4.75 mm) openings] is conventionally referred to as fine aggregate or sand, while all material that is retained on the #4 sieve is referred to as coarse aggregate, gravel, or stone. By carefully grading the material and selecting an optimal particle size distribution, a maximum packing density can be achieved, where the smaller particles fill the void spaces between the larger particles. Such dense packing minimizes the amount of cement paste needed and generally leads to improved mechanical and durability properties of the concrete.

The aggregate constitutes typically 75% of the concrete volume, or more, and therefore its properties largely determine the properties of the concrete. For the concrete to be of good quality, the aggregate has to be strong and durable and free of silts, organic matter, oils, and sugars. Otherwise, it should be washed prior to use, because any of these impurities may slow or prevent the cement from hydrating or reduce the bond between the cement paste and the aggregate particles.

Fig. 1. Workers placing and vibrating concrete on a bridge deck including epoxy-coated reinforcing steel. (*Portland Cement Association*)

Admixtures. While aggregate, cement, and water are the main ingredients of concrete, there are a large number of mineral and chemical admixtures that may be added to the concrete. The four most common admixtures will be discussed.

1. Air-entraining agents are chemicals that are added to concrete to improve its freeze–thaw resistance. Concrete typically contains a large number of pores of different sizes, which may be partially filled with water. If the concrete is subjected to freezing temperatures, this water expands when forming ice crystals and can easily fracture the cement matrix, causing damage that increases with each freeze–thaw cycle. If the air voids created by the air-entraining agent are of the right size and average spacing, they give the freezing water enough space to expand, thereby avoiding the damaging internal stresses.

2. Water-reducing admixtures, also known as superplasticizers, are chemicals that lower the viscosity of concrete in its liquid state, typically by creating electrostatic surface charges on the cement and very fine aggregate particles. This causes the particles to repel each other, thereby increasing the mix flowability, which allows the use of less water in the mix design and results in increased strength and durability of the concrete. *See* FLOW OF SOLIDS.

3. Retarding admixtures delay the setting time, which may be necessary in situations where delays in the placement of concrete can be expected. Accelerators shorten the period needed to initiate cement hydration—for example, in emergency repair situations that call for the very rapid development of strength or rigidity.

4. Color pigments in powder or liquid form may be added to the concrete mix to produce colored concrete. These are usually used with white portland cement to attain their full coloring potential. *See* PIGMENT (MATERIAL).

Reinforcing steels. Because of concrete's relatively low tensile strength, it is typically reinforced with steel bars (**Fig. 1**). These bars are produced in standard sizes. In the United States, the identification number of a reinforcing bar refers to the nominal diameter expressed in eighths of an inch. For example, a number 6 bar has a diameter of $^6/_8 = 0.75$ inch. The available bar sizes range in general from 2 to 18. Reinforcing steel usually has a nominal yield strength of 60,000 lb/in.^{2} (414 MPa). To improve the bond strength between the bars and the concrete, the bars are fabricated with surface deformations or ribs. The relatively high cost of steel mandates its sparing use. This means that the concrete is usually assigned the task of resisting compressive forces, while the steel carries primarily the tensile forces. The alkalinity of the cement paste generally provides sufficient protection of the steel against corrosion. However, corrosion protection is often breached, for example, in highway bridge decks with continuous pore structure or traffic-induced cracks that permit the deicing chemicals used in winter to penetrate the protective concrete cover. Additional protective measures may be necessary, such as using epoxy coatings on the bars, noncorrosive steels, or nonmetallic reinforcement (for example, fiber-reinforced polymers). *See* CORROSION.

Other important concrete terminology can be defined. A mixture of cement and water is called cement paste. Cement paste plus fine aggregate is called mortar or concrete matrix. Mortar plus coarse aggregate constitutes concrete. Concrete reinforced with steel or other high-strength material is known as reinforced concrete. *See* MORTAR.

Production of concrete. The properties of the end product depend not only on the various constituent materials listed above but also on the way they are proportioned and mixed, as well as on the methods of placing and curing the composite.

Mix design. It is not possible to predict the strength and other concrete properties solely based on the properties and proportions of the mix components. Therefore, mixes are designed on an empirical basis, often with the help of trial mixes. The objective of the mix design is to assure that the product has specified properties in both the fresh and hardened state. The most important mix design variable is the weight ratio between water and cement, referred to as the w/c ratio. There is a theoretical minimum amount of water needed for the cement to completely hydrate, which can be determined using the equations of hydration chemistry. Any excess water creates pores which, together with any air-filled pores, do not contribute to the material strength. The result is a drastic decrease in strength as a function of increasing the w/c ratio. On the other hand, too low w/c ratios cause poor workability of the concrete. For practical reasons, the w/c ratio typically varies between 0.4 and 0.6. The other important mix design variables are the cement-to-aggregate ratio and the fine-to-coarse aggregate ratio. Also, the maximum aggregate size is of importance. And since cement is the most expensive bulk ingredient, the mix design will generally aim at the least amount of cement necessary to achieve the design objectives.

Construction practice. The material obtained immediately upon mixing of the various concrete ingredients is called fresh concrete, while hardened concrete results when the cement hydration process has advanced sufficiently to give the material mechanical strength. Concrete that is batched and mixed in a plant and then transported by truck in its fresh, or plastic, state to the construction site for final placement is called ready-mixed concrete. If the resulting structure or highway pavement, for example, remains in place after placement, the concrete is referred to as cast-in-place concrete, whether mixed on-site or off-site. Precast concrete refers to any structure or component that is produced at one site, typically in a precasting plant, and then transported in its hardened state to its final destination. The controlled environment of a precasting plant generally permits higher quality control of the product than is possible with cast-in-place concrete produced at a construction site. *See* CONSTRUCTION METHODS; PAVEMENT.

Code-writing organizations, such as the American Society for Testing and Materials, the American Concrete Institute (ACI), and the American Association of State Highway and Transportation Officials (AASHTO), have published detailed specifications and recommendations for measuring, mixing, transporting, placing, curing, and testing concrete. A proper mix design assures that the concrete mix is well proportioned. The mixing time should be sufficient to assure a uniform mixture. When placing the concrete, care should be taken to avoid segregation. For example, if dropped too far, the heavy or big aggregate particles can settle and lighter mix components, such as water, tend to rise. The concrete is conveyed from the mixing truck to its final destination in dump buckets by cableways or cranes or by pumping through pipelines. In modern high-rise building construction, concrete has been pumped as high as a thousand feet (330 m).

During placement, large amounts of air are entrapped in the mix, which lowers the strength of the hardened concrete. Much of the air is removed by compaction, which is achieved by either immersing high-frequency vibrators into the fresh concrete or attaching them to the outside faces of the formwork (Fig. 1). Care must be taken to avoid excessive vibration; otherwise the heavy aggregate particles settle down and the light mixing water rises to the surface.

For underwater construction, the concrete is placed in a large metal tube, called a tremie, with a hopper at the top and a valve arrangement at the submerged end. For so-called shotcrete applications such as tunnel linings and swimming pools, the concrete mixture is blown under high pressure through a nozzle directly into place to form the desired surface.

Before the concrete sets and hardens, it is relatively easy to give its exposed surfaces the desired finish. Surfaces cast against forms can be given various textures by using form liners or treating the surfaces after forms are removed. Hardened surfaces can be textured by grinding, chipping, bush-hammering, or sandblasting.

Curing. Once the concrete has been placed and compacted, it is critical that none of the mixing water needed for cement hydration is lost. This is the objective of curing. For example, in hot or dry weather large exposed surfaces will lose water by evaporation. This can be avoided by covering such surfaces with sheets of plastic or canvas or by periodically spraying them with water. In precast concrete plants, concrete elements are often steam-cured, because the simultaneous application of hot steam and pressure accelerates the hydration process, which permits high turnover rates for the formwork installations.

Quality control. To assure that the finished material has the specified properties, quality assurance and quality control procedures need to be implemented. From a public safety viewpoint, strength is the most important property. To assure adequate strength,

Fig. 2. Concrete slump test with a slump of 1.5 in., typical for pavement work. (*Portland Cement Association*)

such as determining the time of safe formwork removal, concrete batches are sampled by casting test cylinders at the same time and place as the structure being built. These cylinders are then tested by accredited laboratories to determine their strength. If the in-situ strength of existing structures needs to be evaluated, concrete cores may be drilled from selected parts of the structure and tested in the laboratory. There are also nondestructive test methods available to determine various properties of hardened concrete.

Properties of fresh concrete. The most important property of fresh concrete is its workability or flowability, because this determines the ease with which it can be placed. It is determined using a slump test, in which a standard truncated metal cone form is filled with fresh concrete (**Fig. 2**). The mold is then lifted vertically, and the resulting loss in height of the concrete cone, or the slump value, is indicative of the concrete's workability. For very liquid mixes, the flow test is performed, which is similar to the slump test, except that the mean diameter of the cake formed by the fresh concrete (or mortar) is measured.

A short while after casting, the concrete stiffens and loses its plasticity. The time of setting can be determined by repeatedly dropping a calibrated needle into the fresh concrete and measuring the time when the needle no longer sinks in.

Properties of hardened concrete. By far, the most important property of hardened concrete is its compressive strength. Since this strength continues to increase with continuing cement hydration, it is a function of age which is the time after casting. In the United States, the strength is determined 28 days after casting by loading standardized test cylinders up to failure. In Europe, test cubes are often used. Most commercially produced concrete has compressive strengths between 3000 and 6000 lb/in.^{2} (20 and 40 MPa). If loaded in tension, the material fails at a stress much lower than that, typically of the order of 10% of the compressive strength. Because of this low (and unreliable) tensile strength, concrete is usually reinforced with steel bars. *See* STRESS AND STRAIN.

During hydration and especially if allowed to dry after hardening, the concrete volume decreases by a small amount because of shrinkage. If this shrinkage is restrained somehow, it can lead to cracking. Shrinkage deformations caused by drying can be reversed only partially upon wetting. A concrete member or structure subjected to external load will undergo deformations which, up to a point, are proportional to the amount of applied load. If these loads remain in place for an appreciable time (months or years), these deformations will increase due to a material property called creep. Even for regular concrete mixes, creep deformations can be two or three times as high as the initial elastic deformations, especially if the concrete is loaded at a very young age. When designing concrete structures, such creep and shrinkage deformations must be accounted for. *See* CREEP (MATERIALS); ELASTICITY.

Durability. Durability is the ability of a material (or structure) to maintain its various properties throughout its design or service life. Some concrete structures built by the Romans served for over 2000 years. A material that loses its strength in time, for whatever reason, cannot be considered durable.

There can be numerous causes for loss of durability or deterioration of concrete structures. The most common one is an excessive amount of cracking or pore structure. Most concrete structures contain numerous cracks. But as long as these remain small (of the order of 0.25 mm or less), they are generally invisible to the naked eye, and the concrete remains basically impermeable to salts and other aggressive agents, so that it can continue to protect the reinforcing steel against corrosion. Larger cracks provide easy access for such agents to the steel, thereby promoting corrosion. Since the steel corrosion products occupy a larger volume than sound steel, they produce internal pressure during expansion and can spall off the protective concrete cover, the loss of which may render the structure unsafe to resist loads.

The concrete itself may deteriorate or weather, especially if subjected to many cycles of freezing and thawing, during which the pressure created by the freezing water progressively increases the extent of internal cracking. In addition, carbon in the atmosphere can react chemically with the cement hydration products. This process is known as carbonation. It lowers the pH of the concrete matrix to the point where it can no longer protect the steel against corrosion.

Most types of aggregate used for concrete production are inert; that is, they do not react chemically with the cement or hydration products. However, there are various aggregate types, including those containing amorphous silica such as common glass, which react chemically with the alkali in the cement. In the presence of moisture, the alkali–aggregate reaction products can swell and cause considerable damage. The deterioration of numerous major structures and highway pavements has been attributed to such reactions, especially alkali–silica reaction, often after years of seemingly satisfactory service. Other common causes of chemical attack are sulfates found in soils, chlorides in seawater, acid rain, and other industrial pollutants. Generally, structures built with well-designed concrete mixes, having low porosity or high density and minimal cracking, are likely to resist most causes of chemical attack, although for service in particularly aggressive environments special countermeasures may have to be taken.

Under repeated load applications, structures can experience fatigue failure, as each successive load cycle increases the degree of cracking and material deterioration to the point where the material itself may gradually lose its strength or the increased extent of cracking is the source of loss of durability.

Thermal and other properties. The heavy weight of concrete [its specific gravity is typically 2.4 g/cm^3 (145 lb/ft^3)] is the source of large thermal mass. For this reason, massive concrete walls and roof and floor slabs are well suited for storing thermal energy. Because of this heat capacity of concrete, together with its reasonably low thermal conductivity, concrete structures can moderate extreme temperature cycles and increase the comfort of occupants. Well-designed concrete mixes are impermeable to liquids and therefore suitable for storage tanks without the need for impermeable membranes or liners. Although steel reinforcing bars conduct electricity and influence magnetic fields, the concrete itself does neither. *See* CONCRETE SLAB; FLOOR CONSTRUCTION; ROOF CONSTRUCTION.

Special concretes and recent developments. Concrete is an engineered material, with a variety of specialty products designed for specific applications. Some important ones are described below.

Lightweight concrete. Although the heavy weight or large mass of typical concrete members is often an advantage, there are situations where this is not the case. For example, because of the large stresses caused by their own heavy weight, floor slabs are often made lighter by using special lightweight aggregate. To further reduce weight, special chemical admixtures are added, which produce large porosity. Such high porosity (in either the matrix or the aggregate particles themselves) improves the thermal resistance of the concrete as well as sound insulation, especially for higher frequencies. However, because weight density correlates strongly with strength, ultralightweight concretes [1.1 g/cm^3 (70 lb/ft^3) and less] are used only for thermal or sound insulation purposes and are unsuitable for structural applications.

Heavyweight concrete. When particularly high weight densities are needed, such as for shielding in nuclear reactor facilities, special heavyweight aggregate is used, including barite, limonite, magnetite, scrap metal, and steel shot for fine aggregate. Weight densities can be achieved that are twice that of normal-weight concrete.

Architectural concrete. Concrete surfaces that remain exposed may call for special finishes or textures according to the architect's desires. Textures are most readily obtained by inserting special form liners before casting the concrete. Sometimes the negative imprint of roughly sawn timber is considered attractive and left without further treatment. Other surface textures are obtained by sandblasting, bush-hammering, and similar treatments. Ordinary portland cement gives concrete the typical gray color. By adding color pigments to the mix, a large variety of colors can be produced, especially in combination with white portland cement. Concrete mixed with specialty aggregate, such as marble, and ground smooth is known as terrazzo concrete, which is very popular for decorative surfaces on floors and walls. Recently, crushed postconsumer glass has been used as aggregate for decorative applications because of the esthetic possibilities, provided suitable countermeasures against alkali–silica reaction are taken (**Fig. 3**).

Fiber-reinforced concrete. The concrete matrix can be reinforced with short, randomly distributed fibers. Fibers may be metallic (primarily steel), synthetic (such as polypropylene, nylon, polyethylene, polyvinyl alcohol, and alkali-resistant glass), or natural (such as sisal, coconut, and rice husk). Such fibers are typically used in addition to conventional steel reinforcement, but in some applications as its replacement. For example, precast glass-fiber-reinforced building façade elements are widely used in the United States. By being uniformly distributed and randomly oriented, the fibers give the concrete matrix tensile strength, ductility, and energy absorption capacities that it otherwise would not have. In particular, when these fibers are engineered to optimize the fracture energy, so-called high-performance fiber-reinforced concrete is obtained, which has remarkable deformational characteristics and extraordinary resistance to blast and impact loads. In the

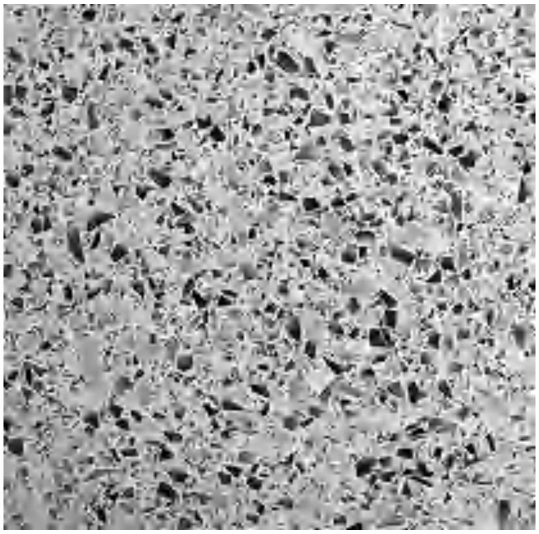

Fig. 3. Glass concrete tile. (*C. Meyer*)

concrete industry, it is very common to add small amounts of polypropylene fibers to reduce the extent of shrinkage cracking.

Textile-reinforced concrete. Whereas in fiber-reinforced concrete the fibers are short [usually no longer than 2 in. (5 cm)] and discontinuous, textile-reinforced concrete contains continuous woven or knitted mesh or textiles. Conceptually, such reinforcement acts similarly to conventional steel reinforcing bars or welded steel wire fabrics. But these fabric materials are noncorrosive and can have mechanical properties that are superior to those of steel. The fabrics can be premanufactured in a wide variety of ways, thereby lending themselves to new applications, especially for repairing or strengthening existing concrete structures. *See* TEXTILE.

Polymer-modified concrete. In polymer-modified concrete, also known as latex-modified concrete, a polymer is added to improve the material's strength, imperviousness, or both. In applications such as highway bridge decks, often a layer of latex-modified concrete is placed on top of a regular reinforced concrete deck for additional protection of the steel reinforcement. In polymer concrete, the hydraulic cement is replaced by an organic polymer as the binder. *See* POLYMER; POLYMERIC COMPOSITE.

Roller-compacted concrete. This type of concrete is formulated with very low contents of portland cement and water and therefore is of relatively low-cost. It is often used for pavements and dams. It can be transported by dump trucks or loaders, spread with bulldozers or graders, and compacted with vibratory rollers. Because the cement content is so low, the heat of hydration does not cause the kind of problems encountered in dams built with conventional concrete.

Ultra-high-strength concrete. Whereas concretes with compressive strengths of 6000 to 12,000 lb/in.^{2} (40 to 85 MPa) can now be categorized as high-strength, a new technology has been developed that results in strengths of 30,000 lb/in.^{2} (200 MPa) and higher. The key ingredient of this ultra-high-strength concrete is a reactive powder; therefore, it is also known as reactive-powder concrete. Other characteristics of this material are low water–cement ratios, carefully selected high-strength aggregates, and small steel fibers.

Self-leveling concrete. The need for good workability has been mentioned. The need for highly skilled workers who can properly compact concrete at the construction site prompted researchers in Japan to optimize the mix design such that the fresh concrete can flow into place without the need for further vibration. The main challenge was to obtain a low-viscosity mix without the threat of desegregation. This innovation is particularly important in applications with dense steel reinforcement, which traditionally have caused severe difficulties of producing high-quality concrete.

"Green" concrete. Concrete is by far the most widely used building material. Well over 10 billion tons are produced worldwide each year, requiring enormous natural resources. Also, it has been estimated that the production of 1 ton of portland cement causes the release of 1 ton of carbon dioxide (CO_2) into the atmosphere, a gas that is known to contribute to global warming. Together with the large amounts of energy required to produce portland cement, the cement and concrete industry has a major impact on the environment worldwide. Efforts are underway to reduce this impact and transform the industry to conform to the principles of sustainable development. The most significant step is the replacement of portland cement by other cementitious or pozzolanic materials, preferably materials that are by-products of industrial processes, such as fly ash (the by-product of coal-burning power plants) and granulated blast furnace slag (a by-product of the steel industry). To reduce the need for virgin aggregate, recycled concrete is the most promising approach, because construction debris, in particular demolished concrete, constitutes a major component of solid waste that fills up sparse landfill capacity. These recent developments are much more advanced in Europe and Japan than in the United States. But the "green" building movement is gaining momentum there as well, and for the concrete industry to maintain its dominant position within the construction industry, it is undertaking major efforts to make concrete a more "green" material.

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Concrete beam

A structural member of reinforced concrete placed horizontally to carry loads over openings.

Because both bending and shear in such beams induce tensile stresses, steel reinforcing tremendously increases beam strength. Usually, beams are designed under the assumption that tensile stresses have cracked the concrete and the steel reinforcing is carrying all the tension. *See* STRESS AND STRAIN.

Two design theories are used, elastic design and ultimate-load design.

Elastic design. The following assumptions are made for elastic design:

1. Plane sections remain plane after bending and are perpendicular to the longitudinal fibers.
2. The stress-strain curve is a straight line.
3. The ratio n of the modulus of elasticity of steel E_s to that of concrete E_c is a constant $n = E_s/E_c$
4. The concrete does not carry tensile stress.

Transformed section. One approach to elastic design of reinforced concrete beams is to convert the steel to concrete. Because the steel and concrete are assumed to be firmly bonded and thus strained the same amount, the stress in the steel is n times the concrete stress. Hence the steel area may be replaced by an equivalent concrete area which is n times as large (**Fig. 1**).

If the equivalent area is placed at the same level as the steel and the moment of inertia I computed for the transformed section, the bending stresses can be computed from the simple flexural formula $f = Mc/I$ where M is the bending moment and c the distance from the neutral axis to the level at which stresses are to be computed.

Rectangular beams. The following formulas can be derived from the basic assumptions of elastic theory. Equation (1) locates the neutral axis, given steel and

$$\frac{nf_c}{f_s} = \frac{k}{1-k} \tag{1}$$

concrete extreme stresses, where n is the ratio of the modulus of elasticity of steel to that of concrete, f_c is the stress in the extreme fiber of the concrete, f_s is the stress in the steel, and k is the ratio of the distance between the top of the beam and the neutral axis to the distance between the top of the beam and the steel (**Fig. 2**).

The design equation for equal moment resistance of concrete and steel (balanced design) is Eq. (2).

$$k = \frac{1}{1 + f_s/nf_c} \tag{2}$$

Equations (3)–(6) are review equations.

$$k = \sqrt{2np - (np)^2} - np \tag{3}$$

$$j = \frac{1-k}{3} \tag{4}$$

$$M_c = {}^1/_2 f_c kjbd^2 \tag{5}$$

$$M_s = f_s A_s jd \tag{6}$$

Here p is the ratio of effective area of tension reinforcement to effective area of concrete in beams, j is the ratio of lever arm of resisting couple to depth d, M_c is the moment resistance of the concrete, b is the width of the rectangular beam or width of flange of the T beam, d is the depth from the compressive surface of beam or slab to center of longitudinal tension reinforcement, M_s is the moment resistance of the steel, and A_s is the steel area.

When M_s is less than M_c, the capacity of the steel determines the maximum moment that the beam will carry. The beam is called underreinforced. If the beam is loaded to failure, the steel rather than the concrete determines the maximum load that is sustained.

When M_c is less than M_s, the concrete determines the maximum moment the beam will carry. The beam is said to be overreinforced. Usually, overreinforced beams are avoided because they are not considered economical and failure may occur without warning.

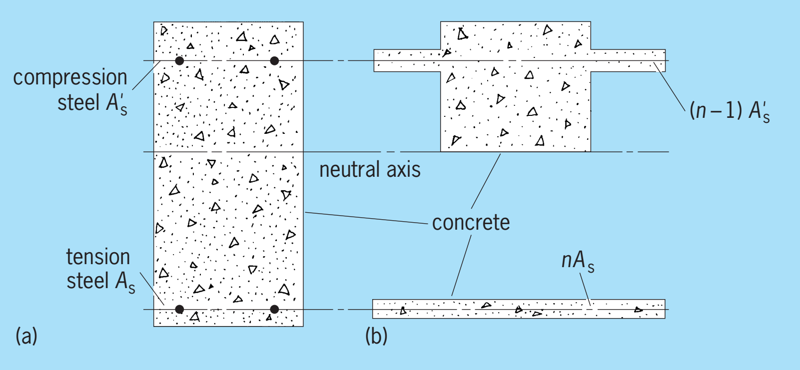

Fig. 1. Sketch of concrete beam. (*a*) Actual beam section. (*b*) Same section transformed. The use of the term $(n-1)A'_s$ prevents compression steel area from being included twice when computing moment of inertia of section; $(n-1)A'_s = nA'_s - A'_s$, because computations require the equivalent steel area to be added to the original concrete area above the neutral axis.

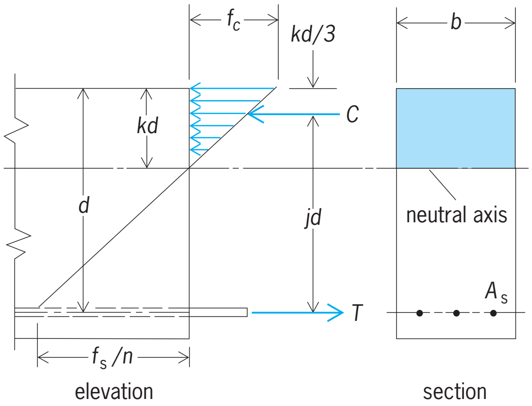

Fig. 2. Stress distribution in a rectangular beam designed according to elastic theory. *C* is total compressive force in concrete and *T* is total tensile stress in longitudinal reinforcement.

To design a rectangular beam by the elastic theory: (1) Select allowable unit stresses and determine k from the formula for balanced design; (2) compute j; (3) assuming the resisting moment of the concrete equal to the bending moment on the section, calculate bd^2 and select values for b and d; and (4) determine the steel area by equating the resisting moment of the steel to the bending moment on the section. This equation indicates that the amount of steel required can be reduced by increasing the depth. If the depth is fixed and an overreinforced beam results, it may be economical to use compression steel.

Compression-reinforced rectangular beams. Reinforcement may be added in the compression zone of concrete beams when the resisting moment of the concrete is less than the bending moment on the section or to avoid an overreinforced design. The compression steel is assumed to act as in plastic design; the Building Code Requirements of the American Concrete Institute allow the steel to take twice the stress given by elastic-theory formulas, provided the allowable tensile stress of the steel is not exceeded. Formulas for design of beams with both tension and compression reinforcement can be derived from the elastic theory in the same manner as for beams with tension reinforcement only, but they are too complicated for ordinary use. Equations (7)–(12) are either exact or a close approximation.

$$k = \frac{1}{1 + f_s/nf_c} \tag{7}$$

$$f_s' = nf_c\frac{kd - d'}{d - kd} \tag{8}$$

$$A_s = \frac{M}{f_s jd} \tag{9}$$

$$M_c = {}^1/_2 f_c bkd\left(d - \frac{kd}{3}\right) \tag{10}$$

$$M_s' = M - Mc \tag{11}$$

$$A_s' = \frac{M_s'}{2f_s'(d - d')} \tag{12}$$

k = ratio of distance between top of beam and neutral axis to the distance between top of beam andtension steel
f_s = allowable steel stress
f_c = allowable concrete stress
n = ratio of modulus of elasticity of steel to that of concrete
f_s' = stress in compression steel computed from elastic theory formula
d' = distance from top of beam to compression steel
A_s = area of tension steel
M = bending moment on the section
jd = moment arm of the tensile
jd = reinforcement (assumed)
M_c = resisting moment of the concrete
b = width of beam
d = distance from top of beam to tension steel
M_s' = resisting moment of the compression steel
A_s' = area of compression steel

Concrete T beams. A slab cast integrally with a rectangular concrete beam usually is assumed to assist the beam in carrying loads. In regions of positive bending moment, the two act together as a T beam. In regions of negative moment, the beam is designed as a rectangular section because the slab is in tension and is assumed not to be able to resist such stresses, which must be taken by the reinforcing. *See* CONCRETE; CONCRETE SLAB.

If the neutral axis of a T beam is within the slab, it is designed as a rectangular beam, with width b the same as that of the flange, to resist bending moments. For shear, however, only the width of stem b' can be assumed to be effective.

If the neutral axis falls within the stem, the section can be designed as a T beam. However, the compression in the stem is negligible and can be ignored to simplify computations.

The American Concrete Institute's code recommends the following limits for the part of the slab that can be considered effective as the flange: (1) b shall be less than one-fourth the span length, (2) the overhanging width of flange shall not exceed eight times the slab thickness, and (3) the overhanging width shall not exceed one-half the clear distance between beams.

If t is the flange thickness and the remaining symbols are the same as for elastic-theory design of rectangular beams, Eqs. (13) through (20) can be used

$$k = \frac{1}{1 + f_s/nf_c} \tag{13}$$

$$\frac{f_s}{f_c} = \frac{bt(2kd - t)}{2A_s kd} \tag{14}$$

$$kd = \frac{2ndA_s + bt^2}{2nA_s + 2bt} \tag{15}$$

$$z = \frac{t(3kd - 2t)}{3(2kd - t)} \tag{16}$$

$$jd = d - z \tag{17}$$

$$M_s = A_s f_s jd \tag{18}$$

$$M_c = \frac{f_c btjd}{2kd}(2kd - t) \tag{19}$$

$$f_c = \frac{f_s}{n}\left(\frac{kd}{d - kd}\right) \tag{20}$$

for T beams when stem compression is neglected.

The shear unit stress in T beams is computed from Eq. (21), where V is the shear on the section. *See*

$$v = \frac{V}{b'd} \tag{21}$$

ELASTICITY; HOOKE'S LAW; YOUNG'S MODULUS.

Ultimate-load design. Other names for ultimate-load design are ultimate-strength design, limit-load design, and the plastic design. Design assumptions differ from those of the elastic theory principally in that the stress-strain curve is not a straight line. Instead of being designed to carry allowable unit stresses, as in the elastic theory, beams are proportioned to carry at ultimate capacity the design load multiplied by a safety factor.

Among the reasons for using ultimate-load design are the following:

1. The elastic theory is not corroborated with sufficiently great accuracy by beam tests.
2. It is logical to use different safety factors for live and dead loads. Different factors can easily be used with ultimate-load design but not with elastic design.
3. Column design is based on a modified ultimate load theory. To avoid inconsistency, structural members subjected to both bending and compressive stress should also be designed by ultimate-load theory.

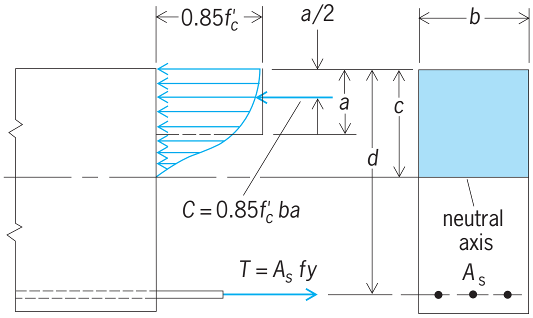

Fig. 3. Stress distribution in a rectangular beam under ultimate load; *T* and *C* are as in Fig. 2.

4. The ultimate strength of beams carrying both bending and axial compression, as determined in tests, conforms closely with ultimate-load theory.

Rectangular beams. The comprehenssive stress distribution may be assumed to be a rectangle, parabola, trapezoid, or any other shape that conforms to test data. Maximum concrete stress is assumed to be $0.85f'_c$, where f'_c is the compressive strength of a standard-test concrete cylinder at 28 days (**Fig. 3**).

When the moment resistance of the steel is less than that of the concrete, the bending moment that a rectangular beam with only tension reinforcement can sustain under ultimate load is Eq. (22).

$$\begin{aligned} M_u &= \phi\left[A_s f_y (d - a/2)\right] \\ &= \phi\left[bd^2 f'_c q(1 - 0.59q)\right] \end{aligned} \qquad (22)$$

A_s = area of tension reinforcement
f_y = yield point stress of steel
f'_c = comprehensive strength of standard-test concrete cylinder at 28 days
ϕ = reduction factor = 0.90 for this type of beam in flexure
b = width of beam
d = distance from top of beam to centroid of the steel
a = depth of rectangular stress block
$q = A_s f_y / bdf'_c$

Reinforcement ratio $p = A_s/bd$ should not exceed $0.75p_b$, where p_b is given by Eq. (23), and k_1 =

$$p_b = \frac{0.85k_1 f'_c}{f_y}\left(\frac{87,000}{87,000 + f_y}\right) \qquad (23)$$

0.85 for values of f'_c up to 4000 lb/in.^{2}, 0.80 for 5000 lb/in.^{2}, and 0.75 for 6000 lb/in.^{2}.

Compression-reinforced rectangular beams. Based on a nonlinear stress-strain relation, the bending moment that a rectangular beam with both compression and tension reinforcement can sustain under ultimate loads is shown in Eq. (24).

$$M_u = \phi[(A_s - A'_s)f_y(d - a/2) + A'_s f_y(d - d')] \qquad (24)$$

A_s = area of tension steel
A'_s = area of compression steel
f_y = yield point stress of the steel
d = distance from top of beam to centroid of tension steel
d' = distance from top of beam to centroid compression steel
$a = (A_s - A'_s)f_y/0.085f'_c b$
b = width of beam
f'_c = compressive strength of standard-test concrete cylinder at 28 days

Equation (24) holds only if Eq. (25) is true, where

$$\begin{aligned} (p - p') &\geq 0.85k_1 \frac{f'_c d'}{f_y d}\left(\frac{87,000}{87,000 - f_y}\right) \\ &\leq 0.75p_b \end{aligned} \qquad (25)$$

$p = A_s/bd$; $p' = A'_s/bd$; and p_b and k_1 are the same as for beams with tension steel only.

Concrete T beams. Two cases should be considered, one with a relatively thick slab and one with a thin slab. If the flange thickness exceeds $1.18qd/k_1$, where $q = pf_y/f'_c$, the bending moment under ultimate load may be taken to be the same as that for a rectangular beam with tension reinforcement only. The value of p used in computing q should be A_s/bd, with b the width of the flange. For thinner flanges, use Eq. (26) to compute bending moment.

$$\begin{aligned} M_u = \phi[(A_s - A_{sf})f_y(d - a/2) \\ + A_{sf} f_y(d - 0.5t)] \end{aligned} \qquad (26)$$

$A_{sf} = 0.85f'_c(b - b)t/f_y$
f_y = yield point stress of the steel
t = flange thickness
b = width of flange
b' = width of stem
d = distance from top of beam to centroid of tension steel
$a = (A_s - A_{sf})f_y/0.85f'_c b'$

Equation (26) holds only if $p_w - p_f$ does not exceed $0.75p_b$, where $p_w = A_s/bd$, $p_f = A_{sf}/bd$, and p_b is the same as for beams with tension reinforcement only, as in Eq. (23).

Shear and bond. Maximum unit shear stress v acting on a section of a beam subjected to total shear V is given by Eq. (27), where b is the beam width, and

$$v = \frac{V}{bd} \qquad (27)$$

d is depth from top of beam to the tensile steel. The bond stress can be computed from Eq. (28), where

$$u = \frac{V}{\sum_o jd} \qquad (28)$$

Σ_o is the sum of the bar perimeters. This formula applies only to tension steel. Bond stresses will be at a maximum where shear is a maximum and the steel is in the tension side of the concrete.

To develop a given bar stress through bond, a bar should be embedded a length L at least equal to Eq. (29), where a is the side of a square bar or the

$$L = \frac{f_s a}{4u} \qquad (29)$$

diameter of a round bar. This length of embedment is called anchorage. Usually, bars are extended 10 diameters past the section where they are no longer required for bending stress.

Shear in itself is not as important in the design of a concrete beam as the tensile stresses that accompany it on a diagonal plane. To resist these stresses, concrete beams should be reinforced with bent-up bars or with stirrups. The latter are bars placed vertically or on an incline in a beam. They may be the legs of a single U-shaped bar or the sides of a rectangle.

The shear V' taken by stirrups is assumed to be the total shear on the section at which the stirrups are to be placed, less the shear taken by the concrete, vbd. The cross-sectional area of the stirrups needed at a section is given by Eq. (30), where f_v is the allowable

$$A_v = \frac{V's}{f_v d} \qquad (30)$$

tensile stress of the steel, and s is the stirrup spacing.

If the stirrups, instead of being vertical, are laid at an angle α with the horizontal, greater steel area is required, as in Eq. (31). Every potential 45° crack

$$A_v = \frac{V's}{d(\sin\alpha + \cos\alpha)f_v} \qquad (31)$$

should be crossed by at least one line of reinforcement.

If the area of the stirrups is given, the spacing can be computed from the two formulas above. The first stirrup is usually placed as close to the support as practical, generally 2 in. (5 cm). Stirrups should be placed throughout a beam, even if theoretically they are not needed. They serve also as supports for the longitudinal steel. When not required for diagonal tension, stirrups should be placed at most 18 in. (45 cm) apart.

It is common practice to cut off bars or bend them up where they are no longer needed to resist tension at the bottom of the beam. The bent bars serve as diagonal-tension reinforcement and tensile reinforcement at the top of the beam over the support.

Frederick S. Merritt

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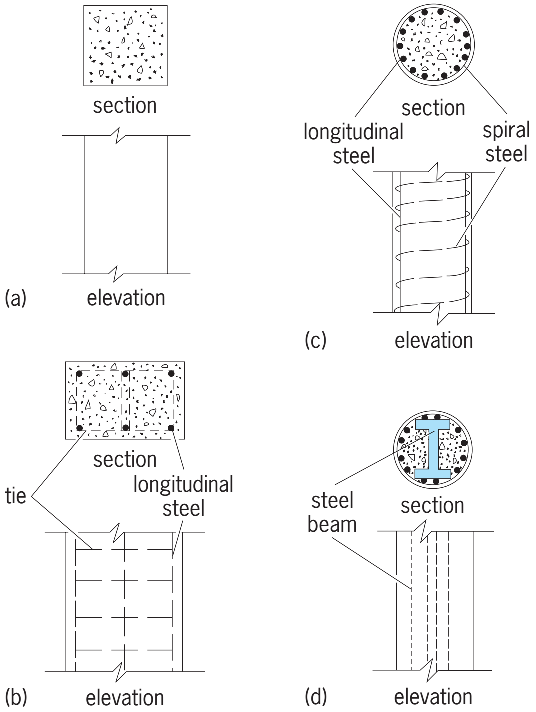
Concrete column

A structural member subjected principally to compressive stresses. Concrete columns may be unreinforced, or they may be reinforced with longitudinal bars and ties (tied columns) or with longitudinal bars and spiral steel (spiral-reinforced columns). Sometimes the columns may be a composite of structural steel of cast iron and concrete (see **illus.**).



Column types. (*a*) Plain concrete. (*b*) Tied column. (*c*) Spiral-reinforced column. (*d*) Composite column.

Plain concrete columns. Unreinforced concrete columns are seldom used because of transverse tensile stresses and the possibility of longitudinal tensile stresses being induced by buckling or unanticipated bending. Because concrete is weak in tension, such stresses are generally avoided.

When plain concrete columns are used, they usually are limited in height to five or six times the least thickness. Under axial loading, the load divided by the cross-sectional area of the concrete should not exceed the allowable unit compressive stress for the concrete.

Axially loaded reinforced columns. Reinforced concrete columns are designed by ultimate-load theory. Two types of column are considered: short and long. Those whose length is three to ten times their least lateral dimension are called short columns.

For spiral-reinforced short columns, the American Concrete Institute code gives the formula for the allowable load in pounds shown in Eq. (1), where

$$P = 0.25 f'_c A_g + f_s A_s \qquad (1)$$

f'_c is the 28-day compressive strength of a standard concrete test cylinder in pounds per square inch (lb/in.^{2}), A_g the gross area of section in square inches, f_s the allowable unit stress for steel in pounds per square inch, and A_s the area of reinforcing steel in square inches.

For a tied column, the allowable load is 85% of that for a spiral-reinforced column. Spiral-reinforced columns are stronger because columns tend to fail by a lateral bursting of the concrete as the longitudinal bars bend outward, and spiral reinforcing is more effective than ties in restraining the concrete. If spirals are used, the longitudinal bars should be arranged in a circle.

For long columns, the allowable load is reduced from that permitted for short columns because of the possibility of buckling. When *h*/*d*, the ratio of unsupported length of column to least lateral dimension, is equal to or greater than 10, one should use the appropriate reduction factor given in Sec. 916 of the Building Code Requirements for Reinforced Concrete (ACI 318–63).

Spiral reinforcement is determined from Eq. (2),

$$p' \geq \frac{0.45(R-1)f'_c}{f'_s} \qquad (2)$$

where p' is the ratio of the volume of spiral reinforcement to the volume of the spiral core (out-to-out of the spiral), R is the ratio of gross area to core area, and f'_s is the yield-point stress of spiral steel, with a maximum of 60,000 lb/in.^{2}

Composite columns. A concrete compression member having a structural steel or cast iron core with a cross-sectional area not exceeding 20% of the gross area of the column is called a composite column. Spiral and longitudinal reinforcing also may be incorporated in the concrete.

The allowable load in pounds on a composite column is given by Eq. (3), where A_c is the net area of

$$P = 0.225A_c f'_c + f_r A_r + f_s A_s \qquad (3)$$

the concrete section (A_g-A_r-A_s), A_s is the area of longitudinal reinforcement other than the metal core, A_r is the cross-sectional area of the structural steel or cast iron core, f_r is the allowable unit stress for the core, and f_s is the allowable unit stress for the longitudinal reinforcement.

If the core area is 20% or more of the gross area and the concrete is at least 2 in. (5 cm) thick over all metal except rivet heads, the members is called a combination column. If the concrete is to be allowed to share the load with the core, the concrete must be reinforced; usually wire fabric is wrapped completely around the core.

Combined bending and axial load. Because columns are designed by ultimate-load theory and this theory has also been developed for beams, it is logical to design columns subjected to both bending and axial loads by ultimate-load theory. The ultimate load is given by Eqs. (4) and (5), where f'_c is the compressive

$$P_u = \phi(0.85f'_c ba + A'_s f_y - A_s f_s) \qquad (4)$$

$$P_u e = \phi[0.85f'_c ba(d - a/2) + A'_s f_y(d - d')] \qquad (5)$$

strength of concrete at 28 days; f_y is the yield strength reinforcement; f_s is the calculated stress in reinforcement when less than yield strength; A'_s is the area of compression reinforcement; A_s is the area of tension reinforcement; e is the eccentricity of axial load at the end of the member measured from centroid of tension reinforcement; a is the depth of equivalent rectangular compression-stress block; b is the width of compression flange; d is the distance from extreme compression fiber to centroid of tension steel; d' is the distance from extreme compression fiber to centroid of compression steel; and ϕ is a capacity reduction factor. It equals 0.75 for spiral-reinforced members and 0.70 for tied members.

For strength reduction factors when length-thickness ratio exceeds 10, one should consult Sec. 916 of the Building Code Requirements for Reinforced Concrete (ACI 318–63). *See* CONCRETE SLAB; REINFORCED CONCRETE.

Frederick S. Merritt

Concrete slab

A shallow, reinforced-concrete structural member that is very wide compared with depth. Spanning between beams, girders, or columns, slabs are used for floors, roofs, and bridge decks. If they are cast integrally with beams or girders, they may be considered the top flange of those members and act with them as a T beam. *See* CONCRETE; CONCRETE BEAM.

One-way slab. A slab supported on four sides but with a much larger span in one direction than in the other may be assumed to be supported only along its long sides. It may be designed as a beam spanning in the short direction. For this purpose a 1-ft width can be chosen and the depth of slab and reinforcing determined for this unit.

Some steel is also placed in the long direction to resist temperature stresses and distribute concentrated loads. The area of the steel generally is at least 0.20% of the concrete area.

Two-way slab. A slab supported on four sides and with reinforcing steel perpendicular to all sides is called a two-way slab. Such slabs generally are designed by empirical methods. A two-way slab is divided into strips for design purposes.

The American Concrete Institute (ACI) code recommends the following design method: Divide the slab in both directions into a column strip and middle strip (**Fig. 1**). If the ratio *S*/*L* of the short span to the long span is equal to or greater than 0.5, the width

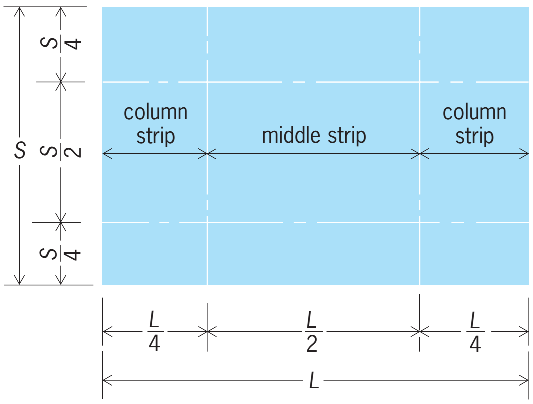


Fig. 1. A two-way slab in strips for design purposes.

of the middle strip extending in the short direction equals $L/2$, as shown. If S/L is less than 0.5, the width of the middle strip in the short direction is $L - S$; the remaining width is divided equally between the two column strips. However, when S/L is less than 0.5, most of the load would be carried in the short direction, and it would be desirable to design the slab as a one-way slab.

A table in the ACI code gives coefficients for calculation of the bending moments in the middle strip for different values of S/L and different types of panels. The moment in the column strip is assumed to be two-thirds that in the middle strip. The reinforcing steel area is determined from $A_s = M/f_s jd$, where M is the bending moment, f_s the tensile unit stress in longitudinal reinforcement, and j the ratio of lever arm of resisting couple to d, the depth from compressive surface of beam or slab to center of longitudinal tension reinforcement.

In the design of the beams that support a two-way slab along its sides, the load is assumed to be uniform over the slab and distributed to the beams as shown in **Fig. 2**. If w is the slab load in lb/ft^2, moments in the beams may be approximated by assuming the beams loaded with the following equivalent uniform loads: for the short span, $wS/3$; for the long span, $wS(3 - S^2/L^2)/6$.

Flat slabs. When a slab is supported directly on columns, without beams and girders, it is called a flat plate or flat slab (**Fig. 3**).

A flat plate generally is of uniform thickness throughout. Usually, the columns also have constant dimensions throughout the story height below the slab (excluding the portion forming capitals, which are discussed later). In designing such construction, it is necessary to investigate shear and diagonal tension in the vicinity of the columns; frequently, reinforcements which are known as shear heads are embedded at the column tops.

In flat-slab construction it is customary to flare out the columns at the top to form capitals so as to give the slab-column junction greater rigidity. The capital is usually sloped at 45°. For exterior columns the capital is sometimes only a bracket that projects inward.

Flat slabs generally are thickened in the region around the columns. The thickened portion, called a drop panel, may be extended until it reaches from column to column, forming shallow beams and giving the effect of a paneled ceiling.

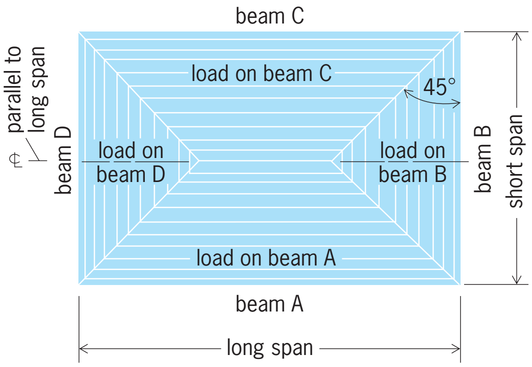


Fig. 2. Load distribution assumed for beams supporting a uniformly loaded two-way slab.

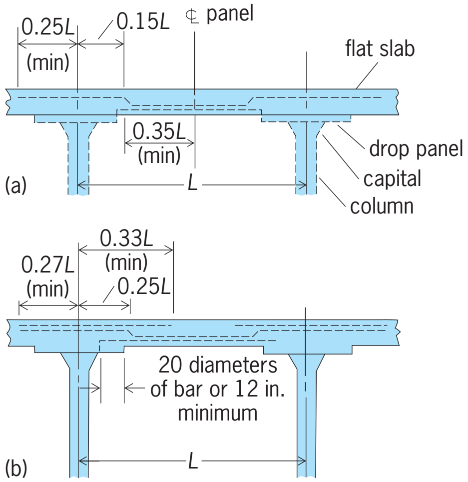


Fig. 3. Details of a flat slab drawn in cross section at two points. (*a*) Middle strip. (*b*) Column strip. *L* is the center-to-center distance between columns.

Although thicker and more heavily reinforced than slabs in beam-and-girder construction, flat slabs are advantageous because they offer no obstruction to passage of light (as beam construction does); savings in story height and in the simpler formwork involved; less danger of collapse due to overload; and better fire protection with a sprinkler system because the spray is not obstructed by beams.

Flat slabs may be reinforced in several ways:

1. *Two-way system.* When the columns are arranged to form rectangular bays, the reinforcing steel may be placed in two directions, perpendicular to the column lines. Design is based on column strips and middle strips, similar to that for a two-way slab.

2. *Four-way system.* Column strip steel is similar to that for a two-way slab. But middle-strip reinforcing consists of diagonal bands of steel extending over the columns.

3. *Circumferential system.* Bars are placed in the top of the slab in concentric rings around the columns, also radially. Similar radial and circular bars are placed in the bottom of the slab in the central portion.

4. *Three-way system.* When columns are arranged so that lines joining them would form triangles, the reinforcing steel may be laid parallel to the column lines.

Design of flat slabs and flat plates is based on empirical formulas. The ACI code presents design rules that are widely used. *See* CONCRETE COLUMN; REINFORCED CONCRETE.

Frederick S. Merritt

Concretion

A loosely defined term used for a sedimentary mineral segregation that may range in size from inches to many feet. Concretions are usually distinguished from the sedimentary matrix enclosing them by a difference in mineralogy, color, hardness, and weathering characteristics. Some concretions show definite sharp boundaries with the matrix, while others have gradational boundaries. Most concretions are composed dominantly of calcium carbonate, with or without an admixture of various amounts of silt, clay, or organic material. Less common are the clay-ironstone concretions characteristic of the Carboniferous coal measures in many parts of the world. The latter are mixtures of iron carbonate minerals and iron silicate minerals. Coal balls are calcareous concretions, found in or immediately above coal beds, in which there may be a high percentage of original plant organic matter, showing wonderfully preserved plant fossils in a noncompressed condition. Concretions are normally spherical or ellipsoidal; some are flattened to disklike shapes. Frequently a concretion is dumbbell-shaped, indicating that two separate concretionary centers have grown together. *See* COAL BALLS; SEDIMENTARY ROCKS.

Raymond Siever

Concurrent processing

The simultaneous execution of several interrelated computer programs. A sequential computer program consists of a series of instructions to be executed one after another. A concurrent program consists of several sequential programs to be executed in parallel. Each of the concurrently executing sequential programs is called a process. Process execution, although concurrent, is usually not independent. Processes may affect each other's behavior through shared data, shared resources, communication, and synchronization.

Concurrent programs can be executed in several ways. Multiprogramming systems have one processing unit and one memory bank. Concurrent process execution is simulated by randomly interleaving instructions of the sequential programs. All processes have access to a common pool of data. In contrast, multiprocessing systems have several processing units and one memory bank. Processes are executed in parallel on the separate processing units while sharing common data. In distributed systems, or computer networks, each process is executed on its own processor with its own memory bank. Interaction between processes occurs by transmission of data from one process to another along a communication channel. *See* DISTRIBUTED SYSTEMS (COMPUTERS); MULTIPROCESSING.

Uses and examples. Concurrent programs are inherently more complex to create and to execute than sequential programs. However, concurrent programs are often more appropriate than sequential programs for a particular computing environment. Additionally, concurrent programs often perform the same tasks much more efficiently than sequential programs.

Historically, one of the first uses of concurrent processing was in operating systems. The operating system of a computer is the software that provides an interface between the user, the computer, and input/output devices such as terminals, printers, and disk drives. If the computer is to support a multiuser environment, the operating system must employ concurrent programming techniques to allow several users to access the computer simultaneously. The operating system should also permit several input/output devices to be used simultaneously, again utilizing concurrent processing. *See* MULTIACCESS COMPUTER; OPERATING SYSTEM.

Concurrent programming is also used when several computers are joined in a network. An airline reservation system is one example of concurrent processing on a distributed network of computers. Agents at many different locations on different computers simultaneously book passenger reservations. The concurrent program controlling the system allows this simultaneity while ensuring that the parallel processes do not conflict, for example, that two agents do not book the same seat on the same flight for two different passengers. *See* LOCAL-AREA NETWORKS; WIDE-AREA NETWORKS.

A simple example of a task that can be performed more efficiently by concurrent processing is a program to calculate the sum of a large list of numbers. A sequential program must iterate through each element of the list, accumulating the sum. In a concurrent program, several processes can simultaneously compute the sum of a subset of the list, after which these sums are added to produce the final total. Depending on the size of the list and the number of processes, the concurrent program may perform the computation in only a small fraction of the time required by the sequential program.

Process interaction. The processes of a concurrent program are usually required to interact and cooperate. An operating system must ensure that processes coordinate the use of shared resources such as printers, memory, and processors. An airline reservation system must ensure that conflicting reservations are not made at different sites. The processes of a concurrent program to sum a list of numbers must cooperate to combine their subtotals into a final total. Many tasks also require concurrent processes to synchronize certain actions. For example, a process controlling a sensor that produces data at a varying rate must be synchronized with a process that reads and analyzes these data.

In multiprogramming and multiprocessing systems, communication and synchronization are achieved through shared variables. Certain memory locations contain data to be read and modified by several processes, such as the number of disk drives available, the next process to send a file to the printer, the number of elements in a buffer, or the total of a sublist of numbers. Reading and writing of shared variable values must be synchronized to avoid undesirable situations. For example, one process may read a shared value in order to update it, and a second process may change the value before the first process is completed. The change in the second process is lost when the first process finally performs its update. This is known as the lost update problem, and it is prevented by ensuring that processes have the ability to gain exclusive access to shared variables for the duration of an operation.

Distributed systems have no shared memory; communication and synchronization are achieved by transmitting messages along shared communication links. Communication can be either synchronous or asynchronous. With synchronous communication, both the sending and receiving processes must be ready to communicate before a message is actually transmitted. With asynchronous communication, the sending process may transmit messages whether or not the receiving process is prepared to receive them. The sent messages are held in a queue until requested by the receiving process. Synchronous communication is used when coordination between processes may be required, as in a series of computers controlling an automated assembly line. Asynchronous communication is used when coordination between processes is not required, as in the transmission of electronic mail messages from one computer to another. *See* DATA COMMUNICATIONS; ELECTRONIC MAIL.

Creating concurrent programs. Concurrent programs can be created explicitly or implicitly. Explicit concurrent programs are written in a programming language designed for specifying processes to be executed concurrently. Implicit concurrent programs are created by a compiler that automatically translates programs written in a sequential programming language into programs with several components to be executed in parallel.

Many programming languages provide facilities for creating concurrent programs. These languages typically include a component for specifying sequential programs and a component for combining and coordinating several sequential programs into one concurrent program. Examples of such languages are Ada, Communicating Sequential Processes (CSP), Concurrent Pascal, Mesa, Modula, and Synchronizing Resources (SR).

Compilers that translate sequential programs into concurrent programs are called parallelizing compilers. They employ a technique called dependency analysis to identify regions of a sequential program that are independent and may therefore be executed in parallel. The regions may be as large as several hundred lines of code or as small as a single arithmetic operation. The object of a parallelizing compiler is to introduce as much parallelism as possible in order to increase the speed of the program. *See* PROGRAMMING LANGUAGES. Jennifer Widom

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Concussion

Mild traumatic brain injury, due to externally inflicted trauma. While such injury has many symptoms, there is often no physical evidence of damage to the brain. It is clinically manifested by at least one of the following:

Loss of consciousness for 30 minutes or less.

Posttraumatic amnesia for less than 24 hours.

An initial score of 13–15 on the Glasgow Coma Scale, which measures eye, verbal, and motor responses. [Scores can range from 3 (deep coma) to 15 (fully awake).]

Alteration in mental state at time of injury (for example, feeling dazed, disoriented, or confused).

Individuals with concussion do not experience focal neurological deficits (that is, they have no paralysis or sensory loss) and imaging studies (such as computerized tomography and magnetic resonance imaging usually do not show evidence of brain damage. However, after concussion the afflicted persons may experience:

Cognitive deficits (for example, difficulties with concentration and attention, a decrease in information processing speed, and deficits in executive functioning and memory).

Affective disorders (for example, irritability, anxiety, and depression).

Somatic complaints (such as headaches, dizziness, nausea, insomnia, fatigue, and sensory disturbances).

Most of these symptoms disappear within weeks or months, but approximately 15% of individuals continue to experience such symptoms, a condition often referred to as postconcussion syndrome. Actual causes and influencing factors of postconcussion syndrome are much debated but may involve premorbid (preexisting) conditions, psychological reactions, age, mechanism of injury, as well as unidentified organic (physical) disorders.

Since most symptoms of concussion resolve spontaneously and no specific treatment has been validated scientifically, management initially is “wait and see.” It is prudent for the individual to promptly undergo a brief neuropsychological assessment and receive appropriate rest. If difficulties persist beyond 6 months, a comprehensive neuropsychological evaluation is indicated. Individuals with persistent complaints months after the injury may benefit from psychotherapy, pain management, cognitive rehabilitation, physical therapy, judicious use of medications, professional counseling, and group support. *See* BRAIN; COGNITION. Kristjan T. Ragnarsson

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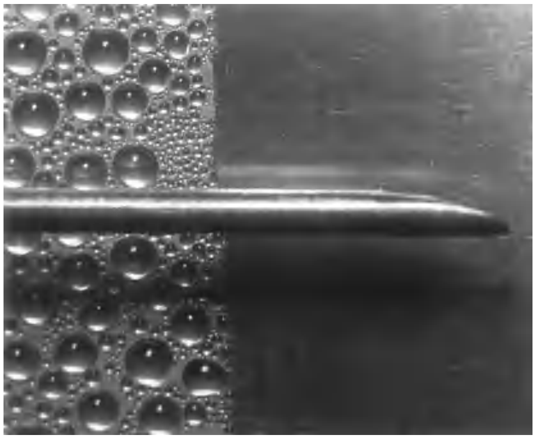
Condensation

A phase-change process in which vapor converts into liquid when the temperature of the vapor is reduced below the saturation temperature corresponding to the pressure in the vapor. For a pure vapor this pressure is the total pressure, whereas in a mixture of a vapor and a noncondensable gas it is the partial pressure of the vapor. Sustaining the process of condensation on a cold surface in a steady state requires cooling of the surface by external means. Condensation is an efficient heat transfer process and is utilized in various industrial applications. Condensation of vapor on a cold surface can be classified as film-wise or drop-wise. Direct-contact condensation refers to condensation of vapor (bubbles or a vapor stream) in a liquid or condensation on liquid droplets entrained in the vapor. If vapor temperature falls below its saturation temperature, condensation can occur in the bulk vapor. This phenomenon is called homogeneous condensation (formation of fog) and is facilitated by foreign particles such as dust. *See* GAS; HEAT TRANSFER.

Film condensation. A thin film of liquid forms upon condensation of vapor on a cold surface that is well wetted by the condensate (see **illus.**). The liquid film flows downward as a result of gravity. The temperature drop between the vapor-liquid interface of the film and the surface of the solid on which vapor condenses is representative of the condensation resistance, which is inversely proportional to the condensation heat transfer coefficient. The film is initially laminar in the direction of flow. As the mass flow rate through the film and, in turn, the thickness of the film increase due to addition of condensate, ripples start to form on the free surface of the film. The ripples form as a result of capillary and inertia forces, and generally begin at a Reynolds number of about 30, where the Reynolds number is based on the average velocity of the condensate in the film, four times the thickness of the film, and the kinematic viscosity of the condensate. The film becomes turbulent when the Reynolds number attains a value of about 1800. *See* REYNOLDS NUMBER; SURFACE TENSION; TURBULENT FLOW.



Steam at atmospheric pressure condensing on a vertical copper surface. Film condensation is visible on the right side, and dropwise condensation in the presence of a promoter is visible on the left side. The horizontal tube is a thermocouple. (*J. F. Welch and J. W. Westwater, Department of Chemical Engineering, University of Illinois, Urbana*)

The earliest work on laminar film condensation was performed by W. Nusselt in 1916. He assumed that the vapor was pure, stagnant, and at its saturation temperature; that inertia and convective contributions in the film were small; and that thermophysical properties of the condensate film could be evaluated at the mean temperature of the film. He then obtained the equation below for the dimensionless average heat transfer coefficient, or Nusselt number.

$$\mathrm{Nu} = \frac{\bar{h}L}{k_\ell} = C\left[\frac{\rho_\ell g(\rho_\ell - \rho_v)h_{fg}L^3}{\mu_\ell k_\ell (T_{\mathrm{sat}} - T_W)}\right]^{1/4}$$

Here, $\bar{h}$ is the average heat transfer coefficient for film condensation, L is the plate height over which laminar film condensation occurs, k_ℓ is the thermal conductivity of the liquid, ρ_ℓ is the density of liquid, ρ_v is the density of vapor, h_{fg} is the latent heat of vaporization, μ_ℓ is the molecular viscosity, T_{sat} is the saturation temperature, and T_W is the surface temperature. The latent heat of vaporization and vapor density correspond to the saturation condition in the vapor. From the form of the equation, it follows that average heat transfer coefficients are higher for small bodies (small L). For condensation of steam, typical values of the heat transfer coefficient $\bar{h}$ are of the order of 5000 W/($\mathrm{m}^2 \cdot \mathrm{K}$). *See* CONDUCTION (HEAT); EVAPORATION; VISCOSITY.

The dimensionless constant C in the equation above is of order unity and varies with geometry. For a vertical plate, $C = 0.943$. Other geometries, such as tubes and spheres, can be analyzed. The latent heat term h_{fg} is also modified by convection and subcooling in the film. If ripples form or turbulence ensues in the film, new formulas and correlations are needed.

Bulk motion of vapor in the direction of the flow of the condensate film tends to increase the heat transfer coefficient from that given by the equation above. If the vapor is at a temperature higher than the saturation temperature, the vapor must be cooled to saturation temperature before it is condensed. As such, the vapor superheat tends to increase the condensation heat transfer rate; however, the condensate mass flow rate decreases. The presence of noncondensable gases in the vapor can substantially reduce the condensation heat transfer rate because of the additional resistance imposed by the diffusion of the vapor to the interface. In the presence of noncondensables, the mass flow rate of the condensate also decreases. In refrigeration and air-conditioning systems, film condensation occurs inside tubes. Since vapor and condensate flow simultaneously through the tube and the fractional cross-sectional area occupied by each phase changes in the direction of the flow, different flow configurations or regimes are encountered which in turn influence the condensation heat transfer coefficients.

Dropwise condensation. On surfaces that are not well wetted, vapor may condense in the form of droplets (see illus.). The droplets form on imperfections such as cavities, dents, and cracks on the surface. The droplets of 10–100 μm diameter contribute most to the heat transfer rate. As a droplet grows to a size that can roll down the surface because of gravity, it wipes the surface of the droplets in its path. In the wake behind the large droplet, numerous smaller droplets form and the process repeats. The heat transfer coefficients with dropwise condensation can be one to two orders of magnitude greater than that for film condensation. Thus, dropwise condensation is preferable to film condensation. Attempts have been made to deposit an ultrathin coating of a nonwetting material such as Teflon on the condensing surface to promote dropwise condensation. However, in heat exchange equipment, because of the buildup of foreign material on the surface or degradation of the promoter layer, dropwise condensation shifts with time to film condensation. Therefore, equipment is designed on the basis of film condensation.

Direct contact condensation. Condensation of vapor bubbles in a host liquid and condensation on droplets entrained in vapor are also very efficient heat transfer processes, especially when the vapor-liquid interface oscillates. The magnitude of the heat transfer coefficient depends on several variables such as the size of the bubble or droplet, liquid subcooling, the relative velocity between the continuous and the discontinuous phase, and the appropriate thermophysical properties of the two phases. V. K. Dhir

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Conditioned reflex

A learned response performed by a trained animal to a signal that was previously associated with an event of consequence for that animal. Conditioned reflex (CR) was first used by the Russian physiologist I. P. Pavlov to denote the criterion measure of a behavioral element of learning, that is, a new association between the signal and the consequential event, referred to as the conditioned stimulus (CS) and unconditioned stimulus (US), respectively. In Pavlov's classic experiment, the conditioned stimulus was a bell and the unconditioned stimulus was sour fluid delivered into the mouth of a dog restrained by harness; the conditioned stimulus was followed by the unconditioned stimulus regardless of the dog's response. After training, the conditioned reflex was manifested when the dog salivated to the sound of the bell.

Classical conditioning. Ideally, certain conditions must be met to demonstrate the establishment of a conditioned reflex according to Pavlov's classical conditioning method. Before conditioning, the bell conditioned stimulus should attract the dog's attention or elicit the orienting reflex (OR), but it should not elicit salivation, the response to be conditioned. That response should be specifically and reflexively elicited by the sour unconditioned stimulus, thus establishing its unlearned or unconditioned status. After conditioned pairings of the conditioned stimulus and the unconditioned stimulus, salivation is manifested prior to the delivery of the sour unconditioned stimulus. Salivation in response to the auditory conditional stimulus is now a "psychic secretion" or the conditioned reflex.

This simple conditioned reflex was important to Pavlov because it presumably demonstrated concretely a new temporary connection in the brain, a neural connection established by training between the auditory apparatus and salivary mechanisms. It provided him with an opportunity to study the psyche objectively. "Here we have exact and constant facts," Pavlov said, "facts that seem to imply intelligence." He had already won the Nobel Prize in Physiology or Medicine for his studies of digestion and its associated secretory reflexes. He knew that the food stimuli contracted oral receptors, and how the impulses were transmitted via centripetal nerves to a specific area of the brainstem. He knew that this reflexive mechanism controlled salivation by centrifugal nerves, so as to match the quality and quantity of saliva precisely with the nature of oral stimulation in accordance with the "wisdom of the body." He understood how the auditory conditioned stimulus might control the head-turning orienting reflex in the dog. But the final mystery was how the auditory conditioned stimulus gained control over the salivary reflex through conditioning or, in other words, how the bell became a stimulus substitute for food. Pavlov's goal was to elucidate these new pathways of control in the brain, and that task was not completed. But to this day, Pavlov's methods provide important guidelines for basic research upon brain mechanisms in learning and memory.

By 1909, other Russian workers had extended the study of the conditioned reflex to other stimulus-reflex combinations in dogs and humans, and since that time scientists all over the world have paired a vast array of stimuli with an enormous repertoire of reflexes to test conditioned reflexes in representative species of almost all phyla, classes, and orders of animals. As a result, classical conditioning is now considered a general biological or psychobiological phenomenon which promotes adaptive functioning in a wide variety of physiological systems in various phylogenetic settings.

Selective learning and homeostatic feedback. The unconditioned stimulus is usually contact with a object or event that is significant for survival, evoking pleasure or pain. This is only a rough guide because some "pleasures" (for example, drugs and alcohol) can be ultimately detrimental. Food, the most popular unconditioned stimulus, is vital for survival. Consumption is followed by digestion which provides feedback (FB) to adjust the palatability of food commensurate with its homeostatic effect. If food is nutritious, it tastes "good" next time. If food is followed by nausea induced by injection, conditioned food aversion is acquired and the food tastes "bad." Therefore the entire conditioning sequence is composed of two different associative processes denoted as CS-US-FB. The first CS-US link and the second US-FB link differ in many ways. For rapid one-trial learning: (1) The CU-US interval must be a matter of seconds, but the US-FB interval can be a matter of hours. (2) The unconditioned stimulus must be presented to an alert subject, but the feedback is completely effective when delivered to a subject asleep under anesthesia. (3) After CS-US training, the subject gains a precise appreciation of both stimuli and their association in time and space and modifies its behavior accordingly. But after conditioned food aversion training the hedonic value of the unconditional stimulus is modified even in the absence of any memory of its association with the nauseous feedback. The subject often approaches the unconditioned stimulus again and rejects it in surprise and disgust.

Furthermore, while many different conditioned stimuli can easily be linked with food unconditioned stimulus, there is a strong selective affinity of the food feedback for taste. In the complete absence of taste, even an aversion to odor paired with poison is absent or weak. With repeated trials, the aversion spreads to other cues associated with feeding. In descending order of effectiveness, these cues are oral stimuli other than taste or odor, visual and tactual aspects of the food, visual and tactual aspects of the food locus, and auditory stimulation paired with food. All these cues are potentiated when accompanied by taste. Natural selection resulted in this specialized US-FB learning system to protect the gut from natural toxins. Charles Darwin was concerned with the mechanisms by which natural toxins protected poisonous insect larvae from predators. Subsequent research revealed that the predators acquired a conditional food aversion for such insects and their mimics; thus the US-FB association has been called Darwinian conditioning.

A brief electric shock impinging on the skin, also a well-known unconditioned stimulus, engages another specialized CS-US-FB system designed by natural selection to protect the skin from predatory attacks. Since the attack is usually swift and preceded by vibrations in the substrate, an immediate noise-shock combination is about as effective for conditioned fear as a delayed taste-toxin combination is for conditioned food aversion. Conversely, taste-shock and noise-toxin are relatively ineffective combinations for rapid conditioning because these stimuli impinge upon two different integrative systems. The shock unconditioned stimulus is followed by an endogenous analgesic feedback that raises the pain threshold. This feedback action is of long duration and is also effective in subjects sleeping under anesthesia. US-FB relationships have not been elucidated for other unconditoned stimulus events, but there is evidence that they exist. Core temperature of the body is apparently feedback for thermal skin receptors. When core temperature is low, a warm unconditioned stimulus is pleasant to the skin. When the core is warmed, the same unconditioned stimulus is unpleasant. In mating behavior of mammals, reproductive success seems to make odors associated with mates more attractive.

Instrumental conditioning. In this procedure the experimenter selects a response (R) emitted by the animal and reinforces it with an unconditioned stimulus. R-US methodology is favored by B. F. Skinner. For example, consider an operant conditioning situation in which a pigeon is placed in the Skinner box with a key or target connected to a food delivery mechanism. Whenever the key illuminates, the pigeon can obtain food by depressing it. Skinner's procedure differs from Pavlov's situation in that the subject is unrestrained, and food is contingent upon depression of the key whenever the light is on. No key press, no food; thus the birds appeared to be working for the pay of food in economic fashion. Skinner, avoiding physiological mechanisms, defined his conditioned reflex as a depression of the key and called it an operant; his pigeon was operating the key to get food. However, high-speed photographs indicated that the pigeon pecked at the target in the same way it pecked at grain. When depressing the lighted key to get water, the pigeon worked the key with the same action it used to drink water. For other birds, the key was disconnected from the food delivery mechanism and seeds were delivered regardless of the pigeon's response, a procedure called autoshaping. These pigeons also learned to peck at the lighted key as if it were a substitute for food. The pigeon's peck, like the dog's salivation, is a Pavlovian conditioned reflex that is characteristic of the consummatory phase of learning.

True instrumental learning is displayed by subjects long before they gain their consummatory objective. For example, E. L. Thorndike confined hungry cats in a puzzle box and placed the food (unconditioned stimulus) outside. Manipulation of a trigger (the response) released the cat, giving access to food. Another procedure is to place a hungry rat in the starting box and to provide food at the end of a maze with cul-de-sacs along the way. With repeated trials in such apparatus, animals will reduce extraneous responses and decrease time from start to finish. With prolonged training under controlled conditions, subjects can combine CS-US and R-US units into long instrumental sequences. However, behavioral units and sequences do not provide a complete answer to the question "What is learned?" Laboratory studies and detailed observations under natural conditions indicate that animals often forego satisfaction of needs to spontaneously explore their surroundings, acquiring memorial representation or a cognitive map of the spatial and temporal relationships among many stimuli. With this cognitive map well in hand, they will exhibit novel shortcuts, detours, strategies, and expectations, modifying instrumental means to achieve desired ends. After consumption, these incentives to action are automatically reevaluted in accordance with their homeostatic utility. *See* COGNITION; MEMORY. John Garcia

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Conductance

The real part of the admittance of an alternating-current circuit. The admittance Y of an alternating-current circuit is a complex number given by Eq. (1). The real part G is the conductance. The units

$$Y = G + jB \tag{1}$$

of conductance, like those of admittance, are called siemens or mhos. Conductance is a positive quantity. The conductance of a resistor R is given by Eq. (2).

$$G = \frac{1}{R} \tag{2}$$

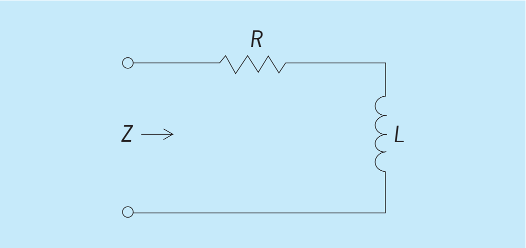
In general the conductance of a circuit may depend on the capacitors and inductors in the circuit as well as on the resistors. For example, the circuit in the **illustration** has impedance at frequency ω given by Eq. (3) and admittance given by Eq. (4), so that the conductance, given by Eq. (5), depends on the inductance L as well as the resistance R. *See* ADMITTANCE; ALTERNATING-CURRENT CIRCUIT THEORY; ELECTRICAL IMPEDANCE.

$$Z = R + jL\omega \tag{3}$$

$$Y = \frac{1}{R + jL\omega} \tag{4}$$

$$G = \frac{R}{R^2 + L^2\omega^2} \tag{5}$$

J. O. Scanlan



Circuit with a resistor and inductor in series.

Conduction (electricity)

The passage of electric charges due to a force exerted on them by an electric field. Conductivity is the measure of the ability of a conductor to carry electric current; it is defined as the ratio of the amount of charge passing through unit area of the conductor (perpendicular to the current direction) per second divided by the electric field intensity (the force on a unit charge). Conductivity is the reciprocal of resistivity and is therefore commonly expressed in units of siemens per meter, abbreviated S/m. *See* ELECTRICAL RESISTIVITY.

The magnitude of the conductivity of a material or system is determined by two properties: the number n of its charges in unit volume that are free to move in the field, and how effectively the field can move them. Acted on by the field, which accelerates them, and by the resistance of the material to their motion, the free charges achieve a drift velocity that is proportional to the electric field intensity. The mobility μ of the charges is defined as the ratio of this drift velocity to the field. From the above definition of the conductivity σ, it follows directly that $\sigma = ne\mu$, where e is the charge of a free carrier and n is the number of free carriers per unit volume.

Electron and hole conduction. In metals and semiconductors (such as silicon, of which transistors are made) the charges that are responsible for current are free electrons and holes (which, as missing electrons, act like positive charges). These are electrons or holes not bound to any particular atom and therefore able to move freely in the field. Conductivity due to electrons is known as n-type conductivity; that due to holes is known as p-type. *See* HOLE STATES IN SOLIDS; SEMICONDUCTOR.

The conductivity of metals is much higher than that of semiconductors because they have many more free electrons or holes. The free electrons or holes come from the metal atoms. Silver is the highest-conductivity metal, with a room-temperature conductivity of 7×10^7 S/m. Copper has almost as high a room-temperature conductivity, 5.9×10^7 S/m. Semiconductors differ from metals in two important respects. First, the semiconductor atoms do not contribute free electrons or holes unless thermally excited, and second, free electrons or holes can also arise from impurities or defects. The latter process may also require thermal excitation, but the temperature rise needed is smaller than that for exciting electrons and holes from the semiconductor atoms. These two differences cause the conductivity of semiconductors, in contrast to that of metals, to be quite dependent on temperature and on their purity. Pure silicon, for example, has a room-temperature conductivity of 3×10^{-4} S/m. If impurities such as aluminum or arsenic are added, a process called doping, the conductivity of silicon can be raised to 10^5 S/m and even higher. Gallium arsenide, of which laser diodes are made, when pure has a room-temperature conductivity of 2×10^{-7} S/m, but it can also be doped, for example, with silicon, to 10^5 S/m.

An exception to some of the rules stated above has been found in conjugated polymers. Polyacetylene, for example, although a semiconductor with extremely high resistance when undoped, can be doped so heavily with certain nonmetallic impurities (iodine, for example) that it attains a conductivity comparable to that of copper. *See* ORGANIC CONDUCTOR.

In metals, although the number of free carriers does not vary with temperature, an increase in temperature decreases conductivity. The reason is that increasing temperature causes the lattice atoms to vibrate more strongly, impeding the motion of the free carriers in the field. This effect also occurs in semiconductors, but the increase in number of free carriers with temperature is usually a stronger effect. At low temperatures the thermal vibrations are weak, and the impediment to the motion of free carriers in the field comes from imperfections and impurities, which in metals usually does not vary with temperature. At the lowest temperatures, close to absolute zero, certain metals become superconductors, possessing infinite conductivity. *See* ELECTRICAL CONDUCTIVITY OF METALS; SUPERCONDUCTIVITY.

Although there is no material that does not conduct electricity at all, that is, behaves as a perfect insulator, there are materials that are very poor conductors. Examples are ceramics, with conductivities of 10^{-12} to 10^{-14} S/m; amorphous selenium, with a conductivity of 10^{-14} S/m; and paraffin, with 3×10^{-17} S/m. *See* ELECTRIC INSULATOR.

Ionic conduction. Electrolytes conduct electricity by means of the positive and negative ions in solution. In ionic crystals, conduction may also take place by the motion of ions. This motion is much affected by the presence of lattice defects such as interstitial ions, vacancies, and foreign ions. *See* ELECTROLYTIC CONDUCTANCE; IONIC CRYSTALS.

Ionic conduction can also take place in a gas by using a strong electric field to ionize the gas molecules. If enough ions are formed, there may be a spark. *See* ELECTRIC SPARK; ELECTRICAL CONDUCTION IN GASES.

Vacuum conductivity. Electric current can flow through an evacuated region if electrons or ions are supplied. In a vacuum tube the current carriers are electrons emitted by a heated filament. The conductivity is low because only a small number of electrons can be "boiled off" at the normal temperatures of electron-emitting filaments. *See* ELECTRON EMISSION; ELECTRON MOTION IN VACUUM; VACUUM TUBE.

Esther M. Conwell

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Conduction (heat)

The flow of thermal energy through a substance from a higher- to a lower-temperature region. Heat conduction occurs by atomic or molecular interactions. Conduction is one of the three basic methods of heat transfer, the other two being convection and radiation. *See* CONVECTION (HEAT); HEAT RADIATION; HEAT TRANSFER.

Steady-state conduction is said to exist when the temperature at all locations in a substance is constant with time, as in the case of heat flow through a uniform wall. Examples of essentially pure transient or periodic heat conduction and simple or complex combinations of the two are encountered in the heat-treating of metals, air conditioning, food processing, and the pouring and curing of large concrete structures. Also, the daily and yearly temperature variations near the surface of the Earth can be predicted reasonably well by assuming a simple sinusoidal temperature variation at the surface and treating the Earth as a semi-infinite solid. The widespread importance of transient heat flow in particular has stimulated the development of a large variety of analytical solutions to many problems. The use of many of these has been facilitated by presentation in graphical form.

For an example of the conduction process, consider a gas such as nitrogen which normally consists of diatomic molecules. The temperature at any location can be interpreted as a quantitative specification of the mean kinetic and potential energy stored in the molecules or atoms at this location. This stored energy will be partly kinetic because of the random translational and rotational velocities of the molecules, partly potential because of internal vibrations, and partly ionic if the temperature (energy) level is high enough to cause dissociation. The flow of energy results from the random travel of high-temperature molecules into low-temperature regions and vice versa. In colliding with molecules in the low-temperature region, the high-temperature molecules give up some of their energy. The reverse occurs in the high-temperature region. These processes take place almost instantaneously in infinitesimal distances, the result being a quasi-equilibrium state with energy transfer. The mechanism for energy flow in liquids and solids is similar to that in gases in principle, but different in detail.

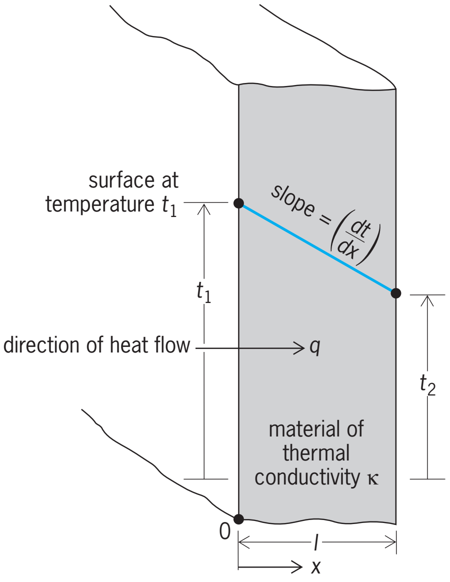

Fig. 1. Heat flow by conduction.

Fourier equation. The mathematical theory as well as the practical calculation of heat conduction is based on a macroscopic interpretation, as contrasted to the basic microscopic mechanism just described. From a physical point of view, it is reasoned that the steady heat flow from a surface (**Fig. 1**) at temperature t_1 to a parallel surface at t_2 is directly proportional to $(t_1 - t_2)$, the area A normal to the direction of flow, and the time of flow τ, and inversely proportional to the distance l between the two planes. These factors are modified by a coefficient κ accounting for the heat-conducting nature of the particular substance between the two planes. Thus, the heat flow Q (in British thermal units, for example) is given by Eq. (1). In terms of the time rate of flow $q = Q/\tau$

$$Q = \kappa A \frac{t_1 - t_2}{l} \tau \tag{1}$$

through an infinitesimally thin layer *dx,* in which the temperature change is *dt,* this becomes Eq. (2). The

$$q = -\kappa A \frac{dt}{dx} \tag{2}$$

minus sign is conventionally included to make q positive when heat flows in the increasing direction of x, since dt/dx is then negative. Although this equation was first proposed by J. Biot, it is named after J. Fourier in honor of Fourier's extensive contributions to the theory of heat conduction.

Thermal conductivity. The coefficient κ in Eqs. (1) and (2), called the thermal conductivity, is an important property of matter. It accounts for the heat–conducting ability of a substance, and depends not only on the particular substance involved, but also on the state of that substance. The Fourier equation is essentially a definition of κ which (Fig. 1) can be interpreted as the rate of heat flow per unit of area normal to the direction of flow when a unit temperature difference exists in unit length. Thus from Eq. (2) is derived Eq. (3), where κ is seen to have

$$\kappa = \frac{-q/A}{dt/dx} = \frac{q/A}{(t_1 - t_2)/l} \tag{3}$$

the dimensions of a heat rate per unit area and per unit of temperature gradient. In the cgs system, it can be expressed in cal/(s) · (cm^2)(°C/cm), which is equivalent to cal/(s)(cm)(°C). In engineering, the units most frequently used are Btu/(h)(ft)(°F).

Considerable progress has been made in the interpretation of thermal properties from theories of matter. This is particularly true for gases, where theory involving intermolecular forces has yielded very accurate results. The process of heat conduction in liquids is believed to be similar to that of sound transmission. In dielectric solids, energy is transmitted primarily by means of waves traveling through the atomic lattice; in metals, the electrons behave like an electron gas and provide for energy transfer as well as electrical conduction. This is the basis of the Widemann-Franz law, which states that $\kappa/\sigma T =$ constant (σ is the electrical conductivity and T the absolute temperature). *See* INTERMOLECULAR FORCES; KINETIC THEORY OF MATTER; THERMAL CONDUCTION IN SOLIDS.

For materials occurring as crystalline or amorphous solids, the general trend of κ at atmospheric pressure throughout the three physical states is as shown in **Fig. 2**. The numerical value at the maximum, which occurs near absolute zero in crystalline substances, is comparatively high. For example, the κ of a copper crystal at 20 K has been found to be 7050 Btu/(h)(ft)(°F)—more than 30 times its value at room temperature. Thermal conductivity of solids is discussed in a later section.

Because of the complexity and incomplete understanding of the mechanisms responsible for heat conduction, values of κ are usually determined experimentally. Results for typical gases, liquids, and solids in appropriate temperature ranges are shown in **Fig. 3**. The effect of pressure is significant primarily in gases.

Differential equation of conduction. The evidence of heat flow by conduction through a substance is the variation of the temperature with location and time.

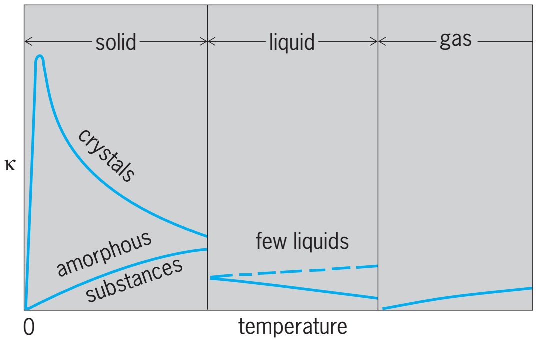

Fig. 2. General variation of thermal conductivity with temperature throughout the three physical states. (*After L. S. Kowalczyk, Trans. ASME, 77:1021–1035, 1955*)

If the temperature as a function of the space coordinates and time is known or can be determined, the heat flow at any location and in any direction can be specified by appropriate differentiation. A given problem is normally attacked by solving the differential equation governing the temperature distribution in a homogeneous substance and making this solution fit the prescribed initial or boundary conditions. This differential equation, essentially an expression of the first law of thermodynamics applied to the heat flow, is derived by making a heat balance on an elemental volume in a medium (**Fig. 4**).

Considering first the x direction, the net heat flow into the element in time $\Delta\tau$ is the difference between the flowing in on the left minus that flowing out on the right; or, applying Eq. (1), Eq. (4) is obtained.

$$\Delta Q_x = -\kappa\ \Delta y\ \Delta z \left(\frac{\partial t}{\partial x}\right)_x \Delta\tau - \left[-\kappa\ \Delta y\ \Delta z \left(\frac{\partial t}{\partial x}\right)_{x+\Delta x} \Delta\tau\right] \qquad (4)$$

Accounting for the variation of κ with temperature is extremely difficult and may make the analytical solution of a problem impossible. Because of this, it is customary to use an appropriate average value which is regarded as constant. Equation (4) can then be rearranged to read as Eq. (5*a*), which, as $\Delta x \to 0$, becomes Eq. (5*b*). Similar expressions apply for the y and z directions. Heat generated within the

$$\Delta Q_x = \kappa\ \Delta y\ \Delta z\ \Delta x \frac{\left(\dfrac{\partial t}{\partial x}\right)_{x+\Delta x} - \left(\dfrac{\partial t}{\partial x}\right)_x}{\Delta x} \Delta\tau \qquad (5a)$$

$$\Delta Q_x = \kappa\ \Delta x\ \Delta y\ \Delta z\ \Delta\tau \frac{\partial^2 t}{\partial x^2} \qquad (5b)$$

element at a uniform rate G per unit volume and time would add an amount $G\ \Delta x\ \Delta y\ \Delta z\ \Delta\tau$.

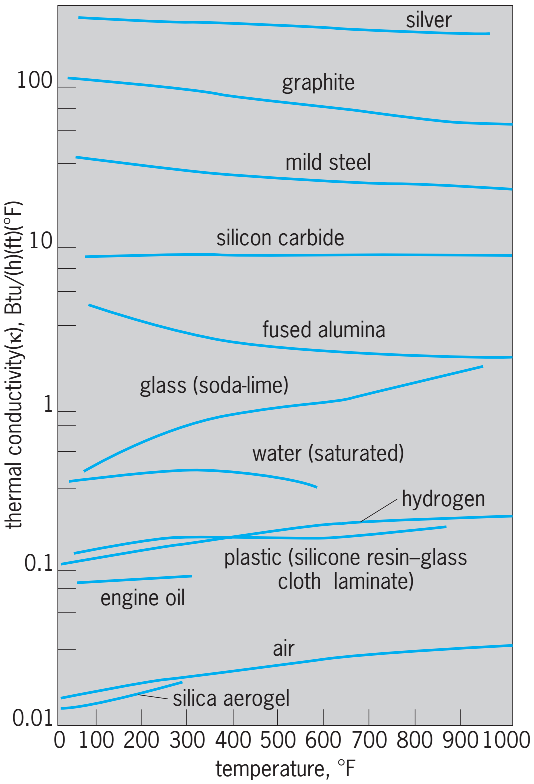

Fig. 3. Thermal conductivities of some typical examples of gases, liquids, and solids. °C = (°F − 32)/1.8.

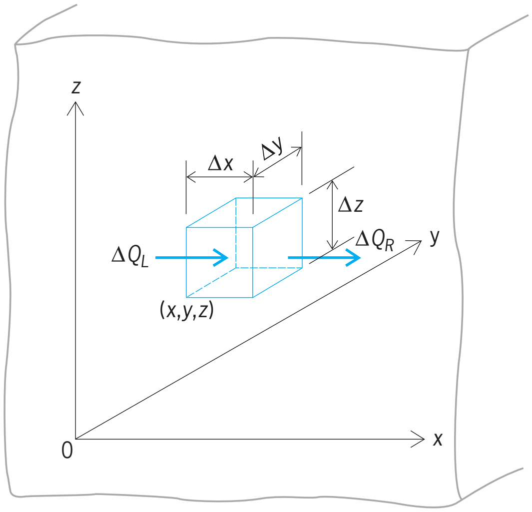

Fig. 4. Diagram of the heat flow through an elemental volume in a homogeneous medium.

The net heat flow into the element would be manifest as stored energy and would be equal to notation (6), where w is the specific weight (weight per

$$\Delta x\ \Delta y\ \Delta z\ wc\ \Delta t \qquad (6)$$

unit volume) of the medium, c its specific heat, and Δt the temperature rise in the time increment $\Delta\tau$. Equating the net flow into the element to that stored and letting Δx, Δy, Δz, and $\Delta\tau \to 0$ leads to Eq. (7).

$$\kappa\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right) + G = wc\,\frac{\partial t}{\partial \tau} \qquad (7)$$

When no heat source is present, Eq. (7) becomes Eq. (8). The ratio $\kappa/wc = \alpha$ is defined as the ther-

$$\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right) = \frac{1}{\kappa/wc}\frac{\partial t}{\partial \tau} = \frac{1}{\alpha}\frac{\partial t}{\partial \tau} \qquad (8)$$

mal diffusivity, and is the significant thermal property of a material for transient heat flow (**Fig. 5**). Equation (8) will be recognized as the equation governing a potential field written in terms of temperature. Similar equations are satisfied by other potential field phenomena, such as electricity, magnetism, diffusion, and ideal fluid flow. Because of this, solutions to problems in one field are applicable to analogous systems in the others. Also, an experimental solution of a problem in one field may be obtained from an analogous system in another. *See* POTENTIALS.

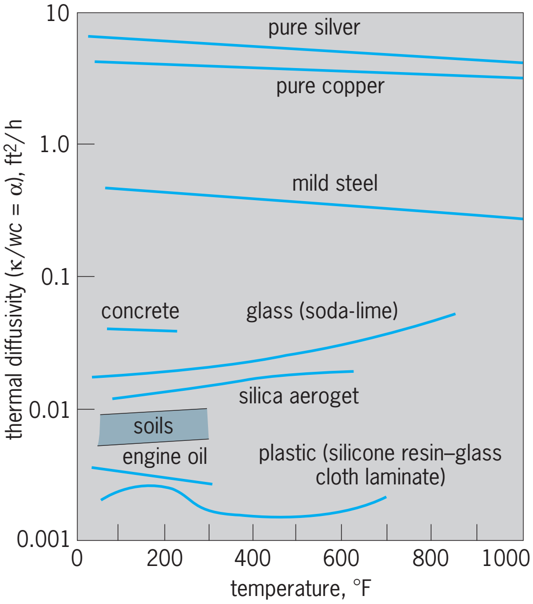

Fig. 5. Thermal diffusivities of some materials. °C = (°F − 32)/1.8.

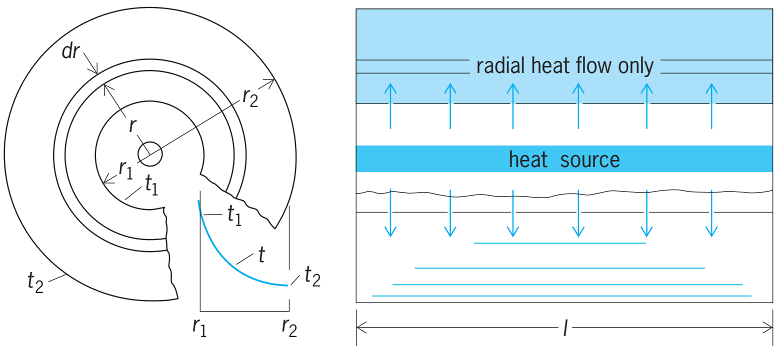

Fig. 6. Steady-state conduction. Diagrams show the temperature distribution for steady radial heat flow through a circular cylinder wall.

Steady-state conduction. When the temperature at all locations is constant with time or, mathematically, when $\partial t/\partial \tau = 0$, steady-state conduction exists. Many important practical problems fall in this category, the most familiar being heat flow through a wall and a hollow cylinder. Referring to Fig. 1 and assuming no heat generation within the wall, Eq. (8) reduces to Eq. (9). The terms $\partial^2 t/\partial y^2$ and $\partial^2 t/\partial z^2$ are

$$\frac{\partial^2 t}{\partial x^2} = 0 \tag{9}$$

eliminated, since t is considered to vary only with x. The desired temperature distribution is obtained by integrating Eq. (9) twice and evaluating the two constants from the known temperatures at $x = 0$ and $x = l$. This leads to Eq. (10). Application of Eq. (2) to obtain q yields Eq. (11).

$$t = t_1 - (t_1 - t_2)\,\frac{x}{l} \tag{10}$$

$$q = \kappa A \frac{(t_1 - t_2)}{l} \tag{11}$$

In the case of steady radial heat flow through a cylindrical wall (**Fig. 6**), Eq. (2) is applicable to any imaginary thin annular ring in the wall; thus Eq. (12)

$$q = -\kappa A \frac{dt}{dr} = -\kappa 2\pi r l \frac{dt}{dr} \tag{12}$$

is obtained. Integration from $t = t_1$ to t, and r_1 to r leads to Eq. (13), which indicates that the effect

$$t = t_1 - q \frac{\ln (r/r_1)}{2\pi \kappa l} \tag{13}$$

of the increasing area for heat flow is to produce a logarithmic variation in the temperature, as shown by the curve in the left part of Fig. 6.

Heat flow through a cylindrical wall is usually expressed in the same form as Eq. (11), written as Eq. (14). Solving Eq. (13) for q and substituting in

$$q = \kappa A_m \frac{t_1 - t_2}{r_2 - r_1} \tag{14}$$

Eq. (14) shows that the appropriate value for A_m must be as given in Eq. (15), which is called the logarithmic-mean area.

$$A_m = \frac{A_2 - A_1}{\ln (A_2/A_1)} \tag{15}$$

If the rate of heat flow and the inner and outer temperatures of a plane wall or hollow cylinder are measured during steady heat conduction, values of κ can be determined from Eq. (11) or Eq. (14). Because of the simplicity of the equations and the physical systems, most devices for measuring thermal conductivity are based on these types of heat flow.

Interface resistance. Now consider steady-state heat flow through a wall composed of two or more layers of material, each with different uniform thermal properties. If the surfaces of the various layers are very smooth and in very good contact with each other, the temperature distribution will be continuous. At any interface (**Fig. 7***a*), since q is constant, Eq. (16) holds. This shows that there is a disconti-

$$\kappa_1 \left(\frac{dt}{dx}\right)_1 = \kappa_2 \left(\frac{dt}{dx}\right)_2 \tag{16}$$

nuity in the temperature gradient due to the change in κ.

Actual surfaces, even polished ones, are not smooth but have small projections and depressions.

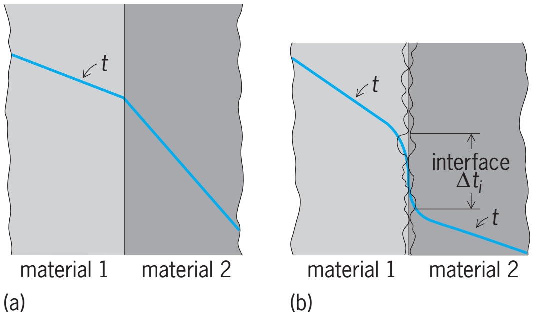

Fig. 7. Temperature distribution through composite wall. (*a*) With perfect interface contact. (*b*) For typical actual surfaces.

Consequently, when two surfaces are brought together, contact occurs primarily at projecting spots, as illustrated in Fig. 7*b*. The resulting contact area is only a small fraction of the nominal contact area. Plastic deformation at the points of contact of one or both materials usually occurs with the application of force to hold them together. Heat flows through both the small contact areas and the substance (usually a gas or liquid) filling the voids between the contacting protuberances.

The impairment to the heat-flow path caused by this imperfect contact is referred to as contact resistance. This is determined by extrapolating the measured temperature distribution in each material to the apparent interface location (Fig. 7*b*). The quotient of the resulting temperature difference Δt_i thus determined and the heat flux defines an interface resistance $R_i = \Delta t_i/q$. R_i depends on the roughnesses of the surfaces, the gas or liquid filling the voids, and the contact pressure. In general, the effect of contact resistance is significant only at low (for example, below 100 lb/in.^{2} or 700 kPa) interface pressures.

Internally generated heat. Conduction of heat generated internally occurs, for example, in the fuel elements used in nuclear reactors. Many of these elements are essentially long, flat plates over which a coolant flows. It is usually necessary to clad the fissionable material to prevent corrosion and keep radioactive particles from entering the coolant (**Fig. 8**). This cladding is undesirable from a heat-transfer standpoint, and is made as thin as possible and of the best adaptable heat-conducting material. Consequently, the temperature drop through it is usually small. *See* NUCLEAR REACTOR.

To illustrate the effect of the heat generation, assume that it is uniform with space and time in the radioactive material of Fig. 8 [that is, G in Eq. (7) is constant]. Heat flow from the ends of the elements and parallel to the flow direction of the coolant is negligible.

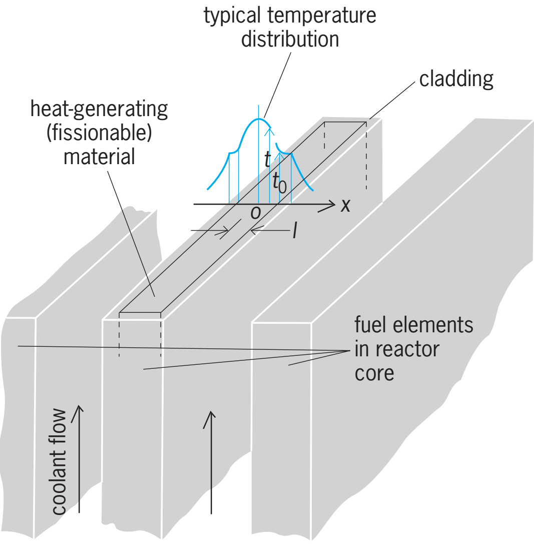

Fig. 8. Temperature distribution in reactor fuel plate.

Therefore, Eq. (7) reduces to Eq. (17). A solution

$$\frac{d^2t}{dx^2} + \frac{G}{\kappa} = 0 \tag{17}$$

for t is obtained by integrating twice and applying the boundary conditions (considering cooling to be the same on each side) $dt/dx = 0$ at $x = 0$ and $t = t_0$ at $x = l$. The result shows the temperature distribution to be parabolic, as in Eq. (18). The rate of heat transfer to the coolant is obtained by differentiating Eq. (18) with respect to x, evaluating at $x = l$, and substituting in Eq. (2).

$$t = t_0 + \frac{G}{2\kappa}(l^2 - x^2) \tag{18}$$

Since the heat generation rate is frequently dependent on the temperature, G will be more complex, possibly making an analytical solution impossible. Numerical methods of solution are then employed.

Periodic and transient conduction. These are the two kinds of non-steady-state heat flow. Periodic means a quasi-steady-state condition in which the temperature and heat flow at any location in a body vary continuosly with time, but pass through the same series of values in a definite period of time, τ_0. A transient state results when the heat flow at any location is momentarily or permanently changed. The duration of the transient period is the time required for the system to return to its original or a new steady-state condition. A transient change may be superimposed on a periodic variation.

Restricting consideration to examples in which no heat generation is present, the fundamental differential equation to be satisfied for either periodic or transient heat flow is Eq. (8). An interesting application is the temperature variation in the Earth due to the diurnal temperature variation, or to a sudden change in surface temperature. Equation (8) reduces in this case to Eq. (19). Assume the existence of a mean temperature of the Earth which is invariable with depth and that its surface temperature has been varying in a steady periodic manner long enough so that the original transient state due to starting the cyclic surface temperature has reached a steady periodic condition. If the surface temperature variation is given by Eq. (20), the appropriate solution to Eq. (19) is given by Eq. (21). This result shows that the temperature distribution looks like a wave traveling into the medium with the amplitude decreasing as the factor $e^{\sqrt{\pi/2\gamma x}}$. Computation of the heat flow by determining $(\partial t/\partial t)_{x\,=\,0}$ from Eq. (21) indicates that heat flows in during one-half of the period τ_0 and out during the other half.

$$\alpha\frac{\partial^2 t}{\partial x^2} = \frac{\partial t}{\partial \tau} \tag{19}$$

$$t = t_0 \cos 2\pi\frac{\tau}{\tau_0} \tag{20}$$

$$t = t_0 e^{-\sqrt{\pi/2\alpha x}} \cos\left(2\pi\frac{\tau}{\tau_0} = \sqrt{\pi/2\alpha}\,x\right) \tag{21}$$

Calculations of the temperature distribution in the Earth over an 8-h interval, using Eq. (21), are shown

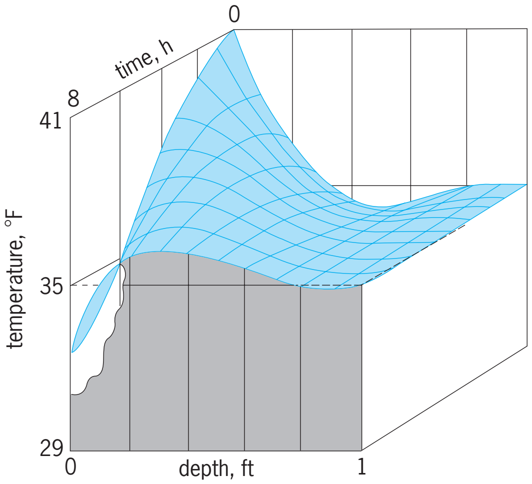

Fig. 9. Temperature distribution in the ground for a daily periodic surface variation. °C = (°F − 32)/1.8.

in **Fig. 9**. In this case the surface temperature varied from 29 to 41°F (−1.6 to 5.0°C) over a 24-h period; the diffusivity of the soil was 0.0065 ft^2/h (6.0×10^{-4} m^2/h).

An illustration of a transient state is the temperature variation resulting from a sudden change of magnitude t_0 in the temperature at the surface of the Earth. When the initial temperature throughout is uniform and taken as the datum, the applicable solution to Eq. (19) is given by Eq. (22). If a body of soil

$$t = \frac{2t_0}{\sqrt{\pi}} \int_0^{x/2\sqrt{\alpha\tau}} e^{-\beta^2}\, d\beta \qquad (22)$$

in the Earth's surface is at a uniform temperature of 40°F (4.4°C) and the surface temperature suddenly drops to 20°F (−6.7°C), Eq. (22) can be applied to determine the depth at which the temperature will have dropped to freezing (32°F or 0°C) in 12 h. Taking $\alpha = 0.0065$ ft^2/h, $t = 32$°F after 12 h is found to occur at $x = 0.27$ ft $= 3.2$ in. $= 8.2$ cm.

Variable thermal conductivity. Most materials are sufficiently homogeneous so that their thermal properties are independent of position. Assuming that they vary only with temperature, the heat balance on the element of Fig. 4 leads to Eq. (23). Upon carrying out the indicated differentiation, Eq. (23) becomes Eq. (24). By introducing a new variable θ called the conductivity potential, notation (25), Eq. (24) can be simplified to Eq. (26).

$$\frac{\partial}{\partial x}\left(\kappa \frac{\partial t}{\partial x}\right) + \frac{\partial}{\partial y}\left(\kappa \frac{\partial t}{\partial y}\right) + \frac{\partial}{\partial z}\left(\kappa \frac{\partial t}{\partial z}\right) + G = wc\,\frac{\partial t}{\partial \tau} \qquad (23)$$

$$\kappa\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right) + \frac{\partial k}{\partial t}\left[\left(\frac{\partial t}{\partial x}\right)^2 + \left(\frac{\partial t}{\partial y}\right)^2 + \left(\frac{\partial t}{\partial z}\right)^2\right] + G = wc\,\frac{\partial t}{\partial \tau} \qquad (24)$$

$$\theta = \int_0^t \kappa\, dt \qquad (25)$$

$$\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} + \frac{\partial^2 \theta}{\partial z^2} + G = \frac{1}{\alpha}\frac{\partial \theta}{\partial \tau} \qquad (26)$$

Equation (26) has exactly the same form as Eq. (7). In many cases the variation of α with temperature (Fig. 5) is less than that of κ so that a mean constant value may be selected. This is true, for example, of metals at temperatures near absolute zero. In such cases, if G is not a function of t (or no heat source is present), solutions for constant α will apply with θ replacing t, provided that the boundary conditions are specified in terms of t or $\kappa(\partial t/\partial n)$ where n represents the variables x, y, z.

The utility of the conductivity potential is demonstrated in the calculation of the heat leak to a liquid-nitrogen tank through a support rod. Consider steady-state conditions with the exposed end of the rod at 300 K and the other at 77.3 K. Also assume there are no losses from the side of the rod which is 1 cm^2 in cross section, is 15 cm long, and is made of stainless steel (for which κ decreases from 0.15 at 300 K to 0.08 W/cm K at 77.3 K). At any location q is given by Eq. (27). Since q is constant, Eq. (28) holds. Then Eqs. (29) follows.

$$q = -A\,\kappa\,\frac{dt}{dx} \qquad (27)$$

$$\frac{q}{A}\int_0^L dx = -\int_{t_1}^{t_2} \kappa\, dt = \int_0^{t_1} \kappa\, dt - \int_0^{t_2} \kappa\, dt \qquad (28)$$

$$\frac{qL}{A} = \theta_1 - \theta_2 \quad q = A\,\frac{\theta_1 - \theta_2}{L} = 1\,\frac{30 - 3.3}{15} = 1.78 \text{ W} \qquad (29)$$

Warren H. Giedt

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Conduction band

The electronic energy band of a crystalline solid which is partially occupied by electrons. The electrons in this energy band can increase their energies by going to higher energy levels within the band when an electric field is applied to accelerate them or when the temperature of the crystal is raised. These electrons are called conduction electrons, as distinct from the electrons in filled energy bands which, as a whole, do not contribute to electrical and thermal conduction. In metallic conductors the conduction electrons correspond to the valence electrons (or a portion of the valence electrons) of the constituent atoms. In semiconductors and insulators at sufficiently low temperatures, the conduction band is empty of electrons. Conduction electrons come from thermal excitation of electrons from a lower energy band or from impurity atoms in the crystal. *See* BAND THEORY OF SOLIDS; ELECTRIC INSULATOR; ELECTRICAL CONDUCTIVITY OF METALS; SEMICONDUCTOR; VALENCE BAND. H. Y. Fan

Conductor (electricity)

Metal wires, cables, rods, tubes, bus-bars, and any other conducting media used for the purpose of carrying electric current. Although any metal assembly or structure can conduct electricity, the term conductor usually refers to the component parts of the current-carrying circuit or system.

Types of conductor. The most common forms of conductors are wires, cables, and bus-bars.

Wires. Wires employed as electrical conductors are slender rods or filaments of metal, usually soft and flexible. They may be bare or covered by some form of flexible insulating material. They are usually circular in cross section; for special purposes they may be drawn in square, rectangular, ribbon, or other shapes. Conductors may be solid or stranded, that is, built up by a helical lay or assembly of smaller solid conductors (**Fig. 1**).

Cables. Insulated stranded conductors in the larger sizes are called cables. Small, flexible, insulated cables are called cords. Assemblies of two or more insulated wires or cables within a common jacket or sheath are called multiconductor cables.

Bus-bars. Bus-bars are rigid, solid conductors and are made in various shapes, including rectangular, rods, tubes, and hollow squares. Bus-bars may be applied as single conductors, one bus-bar per phase, or as multiple conductors, two or more bus-bars per phase. The individual conductors of a multiple-conductor installation are identical. *See* BUS-BAR.

Sizes. Most round conductors less than $^1/_2$ in. (1.3 cm) in diameter are sized according to the American wire gage (AWG)—also known as the Brown & Sharpe gage. AWG sizes are based on a simple mathematical law in which intermediate wire sizes between no. 36 (0.0050-in. or 0.127-mm diameter) and no. 0000 (0.4600-in. or 11.684-mm diameter) are formed in geometrical progression. There are 38 sizes between these two diameters. An increase of three gage sizes (for example, from no. 10 to no. 7) doubles the cross-sectional area, and an increase of six gage sizes doubles the diameter of the wire.

Sizes of conductors greater than no. 0000 are usually measured in terms of cross-sectional area. Circular mil (cmil) is usually used to define cross-sectional area and is a unit of area equal to the area of a circle 1 mil (0.001 in. or 25.4 micrometers) in diameter.

Fig. 1. End views of stranded round conductor.

Wire lengths are usually expressed in units of feet or miles in the United States. Bus-bar sizes are usually defined by their physical dimensions—height and width in inches or fractions of an inch, and length in feet.

Materials. Most conductors are metals, but there is a wide range of conductivities (as much as a 70-to-1 ratio between different metals). Conductors are usually classified as good conductors, such as copper, aluminum, and silver, and poor conductors, such as iron; alloys of nickel, iron, copper, and chromium; and carbon products. In 1914, the U.S. Bureau of Standards made measurements of a large number of representative samples of copper and established standard values of resistivity and temperature coefficients, which have been adopted by the International Electrotechnical Commission. *See* ELECTRICAL CONDUCTIVITY OF METALS; ELECTRICAL RESISTIVITY; METAL.

Most wires, cables, and bus-bars are made from either copper or aluminum. Copper, of all the metals except silver, offers the least resistance to the flow of electric current. Both copper and aluminum may be bent and formed readily and have good flexibility in small sizes and in stranded constructions. Typical conductors are shown in Fig. 1.

Aluminum, because of its higher resistance, has less current-carrying capacity than copper for a given cross-sectional area. However, its low cost and light weight (only 30% that of the same volume of copper) permit wide use of aluminum for bus-bars, transmission lines, and large insulated-cable installations. *See* ALUMINUM; COPPER.

Metallic sodium conductors were used in 1965 on a trial basis for underground distribution insulated for both primary and secondary voltages. Sodium cable offered light weight and low cost for equivalent current-carrying rating compared with other conductor metals. Because of marketing problems and a few safety problems—the metal is reactive with water—the use of this cable was abandoned. *See* SODIUM.

For overhead transmission lines where superior strength is required, special conductor constructions are used. Typical of these are aluminum conductors, steel reinforced (ACSR), a composite construction of electrical-grade aluminum strands surrounding a stranded steel core (**Fig. 2**). Other constructions include stranded, high-strength aluminum alloy and a composite construction of aluminum strands around a stranded high-strength aluminum alloy core (ACAR). *See* TRANSMISSION LINES.

For extrahigh-voltage (EHV) transmission lines, conductor size is often established by corona performance rather than current-carrying capacity. Thus special "expanded" constructions are used to provide a large circumference without excessive weight. Typical constructions use helical lays of widely spaced aluminum strands around a stranded steel core. The space between the expanding strands is

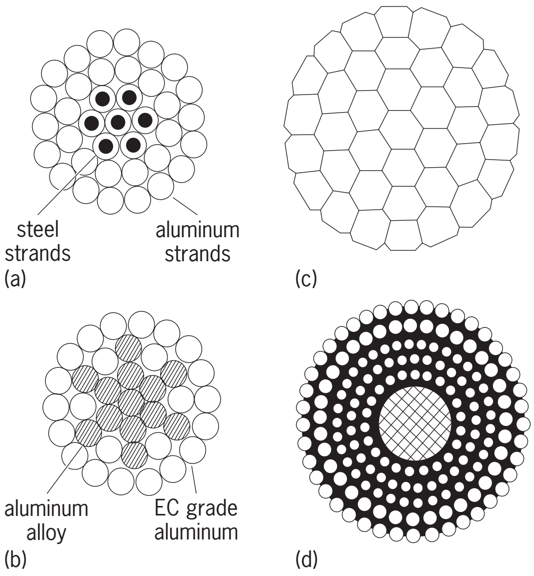

Fig. 2. Aluminum conductors. (*a*) ACSR. (*b*) ACAR. (*c*) Compact concentric stranded conductor. (*d*) Expanded-core concentric stranded conductor.

filled with paper twine, and outer layers of conventional aluminum strands are applied. In another construction the outer conductor stranding is applied directly over lays of widely separated helical expanding strands, without filler, leaving substantial voids between the stranded steel core and the closely spaced outer conductor layers. Diameters of 1.6 to 2.5 in. (41 to 63 mm) are typical. For lower reactance, conductors are "bundled," spaced 6–18 in. (15–45 cm) apart, and paralleled in groups of two, four, or more per phase. Figure 2 shows views of typical aluminum-conductor–steel-reinforced and expanded constructions.

Materials research has focused on amorphous or glassy materials, which include amorphous silicon-based semiconductors and metal alloys that totally lack crystalline structure. *See* AMORPHOUS SOLID.

Bare conductors. Bare wires and cables are used almost exclusively in outdoor power transmission and distribution lines. Conductors are supported on or from insulators, usually porcelain, of various designs and constructions, depending upon the voltage of the line and the mechanical considerations involved. Voltages as high as 765 kV are in use, and research has been undertaken into the use of EHV transmission lines, with voltages as high as 1500 kV.

Bare bus-bars are used extensively in outdoor substation construction, in switchboards, and for feeders and connections to electrolytic and electroplating processes. Where dangerously high voltages are carried, the use of bare bus-bars is usually restricted to areas accessible only to authorized personnel. Bare bus-bars are supported on insulators which have a design suitable for the voltage being carried.

Insulated conductors. Insulated electric conductors are provided with a continuous covering of flexible insulating material. A great variety of insulating materials and constructions has been developed to serve particular needs and applications. The selection of an appropriate insulation depends upon the voltage of the circuit, the operating temperature, the handling and abrasion likely to be encountered in installation and operation, environmental considerations such as exposure to moisture, oils, or chemicals, and applicable codes and standards. *See* ELECTRICAL INSULATION.

Magnet wires, used in the windings of motors, solenoids, transformers, and other electromagnetic devices, have relatively thin insulations, usually of enamel or cotton or both. Magnet wire is manufactured for use at temperatures ranging from 220 to 390°F (105 to 200°C). *See* MAGNET WIRE.

Conductors in buildings. Building wires and cables are used in electrical systems in buildings to transmit electric power from the point of electric service (where the system is connected to the utility lines) to the various outlets, fixtures, and utilization devices. Building wires are designed for 600-V operation but are commonly used at utilization voltages substantially below that value, typically 120, 240, or 480 V. Insulations commonly used include thermoplastic, natural rubber, synthetic rubber, and rubber-like compounds. Rubber insulations are usually covered with an additional jacket, such as fibrous braid or poly(vinyl chloride), to resist abrasion. Building wires are grouped by type in several application classifications in the National Electrical Code. *See* ELECTRICAL CODES.

Classification is by a letter which usually designates the kind of insulation and, often, its application characteristics. For example, type R indicates rubber or rubberlike insulation. TW indicates a thermoplastic, moisture-resistant insulation suitable for use in dry or wet locations; THW indicates a thermoplastic insulation with moisture and heat resistance. Other insulations in commercial use include silicone, fluorinated ethylene, propylene, varnished cambric, asbestos, polyethylene, and combinations of these.

Building wires and cables are also available in duplex and multiple-conductor assemblies; the individual insulated conductors are covered by a common jacket. For installation in wet locations, wires and cables are often provided with a lead sheath (**Fig. 3**).

For residential wiring, the common constructions used are nonmetallic-sheath cables, twin- and multiconductor assemblies in a tough abrasion-resistant jacket; and armored cable with twin- and multiconductor assemblies encased in a helical, flexible steel armor as in **Fig. 4**.

Power cables. Power cables are a class of electrical conductors used by utility systems for the

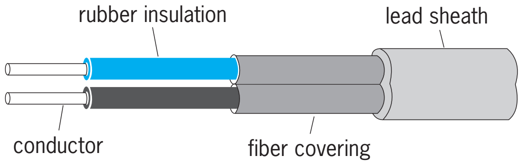

Fig. 3. Rubber-insulated, fiber-covered, lead-sheathed cable, useful for installation in wet places.

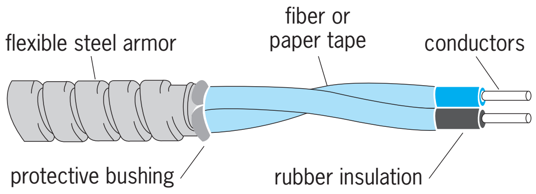

Fig. 4. Two-conductor armored cable.

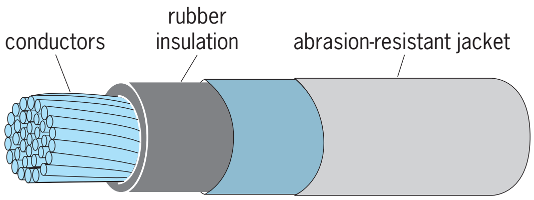

Fig. 5. Rubber-insulated power cable.

distribution of electricity. They are usually installed in underground ducts and conduits. Power cables are also used in the electric power systems of industrial plants and large buildings.

Power-cable insulations in common use include rubber, paper, varnished cambric, asbestos, and thermoplastic. Cables insulated with rubber (**Fig. 5**), polyethylene, and varnished cambric (**Fig. 6**) are used up through 69 kV, and impregnated paper to 138 kV. The type and thickness of the insulation for various voltages and applications are specified by the Insulated Power Cable Engineer Association (IPCEA).

Spaced aerial cable. These cable systems are used for pole-line distribution at, typically, 5–15 kV, three-phase. Insulated conductors are suspended from a messenger, which may also serve as a neutral conductor, with ceramic or plastic insulating spacers, usually of diamond configuration. For 15 kV, a typical system may have conductors with $^{19}/_{64}$-in. (4-mm) polyethylene insulation, 9-in. (23-cm) spacing between conductors, and 20 ft (6 m) between spacers.

High-voltage cable. High-voltage cable constructions and standards for installation and application are described by IPCEA. Insulations include (1) paper, solid type; (2) paper, low-pressure, gas-filled; (3) paper, low-pressure, oil-filled; (4) pipe cable, fully impregnated, oil-pressure; (5) pipe cable, gas-filled, gas-pressure; (6) rubber or plastic with neoprene or plastic jacket; (7) varnished cloth; (8) AVA and AVL (asbestos-varnished cloth).

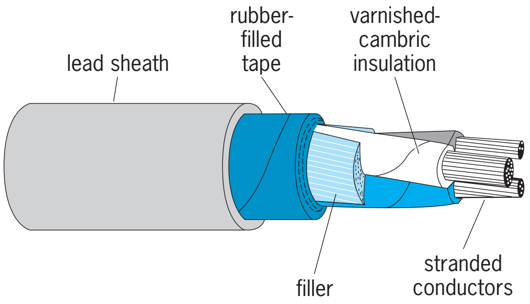

Fig. 6. Varnished cambric-insulated, lead-sheathed power cable, for voltages up to 28 kV.

Underground transmission cables are in service at voltages through 345 kV, and trial installations have been tested at 500 kV. Research has also been undertaken to develop cryoresistive and superconducting cables for transmitting power at high density.

Superconducting cables. It may be possible to apply the phenomenon of superconductivity to help provide more efficient and more compact electrical systems. In the area of electric power transmission, generation, and storage, superconductivity could have a major impact by increasing energy conservation. With the advent, in 1986, of superconducting materials with transition temperatures as high as 125 K (−235°F), there is a possibility of designing superconducting transmission lines that would carry as much as 1 GVA (10^9 W) of power. *See* SUPERCONDUCTING DEVICES; SUPERCONDUCTIVITY.

Busways. Enclosed bus-bar assemblies, or busways, are extensively used for service conductors and feeders in the electrical distribution systems of industrial plants and commercial buildings. They consist of prefabricated assemblies in standard lengths of bus-bars rigidly supported by solid insulation and enclosed in a sheet-metal housing.

Busways are made in two general types, feeder and plug-in. Feeder busways have no provision for taps or connections between the ends of the assembly. Low-reactance feeder busways are so constructed that conductors of different phases are in close proximity to minimize inductive reactance. Plug-in busways have provisions at intervals along the length of the assembly for the insertion of bus plugs.

Voltage drop in conductors. In electric circuits the resistance and (in ac circuits) the reactance of the circuit conductors result in a reduction in the voltage available at the load (except for capacitive loads). Since the line and load resistances are in series, the source voltage is divided proportionally. The difference between the source voltage and the voltage at the load is called voltage drop.

Electrical utilization devices (such as motors, household appliances, and electronic equipment) are designed to operate at a particular voltage or within a narrow range of voltages around a design value. The performance and efficiency of these devices are adversely affected if they are operated at a significantly lower voltage. Incandescent-lamp light output is lowered; fluorescent-lamp light output is lowered and starting becomes slow and erratic; the starting and pull-out torque of motors is seriously reduced.

Voltage drop in electric circuits caused by line resistance also represents a loss in power which appears as heat in the conductors. In excessive cases, the heat may rapidly age or destroy the insulation. Power loss also appears as a component of total energy use and cost. *See* COPPER LOSS.

Thus, conductors of electric power systems must be large enough to keep voltage drop at an acceptable value, or power-factor corrective devices—such as capacitors or synchronous condensers—must be installed. A typical maximum for a building wiring system for light and power is 3% voltage drop from the utility connection to any outlet under full-load condition. *See* WIRING. H. Wayne Beaty

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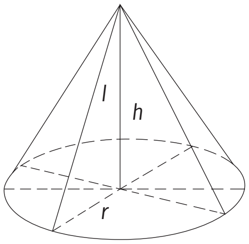
Cone

The solid of revolution obtained by revolving a right triangle about one of its shorter sides is called a cone, or more precisely a right circular cone (see **illus.**).



Right circular cone.

More generally, the term cone is used in solid geometry to describe a solid bounded by a plane and a portion of one nappe of a conical surface. In analytic geometry, however, the term cone refers not to a solid but to a conical surface. This is a surface generated by a straight line which moves so that it always intersects a given plane curve, called the directrix, and passes through a point, called the vertex, not in the plane of the directrix. The generating line in each of its positions is called an element of the cone. The vertex divides the surface into two parts, called nappes, that are congruent to each other in the extended sense (under rotation and reflection combined) but may not be superposable by a rigid motion in three-dimensional space.

If the elements of a cone make equal angles with a line through the vertex, the cone is called a cone of revolution, the line is called the axis of revolution, and the angle is called the semivertical angle ϵ. Plane sections of a cone of revolution are called conic sections.

If the plane makes an angle θ with the axis and does not contain the vertex, the resulting conic section is called nondegenerate and is a circle if $\theta = 90^\circ$, an ellipse if $\epsilon < \theta < 90^\circ$, a parabola if $\theta = \epsilon$, or a hyperbola if $\theta < \epsilon$. In the latter case the plane cuts both nappes of the cone, and the conic section consists of two separate congruent arcs called the branches of the hyperbola.

If the cutting plane contains the vertex of the cone, the conic section is degenerate and consists of a point, a line, or a pair of intersecting lines. Cones whose directrices are conic sections are called quadric cones.

The volume of a solid cone is $V = Bh/3$, where B is the base area included within the directrix, and h is the altitude (or height) measured from the vertex to the plane of the base. The volume V and surface area S of a right circular cone are $V = \pi r^2 h/3$ and $S = \pi rl + \pi r^2$, where r denotes the radius of the base and $l = \sqrt{r^2 + h^2}$ denotes the slant height, measured from vertex to base along an element of the cone.

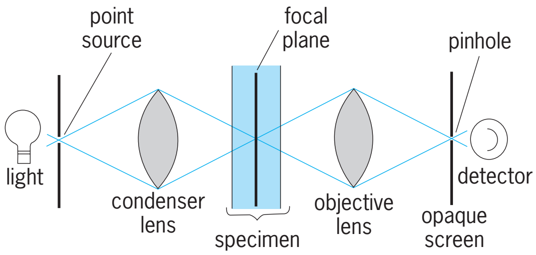
A frustum of a cone is a solid bounded by two parallel planes and a portion of a conical surface. The plane boundaries are called bases. If the bases are circles of radii r and R, the volume of the frustum is $V = (\pi h/3)(r^2 + rR + R^2)$. *See* CONIC SECTION; EUCLIDEAN GEOMETRY. J. Sutherland Frame

Confocal microscopy

A technique that creates high-resolution images of very small objects but differs from conventional optical microscopy in that it uses a condenser lens to focus the illuminating light from a point source into a very small, diffraction-limited spot within the specimen, and an objective lens to focus the light emitted from that spot onto a small pinhole in an opaque screen (see **illus.**). Located behind the screen is a detector capable of quantifying how much light passes through the hole at any instant. Because only light from within the illuminated spot is properly focused to pass through the pinhole and reach the detector, any stray light from structures above, below, or to the side of the spot is filtered out. The image quality is therefore greatly enhanced.

Only the smallest possible spot is illuminated at any one time, and so a coherent image must be built up by scanning point by point over the desired field of view and recording the intensity of the light emitted from each spot. The size of the spot is equal to the ultimate resolution of the instrument and is typically about 0.25 micrometer in diameter and about 0.5 μm deep, although the dimensions vary with the wavelength of the light and the lens system used.

Scanning can be accomplished in several ways, but the most common system is laser scanning. This system uses a pair of mirrors, vibrating at precisely



Schematic diagram of a confocal microscope. Light passes through a point source and a condenser lens to a point on the specimen. Only light coming from that spot is focused again by the objective lens onto a pinhole, through which it passes to reach the detector. Light from structures above or below the focal plane is too diffuse to pass through, and light from structures beside the spot is directed to the side of the pinhole. (*After R. J. Taylor, Confocal microscopy sheds new light on the dynamics of living cells, J. NIH Res., 1(1):113–115, 1989*)

controlled frequencies, which are placed in the path of a laser beam and direct it in a sweeping pattern over the specimen. The intensity of light emitted from each spot is digitally recorded, and the complete set of intensities from each point is displayed on a video screen, allowing the total image to be seen at one time. Because the information is already in a digital form, it can easily be passed to a computer for storage or further analysis.

Although confocal microscopy was first described in 1961, instruments were not available commercially until the late 1980s. They have found applications in several fields, including materials science and the semiconductor industry, but they have a number of advantages that make them particularly useful in the biological sciences. Many dyes used in biological studies are fluorescent and emit light at a wavelength different from the illuminating light. The amount of fluorescence from different parts of a cell, which is often directly proportional to the concentration of a specific intracellular constituent, can be measured far more precisely with a confocal microscope, because of the rejection of interference from other parts of a specimen. Haze from out-of-focus structures above the focal plane is eliminated, and so it is possible to see very clear images from fairly deep within a relatively thick slice of tissue without having to disrupt its three-dimensional organization. A stack of images from successive focal planes can be obtained simply by moving the narrow focal plane through the specimen. That technique makes it relatively easy to build up complex, three-dimensional views of cellular interconnections or subcellular structures. *See* FLUORESCENCE MICROSCOPE.

Robert J. Taylor

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Conformal mapping

A special operation in mathematics in which a set of points in one coordinate system is mapped or transformed into a corresponding set in another coordinate system, preserving the angle of intersection between pairs of curves.

A mapping or transformation of a set E of points in the xy plane onto a set F in the uv plane is a correspondence, Eqs. (1), that is defined for each

$$u = \varphi(x, y) \qquad v = \psi(x, y) \qquad (1)$$

point (x,y) in E and sends it to a point (u,v) in F, so that each point in F is the image of some point in E. A mapping is one to one if distinct points in E are transformed to distinct points in F. A mapping is conformal if it is one to one and it preserves the magnitudes and orientations of the angles between curves (**Fig. 1**). Conformal mappings preserve the shape but not the size of small figures.

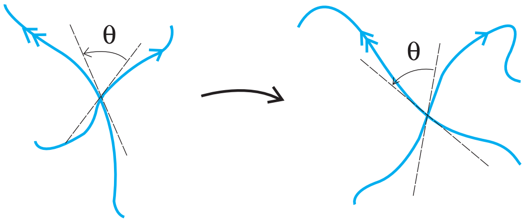

Fig. 1. Angle-preserving property of a conformal mapping.

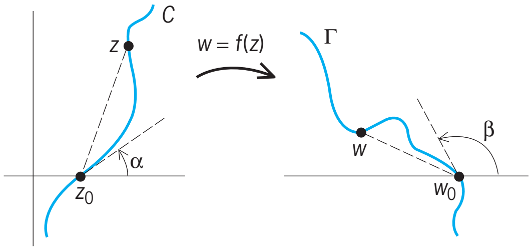

Fig. 2. Illustration for proof that analytic functions preserve angles.

Relation to analytic functions. If the points (x,y) and (u,v) are viewed as the complex numbers $z = x + iy$ and $w = u + iv$, the mapping becomes a function of a complex variable: $w = f(z)$. It is an important fact that a one-to-one mapping is conformal if and only if the function f is analytic and its derivative $f'(z)$ is never equal to zero. This can be seen by considering a function f that is analytic near $z_0 = x_0 + iy_0$, with $f'(z_0) \neq 0$, and mapping a curve C passing through z_0 to a curve Γ passing through $w_0 = f(z_0)$. Then, as a point z tends to z_0 along C, the angle arg $\{z - z_0\}$ tends to the angle α between C and the line $y = y_0$ (**Fig. 2**). But by assumption, expression (2) is valid. In particular,

$$\frac{f(z) - w_o}{z - z_o} \to f'(z_o) \qquad (2)$$

$\arg\{f(z) - w_0\} - \arg\{z - z_0\}$ tends to a limit $\gamma = \arg\{f'(z_0)\}$. In other words, $\arg\{w - w_0\} \to \beta$ as $w \to w_0$ along Γ, where $\beta = \alpha + \gamma$. But any other curve through z_0 is rotated by the same angle γ, so that the mapping preserves the angle between the two curves. In a similar manner, it can be shown that a conformal mapping is necessarily given by an analytic function. *See* COMPLEX NUMBERS AND COMPLEX VARIABLES.

Examples. Some examples of functions that provide conformal mappings (and one that is not conformal) will now be given.

1. The function $w = (z - 1)/(z + 1)$ maps the right half-plane, defined by $\text{Re}\{z\} > 0$, conformally onto the unit disk, defined by $|w| < 1$.

2. The function $w = \log z$ maps the right half-plane conformally onto the horizontal strip defined by $-\pi/2 < \text{Im}\{w\} < \pi/2$.

3. The function $w = z^2$ maps the upper semidisk, defined by $\mathrm{Im}\{z\} > 0$ and $|z| < 1$, conformally onto the unit disk $|w| < 1$ with the segment $0 \leq u < 1$ removed. It doubles angles at the origin, but this is a boundary point which does not lie in the semidisk.

4. The function $w = \bar{z}$ of complex conjugation preserves the magnitudes but not the orientations of angles between curves. It is nowhere conformal.

5. The function $w = z + 1/z$ maps the unit disk $|z| < 1$ conformally onto the extended complex plane (including the point at infinity) with the line segment $-2 \leq u \leq 2$ removed.

6. The Koebe function $k(z) = z(1 - z)^{-2}$ maps the unit disk conformally onto the complex plane with the half-line $-\infty < u \leq -1/4$ removed.

Linear fractional transformations. A linear fractional transformation is a function of the form given by Eq. (3), where *a, b, c*, and *d* are complex constants.

$$w = \frac{az + b}{cz + d} \qquad ad - bc \neq 0 \tag{3}$$

It is also known as a Möbius function. One example is the function $w = (z - 1)/(z + 1)$, discussed above. Simpler examples are magnifications, given by Eq. (4), rotations, given by Eq. (5), and inversion, given by Eq. (6). Every linear fractional transformation is a composition of linear fractional transformations of these three special types. Thus each linear fractional transformation provides a conformal mapping of the extended complex plane onto itself, and in fact the linear fractional transformations are the only such mappings. There is a unique linear fractional transformation which carries three prescribed (distinct) points z_1, z_2, z_3 to prescribed images w_1, w_2, w_3. The most general conformal mapping of the unit disk onto itself is a linear fractional transformation of the form given by Eq. (7).

$$w = az \qquad a > 0 \tag{4}$$

$$w = az \qquad |a| = 1 \tag{5}$$

$$w = 1/z \tag{6}$$

$$w = \frac{z - z_0}{1 - \bar{z}_0 z} \qquad |z_0| < 1 \tag{7}$$

Each linear fractional transformation carries circles to circles and symmetric points to symmetric points. Here a circle means a circle or a line. Two points are said to be symmetric with respect to a circle if they lie on the same ray from the center and the product of their distances from the center is equal to the square of the radius. Two points are symmetric with respect to a line if the line is the perpendicular bisector of the segment joining the two points. As an instance of this general property of linear fractional transformations, the mapping $w = (z - 1)/(z + 1)$ sends the family of circles of Apollonius with symmetric points 1 and -1 (defined by requiring that on each circle the quotient of the distances from 1 and -1 be constant) onto the family of all circles centered at the origin. It carries the orthogonal family of curves, consisting of all circles through the points 1 and -1, onto the family of all lines through the origin (**Fig. 3**).

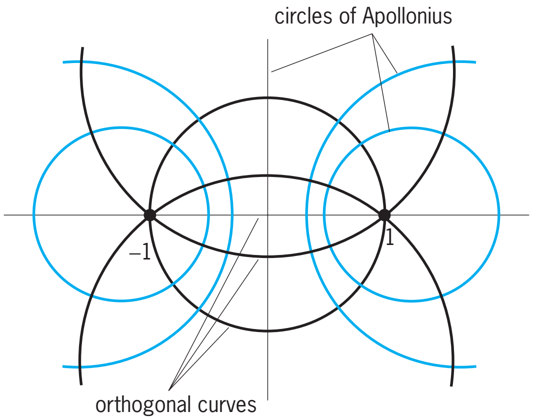

Fig. 3. Circles of Apollonius and members of the orthogonal family of curves.

Applications. Conformal mappings are important in two-dimensional problems of fluid flow, heat conduction, and potential theory. They provide suitable changes of coordinates for the analysis of difficult problems. For example, the problem of finding the steady-state distribution of temperature in a conducting plate requires the calculation of a harmonic function with prescribed boundary values. If the region can be mapped conformally onto the unit disk, the transformed problem is readily solved by the Poisson integral formula, and the required solution is the composition of the resulting harmonic function with the conformal mapping. The method works because a harmonic function of an analytic function is always harmonic. *See* CONDUCTION (HEAT); FLUID-FLOW PRINCIPLES; LAPLACE'S DIFFERENTIAL EQUATION; POTENTIALS.

The term conformal applies in a more general context to the mapping of any surface onto another. A problem of great importance for navigation is to produce conformal mappings of a portion of the Earth's surface onto a portion of the plane. The Mercator and stereographic projections are conformal in this sense. *See* MAP PROJECTIONS.

Riemann mapping theorem. In 1851, G. F. B. Riemann enunciated the theorem that every open simply connected region in the complex plane except for the whole plane can be mapped conformally onto the unit disk. Riemann's proof was incomplete; the first valid proof was given by W. F. Osgood in 1900. Most proofs exhibit the required mapping as the solution of an extremal problem over an appropriate family of analytic univalent functions. (A univalent function is simply a one-to-one mapping.) For instance, the Riemann mapping maximizes $|f'(z_0)|$ among all analytic univalent functions which map the given region into the unit disk: $|f(z)| < 1$. Here z_0 is chosen arbitrarily in the region, and the Riemann mapping has $f(z_0) = 0$.

Multiply connected regions. There is no exact analog of the Riemann mapping theorem for multiply connected regions. For instance, two annuli, $r_1 < |z| < r_2$ and $R_1 < |w| < R_2$, are conformally equivalent if and only if $r_2/r_1 = R_2/R_1$. Any doubly connected region can be mapped conformally onto a (possibly degenerate) annulus. Any finitely connected region (other than a punctured plane) can be mapped conformally onto the unit disk minus a system of concentric circular arcs, or onto the whole plane minus a system of parallel segments, or radial segments, or concentric circular arcs. Other canonical regions are bounded by arcs of lemniscates or logarithmic spirals, or by full circles.

Distortion theorems. Conformal mappings are often studied by considering the class S of functions $f(z)$ which are analytic and univalent in the unit disk and have the normalizing properties $f(0) = 0$ and $f'(0) = 1$. Alternatively, the class S may be defined as the class of all univalent power series of the form $f(z) = z + a_2z^2 + a_3z^3 + \cdots$ that are convergent for $|z| < 1$. The Koebe distortion theorem gives the sharp bounds, Eqs. (8), for all functions f in S and all points

$$\begin{aligned} r(1+r)^{-2} \le |f(z)| \le r(1-r)^{-2} \quad r = |z| \\ (1-r)(1+r)^{-3} \le |f'(z)| \le (1+r)(1-r)^{-3} \end{aligned} \tag{8}$$

z in the disk. The Koebe $^1/_4$-theorem asserts that each function f in S includes the full disk $|w| < {}^1/_4$ in its range. Suitable rotations of the Koebe function (discussed above) show that each of these bounds is the best possible. All of these statements can be deduced from a theorem of L. Bieberbach (1916) that $|a_2| \le 2$ for all functions f in S, with equality occurring only for the Koebe function, given by Eq. (9), or one of

$$k(z) = z(1-z)^{-2} = z + 2z^2 + 3z^3 + \cdots \tag{9}$$

its rotations, given by $e^{-i\theta}k(e^{i\theta}z)$ for some value of θ. Bieberbach conjectured that in general $|a_n| \le n$ for all n. For many years, the Bieberbach conjecture stood as a challenge and inspired the development of powerful methods in geometric function theory. After a long series of advances by many mathematicians, the final step in the proof of the Bieberbach conjecture was taken by L. de Branges in 1984.

Boundary correspondence. The open region inside a simple closed curve is called a Jordan region. Riemann's theorem ensures the existence of a conformal mapping of one Jordan region onto another. C. Carathéodory proved in 1913 that such a mapping can always be extended to the boundary and the extended mapping is a homeomorphism, or a bicontinuous one-to-one mapping, between the closures of the two regions. In fact, Carathéodory proved a much more general theorem which admits inaccessible boundary points and establishes a homeomorphic correspondence between "clusters" of boundary points, known as prime ends. For a conformal mapping of the unit disk onto a Jordan region with a rectifiable boundary, the Carathéodory extension preserves sets of measure zero (or zero "length") on the boundary. It is also angle-preserving at almost every boundary point, that is, except for a set of points of measure zero. If the boundary of the Jordan region has a smoothly turning tangent direction, the derivative of the mapping function can also be extended continuously to the boundary. *See* MEASURE THEORY.

Quasiconformal mappings. A theory of generalized conformal mappings, known as quasiconformal mappings, has evolved. Roughly speaking, a univalent function $w = f(z)$ is said to be K-quasiconformal in a certain region if it maps infinitesimal circles to infinitesimal ellipses in which the ratios of major to minor axes are bounded above by a constant $K \ge 1$. Equivalently, a mapping is quasiconformal if it distorts angles by no more than a fixed ratio. The simplest examples are linear mappings of the form $u = ax + by$, $v = cx + dy$, $ad - bc \ne 0$, where a, b, c, and d are real constants. The 1-quasiconformal mappings are simply the conformal mappings. The notion of a quasiconformal mapping is readily extended to higher dimensions. **Peter L. Duren**

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Conformal optics

Conformal optical systems have outer surfaces whose shape is chosen to optimize the interaction with the environment in which the optical system is being used. The imaging through such conformal optical windows is likely to suffer from extreme aberration, requiring special techniques for correction. *See* ABERRATION (OPTICS).

For example, a conformal optical window might relate to the nose of an infrared-seeking missile. These conformal surfaces permit a beneficial interface with the environment and allow substantial improvements in the overall performance of the vehicle. Recently there has been considerable research into methods of compensating for the aberrations produced by such windows. Computer-intensive methods of design, fabrication, and testing of optics have reached a level where the development of cost-effective methods for insertion of these conformal optics concepts into operational systems appears to be practical.

Applications. Important applications of conformal optics are found in missile and aircraft systems. Missiles and aircraft carry optical sensors for imaging, detection, and ranging that must look at the world through the outer skin of the vehicle. Traditionally, the windows for viewing through the skin of missiles and aircraft have had simple optical forms, such as flats or spheres, that enable the optical tracking systems to operate by using well-known technology. But these optically advantageous windows degrade the performance of the vehicle through increased drag, aerodynamic heating, or other undesirable effects. One example is the use of an optical tracker or seeker on the front end of a missile. These optical systems, usually used with infrared sensors, need to have a wide and unobstructed field of view. The classical solution for the window for these optics is a hemispherical dome mounted at the front of the missile. An optical tracker located within the dome is scanned around the field of view to keep track of a target. The spherical-surfaced-dome approach is easy to accommodate in the design, fabrication, and testing of the system, but the blunt spherical form adds considerable aerodynamic drag to the missile. The use of a conformal window, whose shape conforms more closely to the optimal, pointed ogival shape, reduces the drag of the missile and provides significant gains in the missile's performance. Such ogival shapes produce considerable optical aberration, however.

Similar considerations apply to aircraft. The optical sensors of most combat aircraft are mounted in pods that attach to the wings or other outer surfaces. These pods increase drag and reduce maneuverability and stealth properties of the aircraft. Location of the sensors within the body of the aircraft using traditional flat windows limits their field of view. The use of windows that have surfaces conforming to the desirable aerodynamic shapes of the aircraft is necessary to permit internal, drag-free location of these sensors.

One example of the benefits to be obtained through the appropriate use of conformal optics is a typical missile. Replacement of a hemispherical front-end window by an optimal-shaped ogival window can reduce the drag coefficient by as much as 25%. This reduction of the drag will lead to an increase in range for the same fuel consumption. There are additional advantages such as improved maneuverability of the missile.

The **illustration** shows one possible implementation of a conformal window to replace a conventional optical spherical window. It is a diagram of a conformal window, shaped to provide an improved drag profile for the missile. The optical tracker behind the conformal window can be seen looking toward the side of the missile. The optical tracker no longer sees a simple and constant spherical form for the window at any angle of view. The aspheric shape of the window produces a significant amount of aberration that must be compensated at some location in the optical system. The variation of the aberration with direction of view requires that this correction be dynamic.

There are other applications in which general aspheric optical surfaces are needed. Compact illumination systems require many unique forms of conformal surfaces, sometimes for utilitarian reasons and frequently for design or styling reasons. One growing area of interest comprises unique compact headlight systems for automobiles. Unobscured reflecting imaging systems used in spacecraft or microlithographic optics require nonconventional aspheric shapes for packaging or aberration correction purposes.

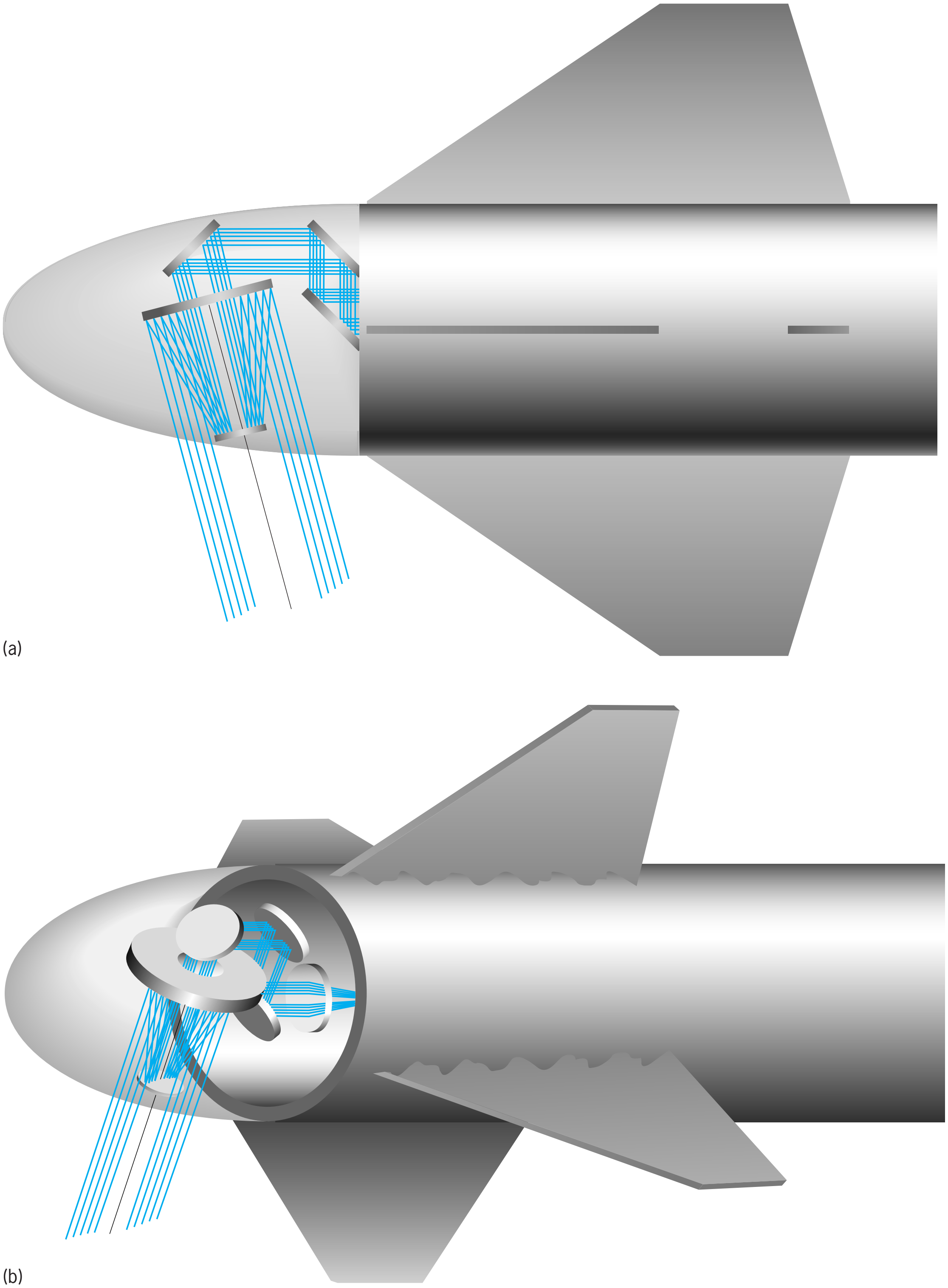
Challenges. The most desirable form for the front end of a missile is a pointed shape called an ogive. This ogival shape reduces the aerodynamic drag on the missile but produces a greatly distorted view of the scene that is viewed through the ogival dome. An optical tracker looking through the dome will see large amounts of aberration. A conformal optical surface is extremely aspheric and cannot be described by traditional surface prescriptions. Traditional optical design and fabrication methods cannot cope with the large amount of aberration that is generated by such conformal shapes. There are no established guidelines for the incorporation of these extreme aspheric conformal surfaces in the design of optical systems.

Fabrication of these conformal surfaces provides a new set of challenges. Traditional optical fabrication is based on the generation and polishing of spherical or flat surfaces by a lapping process. The surface eventually converges to the final required shape as a natural result of the process. Most aspherics used in lenses are minor deviations from these base spherical surfaces. Conformal surfaces require significant departures from traditional optical surfaces. New techniques for shape generation and polishing need to be developed so that conformal surfaces can be successfully fabricated. *See* OPTICAL SURFACES.

Test and measurement of these surfaces provide a new set of challenges. There are no natural nulling tests, which provide an absolute reference for the surface shape. Testing requires new methods of numerically constructing reference surfaces for defining, aligning, and calibrating the conformal surface. The use of these new surfaces as windows for optical systems also provides some new challenges in operation. The alignment between the window and the tracking optics is very critical. Therefore, alignment during installation and field operation must frequently be carried out by new adaptive optical techniques.

All of these new approaches require novel technical solutions within the framework of economic reality. None of these conformal techniques can be inserted into operational practice unless they are cost effective. Thus the cost of introducing conformal surfaces into missiles and aircraft must not exceed a small fraction of the cost benefit.

Design approach. The approach to design with conformal optics does not call for complete abandonment of current understanding of the image-formation process. Optical design methods are based on the description of the wavefront passing through surfaces by use of numerical ray tracing. The understanding of the aberrations arising at surfaces is obtained from an analytic method for describing the surface and the wavefront to stated levels of accuracy. The aberrations produced by general aspheric surfaces defy simple analytic descriptions but can be obtained by fitting of the numerical ray-tracing results. It is found that for most conformal surfaces the local aberration for a wavefront passing through a conformal window can be well described in terms of combinations of simple aberration shapes such as focus, astigmatism, and coma. The variation of these aberrations with location on the window becomes very difficult to describe analytically, leading to a



Geometric optics of an optical tracker behind a conformal window that is shaped to provide an improved drag profile for a missile. Paths of rays through the optical system are shown. (*a*) Side view. (*b*) Oblique view. *(Optical Research Associates)*

design process in which the numerical ray tracing is used to establish the aberration level.

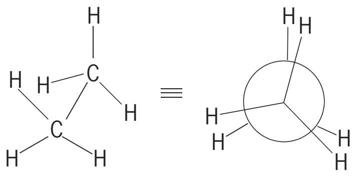
An intuitive grasp of the aberration content of conformal windows can be obtained by graphical presentations of the behavior of the aberrations with respect to the angle of view through the window. New design approaches permit expressing the targets of the design programs in terms of combinations of the sets of aberrations that naturally describe the effect of the conformal windows. New types of nonsymmetric aspheric components are required to compensate these sets of aberrations and are incorporated into the tracker optics. New approaches to tolerancing and assembling of these unusual optical systems are being investigated. *See* GEOMETRICAL OPTICS.

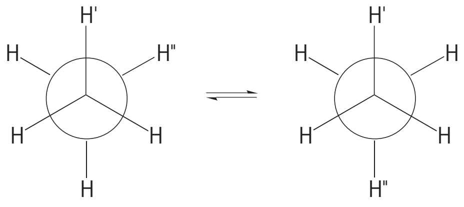
Robert R. Shannon

Conformational analysis

The study of the energies and structures of conformations of organic molecules and their chemical and physical properties. Organic molecules are not static entities. The constituent atoms vibrate and groups rotate about the bond axes. *See* STEREOCHEMISTRY.

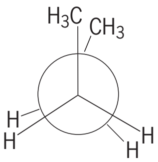
Linear structures. Rotation about the C-C bond in ethane, for example, results in an infinite number of slightly different structures called conformations, two of these are indicated below.

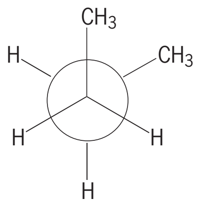

(**1**)

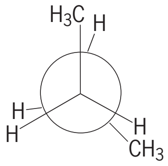

(**2**) (**3**)

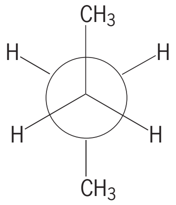
In conformation (**1**) of ethane, the pairs of C-H bonds on the two carbon atoms reside in a plane, and are termed eclipsed. (The circle represents the front-most carbon atom, and the long bonds those from that carbon atom to the hydrogen atoms. The bonds from the circle represent those bonds from the rearward carbon to its hydrogen atoms.) Conformation (**1**) is called the eclipsed conformation. In conformation (**2**), the C-H bonds on one carbon reside between the C—H bonds on the other carbon. Conformation (**2**) is called the staggered conformation. An infinite number of conformations between (**1**) and (**2**) are possible; however, conformations (**1**) and (**2**) are of greatest interest because they are the maximum and minimum energy structures. In conformation (**1**), the electrons in the C-H bonds and the nuclear charges of the hydrogen atoms repel each other, resulting in a higher energy state. In conformation (**2**), the electrons and hydrogen atoms are at their greatest possible separation and the repulsion is at a minimum. The conversion of (**2**) to (**3**) by rotation of one of the methyl groups by 120° requires the input of energy, approximately 3.0 kcal (13 kilojoules) per mole, in order to pass through the eclipsed conformation. This amount is small compared to the thermal energy at room temperature, and the rotation about the C-C bond in ethane occurs at about 10^9–10^{10} times per second.

Butane provides a more complicated case. There are two different eclipsed (**4** and **6**) and two staggered (**5** and **7**) conformations which are designated by the names below the structures. As the methyl group is larger than a hydrogen atom, (**4**) is higher in energy than (**6**), and (**5**) is higher in energy than (**7**) [see **illus.**]. As the molecular weight of an alkane increases, the number of molecular conformations (combinations of all possible individual bond conformations) increases dramatically, although the antiperiplanar conformations are always favored.

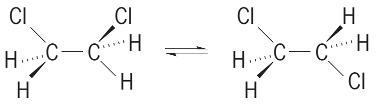

(**4**)
synperiplanar

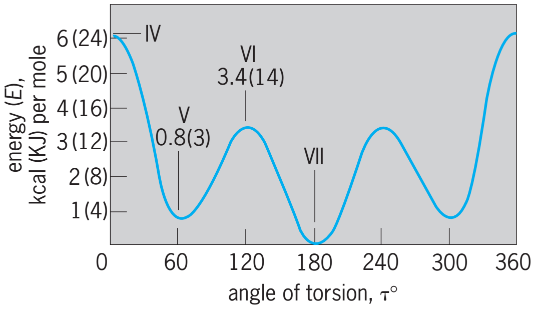

(**5**)
synclinal


(**6**)
anticlinal


(**7**)
antiperiplanar

1,2-Dichloroethane also exists in conformations similar to those of butane (see interconverting conformations below). In the gas phase, the antiperiplanar conformation predominates. This is not due to a steric repulsion in the synclinal conformation, but to C-Cl bond dipole repulsion. (The bond dipole moment arises from the fact that chlorine is more electronegative than carbon.) In a polar solvent, the energy difference between the antiperiplanar and synclinal conformations is decreased due to

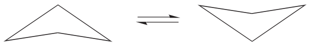

synclinal antiperiplanar



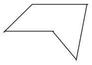
Potential energy diagram for butane. (*After E. L. Eliel et al., Conformational Analysis, Interscience Publishers, 1965*)

stabilization of the synclinal form. In pure liquid 1,2-dichloroethane, the enthalpy difference is zero. Such solvent effects are not observed with nonpolar molecules such as the alkanes.

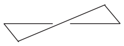
Cyclic structures. These also exist in various conformations. Cyclopropane, a planar structure, can exist in only one conformation. In cyclobutane, slight twisting about the C-C bonds can occur which relieves some of the C-H eclipsing strain energy. Cyclobutane exists in rapidly interconverting so-called butterfly conformations (**8**). Cyclopentane exists in two types of nonplanar conformations: the envelope conformation (**9**) and the half-chair (or twist) conformation (**10**). The flap atom of (**9**), the atom out of the plane of the other four, can migrate around the ring, as can also the twist in (**10**). These motions, called pseudorotation, require very little energy, and cyclopentane presents a very complex conformational system.



(8)

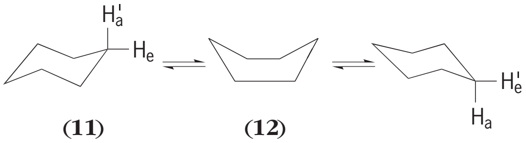


(9)



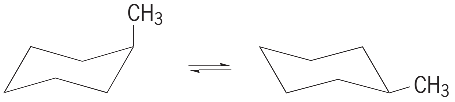
(10)

Cyclohexane exists predominantly in the chair conformation (**11**), in which all C-C bond conformations are of the staggered type. Interconversion between chair conformations occurs rapidly at room temperature, passing through the high-energy, boat conformation (**12**). In the chair conformation, there are two distinctly different types of hydrogen atoms; one set oriented perpendicular to the general plane of the ring, called axial (a) hydrogens, and one set oriented parallel to the plane of the ring, called equatorial (e) hydrogens. These hydrogens interchange orientation on chair interconversion. Axial and equatorial hydrogens possess different chemical and physical properties, although at room temperature the interconversion occurs very rapidly (~10^5 per second), and it is in general not possible to detect the differences. It is easy to design molecules in which the interconversion is not possible and the differences in properties become readily apparent.



(11) **(12)**

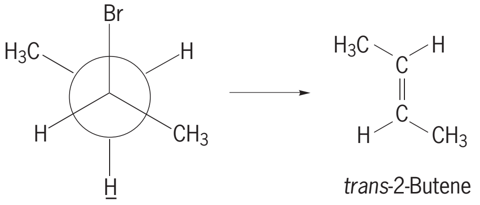
A substituted cyclohexane, for example methylcyclohexane, exists in two different chair conformations which are in equilibrium. In the axial conformation (**13**), the methyl group is in proximity with the other two axial hydrogens on the same side of the ring. This steric repulsion disfavors the axial conformation and favors equatorial conformation (**14**). The measurement of conformational equilibrium constants has allowed the construction of a relative size scale for organic functional groups.



(13) **(14)**

Rotation about C-C bond. Rotation about the C-C double bond requires a very large amount of energy, and is rarely observed except under very forcing conditions. Thus, although *cis*- and *trans*-2-butene can be considered to be conformational isomers, practically this does not occur.

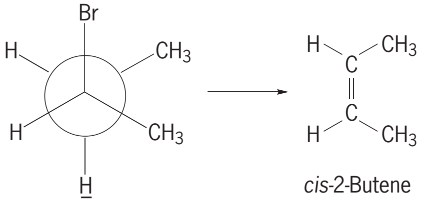
An illustration of how the conformation of a molecule affects a chemical reaction is provided by the elimination of hydrogen bromide from 2-bromobutane, which can exist in either of the two staggered conformations (**15**) and (**16**). The elimination of hydrogen bromide requires that the hydrogen and bromine be antiperiplanar. Thus, the elimination from (**15**) produces *trans*-2-butene [reaction (1)], and from **16**, *cis*-2-butene [reaction (2)].



(1)

trans-2-Butene

(15)



(2)

cis-2-Butene

(16)

Conformational analysis represents a very large area of study and has provided important information on the structures and reactivities of complex natural products such as steroids and alkaloids. *See* MOLECULAR ISOMERISM; STEREOCHEMISTRY. Daniel J. Pasto

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Confuciusornithidae

An extinct family of flying birds that represents one of the most primitive avian groups. It comprises three genera (*Confuciusornis*, *Changchengornis*, and *Jinzhouornis*) and is known exclusively from western Liaoning Province and neighboring areas in northeastern China. Fossils of this group have been collected from the Yixian and Jiufotang formations, which represent freshwater lake deposits that were formed in the Early Cretaceous period 125–120 million years ago.

Confuciusornithids are generally similar in size to *Archaeopteryx* and retain three wing claws and an unreduced phalangeal formula, that is, the phalangeal formula of the hand is 2-3-4 (two phalanges in the first digit, three phalanges in the second digit, and four phalanges in the third digit). The latter may indicate that the hand was used as an aid in climbing or grasping tree trunks and branches, as has also been suggested in the case of *Archaeopteryx* and some of their closely related dinosaurian ancestors. In addition to these primitive features, confuciusornithids share a number of features with modern birds, including a short skeletal tail in which the final few vertebrae are fused together into a pygostyle (or plowshare bone). Tail feathers would have been attached to the pygosyle, suggesting that confuciusornithids were probably better fliers than *Archaeopteryx*. The large and curved toe claws, as well as the toe proportions, suggest that confuciusornithids were arboreal.

The holotype specimen of *Confuciusornis*, the first named confuciusornithid, was discovered in 1993 by an amateur fossil collector and described in 1995 as the earliest known bird to have possessed a horny beak. Unlike living birds, most Mesozoic birds possessed teeth in the jaws; however, all known members of Confuciusornithidae completely lost their teeth. In addition, confuciusornithids have some very specialized skeletal features, such as a hole near the upper end of the humerus (upper arm bone). Although there is as yet no direct evidence concerning the diet of these birds, they probably fed mainly on insects.

Confuciusornis is the only Mesozoic bird that is abundantly represented in the fossil record; at least several hundred specimens are known, due to the exceptional preservation of the fossil assemblages in which they occur. (These deposits, of alternating volcanic ash layers and lake sediments, also yield many other important fossils such as feathered dinosaurs, pterosaur embryos, early mammals, and flowering plants.) In most *Confuciusornis* specimens, the feathers are preserved, including asymmetric flight feathers that indicate powerful flight capability. *Confuciusornis* also displays evidence of sexual dimorphism in the tail feathers; it is generally believed that those with short tail feathers are females, whereas those with a pair of long central tail feathers are males (see **illustration**). In some rare cases, male and female individuals are preserved together on a single slab. The discovery of hundreds of *Confuciusornis* specimens from a relatively small area may also indicate that they were gregarious. Geological evidence, and the abundance of specimens in the same strata, suggests that flocks of these birds may have died in mass mortality events, possibly caused by eruptions of nearby volcanoes. *See* ARCHAEOPTERYX; AVES; FEATHER; FOSSIL.

Zhonghe Zhou

Male *Confuciusornis* with a pair of long central tail feathers from the Early Cretaceous of Liaoning, northeastern China.

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Congenital anomalies

Structural abnormalities of the body that develop during embryogenesis and the fetal period; also called birth defects. Children with significant birth defects need more medical care than other children do, require more frequent hospitalizations, need community support services, and often require special education programs. Among children, over half of all visits to subspecialty medical clinics and admissions to hospitals are for treatment of disorders resulting from errors in embryonic development, chromosomal abnormalities, and genetic and familial disorders. Two-thirds of the deaths of infants and children in pediatric hospitals in developed countries are caused by underlying congenital anomalies.

Incidence. Although any particular birth defect may be rare, birth defects as a group are common. They are identified in 2–3% of newborns and in about an equal percentage later, in the first year of life, as structural defects and development delays become evident.

The overall incidence of congenital anomalies is about the same throughout the world, but certain geographic and racial groups have higher rates of certain disorders. For example, those developmental defects of the brain and spinal cord known as neural tube disorders are much more common in the British Isles than in North America, occurring in 10 per 1000 live births in Ireland as compared with 1–2 per 1000 in Canada and the United States.

Screening. Screening programs are available to identify fetuses and newborns likely to have disorders such as congenital malformations and genetic diseases. Examples of screening include amniocentesis to detect fetal chromosomal abnormalities in mothers over 35 years of age; measurement of maternal serum alpha-fetoprotein levels at 15–16 weeks' gestation to help identify fetuses with certain malformations; and screening of newborns for phenylketonuria, sickle cell disease, thalassemia, galactosemia, and congenital hypothyroidism. *See* ALPHA FETOPROTEIN; PHENYLKETONURIA; SICKLE CELL DISEASE.

Causes. Birth defects can be caused by genetic factors, exposure to malformation-causing agents (teratogens), or a combination of both. It is estimated that single-gene disorders cause 7.5% of birth defects identified in newborns and structural abnormalities of chromosomes cause 6%. Maternal infections that have been transmitted to the embryo or fetus are responsible for 2–3% of congenital anomalies. Maternal diabetes is associated with 1.5% and other maternal diseases with less than 1.5%. Maternal use of drugs and alcohol is responsible in about 1–2% of cases. In more than 50% of newborns with congenital anomalies, however, the specific etiology is not known. *See* DIABETES; FETAL ALCOHOL SYNDROME; HUMAN GENETICS.

Dysmorphology is the area of medicine and science concerned with the cause of congenital anomalies resulting from errors in embryonic development (dysmorphogenesis). The study of normal and abnormal embryonic development allows identification of the latest time in embryogenesis when a malformation could occur. Examples of such times include 28 days of gestation for neural tube defects, 36 days for cleft lip, and 10 weeks for cleft palate. Because the heart is an embryologically complicated organ, different congenital heart defects develop at different times in embryogenesis. Abnormalities of digestive tract formation can occur as early as 30 days of gestation and as late as 10 weeks.

Classification. To facilitate the study, birth defects are divided into malformations, disruptions, deformations, and dysplasias.

Malformations. Malformations are structural defects that are caused by primary errors in morphogenesis. They are classified as major and minor. Major malformations require medical or surgical intervention or are of substantial cosmetic importance. Various defects that were mentioned above are among such malformations. Minor malformations do not require such treatment or do not greatly affect appearance; examples include protruding ears, wide-set eyes, curvature of the fifth finger, webbing of the toes, and many others. Most individuals have two or three minor malformations, and the same minor malformations are frequently found in various family members. An excess of minor malformations is often associated with major malformations.

Disruptions. These are structural defects resulting from interruption of normal morphogenesis, with consequent destruction of previously existing structures and incomplete development of tissues. For example, if the fetus becomes entangled in the amnion (the inner lining of the placental sac), ring constrictions of the limbs can occur.

Deformations. These are congenital anomalies resulting from external compression of a normally formed part of the fetus. The most common deformations are bowing of the lower legs and in-toeing of the feet. In otherwise normal infants, minor deformations usually improve without treatment. If deformations are major, splints and special shoes may be required for correction.

Dysplasias. These are disorders that result from an abnormal organization of cells into tissues; the morphological result is called dyshistogenesis. Examples of such disorders include hemangiomas and lymphangiomas, which result from overgrowth of blood vessels and lymphatic vessels, respectively. Neurofibromatosis is an autosomal dominant genetic disorder that results in overgrowth of neural tissue.

Syndromes. Some individuals have various major and minor congenital anomalies that together form a recognizable pattern, called a syndrome. The medical diagnosis of a specific congenital syndrome in a child aids in determining etiology, identifying associated anomalies that previously were unrecognized, and establishing prognosis. Often, further diagnostic studies are required to confirm the diagnosis of a syndrome. Syndromes can have both genetic and environmental causes.

Teratology. Tetratology is the study of the effect of environmental agents on the developing embryo and fetus. Teratogens are agents that interfere with normal embryonic development. They can cause miscarriages, retard prenatal growth, and produce congenital anomalies or mental retardation.

There are five general groups of teratogens: (1) infectious diseases and agents, including rubella, toxoplasmosis, syphilis, cytomegalovirus, chickenpox, Venezuelan equine encephalitis, and human immunodeficiency virus; (2) physical agents, such as radiation, maternal hyperthermia, and abnormalities of the intrauterine environment; (3) drugs and chemical agents; (4) maternal metabolic and genetic factors, such as diabetes, epilepsy, smoking, and nutritional deficiencies; and (5) paternal factors, although rare. (Paternal exposures contribute mainly to decreased fertility rather than birth defects.)

Treatment, detection, and prevention. Treatment of congenital anomalies is specific for each individual. Individuals with severe or numerous abnormalities usually require multidisciplinary treatment, including such measures as medical management, surgical correction, nursing care, special diets, rehabilitation, prosthetic devices, special education, and community support.

If a couple has had a child with a congenital anomaly, tests may be done in subsequent pregnancies to help detect recurrence. Prenatal tests that are sometimes performed include chorionic villus sampling and amniocentesis to detect chromosomal and some metabolic defects, detailed ultrasound imaging of the fetus to identify significant structural malformations, and fetal echocardiograms to detect congenital heart disease.

Measures that help reduce the risk of having a child with congenital anomalies include avoidance of teratogenic exposures, medical treatment of maternal illnesses, good nutrition, and routine obstetrical care. However, much remains to be learned about the cause, detection, and prevention of congenital anomalies. *See* PREGNANCY. **Margot I. Van Allen**

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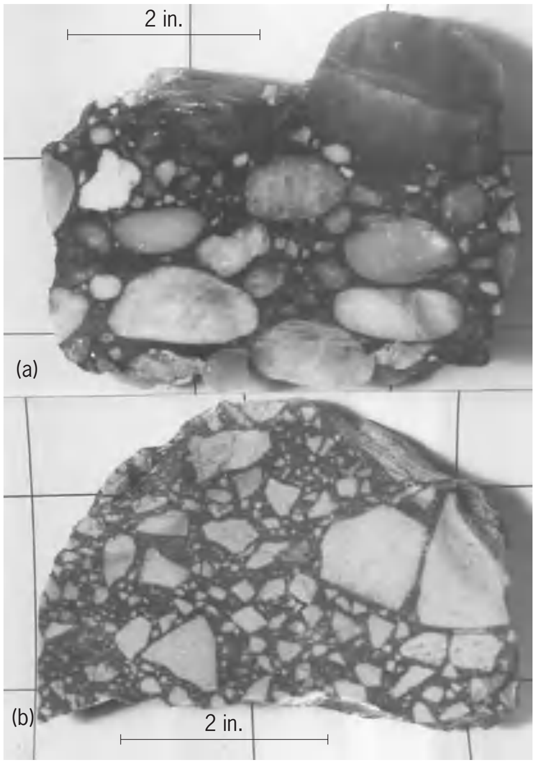
Conglomerate

The consolidated equivalent of gravel. Conglomerates are aggregates of more or less rounded particles greater than 0.08 in. (2 mm) in diameter. Frequently they are divided on the basis of size of particles into pebble (fine), cobble (medium), and boulder (coarse) conglomerates. The common admixture of sand-sized and gravel-sized particles in the same deposit leads to further subdivisions, into conglomerates (50% or more pebbles), sandy conglomerates (25–50% pebbles), and pebbly or conglomeratic sandstones (less than 25% pebbles). The pebbles of conglomerates are always somewhat rounded, giving evidence of abrasion during transportation; this distinguishes them from some tillites and from breccias, whose particles are sharp and angular (see **illus.**).

Conglomerates fall into two general classes, based on the range of lithologic types represented by the pebbles, and on the degree of sorting and amount of matrix present. The well-sorted, matrix-poor conglomerates with homogeneous pebble lithology are one type, and the poorly sorted, matrix-rich conglomerates with heterogeneous pebble lithology are the other. The well-sorted class includes quartz-pebbles, chert-pebble, and limestone-pebble conglomerates. The quartz pebbles were derived from long, continued erosion of the source-rock terrain that resulted in the disappearance of all unstable minerals, such as feldspars and ferromagnesian minerals, that make up most igneous and metamorphic rocks. Typically the quartz-pebble conglomerates are thin sheets that overlie an unconformity and are basal to a series of overlapping marine beds. Chert pebble conglomerates are derived from weathered limestone terrains. Limestone pebble conglomerates seemingly are the result of special conditions involving rapid mechanical erosion and short transport distances; otherwise the limestone would quickly become degraded to finer sizes and dissolve. The well-sorted conglomerates tend to be distributed in thin, widespread sheets, normally interbedded with well-sorted, quartzose sandstones. *See* UNCONFORMITY.

The poorly sorted, lithologically heterogeneous conglomerates include many different types, all related in having very large amounts of sandy or clayey matrix and pebbles of many different rock classes. The graywacke conglomerates are the outstanding representatives. They are composed of pebbles, many times only slightly rounded, or many different kinds of igneous and metamorphic rock as well as sedimentary rocks, bound together by a matrix that is a mixture of sand, silt, and clay. They seem to have been formed from the products of rigorous mechanical erosion of highlands and transported in large part by turbidity or density currents.



Lithified gravels. (*a*) Conglomerate, composed of rounded pebbles. (*b*) Breccia, containing many angular fragments. 2 in. = 5 cm. (*Specimens from Princeton University Museum of Natural History; photo by Willard Starks*)

Another representative of the poorly sorted class is fanglomerate, a conglomerate formed on an alluvial fan. Fanglomerates in many cases are much better sorted than the graywacke conglomerates but have heterogeneous pebble composition. A tillite is another representative of this class of conglomerate. All of these poorly sorted conglomerates tend to occur in fairly thick sequences, and some of them, typically the fanglomerates, are wedge-shaped accumulations. *See* SEDIMENTARY ROCKS; TURBIDITY CURRENT.

Special types of conglomerates, such as volcanic conglomerates and agglomerates and some intraformational conglomerates composed of shale pebbles or deformed limestone pebbles, do not seem to fall easily into either class. Some of the shale and limestone intraformational conglomerates have formed from the tearing up of previously deposited beds at the sea bottom while they were still relatively soft and only partially consolidated. Because of the angularity of some of these pebbles, they have often been called breccias. *See* BRECCIA; GRAVEL; GRAYWACKE; TILL.

Raymond Siever

Conglutination

A term used in serology to describe the completion or enhancement of an incomplete agglutinating system by the addition of certain substances. Some bacteria or erythrocyte suspensions do not exhibit the visible agglutination ordinarily expected after they have been coated with their specific antibodies and complement. Further addition of a conglutinating agent—normal bovine serum—however, initiates visible agglutination. Complement is an essential component of the system. The conglutination reagent is itself without effect in the absence of antibody and complement. Similar overall actions, such as agglutination of Rh^+ cells, occur when human serum, gelatin, or bovine serum albumin are added to the incomplete Rh antibodies found in some sera, but since this enhancing effect occurs also in the absence of complement, these reactions probably are to be distinguished in mechanism from that of the traditional conglutination. *See* BLOOD GROUPS.

Like the related complement-fixation reaction, the conglutination reaction can be used for a variety of serological diagnostic reactions in bacterial and viral infections. *See* AGGLUTINATION REACTION; COMPLEMENT-FIXATION TEST; SEROLOGY.

Henry P. Treffers

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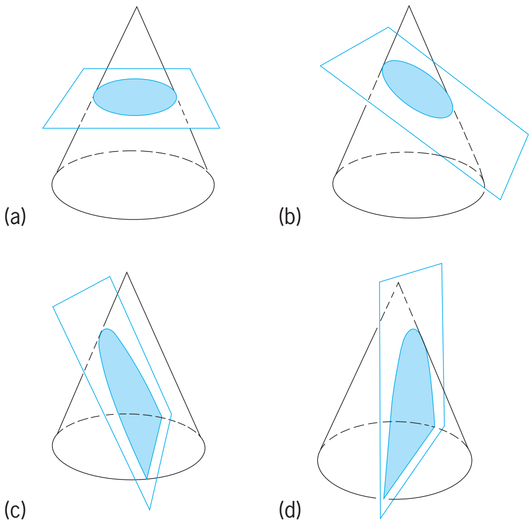
Conic section

One of the class of curves in which a plane may cut a cone (surface) of revolution. They were extensively studied by the ancient Greeks. The section is a parabola if the plane is parallel to an element of the cone, an ellipse or circle if the plane cuts all elements of one nappe (but does not go through the apex), and a hyperbola if the plane cuts elements of both nappes (for example, the plane parallel to the cone's axis of revolution) and does not go through the apex (see **illus.**) If a line g intersects the cone's axis perpendicularly at a point distinct from the apex, a plane that revolves about g will cut all three kinds of conics from the cone. If a plane contains the cone's axis, it intersects the cone in a pair of lines (a degenerate hyperbola); if it goes through the apex but does not contain the axis, it has in common with the cone either the apex alone (degenerate ellipse) or an element of the cone (degenerate parabola).



Four conic sections. (*a*) Circle. (*b*) Ellipse. (*c*) Parabola. (*d*) Hyperbola.

Algebraic definitions. After the advent of analytic geometry, the synthetic method used by the Greeks to develop the properties of conics gave way to algebraic procedures which, using other definitions, divorced these curves from their original relationship to cones and regarded them as graphs of second-degree equations in cartesian coordinates x, y. Let plane π cut all the elements of one nappe of a cone C (π not perpendicular to the cone's axis and not passing through the apex), and let E denote the curve of intersection of π and C. To show that E is an ellipse, consider the spheres S_1 and S_2 inside C that are tangent to π and to all the elements of C and that lie on the opposite sides of π. The contact points of S_1 and S_2 with C form circles whose planes π_1 and π_2 are perpendicular to the axis of C. Let F_1 and F_2 denote the contact points of S_1 and S_2, respectively,with π. If P is any point of E, then Eqs. (1) holds, where Q_1, Q_2

$$\text{dist}\,(P, F_1) = \text{dist}\,(P, Q_1) \tag{1a}$$

$$\text{dist}\,(P, F_2) = \text{dist}\,(P, Q_2) \tag{1b}$$

are those contact points of S_1, S_2, respectively, that lie on the element of C through P. Since dist (P,Q_1) + dist (P,Q_2) is the (constant) distance between the parallel planes π_1, π_2, then Eq. (2) holds, and so E is

$$\text{dist}\,(P, F_1) + \text{dist}\,(P, F_2) = \text{constant} \tag{2}$$

an ellipse. The directrices of E are the lines in which π_1, π_2 intersect π. *See* ANALYTIC GEOMETRY.

Conics are basic in astronomy, where it is shown that the newtonian inverse-square law of gravitation implies that the orbits of the planets are ellipses, with the Sun at one focus. Other heavenly bodies, certain comets, for example, have parabolic and hyperbolic paths.

Projective geometry. The third phase in the study of conic sections began with the development of projective geometry. In that subject it is shown that the locus of the points of intersection of two projective (nonperspective), coplanar (nonconcentric) pencils of lines is a nondegenerate (point) conic. All nondegenerate conics are projectively equivalent; that is to say, if C_1, C_2 are any two such conics, there is a projective transformation of their plane into itself that transforms C_1 into C_2. Conics may be classified into types by their behavior with respect to an arbitrarily selected line g, say the ideal line of the plane. In the geometry (affine) obtained by considering only those projective transformations that transform g into itself, a conic is a hyperbola, a parabola, or an ellipse accordingly as the number of points that the conic has in common with g is two, one, or none, respectively. Dual to point conics are line conics, the locus of all lines joining corresponding points of two projective (not perspective), coplanar (not collinear) point ranges. The tangents to a point conic form a line conic, and the contact points of a line conic form a point conic. One of the most famous theorems concerning conics was proved by the French philosopher-mathematician Blaise Pascal in 1640, when only 16 years old. The theorem asserts that if six points A_i, with $i = 1, 2, \ldots, 6$, are on a conic, then the intersections P,Q,R of the lines (A_1, A_2) and (A_4, A_5), (A_2, A_3) and (A_5, A_6), (A_3, A_4) and (A_6, A_1), respectively, lie on a line. This theorem, together with its converse (which is also valid) had numerous interesting consequences. The Brianchon theorem, proved 166 years later, is its dual. It states that if a hexagon circumscribes a conic, the three lines joining the three pairs of opposite vertices are concurrent. *See* CONE; ELLIPSE; HYPERBOLA; PARABOLA; PROJECTIVE GEOMETRY.

Leonard M. Blumenthal

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Conjugation and hyperconjugation

A higher-order bonding interaction between electron orbitals on three or more contiguous atoms in a molecule, which leads to characteristic changes in physical properties and chemical reactivity. One participant in this interaction can be the electron pair in the π-orbital of a multiple (that is, double or triple) bond between two atoms, or a single electron or electron pair or electron vacancy on a single atom. The second component will be the pair of π-electrons in an adjacent multiple bond in the case of conjugation, and in the case of hyperconjugation it will be the pair of electrons in an adjacent polarized σ-bond (that is, a bond where the electrons are held closer to one atom than the other due to electronegativity differences between the two atoms). *See* CHEMICAL BONDING.

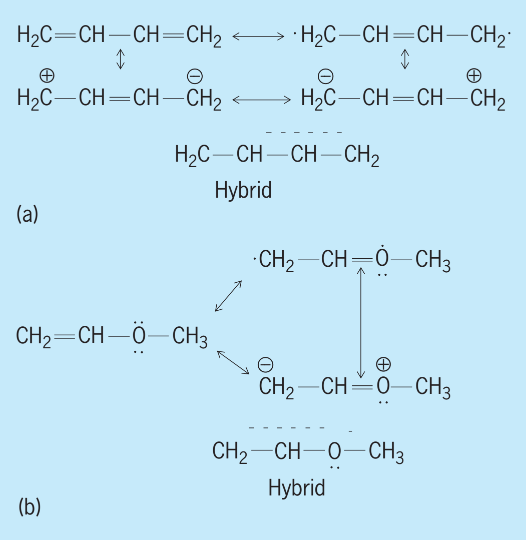

Fig. 1. Conjugated molecules. Broken overbars indicate the effects of conjugation. (*a*) 1,3-Butadiene. (*b*) Methyl vinyl ether.

Conjugation. The conjugated orbitals reside on atoms that are separated by a single bond in the classical valence-bond molecular model, and the conjugation effect is at a maximum when the axes of the component orbitals are aligned in a parallel fashion because this allows maximum orbital overlap. Conjugation thus has a stereoelectronic requirement, or a restriction on how the participating orbitals must be oriented with respect to each other. Two simple examples are shown in **Fig. 1**; in 1,3-butadiene ($H_2C{=}H\underline{C{-}C}H{=}CH_2$) conjugation occurs between the p orbitals (π-bonds) of the two double bonds, and in methyl vinyl ether ($H_2C{=}H\underline{C{-}O}{-}CH_3$) the nonbonding sp^3 orbital on oxygen is conjugated with the p orbitals of the double bond. This interaction is manifest in an effective bond order between single and double for the underlined single bond.

If the component orbitals are orthogonal (at right angles) to each other, or if the atoms bearing these orbitals are separated by more than one single bond or by no bond, the molecule is not conjugated. Two examples of molecules which do not exhibit conjugation are 1,4-pentadiene ($H_2C{=}CH{-}CH_2{-}CH{=}CH_2$) and allene ($H_2C{=}C{=}CH_2$), the former because there is more than one single bond between the component orbitals and the latter because the component orbitals are orthogonal to each other and are not separated by a single bond.

Chemists have used the conjugation rationale since the midnineteenth century, and it has become well accepted. The valence-bond model of conjugation invokes delocalization: the participating electrons are no longer localized or fixed on a particular atom or between a pair of atoms, but are shared throughout the conjugated orbitals. This increases their entropy, which contributes to a lower overall energy and generally results in greater stabilization for the molecule. From the valence-bond point of view, conjugated molecules are viewed as a weighted average hybrid of two or more valence-bond structures as shown in Fig. 1 for the two examples. Thus butadiene has a major contribution from the standard valence-bond structure, $H_2C{=}CH{-}CH{=}CH_2$, but the diradicals or the structures with separation of charge are valid alternative representations, and the same is true for methyl vinyl ether. The effects of conjugation are suggested by the broken lines on the hybrid structures in Fig. 1. When more orbital units are linked together or conjugated, more resonance structures can be drawn, and the molecule will be more stable and behave less according to the expectation based on the simple structure drawn from the classical valence-bond model. *See* DELOCALIZATION; ENTROPY; RESONANCE (MOLECULAR STRUCTURE); STRUCTURAL CHEMISTRY.

Three of the four resonance contributors for butadiene are drawn with only one multiple bond compared to the two multiple bonds in the standard valence-bond structure (Fig. 1*a*); this is known as sacrificial conjugation, in that some bonds in the standard depiction are sacrificed. In methyl vinyl ether (Fig. 1*b*) and in molecules or chemical intermediates, the different pictures drawn for the resonance contributors have the same number of multiple bonds; this is known as isovalent conjugation and results in a greater resonance energy stabilization than in the case of sacrificial conjugation. Other examples of isovalent conjugation include the allyl cation ($CH_2{=}CH{-}CH_2^+$ and $C^+H_2{-}CH{=}CH_2$) and benzene.

Conjugation is better understood by considering the molecular orbitals which can be approximated by the mathematical combination of the wave functions for the constituent atomic *s* and *p* orbitals (and *d* orbitals for elements beneath the first row of the periodic table). **Figure 2** shows simple pictorial results of complex molecular orbital (MO) calculations for the π-electrons in butadiene; here the σ bonds are neglected for clarity. The combination of four atomic *p* orbitals (two each for each of the double bonds) leads to four molecular orbitals. Each of the molecular orbitals is a quartet of "*p*-like" orbitals of different size (determined by calculation) situated on the four carbon atoms of butadiene (C^1–C^4). The four π-electrons are placed in these orbitals from the bottom up, so that the two lowest-energy orbitals, MO #1 and MO #2, both contain paired electrons. These two molecular orbitals thus account for the π-bonding in butadiene. In MO #1 the continuous bonding across all four lobes can be seen, with the highest orbital density between C^2 and C^3. In MO #2 there is a phase change between C^2 and C^3, with consequent repulsion between the adjacent lobes, but this repulsion is relatively less important because the electron orbital density (depicted as orbital size) is much lower here. In both of these molecular orbitals, the bonding interactions between $C^1{-}C^2$ and $C^3{-}C^4$ are in phase and add up to strong π-bonds. Thus, the π-delocalization interaction across $C^2{-}C^3$ that characterizes conjugation appears very naturally from the molecular orbital description. *See* MOLECULAR ORBITAL THEORY.

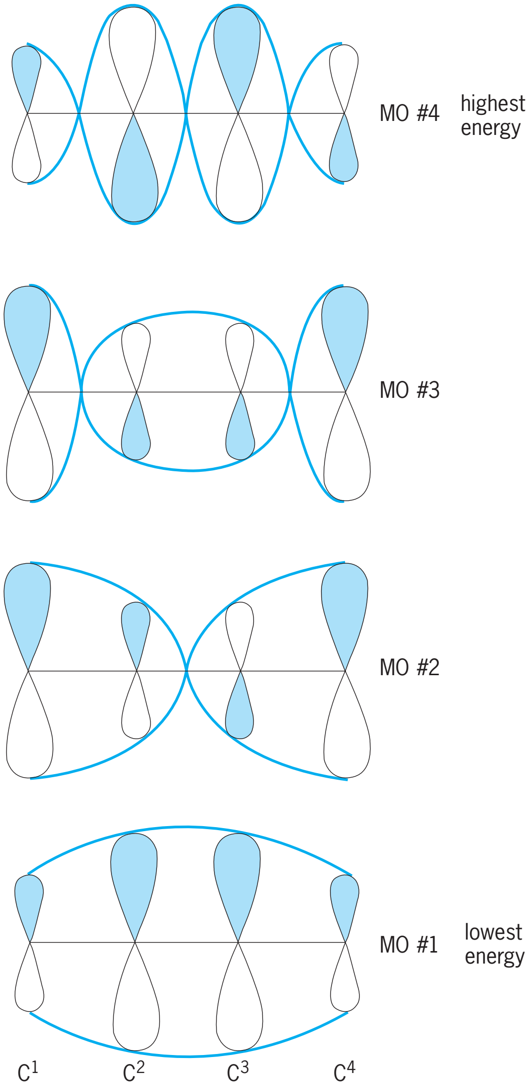

Fig. 2. Molecular orbital (MU) diagram for butadiene as determined by calculation. Algebraic phase is indicated by the presence or absence of tint. Orbital density is depicted as orbital size.

Hyperconjugation. This concept posits the conjugation of polarized σ-bonds with adjacent π-orbitals, and was introduced in the late 1930s by R. S. Mulliken. This rationale was used to explain successfully a wide variety of chemical phenomena; however, the confusing adaptation of the valence-bond model necessary to depict it and its inappropriate extension to some phenomena led to difficulties. The advent of the molecular orbital treatment has eliminated many of these difficulties.

Early on, hyperconjugation was used to explain the stabilization by alkyl groups of carbocations, or positively charged trivalent carbon. **Figure 3** shows how the orbitals of the σ-bonds of a methyl group (H_3C) exert a hyperconjugative stabilizing

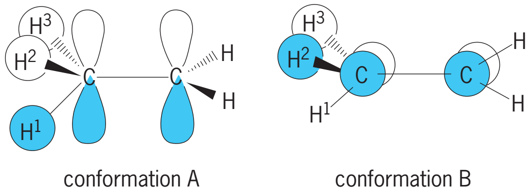

Fig. 3. Diagram showing hyperconjugative effect of orbitals of the σ-bonds of a methyl group (H_3C) on a neighboring *p* orbital of a methylene group (CH_2). Algebraic phrase is indicated by the presence or absence of tint.

effect upon a neighboring *p* orbital on a methylene group (CH_2). The bonding molecular orbitals of the methyl group utilize aspects of its carbon *p* orbitals; in both of the conformations or rotations the methyl group has such an orbital which overlaps in phase with the neighboring *p* orbital on CH_2. As hydrogen is an electropositive atom, the methyl group acts as an electron donor to stabilize an empty *p* orbital and to destabilize a filled *p* orbital on the right-hand carbon. This is in accord with empirical observations. If H^1 is replaced with some other atom X, the hyperconjugative effect of X will be at a maximum in conformation A, where there is orbital density on X, and it will be at a minimum in conformation B, where X is in the nodal or null plane. If X is a more electropositive atom such as silicon, the C-X bond is a donor bond and will stabilize an adjacent empty *p* orbital, such as in a cation. If X is a more electronegative element such as fluorine, the C-X bond is an acceptor bond and will stabilize an adjacent filled *p* orbital such as in an anion; this result accords with experiment as well. The donor and acceptor effects are also important where the single *p* orbital is replaced by a multiple bond. *See* REACTIVE INTERMEDIATES.

Physical properties and chemical reactivity. The most notable differences in physical properties attributed to conjugation are as follows: (1) The single bonds lying between the two orbital components are shortened. For example, the length of the C^2-C^3 bond in butadiene is 0.148 nanometer, as compared to 0.154 nm for the carbon-carbon single bond in ethane. This shortening can also be explained by the changes in orbital hybridization at these carbons. (2) Electronic absorption spectra begin at significantly longer wavelengths for conjugated than for related unconjugated molecules. (3) Ionization potentials are lower than for isomeric unconjugated molecules. (4) Related to points 2 and 3 is the fact that polarizabilities are larger for conjugated than for the corresponding unconjugated dienes. Polarizability is the ease with which the electron orbitals (electron clouds) of the molecule can be distorted through dipole-dipole interactions with other molecules, ions, atoms, or electrons; it is generally a measure of how loosely the electrons are held by the nuclei. (5) As compared with predictions from formulas for unconjugated molecules, conjugated molecules show lower energies, for example, about 6 kcal/mol (25 kilopascals/mol) lower for 1,3-butadiene than for unconjugated dienes; the excess is describable theoretically as resonance energy (valence-bond picture) or delocalization (molecular orbital theory picture). (6) The magnitude and orientation of dipole moments can be derived from hyperconjugation arguments, although the aforementioned differences in hybridization can also explain this. *See* BOND ANGLE AND DISTANCE; DIPOLE MOMENT.

In terms of changes in chemical reactivity, the following are exemplary: (1) The acidity of carboxylic acids stems from the conjugation stabilization of their ionized forms. (2) The addition of many chemical reactants takes place across the conjugated system (conjugate addition) rather than at the isolated double bonds, for example, the addition of bromine to butadiene to give a mixture of 1,4-dibromo-2-butene and 1,2-dibromo-3-butene. (3) The well-recognized orientation rules for the addition of chemical reagents to substituted benzenes and other aromatic systems can be rationalized through conjugated intermediates. (4) The facile formation of an anion from cyclopentadiene and of a cation from cycloheptatriene derives from the conjugation stabilization for those ions. (5) The chemistry of unsaturated organosilicon compounds can be explained only by hyperconjugation effects. (6) Certain changes in chemical reaction rates that occur when hydrogen atoms are substituted by deuterium atoms are clearly hyperconjugative effects.

A number of scientific phenomena depend on the properties of conjugated systems; these include vision (the highly tuned photoreceptors are triggered by molecules with extended conjugation), electrical conduction (organic semiconductors such as polyacetylenes are extended conjugated systems), color (most dyes are conjugated molecules designed to absorb particular wavelengths of light), and medicine (a number of antibiotics and cancer chemotherapy agents contain conjugated systems which trap enzyme sulfhydryl groups by conjugate addition). *See* VALENCE.

Matthew F. Schlecht

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Connecting rod

A link in several kinds of mechanisms. Usually one end of a connecting rod is intended to follow a circular path, while the other end follows a path along a straight line or a curve of large radius. The term is sometimes applied, however, to any straight link that transmits motion or power from one linkage to another within a mechanism. **Figure 1** shows conventional arrangements of connecting rods in typical mechanisms. In some applications (for example, the connecting rod between the crank and an overhead oscillating member or walking beam in a well-drilling

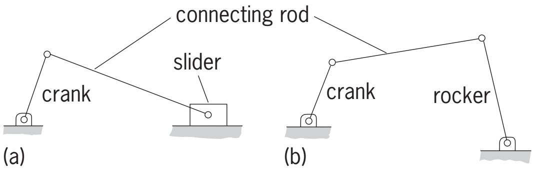

Fig. 1. Connecting rod in (*a*) slider-crank mechanism and (*b*) crank-and-rocker mechanism.

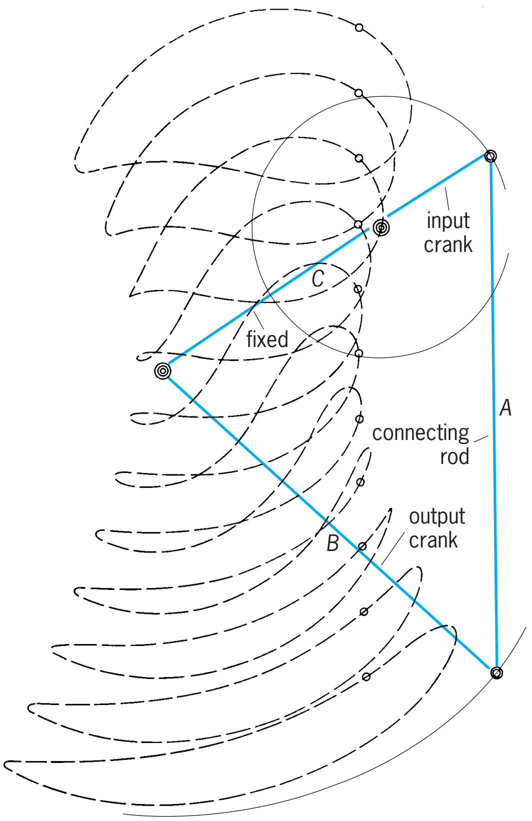

Fig. 2. Paths of points on connecting-rod plane traced by four-bar crank-and-rocker mechanisms for $A = 4.0$, $B = 3.5$, $C = 2.0$. (*After J. A. Hrones and G. L. Nelson, Analysis of Four-Bar Linkage*, John Wiley and Sons, *1951*)

rig, or between the steering column and cross-links in an automobile) the connecting rod is called a pitman. *See* AUTOMOTIVE STEERING.

The connecting rod of the four-bar linkage, often called the coupler, has special significance. The motion of its plane can now be synthesized to furnish desired paths for points not necessarily on the straight line *AB* (coupler-point paths), or desired positions of the entire connecting-rod plane. The connecting rod is then not primarily used for transmission of force or motion from input to output crank, but the entire mechanism is employed to impart to the connecting-rod plane certain displacements, and sometimes velocities and accelerations. **Figure 2** illustrates paths traced by various points in the plane of the rod, also revealing some velocities and accelerations there. *See* FOUR-BAR LINKAGE; MECHANISM.

Douglas P. Adams

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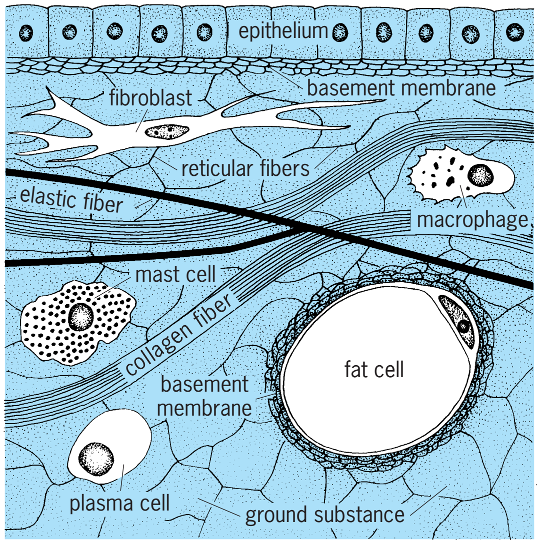
Connective tissue

One of the four primary tissues of the body. It differs from the other three tissues in that the extracellular components (fibers and intercellular substances) are abundant. It cannot be sharply delimited from the blood, whose cells may give rise to connective tissue cells, and whose plasma components continually interchange with and augment the ground substance of connective tissue. Bone and cartilage are special kinds of connective tissue. *See* BLOOD.

Functions. The functions of connective tissues are varied. They are largely responsible for the cohesion of the body as an organism, of organs as functioning units, and of tissues as structural systems. This cohesive function is achieved through their permeation of other tissues of the body. The connective tissues are essential for the protection of the body both in the elaborate defense mechanisms against infection and in repair from chemical or physical injuries. Nutrition of nearly all cells of the body and the removal of their waste products are both mediated through the connective tissues.

Connective tissues are important in the development and growth of many structures. Constituting the major environment of most cells, they are probably the major contributor to the homeostatic mechanisms of the body so far as salts and water are concerned. They act as the great storehouse for the body of salts and minerals, as well as of fat. The connective tissues determine in most cases the pigmentation of the body. Finally, the skeletal system (cartilage and bones) plus other kinds of connective tissue (tendons, ligaments, fasciae, and others) make motion possible.

Cellular components. The connective tissues consist of cells and extracellular or intercellular substance (see **illus.**). The cells include many



Components of connective tissue.

varieties, of which the following are the most important: (1) fibroblasts—variable in shape, frequently outstretched to form many fine processes, some as small as 20–30 nanometers; (2) macrophages (histiocytes)—variable in shape, strongly motile or outstretched, frequently with numerous minute cell processes, highly phagocytic (the ability to take particulate material into the cytoplasm); (3) mast cells—frequently large, ameboid, nucleus centrally located, cytoplasm very often packed with granules about 0.4 micrometer in diameter; (4) plasma cells—generally ovoid, weakly ameboid, nucleus eccentric, granular cytoplasm staining strongly with basic dyes (toluidine blue, methylene blue, hematoxylin); (5) melanocytes—cytoplasm of highly branched cells filled with minute granules which appear yellow or brown because of the melanin they contain; and (6) fat cells of two kinds: (a) yellow fat cells—very large (80 μm or more), generally spherical, with a thin shell of protoplasm (3.0–0.1 μm or less) enclosing a single enlarged fat droplet which appears yellowish; and (b) brown fat cells—moderately large, generally spherical, with small droplets of variable size (about 2 μm or less), scattered in the cytoplasm. In addition, connective tissues may contain, especially in the vicinity of small blood vessels, undifferentiated mesenchymal cells which may be considered as potentially embryonic, and blood cells which have wandered through the walls of blood vessels, including lymphocytes and polymorphonuclear granular leukocytes. It is especially important to realize that most of the cells of the connective tissue are developmentally related even in the adult; for example, fibroblasts may be developed from histiocytes or from undifferentiated mesenchymal cells.

Extracellular components. The extracellular components of connective tissues may be fibrillar or nonfibrillar. The fibrillar components are (1) reticular fibers which may be stained differentially with certain silver stains; (2) collagenous fibers which have a longitudinally striated appearance with the light microscope and are readily stainable with the acid dyes cosin and aniline blue; and (3) elastic fibers which are highly refractile, appear slightly yellowish, and may be stained differentially by certain dyes like orcein. With the higher resolution achieved with the electron microscope, both reticular and collagenous fibers are seen to be made up of smaller fibrils of about 20–100 nm in diameter, each with an internal cross-banded structure which is repeated on an average of every 64 nm. The unit of structure is tropocollagen. This is an elongated protein molecule about 300 nm long and about 1.3 nm in diameter, and is made up of three subunits. These are wound spirally around each other in very specific manners. The elastic fibers are also resolvable into finer fibrils which may be 8 nm or larger in diameter. All fibers visible with the light microscope are thus composed of bundles of submicroscopic fibrils visible only with the electron microscope. In addition, there are many collagenous and elastic fibers composed of the same fibrillar constituents which are too fine to be visible with the light microscope (fibers that are less than 0.2 μm in diameter). *See* COLLAGEN.

The nonfibrillar component of connective tissues appears amorphous with the light microscope and is the matrix in which cells and fibers are embedded. It consists of two groups of substances: (1) those probably derived from secretory activity of connective tissue cells including mucoproteins, protein-polysaccharide complexes, tropocollagen, and antibodies; and (2) those probably derived from the blood plasma, including albumin, globulins, inorganic and organic anions and cations, and water. In addition, the ground substance contains metabolites derived from, or destined for, the blood.

The ground substance of local origin and the tissue fluid of hematogenous origin are not only coextensive but are dynamically related in a two-phase system. The two phases of this thermodynamic system are probably recognizable in the electron microscope as a series of small, watery vacuoles (about 60 nm in diameter) embedded in a denser matrix. The basement membrane is a specially differentiated sheetlike part of the ground substance (10–50 nm thick) which underlies directly many epithelia, and encloses muscle fibers and fat cells. It is denser than the adjacent ground substance, with which it is continuous, and may contain fibrils. There is some evidence that epithelial cells may contribute some constituents to the basement membrane.

Classification. All the manifold varieties of connective tissue may contain all the cells and fibers discussed above in addition to ground substance. They differ from each other in the relative occurrence of one or another cell type, in the relative proportions of cells and fibers, in the preponderance and arrangement of one or another fiber, and in the relative amount and chemical composition of ground substance. In the classification which follows, some of these differences are pointed out.

1. Irregularly arranged connective tissue—which may be loose (subcutaneous connective tissue) or dense (dermis). The dominant fiber type is collagen, though others may be present. The fibers are irregularly interwoven and the cells irregularly distributed. The looser type has more ground substance than the denser type.

2. Regularly arranged connective tissue—primarily collagenous—with the fibers arranged in certain patterns depending on whether they occur in tendons or as membranes (dura matter, capsules, fasciae, aponeuroses, or ligaments). *See* TENDON.

3. Mucous connective tissue—ground substance especially prominent (umbilical cord).

4. Elastic connective tissue—predominance of elastic fibers or bands (ligamentum nuchae) or lamellae (aorta). *See* LIGAMENT.

5. Reticular connective tissue—fibers mostly reticular, moderately rich in ground substance, frequently numerous undifferentiated mesenchymal cells. In contrast with collagenous fibers which are unbranched, reticular fibers are branched and may be selectively stained by silver methods. These branched fibers, however, consist of submicroscopic

fibrils which have the same submicrostructure as unbranched collagen fibrils.

6. Adipose connective tissue—yellow or brown fat cells constituting chief cell type, reticular fibers most numerous. *See* ADIPOSE TISSUE.

7. Pigment tissue—melanocytes numerous.

8. Cartilage—cells exclusively of one type, derived from mesenchymal cells. The latter persist even in the adult in the perichondrium which encloses cartilage. The extracellular matrix is of three types: (1) hyaline (joint cartilage), containing no bundles of fibers; (2) fibrocartilage (patella), containing numerous coarse bundles of collagen fibers; and (3) elastic cartilage (external ear), containing elastic fibers. Hyaline cartilage does, however, contain collagen fibrils of submicroscopic dimensions. In all three types of cartilage, the fibrils and fibers are embedded in a homogeneous matrix, which is almost entirely composed of protein-polysaccharide complex, whose predominant polysaccharide is chondroitin sulfate. *See* CARTILAGE.

9. Bone—cells predominantly osteocytes, but also include fibroblasts, mesenchymal cells, endothelial cells, and osteoclasts. The fibers are almost entirely collagenous in nature, and may be highly organized into osteones. The fibers are embedded in a ground substance matrix. The outstanding property of bone is its hardness, due to deposition in the extracellular regions of many minute crystals of a calcium mineral, apatite. *See* BONE.

In some forms of connective tissue (fat), blood capillaries are extremely numerous. In others (cartilage and dentine), blood capillaries are lacking. Tendon is nearly avascular, and bone is also poorly supplied with blood capillaries. But all these different kinds of connective tissue must be supplied with nutrients and oxygen and must be drained of metabolic waste products in order to maintain the cells, however sparse, in a functional condition, and to effect turnover of extracellular components. How an adequate nutritive state is maintained is a great puzzle, and is attracting the attention of research workers. *See* HISTOLOGY.

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Connective tissue disease

Any of a group of diseases involving connective tissue; formerly termed collagen vascular disease. These diseases are clinically and pathologically discrete but have overlapping features. The group includes lupus erythematosus, systemic vasculitis, scleroderma (and systemic sclerosis), polymyositis, and Sjögren's syndrome. Each of the diseases can involve multiple organ systems and is often coupled with various immunologic abnormalities. *See* CONNECTIVE TISSUE.

Lupus erythematosus. This set of diseases includes limited, primarily cutaneous disorders (discoid lupus and subacute cutaneous lupus) and a diffuse systemic illness (systemic lupus erythematosus), all of which are of unknown cause. Also, a lupuslike reaction known as drug-induced lupus can be caused by certain therapeutic agents.

Systemic lupus erythematosus. This is an inflammatory, multisystem disorder in which tissue injury is mediated by immune complexes. In this incompletely understood disorder, lymphocytes known as T cells lose some of their control over the antibody production by lymphocytes known as B cells. Thus, in most individuals with systemic lupus, antibodies are found in the blood serum that are not normally present.

The immunologic events of systemic lupus are influenced by multiple factors. In some families, a genetic predisposition seems to be present. That the disease sometimes flares up after excessive exposure to ultraviolet light emphasizes the importance of environmental factors. Finally, hormonal factors also seem to play a contributing role; eight to nine times as many young women compared with men have systemic lupus; and in some animal models of lupus, femaleness is associated with more severe disease. *See* CELLULAR IMMUNOLOGY.

Although systemic lupus can be an acute and fulminating illness, it is far more often a chronic disorder with long periods (years, sometimes even decades) of remission and good health and with infrequent flareups. With the recognition of the immune markers (that is, autoantibodies) in serum, milder forms of the disorder can now be identified.

The manifestations and course of systemic lupus vary greatly from one individual to another and even in one person over time. Fever and other constitutional symptoms (for example, fatiguability, lack of appetite, and weight loss) are prominent. Skin rashes are common, and the so-called butterfly rash over the nose and cheeks is most characteristic. Joint pain and inflammation (arthritis) are among the common features and often are the first manifestations of the disease. Many other parts of the body—such as the lungs, heart, skeletal muscles, kidneys, and nervous system—can be involved. Small blood vessels at any site may be inflamed. Hematologic abnormalities also can occur when antibodies reactive with cell membrane antigens are present. Anemia and low levels of white blood cells and platelets are common. Certain autoantibodies affect blood clotting and can be associated with clots in blood vessels anywhere in the body. *See* ARTHRITIS; HEMATOLOGIC DISORDERS.

The diagnosis of systemic lupus is based on a combination of clinical and laboratory findings; no single clinical feature or laboratory test makes the diagnosis. Even the characteristic immune markers in serum (that is, the autoreactive antibodies) are not specific. For example, the routine screening test for antinuclear antibodies (ANA), which is positive in 95% of patients with systemic lupus erythematosus, can also be positive in those with the other connective tissue disorders and certain other diseases, as well as some healthy family members of patients with systemic lupus. Discoid lupus and subacute cutaneous lupus are variants, primarily with skin involvement.

Photosensitivity is prominent. Systemic features are infrequent and milder than in systemic lupus erythematosus, and kidney and nervous systems are usually spared. ANA positivity is often present.

Drug-induced lupus. This form subsides when the offending agent is discontinued. Many drugs that are chemically unrelated to each other can produce the disorder. Genetic factors play a role in susceptibility to induction of lupus by at least some drugs.

Cause. Except for drug-related lupus, the cause of systemic lupus and its variants is not known; thus, a rational basis for specific curative therapy does not exist. However, the clinical manifestations of systemic lupus can generally be managed effectively for long years or even decades. Prognosis is steadily improving. Drugs that are used to control the disease by suppressing inflammation and altering the immune system include nonsteroidal anti-inflammatory drugs, an antimalarial agent (hydroxychloroquine), corticosteroids, and immunosuppressive agents. Sound general medical management and vigorous treatment of associated illnesses (especially infections) are essential.

Systemic vasculitis. This is a series of different clinical illnesses that are characterized by intense inflammation in the walls of blood vessels, especially arteries (that is, arteritis). These illnesses differ clinically, pathologically, and with respect to therapeutic responsiveness and outcome. Even the age and sex of the typically affected person varies from one to another.

The clinical pattern of illness varies with the sites of blood vessel involvement and the character of vascular injury. Tissue death in the vessel wall can lead to narrowing, or even blockage, of the vessel or weakening of the wall with formation of an aneurysm. Impaired circulation and altered blood flow result. Symptoms, therefore, can arise not only from the tissue inflammation itself but also from the lack of adequate blood supply in the organ supplied by that vessel. Vasculitis can be a systemic condition or can be confined to a single organ or to the skin. *See* ANEURYSM; CIRCULATION DISORDERS.

Polyarteritis. Formerly called polyarteritis nodosa, polyarteritis most commonly occurs in young adult men. In most instances, the cause of the inflammatory reaction, which affects medium-sized and small arteries, is not known. Sometimes, however, the condition appears to be associated with a viral infection (such as hepatitis B) or to be induced by a drug.

The clinical features of polyarteritis include both nonspecific manifestations of diffuse inflammation and reflections of arterial involvement at specific sites. Fever, fatiguability, and loss of appetite and weight are prominent. Arteritis may occur in the kidney (often associated with high blood pressure), the heart, the liver, and the circulation to the bowel. A peripheral nervous system disease is more frequent than involvement of the central nervous system. Joint pain and arthritis, muscle pain, and vasculitic skin lesions are also common. Polyarteritis varies greatly from one person to another; any one of these features, or any combination, can be present and cause clinical problems.

The laboratory manifestations are mostly nonspecific reflections of tissue inflammation, with elevations of the white blood cell count and platelets. The blood sedimentation rate is a standard test for the presence of an inflammatory process of some type but is nonspecific; it is elevated well above the normal in most individuals with polyarteritis. There is no diagnostic blood test specifically for polyarteritis; the diagnosis is established by either a biopsy of an involved site (for example, muscle or peripheral nerve) or demonstration of structural changes in the arteries by x-ray visualization after injection of dye (an angiogram).

Optimal therapy is yet to be defined, but disease control and prognosis have progressively improved, first with the administration of corticosteroids and in combination with a cytotoxic drug.

Granulomatous arteritis. This category encompasses several rare disorders, including Churg-Strauss syndrome, Wegener's granulomatosis, aortic arch arteritis, and giant cell arteritis. These disorders cause very different clinical problems, but all are generally characterized by the presence of granulomas and giant cells in the affected sites. The causes and mechanisms are unknown. These disorders differ from each other in age group and sex predominantly affected, and prognosis. Early recognition and prompt treatment are key to an optimal outcome. Indeed, without treatment these disorders tend to have a poor prognosis.

Churg-Strauss syndrome is rare. It involves small and medium-sized arteries as well as the smallest arterioles and venules. It is usually associated with pulmonary disease, with an allergic asthmatic component often present. A characteristic feature of this syndrome is a marked increase in the number of white blood cells known as eosinophils, both in peripheral blood and in the affected tissue.

Wegener's granulomatosis is characterized by inflammation of small vessels in the respiratory tract, in the kidneys, and elsewhere. Both the upper respiratory tract (nasopharynx and sinuses) and lungs can be involved; biopsy of lung tissue or upper airways best establishes the diagnosis. Addition of a cytotoxic drug, especially cyclophosphamide, to corticosteroid therapy can reverse the pulmonary process and prevent kidney failure.

Aortic arch arteritis, also called Takayasu's arteritis, occurs almost exclusively in young women. Large and medium-sized arteries that branch off the aorta are involved, with consequent narrowing or even occlusion. Impaired blood flow results, with diminished or absent pulses in the upper extremities and neck; thus this condition is sometimes called the pulseless syndrome. Decreased circulation to the head can impair brain function, with recurrent lightheadedness and fainting or even a stroke. Similarly, impaired coronary artery flow may result in heart failure and the pain of angina. These major complications occur late and can be prevented if the process is recognized and treated early. Diagnosis is established by intra-arterial dye studies that demonstrate characteristic structural changes in the large vessels.

Temporal arteritis occurs mainly in women over 50 years of age and especially in those who are elderly. Aching pain and severe stiffness in the proximal limb-girdle regions (that is, shoulder/arm, pelvis/thigh) are common early manifestations. Later, with temporal artery involvement (in the head), symptoms such as headaches, scalp tenderness, and visual abnormalities can occur. A tender, dilated temporal artery may be found. Visual loss is the most feared complication, and is preventable by prompt corticosteroid therapy. The musculoskeletal pain syndrome, which can be progressive and incapacitating, also promptly responds to steroids.

Primary central nervous system arteritis is rare. Headaches, altered mentation and confusion, decreased level of consciousness, and even coma can occur; infrequently, unexplained seizures can occur.

Hypersensitivity angitis. In this disease there is an intense inflammation of the smaller vessels, especially venules, that represents an adverse immunologic reaction to an offending agent. The agent could be a drug, a foreign protein, or an infectious agent. Skin lesions occur in all cases; they vary in type but typically include localized areas of bleeding into the skin from injured vessels over the feet and ankles. Systemic features also can be present. Henoch-Schönlein purpura is a designation applied to one subset of this disorder.

In all types of hypersensitivity vasculitis, the diagnosis is clinical since there are no specific blood tests. A skin biopsy may support the diagnosis if inflammation of small vessels is found. Treatment focuses on withdrawal of the offending antigen, if known, or treatment of any causal infection, if present. Occasionally, use of corticosteroids may be necessary.

Vasculitis associated with specific diseases. Vasculitis can also be a secondary process occurring along with other connective tissue diseases (for example, systemic lupus, polymyositis, and Sjögren's syndrome) and with rheumatoid arthritis, infections, and malignant neoplasms. The existence of this wide array of underlying disorders suggests that various immunologic pathways can lead to vascular injury. Although the appropriate therapy is generally determined by the associated disease process, emergence of vasculitis may indicate the need to administer, or increase the dosage of, corticosteroids. *See* VASCULAR DISORDERS.

Polymyositis. Polymyositis involves intense inflammation in skeletal muscle that, if untreated, can lead to destruction of muscle fibers. When typical skin lesions are present, the term dermatomyositis is applied. The pathology of these two entities differs and suggests different mechanisms of inflammation.

The cause of polymyositis or dermatomyositis is not known in most cases. These conditions can occur alone or in association with other connective tissue disorders (that is, systemic lupus, scleroderma, and Sjögren's syndrome). Dermatomyositis may sometimes accompany malignant tumors.

Polymyositis may be abrupt or insidious in onset. The dominant manifestation is progressive weakness of the proximal limb-girdle muscle groups. Difficulty rising from a chair, in climbing stairs, lifting modest weights, and keeping the arms elevated are common symptoms. Despite intense inflammation in the skeletal musculature, pain and tenderness of the involved muscles are infrequent. Most serious are the potential involvement of pharyngeal musculature which may impair swallowing, or of the chest muscles, which may impair breathing.

Destruction of muscle fibers causes release into the circulation of various enzymes normally contained in muscle; measuring levels of these enzymes in blood thus aids in diagnosis. Also, inflamed muscle is abnormal in its electrical activity; therefore the test known as an electromyogram yields abnormal results. Finally, muscle biopsy firmly establishes the diagnosis; it can be important in distinguishing polymyositis from noninflammatory disorders affecting muscle. Although polymyositis is presumed to be an immune-mediated process, the mechanisms are obscure. Antinuclear antibodies may be found in the serum. Other less frequent but more myositis-specific autoantibodies may also be present.

The inflammatory process is generally responsive to corticosteroid therapy, but in some cases the addition of a cytotoxic drug, especially methotrexate, is required. In the few individuals with tumor-related polymyositis, appropriate treatment of the malignancy is essential; and when polymyositis occurs together with other connective tissue disorders, such as lupus, the additional features of these illnesses must also be controlled.

If diagnosed early, before loss of muscle fibers and replacement by fibrous scarring is extensive, myositis is reversible; recovery with minimal residual loss of strength is to be expected in almost all patients.

Scleroderma. The term scleroderma means "hard skin," designating a disorder in which increased deposition of collagen fibers in the deeper dermis leads to thickened, leathery, bound-down skin. This deposition is variable in extent and degree. When organ involvement is associated with such skin changes, the term systemic sclerosis is used.

Raynaud's phenomenon, a hyperreactivity to cold exposure with blanching and discoloration of the fingers and toes, is the common initial manifestation and may precede sclerodermatous skin changes by decades. Only a small fraction of those with Raynaud's eventually develop scleroderma or systemic illness; but of those who do have scleroderma, at least 80% will have Raynaud's. Skin changes may be confined to the distal digits or become generalized.

Systemically, the gastrointestinal tract is commonly involved. Difficulty in swallowing and midchest discomfort result from loss of peristalsis in the esophagus. Diarrhea, inability to absorb nutrients, abdominal pain, and distention can occur with bowel involvement and lead to weight loss and wasting. Scarring of the lungs and decreased pulmonary function occur frequently. The most serious lesions are those of the heart and kidney, and may result from vascular abnormalities. Joint inflammation is mild and uncommon; but advanced skin changes, especially in the hands, may restrict joint mobility.

Polymyositis is occasionally present and is the major indication for corticosteroid therapy in this disorder.

A variant called the CREST syndrome (calcinosis, Raynaud's, esophageal dysmotility, sclerodactyl- or scleroderma-like finger, and telangiectasia) is notable because of its mildness and slow progression. It is also referred to as limited scleroderma.

Multiple autoantibodies (including ANA) may be found in serum. The diagnosis is usually a clinical one, based on characteristic skin tightening. A skin biopsy, if peformed, will demonstrate increased collagen fibers in the deeper dermis without any inflammatory reaction.

Management involves treatment of high blood pressure that can arise because of kidney involvement, use of agents to improve circulation by reducing small-vessel spasm, and reducing gastrointestinal complications with special diets and sometimes antibiotics. The drug D-penicillamine may produce improvement in the skin and possibly systemic features. In a few cases, skin changes may subside spontaneously.

Sjögren's syndrome. This condition is characterized primarily by dryness of the membranes due to excretory gland failure, especially dryness of the eyes (xerophthalmia) and mouth (xerostomia) from loss of tears and saliva, respectively. This sicca (dryness) syndrome reflects the infiltration of lacrimal and salivary glands by immunologically competent cells (lymphocytes).

Sjögren's syndrome may be primary or secondary, the latter occurring in the context of another disorder, such as rheumatoid arthritis or systemic lupus. The typical individual with primary Sjögren's syndrome is a woman later in life. In most cases, the sicca complex dominates, but there can be loss of secretions in the skin, bronchial tree, esophagus and stomach, and vaginal vault. In some people with primary Sjögren's, systemic features may evolve. Diagnosis is primarily clinical, but ocular dryness can be quantitated. Lip biopsy of the minor salivary glands can confirm the infiltration by immune cells. Noninvasive scanning of the parotids can confirm the loss of functional glandular structure. Autoantibodies in the blood are common and can aid in differentiating Sjögren's syndrome from other causes of dry eyes and dry mouth, but in no instance is a blood test diagnostic of either Sjögren's or any companion disorder.

Management involves artificially keeping membranes moist (for example, with artificial tears). Extraglandular inflammatory lesions and associated disorders are treated with anti-inflammatory agents and occasionally cytotoxic agents. *See* IMMUNOLOGY; INFLAMMATION; STEROID.

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Conodont

A group of extinct marine animals that are often abundant in strata of Late Cambrian to Late Triassic age, a time span of about 300 million years. Only the mineralized elements, which are usually 0.2 to 2 mm (0.008 to 0.08 in.) in dimension (the largest known reach 14 mm or 0.6 in.), are normally preserved. They are routinely extracted as isolated discrete specimens by chemical degradation of the rock in which they occur. The apatite (calcium phosphate) of which conodont elements are composed is laid down as lamellae. In the earliest euconodonts ("true" conodonts, as opposed to the more primitive, and possibly unrelated, protoconodonts and paraconodonts), the elements comprise an upper crown and a basal body. The basal body occupies a cavity in the base of the crown, but is not present in the majority of post-Devonian species. In advanced conodonts the crown incorporates regular patches of opaque, finely crystalline, white matter.

For many years, conodont taxonomists treated individual element types as separate species. There are three major shape categories, coniform, ramiform, and pectiniform (**Fig. 1**). Coniform elements were dominant in the Cambrian to Early Ordovician and common until the Devonian. They vary in curvature and in cross section, including the development of costae. Ramiform (comblike) elements extend into elongate processes with various arrangements of denticles. Pentiniform elements include straight and arched blades, and may be expanded laterally to form a platform.

Skeletal apparatus. In the 1930s the discovery of "natural assemblages" on bedding surfaces provided direct evidence that each animal possessed a skeletal apparatus consisting of several different kinds of elements. Several hundred such associations have now been found, each representing the skeletal remains of an individual animal. Most are from shales, as their preservation requires that the soft parts of the animal decay undisturbed by currents, so that the skeleton remains intact. Some elements may also become fused into clusters during the diagenesis of the sediments in which they occur, and these, too, give an indication of the configuration of the conodont apparatus. Although most conodont species are still known only from elements scattered in the sediment, it is now conventional practice in conodont taxonomy to reconstruct their skeletal apparatus by using morphological and statistical criteria.

The evidence of bedding-plane assemblages shows that most of the elements in an apparatus were symmetrically paired across the midline. A common type of apparatus in the Upper Paleozoic (Fig. 1*i*) consisted of a set of 7 to 11 ramiform elements (one of which was an unpaired median, bilaterally symmetrical form), followed by a pair of arched blades and, posterior of these, a pair of platform pectiniform elements. Variations in this arrangement occur; early Paleozoic apparatus often consisted of a series of coniform elements alone.

Soft parts. In the absence of preserved soft parts, the nature of the affinities of conodonts was the subject of considerable speculation and debate. Since the discovery of isolated elements in 1856, conodonts have been variously aligned with algae, higher plants, several wormlike phyla, mollusks, arthropods, lophophorates, chaetognaths, and chordates, or have been assigned to a separate phylum, Conodonta. It was not until 1983 that evidence of the soft parts was described by D. E. G. Briggs, E. N. K. Clarkson, and R. J. Aldridge, on the basis of the first of several specimens discovered in lower Carboniferous rocks near Edinburgh, Scotland.

Features of the soft parts are preserved as a calcium phosphate film (**Fig. 2**). They show that conodonts were elongate animals (40–60 mm or 1.6–2.4 in.). The apparatus lies in the head region, behind a bilobed structure which is preserved as a film darker than the rest of the body (**Fig. 3**). All of the Carboniferous examples discovered to date are compacted in lateral view, and the apparatus lies to one side, in some cases beyond the apparent outline of the body. This suggests that the soft tissue which supported the elements is not preserved. The trunk shows clear evidence of V-shaped structures, the apex of the V's pointing anteriorly. These structures are interpreted as muscle blocks, but the nature of two parallel lines which run the length of the

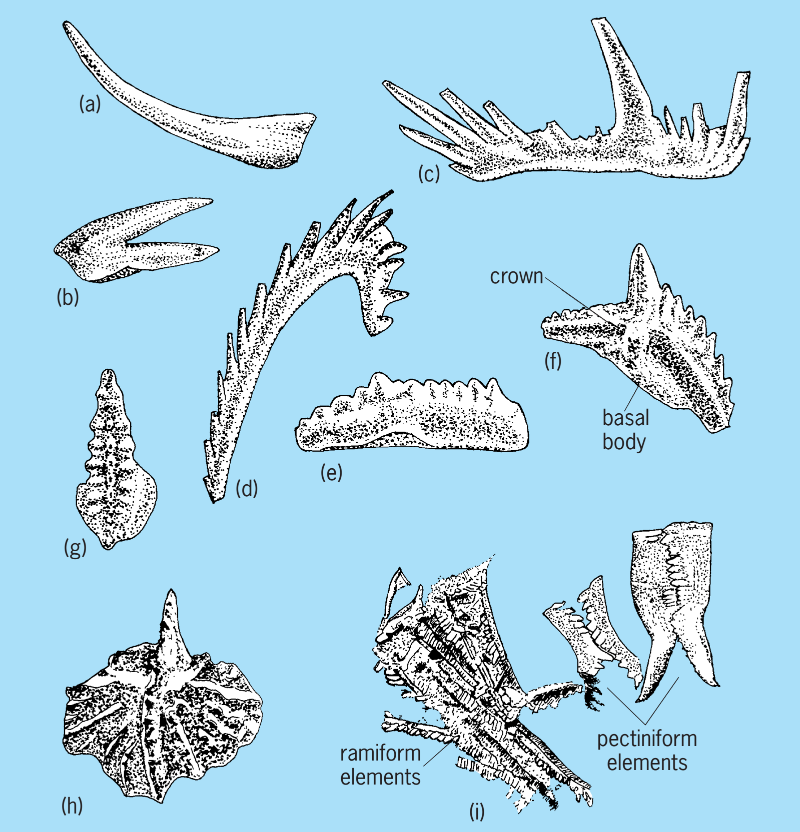

Fig. 1. Conodont elements: (*a*, *b*) coniform elements, (*c*, *d*) ramiform elements, (*e*, *f*) pectiniform blade elements, (*g*, *h*) pectiniform platform elements, (*i*) bedding-plane assemblage.

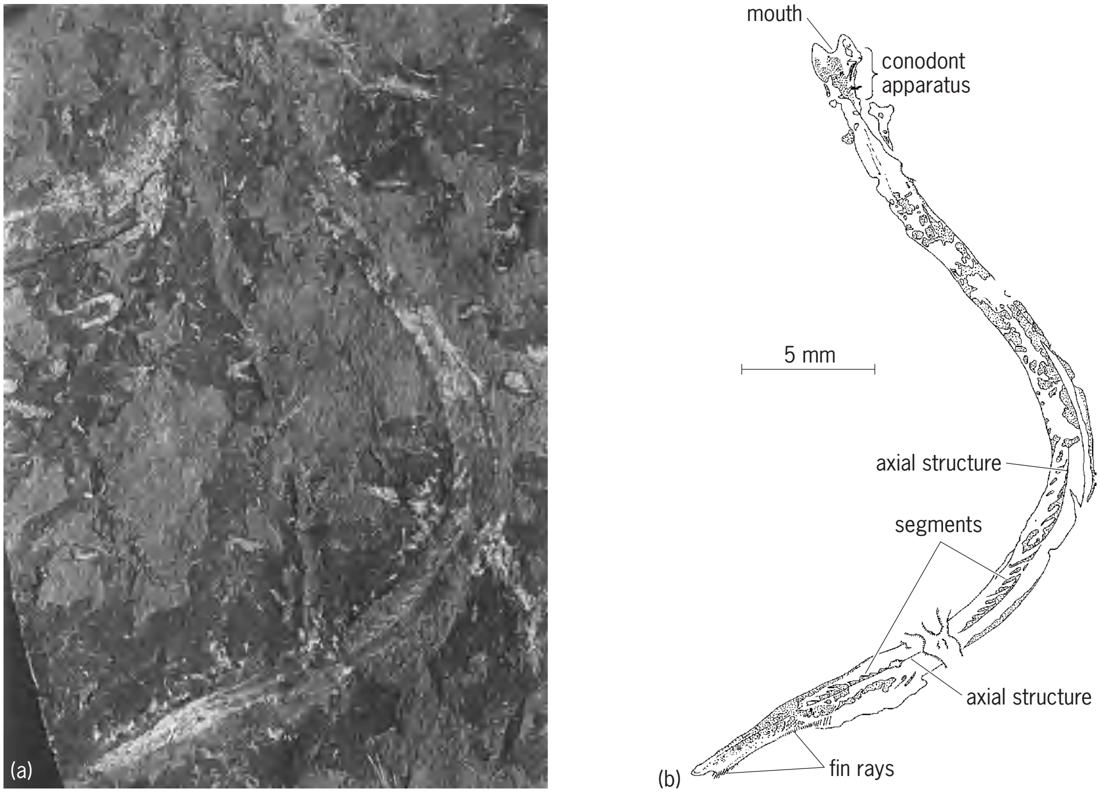

Fig. 2. The first specimen of the conodont animal discovered in Lower Carboniferous rocks in Edinburgh. (*a*) Photograph of specimen. (*b*) Outline of the specimen for comparison. (*From D. E. G. Briggs, E. N. K. Clarkson, and R. J. Aldridge, The conodont animal, Lethaia, 16:1–14, 1983*)

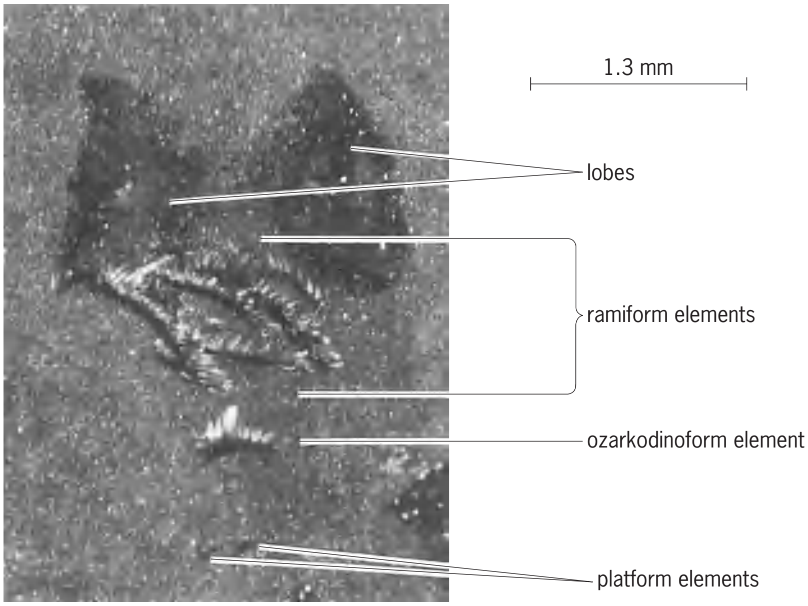

Fig. 3. Head region of the conodont animal, showing the conodont elements on the side of the slab opposing that illustrated in Fig. 2. (*From D. E. G Briggs, E. N. K Clarkson, and R. J. Aldridge, The conodont animal, Lethaia, 16:1–14, 1983*)

trunk is less certain. Fin rays indicate the presence of an asymmetrical fin around the margin of the tail. A single poorly preserved specimen from the Silurian of Wisconsin, the only other example known which shows traces of the soft parts, suggests that the body of some conodonts may have been broader than that in the Scottish specimens.

Biological affinities. The evidence of the soft-part morphology indicates that the conodonts belong within the chordates; it is no longer possible to justify their separation as a phylum, Conodonta. The lack of jaws and of a bony skeleton suggests that they represent a primitive group of jawless craniates, perhaps close to the Myxinoidea (hagfishes). The apparatus is thought to have functioned in food capture. The ramiform elements (or coniform elements in earlier conodonts) appear to be adapted for grasping prey. In later conodonts this would have been processed by the shearing and grinding action of the paired pectiniform elements *See* CHORDATA.

Geological applications. Although the biological affinities of conodonts and the function of the elements were essentially unknown until recently, they have nonetheless been extensively studied because of their important geological applications. Most significant of these is the use of conodont elements in biostratigraphy. Biozonal schemes have been erected for all the systems through which conodonts range, Cambrian to Triassic; the most detailed subdivision is in Upper Devonian strata (conodont subbiozones representing, on average, 0.5 million years). Some conodonts are restricted in their distribution to certain sedimentary environments and can be used to define biofacies. Most conodont biofacies are, at least indirectly, related to depth, as reflected in the contrasts between nearshore and offshore assemblages.

Conodont elements can also be used to determine the thermal history of strata. The color of elements alters from pale yellow through brown to black as their carbon content is fixed during organic metamorphism. This is the basis for a conodont Color Alteration Index (CAI, from 1 to 5) which can be applied in assessing oil and gas potential, and in wider studies of the thermal history of sedimentary basins.

The apatite of which conodont elements are formed is stable and resistant to diagenetic alteration. The trace-element and isotopic-ratio characteristics of the seawater in which the organism lived were retained in the apatite, which can be analyzed to yield significant information about the temperature and chemistry of ancient oceans. Thus an assemblage of conodont elements extracted from a rock sample not only may allow biostratigraphic correlation, but also may give an indication of the paleoenvironment of the locality; the temperature, geochemistry, and oxygen content of the seawater; and the subsequent thermal history of the sedimentary basin. *See* STRATIGRAPHY. Richard J. Aldridge; Derek E. G. Briggs

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Consciousness

Accounting for the sensations or "raw feels" which constitute conscious experience has been a persistent problem for scientific approaches to psychology. In addressing this problem, each new scientific approach has put forth a new account of the relationship between those conscious sensations, as they are privately experienced by individuals, and the nervous system, as it is experienced by scientists.

Fechner on consciousness. In 1860 Gustav Fechner published his *Elemente der Psychophysik*, wherein he developed scientific techniques to measure the magnitudes of conscious sensations such as brightness and loudness, and then derived a mathematical equation to describe the relationship between each sensory magnitude and the physical magnitude which stimulated it. Fechner derived this psychophysical equation as a scientific solution to the mind-body problem. He interpreted it as support for panpsychism, the metaphysical position that all matter is conscious of other matter. His interpretation was based on the equation's implication that a very small physical magnitude stimulates a negative sensation: the consciousness of a magnitude beneath the threshold at which neural substances produce awareness of each other's magnitudes, a conscious sensation such as that experienced by flowers and other nonneural substances.

Inasmuch as the mathematical relationship between psychological sensations and physical stimuli must be derivable from psychoneural and neurophysical equations, Fechner's panpsychist interpretation of his psychophysical equation assumed that the underlying psychoneural equation was a logarithmic equation yielding the negative sensations and that the neurophysical equation was linear. However, critics argued that the logarithmic relationship reflected the neurophysical relationship between the magnitude of the brain state evoked by the stimulus and the magnitude of the physical stimulus itself, both of which are physically and scientifically measurable magnitudes. *See* PSYCHOPHYSICAL METHODS.

Wundt on consciousness. Historically, Wilhelm Wundt convinced the scientific establishment that the methods of science are sufficient to study the sensory data of consciousness. He argued that the inner aspects of conscious experience, the data of psychology, are the only immediately known data of science: that the outer world of physical reality has to be inferred from the data of scientific psychology and, thus, is known only mediately. His scientific studies of perceptual consciousness confirmed that perceptual experience provides no immediate knowledge of external reality.

In logically and experimentally supporting his thesis that the data of scientific psychology constitute the foundation for all sciences, Wundt sought to reduce physical reality to a subset of consciousness itself. Three founders of subsequent approaches to psychology were not satisfied with this effort to rewrite psychophysical and psychoneural equations in purely mental terms. One of them—John Watson, who founded behaviorism around 1913—sought, instead, to reduce mental terms to physical terms. The other two—Sigmund Freud, who founded psychoanalysis around 1900, and Max Wertheimer, who founded Gestalt psychology around 1912—sought to put mental terms on the psychological sides of the psychoneural and psychophysical equations and to put physical terms on the opposite sides.

Freudian reaction to Wundt. By arguing for the existence of unconscious mental events, Freud took issue with both the metaphysical and the methodological underpinnings of Wundt's approach to the psychology of consciousness. If unconscious mental events existed, then much of the mind itself—much of the data of scientific psychology—was no more immediately knowable than the inferred data of physical sciences. Moreover, to the extent that the unconscious mind was actually part of physical reality, Wundt was not justified in treating physical reality as a subset of the mind. In the light of Freud's analysis of the unconscious mind, the psychophysical and psychoneural relationships reemerged as unsolved and problematical relationships.

Behaviorist reaction to Wundt and Freud. In creating and developing behaviorism, Watson introduced both a new methodological approach to psychology and a new metaphysical approach to consciousness. Watson's scientific methods and metaphysical positions were addressed to the psychology of the other. The starting point for behaviorism was the scientist's immediate experience of another organism's behavioral response to a stimulus; metaphysical inferences about conscious events within that other organism were deemed to be unnecessary and unwarranted.

From the standpoint of behaviorism, all scientific conclusions regarding the psychophysical and psychoneural relationships—including Fechner's panpsychist interpretation of his psychophysical equation and Freud's distinction between conscious and unconscious mental events—were meaningless. This did not necessarily imply that mental terms such as consciousness were meaningless. It did imply that the behavioral scientist's physical descriptions of other entities like brains (including the physical description of his or her own brain) could not meaningfully be related to mental descriptions of his or her own consciousness.

From behaviorism to computer models. At the beginning of the twentieth century, Ivan Pavlov and Edward Thorndike initiated psychological research on animals, and Watson's psychology of the other organism provided the rationale for viewing other animals and other people as scientifically equivalent subjects of psychological study. Since the late 1960s, animal-behavior models of psychological processes have been replaced by computer models, and Watson's animal behaviorism has been transformed into a computer behaviorism or a psychology of the other machine. The goal of computer behaviorism is to program computers to produce output responses which observers experience as indistinguishable from human beings' responses. If and when this goal is achieved, computer models of psychological processes will provide logically sufficient explanations of the psychological processes of other human beings. The critical question is whether such computer models of psychological processes would also provide sufficient explanations of the psychological processes of the scientist who consciously experiences the other machine.

Some computer behaviorists argue that neither the scientist's conscious experience nor the computer's lack thereof has any causal effect on behavior. However, a subset of these computer behaviorists believe that any conscious psychological process in the scientist's computerlike brain can actually occur with or without consciousness of that process, implying that the scientist's psychological processes are, in principle, not different from the computer's. Another implication is that the scientist's brain contains a metaphysical subject which can consciously inspect or not inspect the same neural process. Other computer behaviorists adopt the functionalist argument that sensations like blueness and other privately experienced phenomena will "emerge" from any functionally equivalent psychological processes present either in the scientist's computerlike brain or in the other computer studied by the scientist. Metaphysically, computer behaviorism presupposes that the conscious mind is a machine; methodologically, it starts with the scientist's conscious experience of other machines. Another metaphysical and methodological approach, the approach of Gestalt psychology, presupposed also that the mind is a machine, but started instead with the scientist's phenomenal experience of his or her own machine.

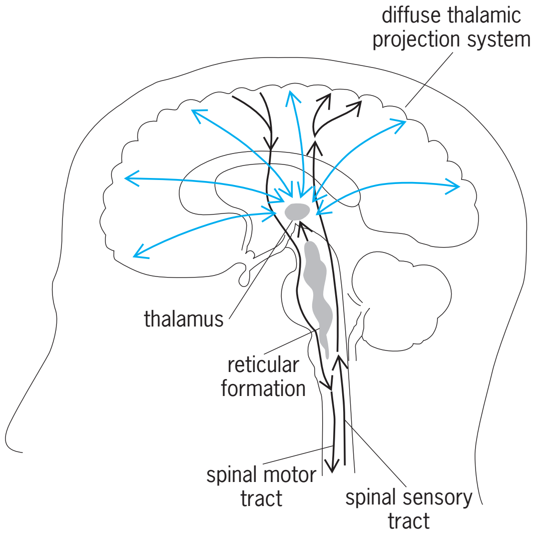
Gestalt reaction to Wundt and behaviorism. While the Gestalt psychologist Max Wertheimer rejected Watson's scientific psychology of the other organism, he also rejected Wundt's contention that nothing in the scientist's immediately known experience corresponds directly with the mediately known physical world. Gestalt psychologists objected that Wundt had restricted his observations to elementary sensations and had not observed the Gestalt, the holistic relationship among the immediately known sensations. According to Gestalt psychology, there was a direct psychophysical correspondence between perceptual experience and physical stimulation.

From Gestalt to mind-brain identity theory. In his effort to rebut Wundt's contention that any psychophysical correspondence is a necessarily indirect, arbitrarily learned, and basically illusory correspondence, Wertheimer adopted the scientist's conscious experience as his starting point and looked for phenomenal evidence to support a direct psychophysical relationship. In so making his case for a direct psychophysical correspondence, he set the stage for the Gestalt psychologist Wolfgang Köhler and other mind-brain identity theorists to argue for a direct psychoneural relationship.

According to mind-brain identity theorists, the scientist's sensations are qualities of particular brain structures in their excited state. Thus, the scientist is "conscious of" neither sensations nor the brain; the scientist is the sensory qualities of his or her brain states. The scientist immediately experiences nothing besides the qualities of the brain states which he or she is; and the scientist's experiential qualities change over time, simply because the patterning of excited structures in his or her brain changes.

According to mind-brain identity theory, a scientist could simultaneously experience his or her own brain both immediately and mediately, by visually experiencing the exposed brain on a television screen. In spite of the fact that such a mediately experienced brain would be a subset of the immediately experienced brain, the scientist could look for mediately experienced brain states which correlate perfectly with immediately experienced sensory qualities. Gestalt psychologists argue that mind-brain identity theory predicts that psychoneural correspondences can be discovered. Scientists adopting a mind-brain identity position have not yet discovered any structural differences in various parts of the brain, much less discovered any correspondences between conscious qualities and brain structures. Robert G. Kunzendorf

Lines of evidence. Psychologists and neuroscientists have developed many productive lines of evidence. Psychological investigations have compared conscious and unconscious processes in selective attention, visual perception, implicit versus explicit learning, conscious availability in problem solving and memory, automatic versus controlled task components, working memory, and so on. Theoretical approaches have emerged, couched in the vocabulary of information processing, cognitive architectures, and adaptive systems. Brain researchers have developed promising lines of evidence, including studies of brain damage (as in amnesia, neglect syndromes, split brain cases, hemispherectomies, and blindsight), as well as normal neurosensory processes, anesthesia, sleep, dreaming, and coma.



Brain structures most closely associated with the conscious experience. (*After B. J. Baars, A Cognitive Theory of Consciousness, Cambridge University Press, 1988*)

The effects of the presence and absence of consciousness reveal enormous neurobehavioral differences between the brain in deep sleep, stupor, or coma compared to when it is wakeful. The anatomical structures required for waking consciousness are well known. They include the brainstem reticular formation, the reticular nuclei of the thalamus (its outer shell), and the fountain of neuronal fibers projecting from the intralaminar nuclei of the thalamus to all parts of the cortex (see **illus.**). Damage to any of these structures will induce coma, whereas massive lesions elsewhere in the brain generally produce no loss of conscious wakefulness; actually, an entire hemisphere can be removed without producing coma.

In many cases, exact experimental comparisons can be made between mental events that are clearly conscious and very similar events that are not. Everyone has experienced repetitive stimuli fading from consciousness (for example, the repeated sound of a noisy refrigerator pump). Sometimes, when such a highly predictable train of events suddenly stops, the stimulus becomes conscious, so that an individual then perceives that something has changed, even though the person was not aware of it while it was taking place. Scientific observations of such habituation phenomena suggest that the nervous system must maintain a rather accurate, unconscious representation of the repetitive stimulus, since a change in any parameter of the stimulus (for example, an increase or decrease in intensity or a change in the temporal pattern) may bring it to consciousness.

Similarly, if someone is spoken to while reading a book, the person's first impulse may be to ask, "What did you say?", but suddenly the memory of what was said comes to mind. The words must have been stored unconsciously, or they would not be remembered a few seconds later.

A useful distinction can be made between conscious experience, that is, what people can report and act upon, and selective attention, which is the ability to choose between alternative streams of conscious contents. Once an individual attends to one dense stream of speech or visual flow, competing trains of stimulation appear to be processed unconsciously. In a classic dichotic listening task, subjects closely monitored sentences presented to one ear. Information presented to the other ear is not reportable under these conditions; it cannot be acted upon voluntarily, and it can be repeated many times without creating recallable memories. This result is consistent with the subjects' reports that the unattended stream was not conscious. However, the meaning of unattended words is in fact processed, since the listeners' understanding of the attended sentences can be influenced by those words.

In subliminal priming, subjects may be exposed to a printed word via one eye, while a visual mask is presented to the other eye in such a way that the target word cannot be reported. The masked word will nevertheless influence the time needed to recognize a related word presented immediately afterward, again suggesting that the unconscious stimulus must be processed and represented unconsciously.

The question is what is the difference between the mental representation of a stimulus when it is conscious versus unconscious. It has been suggested that novel combinations of stimuli require consciousness; unconscious processing may be rigid and automatic. But the unconscious is not simple. Complex tasks such as linguistic analysis, memory search, motor control, executive planning, and emotional response, which often involve abstract representations and symbolic processes, are performed unconsciously. Unconscious processes can be quite formidable in speed, accuracy, and complexity. The functional capacities of conscious and unconscious processes can be compared as follows.

Conscious processes:

1. They are computationally inefficient. Many errors, relatively low speed, and mutual interference occur between processes.
2. The range of contents is great. There is great ability to relate different conscious contents to each other, and conscious events to their unconscious contexts.
3. In regard to access, largely unconscious executive functions can gain control over unconscious specialists via consciousness. Conscious contents can refer to and sometimes trigger other conscious contents. Conscious contents can trigger unconscious automatisms.
4. There is high internal consistency at any single moment, seriality over time, and limited processing capacity.

Unconscious processes:

1. They are very efficient in routine tasks. Few errors, high speed, and little mutual interference occur between processes.
2. Each routine process has a limited range of contents. It is relatively isolated and autonomous, and is relatively context free.
3. Entirely unconscious processes probably have only routine (highly practiced, hard-wired, or both) access to each other.
4. The set of routine, unconscious processes are diverse, can sometimes operate in parallel, and together have great processing capacity.

Methodology. An individual's understanding of consciousness, while no doubt influenced by personal experience, needs to be based on publicly observable events that can be tested and verified by multiple observers. Conscious processes can be operationally defined as the set of events that are claimed by a subject to be conscious and can be reported and acted upon with verifiable accuracy, under optimal reporting conditions. Optimal reporting conditions imply a minimum delay between the conscious event and the report (for example, freedom from distraction). This definition fits existing practice in the study of perception, short-term memory, explicit problem solving, and imagery. *See* MEMORY; PERCEPTION; PROBLEM SOLVING (PSYCHOLOGY).

By contrast, unconscious processes can be operationally defined as those which are not claimed to be conscious, and cannot be reported or acted on, even under optimal reporting conditions, but whose presence can nevertheless be verified. By this definition, automatic processes are unconscious, as are visually masked stimuli, visual objects in blindsight, implicit memory, unattended information, subliminal effects, the details of language processing, and the effects of priming. Again, there is a good fit between this definition and existing scientific practice.

There is a curious asymmetry in the assessment of conscious and unconscious processes. Obtaining verifiable reports is a viable method for specifying conscious events, but unconscious ones are much more difficult to define. William James suggested that because the evidence for unconscious processes could always be challenged there were no unconscious psychological processes at all. This is known as the zero point problem. For example, if a word shown for a few milliseconds cannot be reported, it does not necessarily mean that the person is truly unconscious of the stimulus. There could have been a fleeting awareness that is soon masked or replaced by succeeding events. It is extraordinarily difficult to be sure of the zero point of consciousness.

Alternatively, a criterion for unconscious events can be applied which does not solve the problem exactly but which gives a reasonable basis for consensus. Suppose that a subject is asked to avoid recently primed processes. If the subject cannot do so, those processes are plausibly unconscious. James could argue that by this criterion unconscious events could still be fleetingly conscious, however briefly. The criterion only guarantees that the unconscious event cannot be used in working consciousness—the ability to report and act upon the fleeting stimulus.

Limited capacity system. Most cognitive models formerly did not refer to consciousness explicitly but used terms and mechanisms that were very closely associated with it. For example, one of the first models was short-term memory, which is roughly the domain in which one rehearses telephone numbers while walking from the phone book to the telephone. More broadly, it may include the domain in which individuals mentally talk to themselves. It is true, of course, that not all items in short-term memory are conscious at any single instant. Of the seven digits of a new telephone number that can be mentally rehearsed, only one or two are conscious at any time. Thus, short-term memory is not identical to consciousness but seems to be very closely related.

All phenomena associated with conscious experience are characteristically limited in capacity. A person watching a baseball game on television cannot simultaneously experience a football game overlaid on the same screen, nor can a person follow a normal conversation while performing any other unpredictable, skilled task. Short-term memory is characterized by a limit of seven plus or minus two chunks of information. Voluntary control, which is also intimately involved with conscious experience, seems similarly limited. Finally, the flow of conscious information is relatively serial.

There is a curious dichotomy between limited-capacity models and evidence suggesting that the unconscious parts of the nervous system have enormous capacity. The vast capacity of long-term memory, the great size of the linguistic lexicon, and the large set of available automatic skills are known in a psychological sense. The most obvious illustration of enormous unconscious capacity is the sheer size and complexity of the brain. The cerebral cortex alone has some 50 billion neurons, with similar numbers for the large subcortical mass, the spinal cord, and the great network of peripheral neurons. Each neuron sends an electrochemical signal to its neighbors an average of 40 times per second, up to perhaps 1000 Hz. The system is thoroughly interconnected: Neurons have up to 10,000 connections, and a path can be traced from any single neuron in the brain to any other neuron in seven steps or less. This enormous organ, the most complex in the body, operates concurrently rather than serially and performs highly complex and intelligent tasks with minimal conscious involvement. *See* BRAIN.

Society models. The society model of the nervous system suggests that the great bulk of information processing is performed by local networks that are unconscious, though they are complex, specialized, and intelligent, and operate in parallel and normally very efficiently. Such expert societies have great flexibility in problem solving and control. Repetitive events and routine actions can be handled by specialized processors with minimal conscious involvement. It is possible that conscious experience corresponds to a domain of interaction between the multitude of unconscious experts, one that may act as a global "publicity organ'' or meeting place in the society of intelligent processors. Consciousness in this view serves as an indispensable adaptive function. *See* COGNITION; INFORMATION PROCESSING (PSYCHOLOGY); PSYCHOLOGY.

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Conservation laws (physics)

Principles which state that the total values of specified quantities remain constant in time for an isolated system. Conservation laws occupy enormously important positions both at the foundations of physics and in its applications.

Realization in classical mechanics. There are three great conservation laws of mechanics: the conservation of linear momentum, often referred to simply as the conservation of momentum; the conservation of angular momentum; and the conservation of energy. It is almost impossible to understand the modern form of the conservation laws without understanding their original and simplest realization in the classical mechanics of particles. Therefore, the conservation laws as they appear within that framework will first be discussed, and then their generalization and modification to cover larger domains.

Conservation of momentum. The linear momentum, or simply momentum, of a particle is equal to the product of its mass and velocity. It is a vector quantity. The total momentum of a system of particles is simply the sum of the momenta of each particle considered separately. The law of conservation of momentum states that this total momentum does not change in time.

An important application of this principle is to collisions. For example, in a collision between two bodies of equal mass, starting with opposite velocities, the total momentum is zero. The conservation of momentum states that it will still be zero after the collision. Thus, if the bodies remain intact they must move off again with opposite velocities—though not necessarily the original ones, for both bodies may have been deflected through a common angle. If the collision causes part of one of the original bodies to adhere to the other, the two bodies will again move off in opposite directions, but the heavier one will move slower and the lighter one faster, by factors inversely proportional to their new masses. Even if the bodies shatter into several bits, there are three constraints on the motion of the debris that emerges: each component of the total momentum must vanish. *See* COLLISION (PHYSICS).

This application is typical in showing both the power and the limitations of general conservation laws as they are applied to complex processes. They cannot tell what happens in detail, but they constrain the possibilities in ways that are nontrivial and unequivocal. *See* CONSERVATION OF MOMENTUM; MOMENTUM.

Conservation of angular momentum. The angular momentum of a particle is more complicated. It is also a vector quantity. It is defined with respect to some origin of coordinates O. Let the position P of the particle be specified by the position vector $\overline{r} = \overline{OP}$ pointing from the origin to it; and let its mass and velocity be m and $\overline{v}$ respectively. Then the angular momentum of the particle is defined by the vector product of the position and momentum vectors, Eq. (1). The total

$$\vec{L} = \vec{r} \times (m\vec{v}) \qquad (1)$$

angular momentum of a system of particles is equal to the sum of the angular momenta of each particle separately. The law of conservation of angular momentum states that the total angular momentum of an isolated system is constant in time.

An extremely important instance of the conservation of angular momentum is Kepler's second law of planetary motion, which states that a line drawn from the Sun to a planet sweeps out equal areas in equal times. This would be a geometrical statement entirely equivalent to the conservation of angular momentum if the planet and Sun formed an isolated system. In reality they do not: A planet is subject to gravitational forces from other planets as well as the Sun, so that Kepler's law is only approximately correct. There are many other important applications of the law of conservation of angular momentum to mechanical problems involving rotation, particularly the motion of tops and gyroscopes. *See* ANGULAR MOMENTUM; KEPLER'S LAWS; RIGID-BODY DYNAMICS.

Conservation of energy. The third great conservation law of classical mechanics, conservation of energy, is perhaps the most important of all (although it was the last to be properly appreciated, for reasons discussed below). Energy is a scalar quantity, and it takes two forms: kinetic and potential. The kinetic energy of a particle is defined to be one-half the product of its mass with the square of its velocity, $T = {}^1/_2 mv^2$, and the total kinetic energy of a system of particles is simply the sum of their separate kinetic energies. The potential energy is loosely defined as the ability to do work; more precisely, it is a function V of the particles' positions, such that the force felt by a particle is minus the derivative of the potential energy with respect to that particle's position. The total energy is the sum of the kinetic and potential energies, $E = T + V$, and according to the conservation law it remains constant in time for an isolated system.

The essential difficulty in applying the conservation of energy can be appreciated by considering once again the problem of two colliding bodies. In general, even if they retain their integrity, the bodies emerge from the collision moving more slowly than when they entered. When this happens, the collision is said to be inelastic. An inelastic collision seems to violate the conservation of energy, until it is recognized that the bodies involved may consist of smaller particles. If these particles are shaken up and rattle around within the larger bodies after the collision, their random small-scale motions will require kinetic energy, which robs kinetic energy from the overall coherent large-scale motion of the bodies that are observed directly.

Such difficulties make it more challenging to extract concrete quantitative consequences from the conservation of energy than from the other conservation laws. One of the greatest achievements of nineteenth-century physics was the recognition that small-scale motion within macroscopic bodies could be identified with the perceived property of heat. By measuring the heat created by a given amount of mechanical work, J. P. Joule was able to define a precise mechanical equivalent of heat—for example, how much work it takes to heat a gram of water by one degree. *See* THERMODYNAMIC PRINCIPLES.

The first law of thermodynamics is simply an expression of the conservation of energy, using this concept that energy can take the form of heat (that is, microscopic, random motion) as well as perceived macroscopic motion or potential energy. The idea of heat as microscopic motion is used to explain some of the properties of gases. Finally, careful observations on the microscopic motions of small bodies have experimentally verified the theoretical predictions for this so-called brownian motion in great detail. *See* BROWNIAN MOVEMENT; CONSERVATION OF ENERGY; ENERGY; KINETIC THEORY OF MATTER; STATISTICAL MECHANICS.

Methodology. In Newton's original scheme of mechanics, the notion of force was primary. Later workers obtained simpler and more powerful mathematical formulations of the laws, without changing their physical content, by regarding energy as the primary notion. In modern physics this change in emphasis has become more pronounced, so that, for example, in quantum mechanics the concept of force is hardly ever encountered, but always energy. *See* HAMILTON'S EQUATIONS OF MOTION; LAGRANGE'S EQUATIONS.

Position in modern physics. As physics has evolved, the great conservation laws have likewise evolved in both form and content, but have never ceased to be important guiding principles, and never more so than now. Only a few highlights will be discussed.

Electromagnetism. In order to account for the phenomena of electromagnetism, it was necessary to go beyond the notion of point particles, to postulate the existence of continuous electric and magnetic fields filling all space. An assembly of charged particles can excite propagating waves in the fields. These are interpreted as electromagnetic radiation, of which, for example, light and radio waves are special cases. When such radiation occurs, the total energy of the particles is diminished in a definite way, depending on the amount and type of radiation emitted. Thus, to obtain valid conservation laws, energy (and, for similar reasons, momentum and angular momentum) must be ascribed to the electromagnetic fields. *See* ELECTROMAGNETIC RADIATION; MAXWELL'S EQUATIONS; POYNTING'S VECTOR.

Special relativity. In the special theory of relativity, energy and momentum are not independent concepts. A leading idea of this theory is that the laws of physics take the same form when viewed by two observers who move with respect to one another at a constant velocity. In particular, each observer will associate both a conserved energy and a conserved momentum with a given isolated system. However, the energy reported by one observer is equal to a certain combination of the energy and momentum reported by the other.

Einstein discovered perhaps the most important consequence of special relativity, that is, the equivalence of mass and energy, as a consequence of the conservation laws. He considered a thought-experiment wherein an atom emits equal packets of radiation in opposite directions. He showed that the law of conservation of energy could be valid for this process, as viewed by a moving observer, only if, as a result of the radiation, the atom's mass is diminished, according to Eq. (2), where E is the energy

$$\Delta m = \frac{E}{c^2} \qquad (2)$$

of the radiation emitted and c is the speed of light. In the nineteenth century, the law of conservation of mass was a major item in any discussion of conservation laws. Now this "law" is understood as an approximate consequence of the conservation of energy (valid in the limit $c \to \infty$). *See* CONSERVATION OF MASS; RELATIVITY.

Connection with symmetries. A remarkable, beautiful, and very fruitful connection has been established between symmetries and conservation laws. Thus the law of conservation of linear momentum is understood as a consequence of the homogeneity of space, the conservation of angular momentum as a consequence of the isotropy of space, and the conservation of energy as a consequence of the homogeneity of time. *See* SYMMETRY LAWS (PHYSICS).

General relativity. The development of general relativity, the modern theory of gravitation, necessitates attention to a fundamental question for the conservation laws: The laws refer to an "isolated system," but it is not clear that any system is truly isolated. This is a particularly acute problem for gravitational forces, which are long range and add up over cosmological distances.

Indeed, according to general relativity, a small region of space-time cannot be regarded as isolated, and the conservation laws are not valid. However, special solutions of the equations of general relativity, including model universes which closely model that of the Earth, support the conservation laws as a good approximation, valid over distances and times that are not too large. The relevant feature of these model universes is that they are approximately homogeneous and evolve slowly.

Fortunately, the scales are such that practical applications of the conservation laws are completely unaffected by this limitation. However, there is an important philosophical consequence: The symmetry of physical laws, which, as mentioned above, is closely tied up with the conservation laws, is actually a more fundamental property than the conservation laws themselves, for the symmetries remain valid while the conservation laws, strictly speaking, fail.

Quantum theory. In quantum theory, the great conservation laws remain valid in a very strong sense. Generally, the formalism of quantum mechanics does not allow prediction of the outcome of individual experiments, but only the relative probability of different possible outcomes. One might therefore entertain the possibility that the conservation laws were valid only on the average. However, the power of the conservation laws is much stronger: Momentum, angular momentum, and energy are conserved in every experiment, not just on the average.

How this can be so is one of the strangest yet simplest and most profound aspects of quantum theory. It is helpful to consider the decay of an excited state of an atom, wherein it radiates a single photon. If an apparatus is set up to detect the photon, then for every possible direction there is a probability that the photon will be detected moving in that direction. Now, if after detecting the photon the observer goes back and examines the atom, it will be found to be moving in the opposite direction in such a way that the total momentum is zero, as it was initially. This raises the question of how the atom could "find out" the result of the measurement of the photon. This is one form of what Einstein called the "spooky action-at-a-distance" in quantum mechanics. To interpret this situation, it must be acknowledged that the atom, like the photon, has a range of potential motions, but that these two potentialities, though they can be measured in either order and quite separately, are rigorously correlated. *See* NONRELATIVISTIC QUANTUM THEORY; QUANTUM MECHANICS; QUANTUM THEORY OF MEASUREMENT.

Conservation laws of particle type. There is another important class of conservation laws, associated not with the motion of particles but with their type. Perhaps the most practically important of these laws is the conservation of chemical elements, that is, the principle that, in a chemical reaction, for each chemical element the total number of atoms of that element in the products is equal to the total number of atoms of that element in the original reactants. From a modern viewpoint, this principle results from the fact that the small amount of energy involved in chemical transformations is inadequate to disrupt the nuclei deep within atoms. It is not an absolute law, because some nuclei decay spontaneously, changing the elemental nature of the atoms in which they reside. At sufficiently high energies the "law" of conservation of elements is grossly violated; indeed, a well-developed theory traces the origin of chemical elements to processes occurring within minutes after the big bang, and in stars and supernova explosions. *See* BIG BANG THEORY; NUCLEOSYNTHESIS; RADIOACTIVITY.

Several conservation laws in particle physics are of the same character: They are useful even though they are not exact because, while known processes violate them, such processes are either unusually slow or require extremely high energy. Examples of such approximate conservation laws are the conservation of strangeness, of charm, and of isospin. *See* CHARM; ELEMENTARY PARTICLE; I-SPIN; STRANGE PARTICLES.

Two laws of conservation of particle type deserve special mention: the conservation of electric charge and the conservation of baryon number.

Conservation of electric charge. This law is believed to be exact. In principle, it is very simple to state, involving only counting. Every kind of elementary particle has a definite electric charge, which is an integer times the charge of the electron. The conservation law simply specifies that in any reaction the total electric charge of the reactants is equal to the total electric charge of the products.

Conservation of electric charge is deeply connected to the principle of electromagnetic gauge invariance and to the foundations of electromagnetic theory. One aspect is that the total charge inside a volume can be inferred by measurements of the electric field at a distant bounding surface, according to Gauss's law. Thus, if the charge suddenly changed it would require an instantaneous change in the electric field far away, contrary to the principle that the speed of light limits the transfer of information. *See* ELECTRIC CHARGE; ELECTRODYNAMICS; GAUGE THEORY.

Conservation of baryon number. This law is also very easy to state, as a counting rule. Among the common so-called elementary particles, protons and neutrons are assigned baryon number one—and their antiparticles baryon number minus one—while electrons, positrons, photons, and pions are assigned baryon number zero. A more modern and fundamental perspective is that quarks are assigned baryon number one-third, antiquarks baryon number minus one-third, and all other fundamental particles zero. In either formulation, the law of conservation of baryon number is simply the statement that, in any reaction, the total baryon number of the reactants is equal to the total baryon number of the products. *See* BARYON; QUARKS.

The most important evidence for the law of conservation of baryon number is the stability of the proton. There is no principle, other than this (or some similar conservation law, such as the conservation of lepton number), that forbids, for example, the decay [reaction (3)] of a proton into a neutral pion and a

$$p \rightarrow \pi^0 + e^+ \qquad (3)$$

positron. Yet, whereas otherwise similar decays take place within a small fraction of a second, the lifetime of the proton is greater than 10^{30} years. Despite its accuracy, the law of conservation of baryon number, unlike the law of conservation of electric charge, is not tied up with any known profound dynamical principles. Indeed, important ideas in modern particle physics definitely suggest that the conservation of baryon number is not exactly valid, and difficult but important experiments are planned to search for small violations of it. *See* PROTON.

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Conservation of energy

The principle of conservation of energy states that energy cannot be created or destroyed, although it can be changed from one form to another. Thus in any isolated or closed system, the sum of all forms of energy remains constant. The energy of the system may be interconverted among many different forms—mechanical, electrical, magnetic, thermal, chemical, nuclear, and so on—and as time progresses, it tends to become less and less available; but within the limits of small experimental uncertainty, no change in total amount of energy has been observed in any situation in which it has been possible to ensure that energy has not entered or left the system in the form of work or heat. For a system that is both gaining and losing energy in the form of work and heat, as is true of any machine in operation, the energy principle asserts that the net gain of energy is equal to the total change of the system's internal energy. *See* THERMODYNAMIC PRINCIPLES.

Application to life processes. The energy principle as applied to life processes has also been studied. For instance, the quantity of heat obtained by burning food equivalent to the daily food intake of an animal is found to be equal to the daily amount of energy released by the animal in the forms of heat, work done, and energy in the waste products. (It is assumed that the animal is not gaining or losing weight.) Studies with similar results have also been made of photosynthesis, the process upon which the existence of practically all plant and animal life ultimately depends. *See* METABOLISM; PHOTOSYNTHESIS.

Conservation of mechanical energy. There are many other ways in which the principle of conservation of energy may be stated, depending on the intended application. Examples are the various methods of stating the first law of thermodynamics, the work-kinetic energy theorem, and the assertion that perpetual motion of the first kind is impossible. Of particular interest is the special form of the principle known as the principle of conservation of mechanical energy (kinetic E_k plus potential E_p) of any system of bodies connected together in any way is conserved, provided that the system is free of all frictional forces, including internal friction that could arise during collisions of the bodies of the system. Although frictional or other nonconservative forces are always present in any actual situation, their effects in many cases are so small that the principle of conservation of mechanical energy is a very useful approximation. Thus for a missile or satellite traveling high in space, the dissipative effects arising from such sources as the residual air and meteoric dust are so exceedingly small that the loss of mechanical energy $E_k + E_p$ of the body as it proceeds along its trajectory may, for many purposes, be disregarded. *See* ENERGY; PERPETUAL MOTION.

Mechanical equivalent of heat. The mechanical energy principle is very old, being directly derivable as a theorem from Newton's law of motion. Also very old are the notions that the disappearance of mechanical energy in actual situations is always accompanied by the production of heat and that heat itself is to be ascribed to the random motions of the particles of which matter is composed. But a really clear conception of heat as a form of energy came only near the middle of the nineteenth century, when J. P. Joule and others demonstrated the equivalence of heat and work by showing experimentally that for every definite amount of work done against friction there always appears a definite quantity of heat. The experiments usually were so arranged that the heat generated was absorbed by a given quantity of water, and it was observed that a given expenditure of mechanical energy always produced the same rise of temperature in the water. The resulting numerical relation between quantities of mechanical energy and heat is called the Joule equivalent, or mechanical equivalent of heat. The present accepted value of the 15-degree calorie is $1\ \mathrm{cal}_{15^\circ} = 4.1855 \pm 0.0004$ J; in thermochemical work it is now more common to use the thermochemical calorie, which is defined as $1\ \mathrm{cal} = 4.184$ J exactly.

Conservation of mass-energy. In view of the principle of equivalence of mass and energy in the restricted theory of relativity, the classical principle of conservation of energy must be regarded as a special case of the principle of conservation of mass-energy. However, this more general principle need be invoked only when dealing with certain nuclear phenomena or when speeds comparable with the speed of light (1.86×10^5 mi/s or 3.00×10^5 km/s) are involved. *See* RELATIVITY.

If the mass-energy relation, $E = mc^2$, where c is the speed of light, is considered as providing an equivalence between energy E and mass m in the same sense as the Joule equivalent provides an equivalence between mechanical energy and heat, there results the relation, $1\ \mathrm{kg} = 9 \times 10^{16}$ joules.

Laws of motion. The law of conservation of energy has been established by thousands of meticulous measurements of gains and losses of all known forms of energy. It is now known that the total energy of a properly isolated system remains constant. Some parts or particles of the system may gain energy but others must lose just as much. The actual behavior of all the particles, and thus of the whole system, obeys certain laws of motion. These laws of motion must therefore be such that the energy of the total system is not changed by collisions or other interactions of its parts. It is a remarkable fact that one can test for this property of the laws of motion by a simple mathematical manipulation that is the same for all known laws: classical, relativistic, and quantum mechanical.

The mathematical test is as follows. Replace the variable t, which stands for time, by $t + a$, where a is a constant. If the equations of motion are not changed by such a substitution, it can be proved that the energy of any system governed by these equations is conserved. For example, if the only expression containing time is $t_2 - t_1$, changing t_2 to $t_2 + a$ and t_1 to $t_1 + a$ leaves the expression unchanged. Such expressions are said to be invariant under time displacement. When daylight-saving time goes into effect, every t is changed to $t + 1$ h. It is unnecessary to make this substitution in any known laws of nature, which are all invariant under time displacement. Without such invariance laws of nature would change with the passage of time, and repeating an experiment would have no clear-cut meaning. In fact, science, as it is known today, would not exist.

Duane E. Roller/Leo Nedelsky

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Conservation of mass

The notion that mass, or matter, can be neither created nor destroyed. According to conservation of mass, reactions and interactions which change the properties of substances leave unchanged their total mass; for instance, when charcoal burns, the mass of all of the products of combustion, such as ashes, soot, and gases, equals the original mass of charcoal and the oxygen with which it reacted.

The special theory of relativity of Albert Einstein, which has been verified by experiment, has shown, however, that the mass of a body changes as the energy possessed by the body changes. Such changes in mass are too small to be detected except in subatomic phenomena. Futhermore, matter may be created, for instance, by the materialization of a photon (quantum of electromagnetic energy) into an electron-positron pair; or it may be destroyed, by the annihilation of this pair of elementary particles to produce a pair of photons. *See* ELECTRON-POSITRON PAIR PRODUCTION; LIGHT; MASS; RELATIVITY.

Leo Nedelsky

Conservation of momentum

The principle that, when a system of masses is subject only to forces that masses of the system exert on one another, the total vector momentum of the system is constant. Since vector momentum is conserved, in problems involving more than one dimension the component of momentum in any direction will remain constant. The principle of conservation of momentum holds generally and is applicable in all fields of physics. In particular, momentum is conserved even if the particles of a system exert forces on one another or if the total mechanical energy is not conserved.

Use of the principle of conservation of momentum is fundamental in the solution of collision problems. *See* COLLISION (PHYSICS).

If a person standing on a well-lubricated cart steps forward, the cart moves backward. One can explain this result by momentum conservation, considering the system to consist of cart and human. If both person and cart are originally at rest, the momentum of the system is zero. If the person then acquires forward momentum by stepping forward, the cart must receive a backward momentum of equal magnitude in order for the system to retain a total momentum of zero.

When the principle of conservation of momentum is applied, care must be taken that the system under consideration is really isolated. For example, when a rough rock rolls down a hill, the isolated system would have to consist of the rock plus the earth, and not the rock alone, since momentum exchanges between the rock and the earth cannot be neglected.

Rocket propulsion. The propulsion of a rocket through space can be explained in terms of momentum conservation. Hot gases produced by the combustion of the fuel are expelled at high speed from the rear of the rocket. Although the total mass of these hot gases may not be large, the gases move with such a high velocity that the total momentum associated with them is appreciable. The momentum of the gases is directed backward. For momentum to be conserved, the rocket must acquire an equal momentum in the forward direction. If the rocket carries all the materials needed for the combustion of its fuel, its propulsion does not require air, and it can move through empty space. *See* PROPULSION; ROCKET.

Exploding bomb. An exploding bomb gives another application of the conservation of momentum. The total resultant vector momentum of all the pieces of the bomb immediately after explosion must equal the momentum of the unexploded bomb just before the explosion. *See* EXPLOSIVE.

Proof of principle. The principle of conservation of momentum follows directly from Newton's second and third laws. While the principle will be proved here only for the straight-line motion of a two-particle system, it can be generalized to systems containing any number of particles. A particle is a mass with dimensions so small that rotational effects are negligible. Momentum will also be conserved for rigid bodies large enough that rotation must be considered, since rigid bodies can be treated as assemblies of many particles.

For the one-dimensional motion of an isolated two-particle system, Newton's third law states that the force F_{12} that particle 1 exerts on particle 2 is equal in magnitude and opposite in direction to the force F_{21} that particle 2 exerts on particle 1. Thus Eq. (1) holds.

$$F_{21} = -F_{12} \tag{1}$$

By use of Newton's second law this equation can be expressed in terms of the momenta m_1v_1 and m_2v_2 of particles 1 and 2, respectively, where m_1, m_2, v_1, and v_2 are the masses and velocities of particles 1 and 2, respectively. Then Eq. (2) holds. Integration

$$m_1\frac{dv_1}{dt} = -m_2\frac{dv_2}{dt} \tag{2}$$

gives Eq. (3), where c is a constant. This equation

$$m_1v_1 + m_2v_2 = c \tag{3}$$

expresses the conservation of momentum for two particles moving in the same straight line.

Finally it should be mentioned that angular and linear momentum are independent quantities. A complete description of a system must include both quantities. The angular momentum of a system is conserved under quite general conditions. *See* ANGULAR MOMENTUM; CONSERVATION OF ENERGY; MOMENTUM.

Paul W. Schmidt

Conservation of resources

Management of the human use of natural resources to provide the maximum benefit to current generations while maintaining capacity to meet the needs of future generations. Conservation includes both the protection and rational use of natural resources.

Natural resources. Earth's natural resources are either nonrenewable, such as minerals, oil, gas, and coal, or renewable, such as water, timber, fisheries, and agricultural crops. Natural resources are the basic goods and services that sustain human societies. Renewable resources play central roles in providing air, water, and food. Nonrenewable resources provide the energy essential for industrial economies and are the source of important products ranging from iron tools to silicon chips.

Although humans are entirely dependent upon Earth's natural resources, the combination of growing populations and increasing levels of resource consumption is now degrading and depleting the natural resource base. The world's population stood at 850 million at the onset of the industrial age, sharing the Earth with life forms nearly as diverse as the planet has ever possessed. The global population has grown to nearly seven times as large (6 billion), and the level of consumption of resources is far greater. This human pressure now exceeds the carrying capacity of many natural resources.

Nonrenewable. Nonrenewable resources, such as fossil fuels, are replaced over geologic time scales of tens of millions of years. Human societies will eventually use up all of the economically available stock of many nonrenewable resources, such as oil. Peak oil production in the United States, for example, occurred in 1984 and has since declined significantly as the most easily accessible oil fields have been drained. Clearly, because the stock of nonrenewable resources is fixed, future generations will inherit a world depleted of those important resources. Conservation thus entails actions to use these resources most efficiently and thereby extend their life as long as possible. By recycling aluminum, for example, the same piece of material is reused in a series of products, reducing the amount of aluminum ore that must be mined. Similarly, energy-efficient products help to conserve fossil fuels since the same energy services, such as lighting or transportation, can be attained with smaller amounts of fuel. *See* HUMAN ECOLOGY.

It may be expected that the biggest challenge of resource conservation would involve nonrenewable resources, since renewable resources can replenish themselves after harvesting. In fact, the opposite is the case. Historically, when nonrenewable resources have been depleted, new technologies have been developed that effectively substitute for the depleted resources. Indeed, new technologies have often reduced pressure on these resources even before they are fully depleted. Fiber optics, for example, has substituted for copper in many electrical applications, and it is anticipated that renewable sources of energy, such as photovoltaic cells, wind power, and hydropower, will ultimately take the place of fossil fuels when stocks are depleted. Renewable resources, in contrast, can be seriously depleted if they are subjected to excessive harvest or otherwise degraded, and no substitutes are available for, say, clean water or food products such as fish or agricultural crops. Moreover, when the misuse of biological resources causes the complete extinction of a species or the loss of a particular habitat, there can be no substitute for the esthetic and moral values that many people associate with that diversity of life.

Renewable. The urgent need to conserve renewable resources, particularly biological resources, can be seen in trends associated with major ecosystems. For example, 60% of the world's most important fish stocks are now overfished. Well over one-half of the world's coral reefs are at risk of degradation from human activities. The world has lost nearly half of its original forest cover, and each year an additional 12 million hectares (29.7 million acres) are deforested. These pressures of overharvesting and habitat loss, combined with other pressures such as pollution and the introduction of exotic species (which often outcompete or otherwise threaten native species), are now depleting the very building blocks of living natural resources—the diversity of genes, species, and ecosystems that constitute living systems. *See* ECOSYSTEM; REEF.

The diversity of life is threatened with a massive extinction that could rival the loss of diversity that took place some 65 million years ago around the time that dinosaurs became extinct. Since the 1600s, nearly 500 animal and 650 plant species (mostly vertebrates and flowering plants) are known to have become extinct, and many more species undoubtedly became extinct before they were even identified. The rate of extinctions in groups such as birds and mammals has increased dramatically during this period. Not all species extinctions are necessarily caused by humans. Species went extinct long before humans appeared on the planet, but the background rate of natural extinction is estimated to be nearly 100 times slower than current rates. If the current rate of loss of closed tropical forest (about 1% globally per year) continues until 2030, the number of species these habitats will support will be reduced by 5–10%. This could amount to an additional tens of thousands of extinctions in groups of organisms such as plants.

Current overuse and misuse of renewable living resources cannot be sustained and poses significant economic costs to societies. A critical element of ensuring a sustainable biosphere—one that continues to provide the goods and services from living systems upon which society depends—is thus the conservation of natural resources. "Conservation" is sometimes used synonymously with "protection." More appropriately, however, it refers to the protection and sustainable use of resources. Critical elements of the effective conservation of natural resources include sustainable resource management, establishment of protected areas, and ex situ (off-site) conservation.

Resource management. Some of the most pressing resource conservation problems stem directly from the mismanagement of important biological resources. Many marine fisheries are being depleted, for example, because of significant overcapacity of fishing vessels and a failure of resource managers to closely regulate the harvest. In theory, a renewable resource stock could be harvested at its maximum sustainable yield and maintain constant average annual productivity in perpetuity. In practice, however, fishery harvest levels are often set too high and, in many regions, enforcement is weak, with the result that fish stocks are driven to low levels. A similar problem occurs in relation to the management of timber resources. Short-term economic incentives encourage cutting as many trees as quickly as possible. Without effective resource management policies and enforcement, sound stewardship of forest resources is difficult. *See* FISHERIES ECOLOGY; FOREST MANAGEMENT.

Early conservation efforts primarily involved regulation of wildlife harvests. Historically, hunters often depleted game or commercial species until they were effectively extinct (or completely extinct in the case of such species as passenger pigeons in the United States or the great auk in the north Atlantic). However, in the last half century the development and application of principles of wildlife management has led to more effective regulation of harvests. It is now rare that commercial harvest of individual species threatens a species with extinction, although, as in the case of fisheries, it is still common for some species to be harvested at levels that substantially deplete the population. *See* FOOD WEB.

A number of steps are being taken to improve resource conservation in managed ecosystems. (1) Considerable scientific research has been undertaken to better understand the natural variability and productivity of economically important resources. (2) Many national and local governments have enacted regulations for resource management practices on public and private lands. These include laws regulating management practices (for example, laws that require timber companies to leave buffers of trees standing near rivers and creeks), as well as laws protecting specific resources, such as endangered species. (3) Problems of resource mismanagement often have stemmed from the fact that local residents, who would have a greater incentive to manage for long-term production, had little rights to local resources, whereas the companies or individuals with rights to harvest resources found it economically beneficial to deplete the resource and move on to new regions. In some of these regions, programs recently have been established either to involve local communities more directly in resource management decisions or to return to them resource ownership rights. (4) Efforts are under way to manage resources on a regional or ecosystem scale using methods that have come to be known as ecosystem management or bioregional management. Since the actions taken in one location often influence species and processes in other locations, traditional resource conservation strategies were often focused too narrowly to succeed.

Protected areas. Regardless of the success in better managing resources, the fact remains that human activities now have reshaped much of the land surface to meet human needs. Human changes in land use and land cover, for example, have transformed one-third to one-half of Earth's icefree surface. This is an area equal to North America, South America, and Africa combined. Clearly, without significant management interventions, many species that once lived in these transformed regions are likely to become extinct. One of the most effective strategies to protect species from extinction is the establishment of protected areas designed to maintain populations of a significant fraction of the native species in a region. Worldwide, 9832 protected areas, totaling more than 9.25 million square kilometers (24 million square miles), cover about 8% of land on Earth. Although these sites are not all managed exclusively for the conservation of species, they play an essential role in protecting species from extinction.

Many problems remain, however, in ensuring effective protected-area conservation networks. For example, several regions with important biodiversity still lack effective protected-area networks. In addition, where protected areas have been designated, human and financial resources are not always available to effectively manage the areas, creating "paper parks." Particularly in developing countries, the establishment of protected areas has resulted in conflicts with local communities that had been dependent upon the areas for their livelihood. These challenges are now being addressed through international efforts, such as the International Convention on Biological Diversity, which aims to increase the financing available for protected areas and to integrate conservation and development needs.

Ex situ conservation. The most effective and efficient means for conserving biological resources is to prevent the loss of important habitats and to manage resources for their long-term productivity of goods and services. In many cases, effective conservation in the field is no longer possible. For example, some species have been so depleted that only a few individuals remain in their natural habitat. In these cases, there is no alternative to the ex situ conservation of species and genetic resources in zoos, botanical gardens, and seed banks. Ex situ collections play important conservation roles as well as serving in public education and research. Worldwide, zoos contain more than 3000 species of birds, 1000 species of mammals, and 1200 species of reptiles, and botanic gardens are believed to hold nearly 80,000 species of plants. These collections hold many endangered species, some of which have breeding populations and thus could potentially be returned to the wild. Genebanks hold an important collection of the genetic diversity of crops and livestock.

Much can be done to better conserve the world's natural resources, but in the face of growing pressure on these resources the challenge is growing. One of the most important steps to bolster any conservation activity is to learn more about the target resource. Scientists have identified only about 1.7 million of an estimated 13 million species of plants, animals, fungi, and microbes on Earth. Many more species are described each year. Unless basic scientific information on this biodiversity is obtained, it is unlikely that conservation will be effective. *See* LAND-USE PLANNING; MINERAL RESOURCES; SOIL CONSERVATION; WATER CONSERVATION.

Walter Reid

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Constellation

One of the 88 areas into which the sky is divided. Each constellation has a name that reflects its earliest recognition. Though pictures are associated with the constellations, they have no official status, and constellations have been depicted differently by different artists.

The identifications of the constellations are lost in antiquity. No doubt ancient peoples associated myths with the heavens and imagined pictures connecting or surrounding the bright stars. The names of some constellations have been handed down by the Chaldeans or Egyptians, but most of those that can be seen from midnorthern latitudes have Greek or Roman origins. Star maps are found in various cultures, and constellation figures and myths usually differ from those found in Greek and Roman sources.

Star catalogs and atlases. The catalog of Ptolemy, in Hellenic Alexandria in the second century of the Christian Era, included over 1000 stars grouped into 48 constellations. Many of today's images of constellations are derived from the beautiful engravings by Alexander Mair in Johann Bayer's *Uranometria* (1603) [**Fig. 1**]. Bayer included the constellations listed by Ptolemy and also named 12 new ones containing stars observed on expeditions to the Southern Hemisphere. Bayer originated the scheme of labeling individual stars in constellations with Greek and other letters, roughly in order of brightness, and the genitive form of the constellation name. For example, the bright star Betelgeuse (the second brightest in the constellation Orion) is alpha Orionis (alpha of Orion), and Sirius, the brightest star in the sky, is alpha Canis Majoris (alpha of the Big Dog). In some cases, Bayer labeled stars in order around figures in the sky, as for the Big Dipper. Bayer also used some uppercase (as in the star P Cygni) and lowercase Latin letters. In 1624, Jakob Bartsch placed three new constellations in gaps in Bayer's atlas and separated the southern constellation Crux from Centaurus. Coma Berenices (Berenice's Hair) was also added at about this time, reportedly by Tycho Brahe.

Johannes Hevelius added nine more southern constellations in his 1690 star atlas, *Firmamentum Sobiescianum sive Uranographia*. His figures represent the view of a celestial globe from the outside and thus are reversed from Bayer's. Nicolas Louis de Lacaille added 14 constellations in 1763 from his expedition to the Cape of Good Hope, using names reflecting the mechanical age, such as air pump, microscope, and telescope.

John Flamsteed (1729) and Johan Elert Bode (1801) produced other elegant star atlases, with engravings of constellations. Since the mid-1800s, Ptolemy's largest constellation, Argo Navis, has been divided into Carina, the keel; Puppis, the stern; and Vela, the sails.

Modern star atlases, from the *Millennium Star Atlas* to the *Guide Star Catalogue* compiled in the late 1980s for the use of observers with the Hubble Space Telescope, do not usually show the figures of tradition. *See* ASTRONOMICAL ATLASES; ASTRONOMICAL CATALOGS.

International agreement. In 1928, the International Astronomical Union formally accepted the division

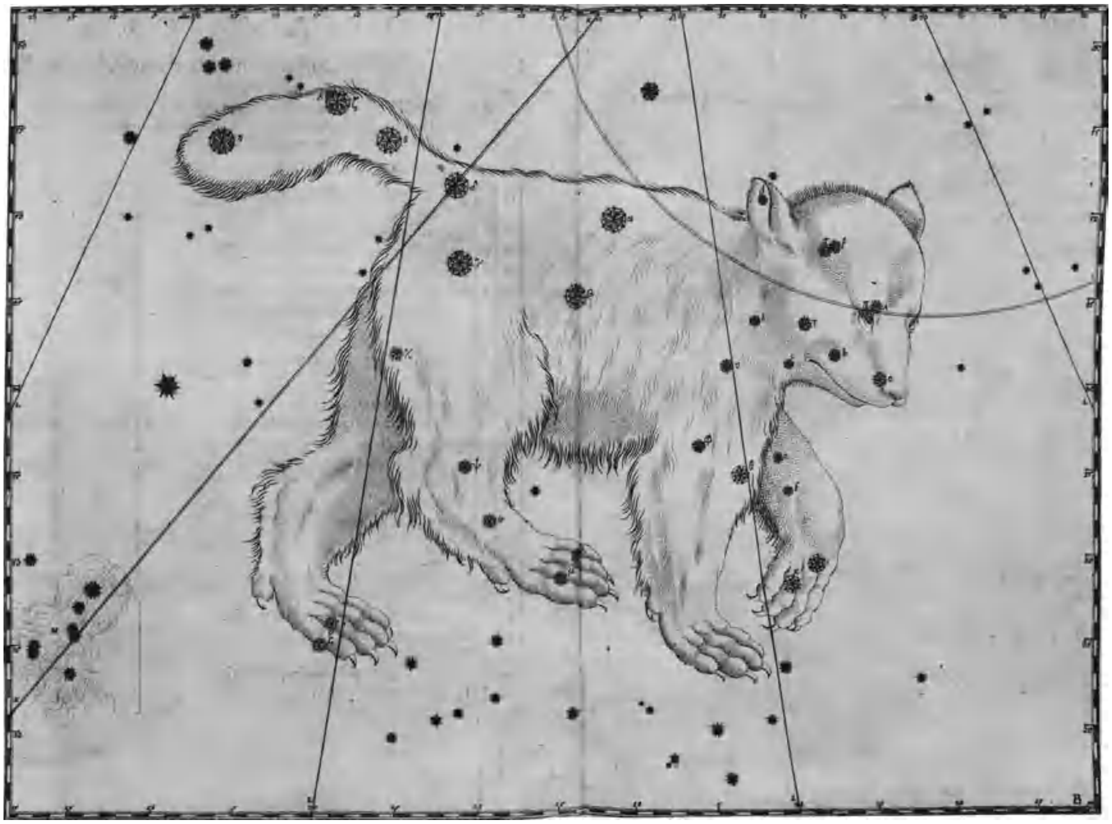

Fig. 1. The constellation Ursa Major from Bayer's star atlas (1603). (*Jay M. Pasachoff collection*)

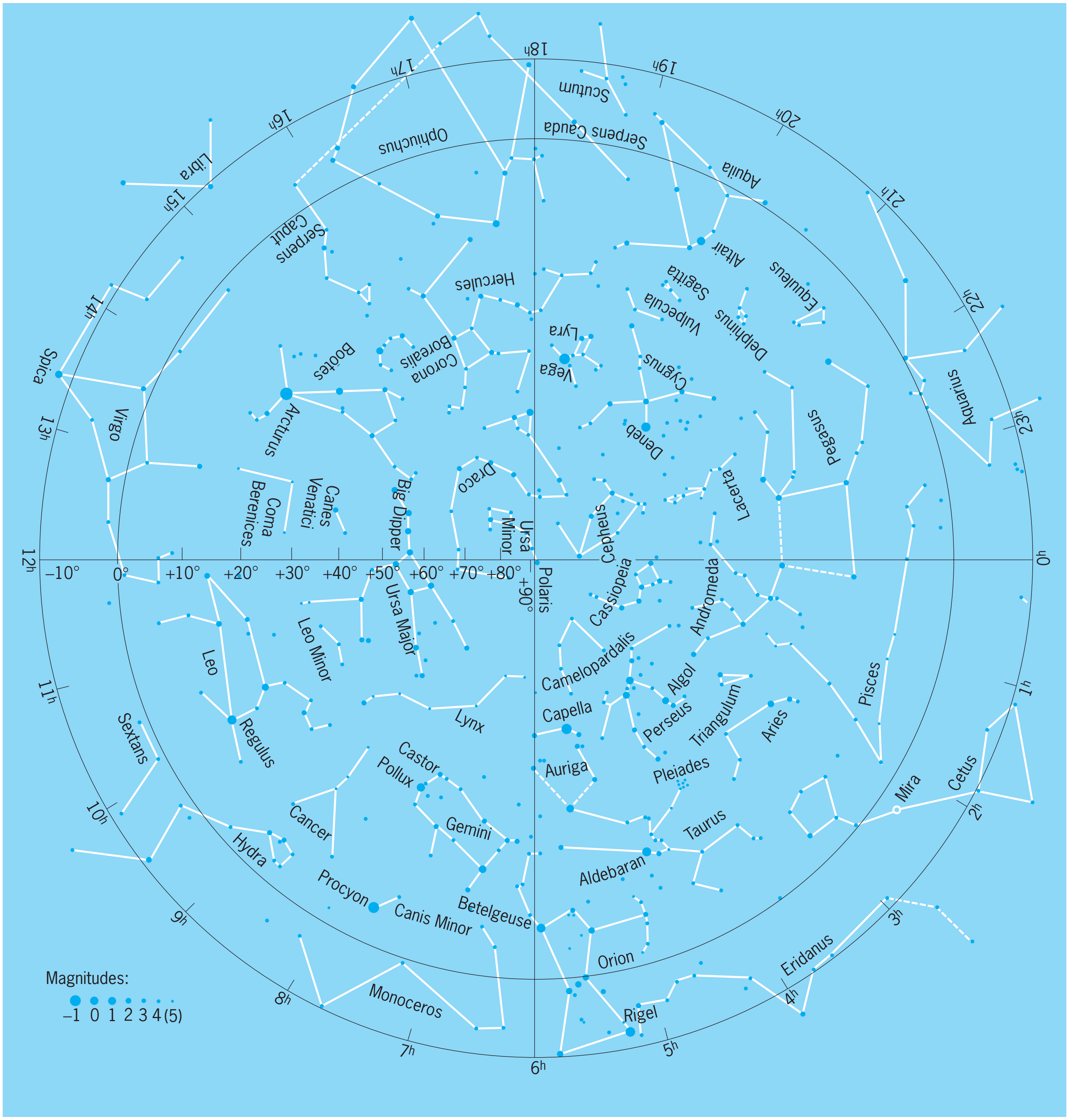

Fig. 2. Constellations of the northern hemisphere; brighter stars are shown by larger dots. (*After J. M. Pasachoff, A Field Guide to the Stars and Planets, Houghton Mifflin, 4th ed., 2000*)

of the sky into 88 constellations (see **table**), with the final list provided 2 years later; each star now falls in only one constellation (**Figs. 2** and **3**). The boundaries follow north-south or east-west celestial coordinates (right ascension and declination lines) from the year 1875; because of precession, the current boundaries do not match rounded values of celestial coordinates. *See* ASTRONOMICAL COORDINATE SYSTEMS; PRECESSION OF EQUINOXES.

Asterisms. Some of the most familiar patterns in the sky are asterisms rather than constellations. For example, the asterism known as the Big Dipper is part of the constellation Ursa Major. The asterism known as the Great Square of Pegasus has three of its corners in Pegasus but the fourth in Andromeda. The Northern Cross is made of stars in Cygnus.

Zodiac. The Sun, the Moon, and the planets move through a band in the sky known as the ecliptic. The

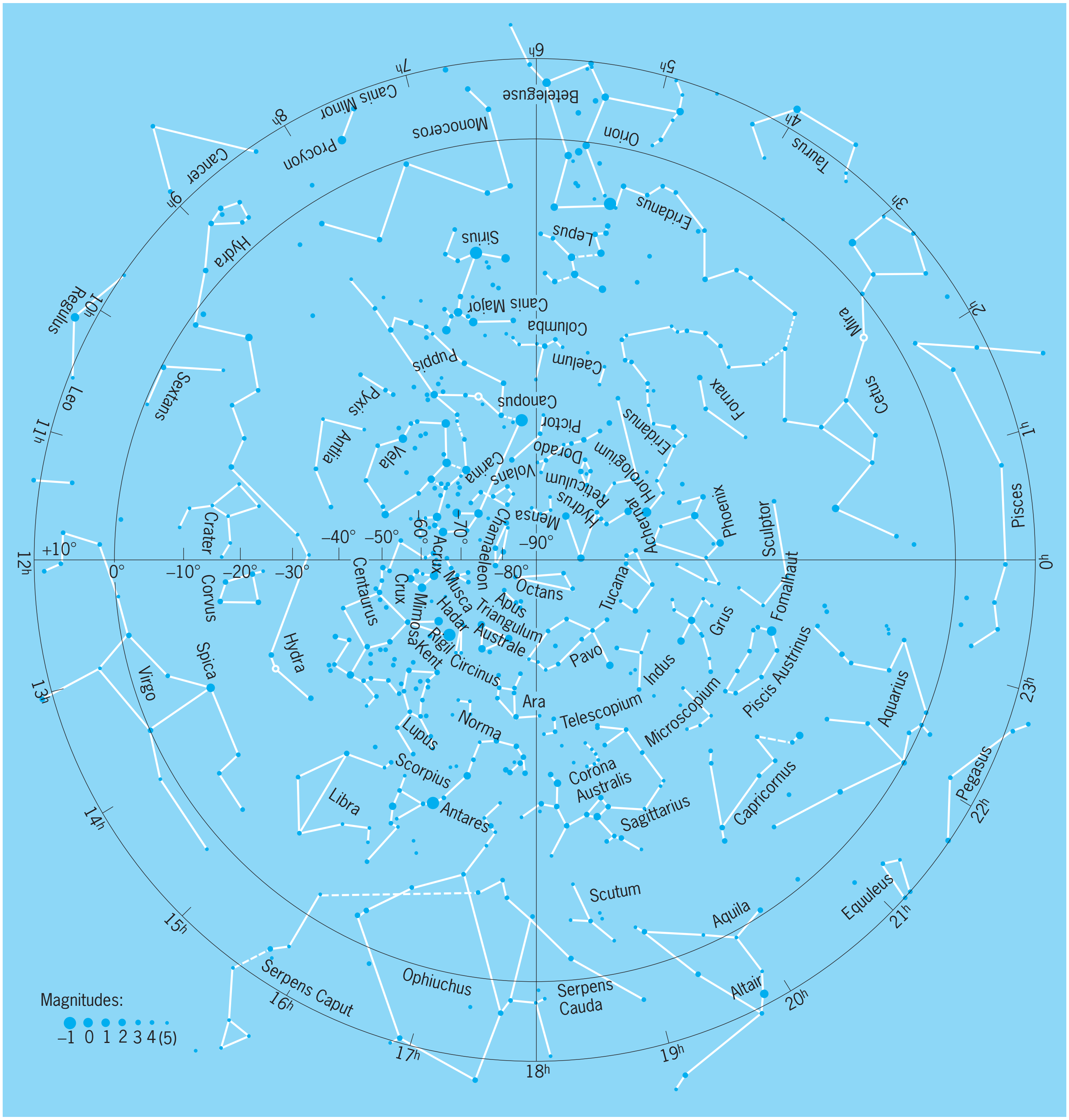

Fig. 3. Constellations of the southern hemisphere; brighter stars are shown by larger dots. (*After J. M. Pasachoff, A Field Guide to the Stars and Planets, Houghton Mifflin, 4th ed., 2000*)

constellations that fall close to the ecliptic through which the Sun traditionally moves are known as the zodiac. Actually, the Sun moves through 13 constellations, and precession has changed the dates at which the Sun passes through the zodiacal constellations. The intersection of the ecliptic and the celestial equator (the extension of the Earth's Equator into the sky) is known as the vernal equinox, or the first point of Aries. It has been used to mark the zero point of the celestial coordinate system. Westward from Aries, the zodiacal constellations are Taurus, the Bull; Gemini, the Twins; Cancer, the Crab; Leo, the Lion; Virgo, the Virgin; Libra, the Scales; Scorpius, the Scorpion; Sagittarius, the Archer; Capricornus, the Seat Goat; Aquarius, the Water Bearer; and Pisces, the Fish. *See* ECLIPTIC; EQUINOX; ZODIAC.

With the advent of equatorial drives on telescopes, astronomers no longer use the constellations to

The constellations[*]

Latin name	Genitive	Abbreviation	English translation
Andromeda	Andromedae	And	Andromeda[†]
Antlia	Antliae	Ant	Pump
Apus	Apodis	Aps	Bird of Paradise
Aquarius	Aquarii	Aqr	Water Bearer
Aquila	Aquilae	Aql	Eagle
Ara	Arae	Ara	Altar
Aries	Arietis	Ari	Ram
Auriga	Aurigae	Aur	Charioteer
Boötes	Boötes	Boo	Herdsman
Caelum	Caeli	Cae	Chisel
Camelopardalis	Camelopardalis	Cam	Giraffe
Cancer	Cancri	Cnc	Crab
Canes Venatici	Canum Venaticorum	CVn	Hunting Dogs
Canis Major	Canis Majoris	CMa	Big Dog
Canis Minor	Canis Minoris	CMi	Little Dog
Capricornus	Capricorni	Cap	Goat
Carina	Carinae	Car	Ship's Keel[‡]
Cassiopeia	Cassiopeiae	Cas	Cassiopeia[†]
Centaurus	Centauri	Cen	Centaur[†]
Cepheus	Cephei	Cep	Cepheus[†]
Cetus	Ceti	Cet	Whale
Chamaeleon	Chamaeleonis	Cha	Chameleon
Circinus	Circini	Cir	Compass
Columba	Columbae	Col	Dove
Coma Berenices	Comae Berenices	Com	Berenice's Hair[†]
Corona Australis	Coronae Australis	CrA	Southern Crown
Corona Borealis	Coronae Borealis	CrB	Northern Crown
Corvus	Corvi	Crv	Crow
Crater	Crateris	Crt	Cup
Crux	Crucis	Cru	Southern Cross
Cygnus	Cygni	Cyg	Swan
Delphinus	Delphini	Del	Dolphin
Dorado	Doradus	Dor	Swordfish
Draco	Draconis	Dra	Dragon
Equuleus	Equulei	Equ	Little Horse
Eridanus	Eridani	Eri	River Eridanus[†]
Fornax	Fornacis	For	Furnace
Gemini	Geminorum	Gem	Twins
Grus	Gruis	Gru	Crane
Hercules	Herculis	Her	Hercules[†]
Horologium	Horologii	Hor	Clock
Hydra	Hydrae	Hya	Hydra[†] (water monster)
Hydrus	Hydri	Hyi	Sea Serpent
Indus	Indi	Ind	Indian
Lacerta	Lacertae	Lac	Lizard
Leo	Leonis	Leo	Lion
Leo Minor	Leonis Minoris	LMi	Little Lion
Lepus	Leporis	Lep	Hare
Libra	Librae	Lib	Scales
Lupus	Lupi	Lup	Wolf
Lynx	Lyncis	Lyn	Lynx
Lyra	Lyrae	Lyr	Harp
Mensa	Mensae	Men	Table (mountain)
Microscopium	Microscopii	Mic	Microscope
Monoceros	Monocerotis	Mon	Unicorn
Musca	Muscae	Mus	Fly
Norma	Normae	Nor	Level (square)
Octans	Octantis	Oct	Octant
Ophiuchus	Ophiuchi	Oph	Ophiuchus[†] (serpent bearer)
Orion	Orionis	Ori	Orion[†]
Pavo	Pavonis	Pav	Peacock
Pegasus	Pegasi	Peg	Pegasus[†] (winged horse)
Perseus	Persei	Per	Perseus[†]
Phoenix	Phoenicis	Phe	Phoenix
Pictor	Pictoris	Pic	Easel
Pisces	Piscium	Psc	Fish
Piscis Austrinus	Piscis Austrini	PsA	Southern Fish
Puppis	Puppis	Pup	Ship's Stern[‡]
Pyxis	Pyxidis	Pyx	Ship's Compass[‡]
Reticulum	Reticuli	Ret	Net

(*cont.*)

The constellations[*] (*cont.*)

Latin name	Genitive	Abbreviation	English translation
Sagitta	Sagittae	Sge	Arrow
Sagittarius	Sagittarii	Sgr	Archer
Scorpius	Scorpii	Sco	Scorpion
Sculptor	Sculptoris	Scl	Sculptor
Scutum	Scuti	Sct	Shield
Serpens	Serpentis	Ser	Serpent
Sextans	Sextantis	Sex	Sextant
Taurus	Tauri	Tau	Bull
Telescopium	Telescopii	Tel	Telescope
Triangulum	Trianguli	Tri	Triangle
Triangulum Australe	Trianguli Australis	TrA	Southern Triangle
Tucana	Tucanae	Tuc	Toucan
Ursa Major	Ursae Majoris	UMa	Big Bear
Ursa Minor	Ursae Minoris	UMi	Little Bear
Vela	Velorum	Vel	Ship's Sails[‡]
Virgo	Virginis	Vir	Virgin
Volans	Volantis	Vol	Flying Fish
Vulpecula	Vulpeculae	Vul	Little Fox

[*] After J. M. Pasachoff, *Astronomy: From the Earth to the Universe*, 6th ed., 2002.
[†] Proper names.
[‡] Formerly formed the consellation Argo Navis, the Argonauts' Ship.

locate objects in the sky. Even amateur telescopes are often equipped with computer locators that point the telescope at objects specified by name or catalog number. Jay M. Pasachoff

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Constraint

A restriction on the natural degrees of freedom of a system. If n and m are the numbers of the natural and actual degrees of freedom, the difference $n - m$ is the number of constraints. In principle $n = 3N$, where N is the number of particles, for example, atoms. In practice n is determined by the number of effectively rigid components. *See* DEGREE OF FREEDOM (MECHANICS).

A holonomic system is one in which the n original coordinates can be expressed in terms of m independent coordinates and possibly also the time. It is characterized by frictionless contacts and inextensible linkages. The new coordinates, $q_1, q_2, \ldots, q_m$, are called generalized coordinates. The equations of equilibrium and of motion may be expressed in terms of these coordinates. *See* LAGRANGE'S EQUATIONS.

Nonholonomic systems cannot be reduced to independent coordinates because the constraints are not on the n coordinate values themselves but on their possible changes. For example, an ice skate may point in all directions but at each position it must point along its path. This is a condition between changes (dx,dy) in the two position coordinates (x,y) and the direction angle θ, as in Eq. (1). This cannot

$$dy = \tan\theta \, dx \tag{1}$$

be put in an integrated form, as in Eq. (2), since a

$$f(x, y, \theta) = 0 \tag{2}$$

skater can pass in different directions repeatedly over a point.

The static equilibrium conditions of a constrained system under impressed forces F_1, F_2, and so on are contained in a general statement, the principle of virtual work or virtual displacement. *See* STATICS; VIRTUAL WORK PRINCIPLE.

A moving constraint is one which changes with time, as in the case of a system on a moving platform. Moving constraints differ from the stationary constraints of static equilibrium in being able to do work. For example, a mass constrained to move on the floor of a rising elevator is carried also in the direction of the (vertical) force of constraint which does work on it. Bernard Goodman

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Construction engineering

A specialized branch of civil engineering concerned with the planning, execution, and control of construction operations for such projects as highways, buildings, dams, airports, and utility lines.

Planning consists of scheduling the work to be done and selecting the most suitable construction methods and equipment for the project. Execution requires the timely mobilization of all drawings, layouts, and materials on the job to prevent delays to the work. Control consists of analyzing progress and cost to ensure that the project will be done on schedule and within the estimated cost.

Planning. The planning phase starts with a detailed study of construction plans and specifications. From this study a list of all items of work is prepared, and related items are then grouped together for listing on a master schedule. A sequence of construction and the time to be allotted for each item is then indicated. The method of operation and the equipment to be used for the individual work items are selected to satisfy the schedule and the character of the project at the lowest possible cost. *See* CONSTRUCTION EQUIPMENT; CONSTRUCTION METHODS.

The amount of time allotted for a certain operation and the selection of methods of operation and equipment are generally determined by the equipment that is readily available to the contractor. After the master or general construction schedule has been drawn up, subsidiary detailed schedules or forecasts are prepared from the master schedule. These include individual schedules for procurement of material, equipment, and labor, as well as forecasts of cost and income.

Execution. The speedy execution of the project requires the ready supply of all materials, equipment, and labor when needed. The construction engineer is generally responsible for initiating the purchase of most construction materials and expediting their delivery to the project. Some materials, such as structural steel and mechanical equipment, require partial or complete fabrication by a supplier. For these fabricated materials the engineer must prepare or check all fabrication drawings for accuracy and case of assembly and often inspect the supplier's fabrication.

Other construction engineering duties are the layout of the work by surveying methods, the preparation of detail drawings to clarify the design engineer's drawings for the construction crews, and the inspection of the work to ensure that it complies with plans and specifications.

On most large projects it is necessary to design and prepare construction drawings for temporary construction facilities, such as drainage structures, access roads, office and storage buildings, formwork, and cofferdams. Other problems are the selection of electrical and mechanical equipment and the design of structural features for concrete material processing and mixing plants and for compressed air, water, and electrical distribution systems.

Control. Progress control is obtained by comparing actual performance on the work against the desired performance set up on the master or detailed schedules. Since delay on one feature of the project could easily affect the entire job, it is often necessary to add equipment or crews to speed up the work. *See* PERT.

Cost control is obtained by comparing actual unit costs for individual work items against estimated or budgeted unit costs, which are set up at the beginning of the work. A unit cost is obtained by dividing the total cost of an operation by the number of units in that operation.

Typical units are cubic yards for excavation or concrete work and tons for structural steel. The actual unit cost for any item at any time is obtained by dividing the accumulated costs charged to that item by the accumulated units of work performed.

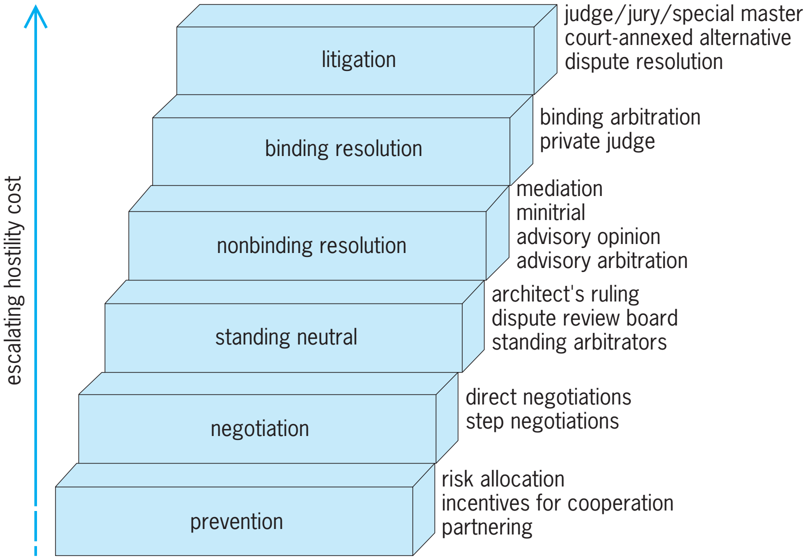
Individual work item costs are obtained by periodically distributing job costs, such as payroll and invoices to the various work item accounts. Payroll and equipment rental charges are distributed with the aid of time cards prepared by crew forepersons. The cards indicate the time spent by the job crews and equipment on the different elements of the work. The allocation of material costs is based on the quantity of each type of material used for each specific item.

When the comparison of actual and estimated unit costs indicates an overrun, an analysis is made to pinpoint the cause. If the overrun is in equipment costs, it may be that the equipment has insufficient capacity or that it is not working properly. If the overrun is in labor costs, it may be that the crews have too many workers, lack of proper supervision, or are being delayed for lack of materials or layout. In such cases time studies are invaluable in analyzing productivity. William Hershleder

Legal aspects. The construction industry is structured by contracts and other legal obligations. Construction company managers are in daily contact with legal requirements that relate to the contractual provisions of the projects that they are designing or constructing. Other legal considerations relate to subcontractor and materials procurement, the law applied to labor relations, and the legal form of a given company's organization. A firm knowledge of the law is absolutely necessary.

The relationship between owner, designer, and constructor has become so complex and open to misunderstandings that a formal legal framework for performing a given project is essential. Projects are governed by a number of legally binding documents. The construction contract typically consists of an agreement, a description of the general conditions for the project, special or supplementary conditions directly related to the project, and a listing of technical requirements or specifications. These documents, together with the project drawings, provide a legally binding description of the project and establish the relationships between the parties to the contract. On large projects this set of documents can be very large and must be understood in detail by the construction management.

It is not uncommon for disputes to arise regarding the legal interpretation of the contract provisions. In many cases, this has led to an adversarial relationship between the owner, designer, and constructor. The contract itself contains mechanisms for the resolution of disputes. Usually, it is beneficial for all parties to negotiate and to come to a mutual agreement. In extreme cases, the parties become so confrontational that a third party is required to resolve the



Steps in resolving a construction dispute.

conflict. In the past, this has resulted in the dispute being presented to a civil court in the form of a claim, with a judge or jury deciding the outcome. In some cases, the contract provides that arbitration will be utilized by the parties to settle disputes. In the United States, the American Arbitration Association (AAA) has developed comprehensive procedures for the reconciliation of contract disputes. Other methods of dispute resolution are shown in the **illustration**.

A large body of law regulates the interactions between workers and management as well as working conditions at the construction site. In the United States, labor laws pertain to the operation of labor unions and specific issues such as minimum pay rates on federally funded projects (Davis Bacon Act). The National Labor Relations Act and other laws established the National Labor Relations Board (NLRB), which acts to resolve disputes between labor and management. The construction worksite is regulated by the Occupational Safety and Health Act (OSHA), originally enacted in 1970. This law requires all employers to provide a safe workplace free of hazards that could cause serious harm to employees. Daniel W. Halpin

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Construction equipment

A wide variety of relatively heavy machines which perform specific construction (or demolition) functions under power. The power plant (which is treated in later paragraphs) is commonly an integral part of an individual machine, although in some cases it is contained in a separate prime mover, for example, a towed wagon or roller. It is customary to classify construction machines in accordance with their functions such as hoisting, excavating, hauling, grading, paving, drilling, or pile driving. There have been few changes for many years in the basic types of machines available for specific jobs, and few in the basic configurations of those that have long been available. Design emphasis for new machines is on modifications that increase speed, efficiency, and accuracy (particularly through more sophisticated controls); that improve operator comfort and safety; and that protect the public through sound attenuation and emission control. The selection of a machine for a specific job is mainly a question of economics and depends primarily on the ability of the machine to complete the job efficiently, and secondarily on its availability.

Hoisting equipment. This class of equipment is used to raise or lower materials from one elevation to another or to move them from one point to another over an obstruction. The main types of hoisting equipment are derricks, cableways, cranes, elevators, and conveyors. *See* BULK-HANDLING MACHINES; HOISTING MACHINES.

Derricks. The two main types of derricks are the guy and the stiff-leg. The former has a mast that is held in a vertical position by guy wires and a boom that can rotate with the mast 360°. In the stiff-leg the mast is tied to two or more rigid structural members, and the rotation of the boom is limited by the position of these members. The derrick is practical only where little mobility is required as in some types of steel erection, excavation of a shaft, or hoisting of materials through a shaft. *See* DERRICK.

Cableway. This is a combination hoist and tram system comprising a trolley that runs on main load cables stretched between two or more towers which may be stationary or tiltable. Since even with towers that can be tilted slightly from side to side the cableway is limited almost entirely to linear movement of materials, its use in construction is restricted to dams, to some dredging and drag-line operations, and in special cases to bridges.

Elevator. The construction elevator, like the passenger elevator, consists of a car or platform that operates within a structural framework and is raised and lowered by cables. Because the elevator can move materials only in a vertical linear direction and because the materials so moved must subsequently be moved horizontally by other means, the elevator is limited to moving relatively light materials on jobs of small areas. *See* ELEVATING MACHINES.

Crane. A crane is basically a fast-moving boom mounted on a frame containing the power supply and mechanisms for moving the boom and for raising and lowering the load-bearing cables that run through sheaves at the top of the boom. Once all cranes in the United States were mobile; that is, they were attached to a chassis mounted on pneumatic tires, crawler treads, or flanged (railroad) wheels. This type of machine is still predominant in all

Fig. 1. Hydraulic truck crane.

operations where mobility is a must. **Figure 1** shows a hydraulic truck crane. However, European and Australian tower cranes and climbing cranes have become popular throughout the United States and the world for high-rise building construction where mobility requirements are negligible. These machines, which carry horizontal or diagonal masts or booms, can “grow” with the construction by climbing with it or by adding sections to their own towers. They have the fast boom and line action of the mobile crane but are not restricted in boom reach.

Conveyor. Occasionally a conveyor is used to raise materials needed for construction of low buildings. This machine, which has a movable endless belt mounted on a frame, can carry only light loads such as bricks and cement sacks and is not practical for buildings of more than one or two floors. A conveyor carrying rock over a railroad yard is shown in **Fig. 2**.

Excavating equipment. This type of equipment is divided into two main classes: standard land excavators and marine dredges; each has many variations.

Standard land excavator. This comprises machines that merely dig earth and rock and place it in separate hauling units, as well as those that pick up and transport the materials. Among the former are power shovels, draglines, backhoes, cranes with a variety of buckets, front-end loaders, excavating belt loaders, trenchers, and the continuous bucket excavator. The second group includes such machines as bulldozers, scrapers of various types, and sometimes the front-end loader.

Power shovel. This has for years been regarded as the most efficient machine for digging into vertical banks and for handling heavy rock. Generally mounted on crawler treads, the power shovel carries a short boom on which rides a movable dipper stick carrying an open-topped bucket. The bucket digs in an upward direction away from the machine and dumps its load by lowering the front of its hinged bottom. **Figure 3** shows power shovels in the process of loading dump trucks.

Front-end loader. This has made heavy inroads into the domain of the power shovel and in time may well replace it in all but the biggest operations. Loaders are built that can handle buckets having 12, 14, and 24 yd^3 (9, 11, and 18 m^3) capacities. The loader, basically an articulated bucket mounted on a series of movable arms at the front of a crawler or rubber-tired tractor, has the advantage of mobility, speed, economy of cost and operation, and light weight. A loader of any given capacity can cost as little as one-half or even one-third as much as a power shovel of the same capacity and requires only one person to run it as opposed to the two or more normally required for the power shovel. **Figure 4** shows a loader operating in a swamp.

Backhoe. This is fundamentally an upside-down power shovel. Its bucket, mounted on a hinged boom, digs upward toward the machine and unloads by being inverted over the dumping point. Backhoes are manufactured as individual machines but more often are attachments mounted on a crawler crane, a rubber-tired truck crane, or a tractor (which usually has a front-end loader bucket at the other end). It is particularly well adapted to the digging of deep trenches.

Dragline. This is a four-sided bucket that is used mainly on soil too wet to support an excavating machine. It is usually carried on a mobile machine mounting a crane boom, but it can also be worked from a cableway where excavating distances are great. The bucket is carried or cast to a point ahead of its support and dropped to the ground. The dragline is designed to excavate and to fill itself as it is drawn across the ground. It empties when its front end is lowered.

Fig. 2. Conveyor carrying rock over a railroad yard.

Fig. 3. Power shovels loading over-the-road rear-dump trucks.

Clamshell. A clamshell is a two-sided bucket that can dig only in a vertical direction. The bucket is dropped while its leaves are open and digs as they close. Formerly, clamshells were suspended from cables on cranes or gantries and worked only under their own weight. Therefore they were imprecise in digging and were practical only in relatively soft soil or loose rock. Presently many clamshell buckets are attached directly to powered booms, are closed hydraulically, and can work with greater precision in dense soils.

Orange peel. This is a multileaved bucket, generally round in configuration. It is normally cable-supported and, like the clamshell, works under its own weight. Like the clamshell, however, it too is being mounted on powered booms and closed hydraulically. One of the commonest uses of the orange peel is the cleaning of small shafts, sewers, and storm drains. Larger sizes are often used for handling broken rock.

Grapple. This group includes a wide variety of special-purpose tined grabs that work on the principle of the clamshell and orange peel. The grapple is used mainly for handling rock, pipe, and logs.

Excavating belt loader. This type of machine is used mainly for loading granular materials from a stockpile, or as a vertical or inclined belt, or as a pair of chains on which are mounted small buckets. Some belt loaders are mobile and can move into a bank under their own power as the material is moved. Others are fixed and are fed by bulldozers which push material onto the belt from above. Their advantage over most excavators lies in their continuous operation.

Trenching machine. This equipment for digging trenches ranges in size from small hand-pushed units

Fig. 4. A loader operating in a swamp.

Fig. 5. A scraper in operation, as it is pulled by a tractor.

used for getting small pipes from streets to private homes to monsters of many tons capable of cutting a 4-ft-wide (1.2-m) swath for 2000 mi (3200 km) of transcontinental pipelines. All, however, work on basically the same principle: A series of buckets, mounted on a chair or a wheel, lift dirt from the ground and deposit it alongside the trench being dug.

Continuous bucket excavator. This excavator works like a trenching machine but is designed to remove earth and loose rock from a wider area and at shallower depths. These machines are self-propelled; they can load trucks in a continuous operation and can switch from a filled to an empty truck in less than 2 s. The continuity of loading and the absence of intermittent activities, such as those necessary in shovel or loader operations, make the continuous bucket excavator a fast, economical machine for large excavating jobs.

Combination excavators and haulers. This classification of construction equipment includes bulldozers, carrying scrapers, self-loading or elevating scrapers, and sometimes front-end loaders.

Bulldozer. This is a curved blade mounted on the front of a crawler or rubber-tired tractor for the purpose of digging and pushing earth and broken rock from one place to another. It is often used in conjunction with a ripper, a heavy tooth or series of teeth mounted on the rear of a tractor to break up rock so that it can be handled by the dozer. Because the amount of dirt the dozer can move at one time is limited by the size of its blade, it is not economical to use the dozer for moving dirt more than a few hundred feet.

Front-end loader. This is sometimes used for moving dirt in the same manner as the dozer, but with the same limitations.

Scraper. This is the most economical of the combination excavating-hauling units for hauls of over a few hundred feet. A wheel-mounted, open-top box or “bowl,” the scraper has a hinged bottom that is lowered to scoop up dirt as the machine moves forward. When the bowl is full, the bottom is closed and the unit is moved to the dumping area, where the bottom is lowered and a hydraulic pushing unit in the back of the bowl moves the dirt out through the opening in the bottom, to spread the dirt as needed. Scrapers are pulled by tractors, most of which are an integral part of the unit. A scraper is shown in **Fig. 5**.

Self-loading or elevating scraper. This group of machines does the same work as the conventional scraper, but in front of the bowl is a series of horizontal plates mounted on moving chains. As the chains move, the plates lift the dirt into the bucket in the same manner as a bucket loader. The advantage of the elevating scraper is that it needs less tractor power during the loading operation.

Marine excavator. Usually called a dredge, the marine excavator is an excavating machine mounted on a barge or boat. Two common types are similar to land excavators, the clamshell and the bucket excavator. The suction dredge is different; it comprises a movable suction pipe which can be lowered to the bottom, usually with a fast-moving cutter head at the bottom end. The cutter churns up the bottom so that the pumps on the barge or boat suck up water and the earth suspended in it. When practical, the pumped material is then piped to land, where the solids settle out, allowing the liquids to run back to the body of water being dredged. When distance to land is too great or where there is no empty land on which to discharge the material, the effluent is pumped into barges in which the settled-out solids are towed to a dump area at a distant point.

Hauling equipment. Excavated materials are moved great distances by a wide variety of conveyances. The most common of these are the self-propelled rubber-tired rear-dump trucks, which are classed as

Fig. 6. A 100-ton (90-metric-ton) rear-dump truck.

over-the-road or off-the-road trucks. The main difference between these two is weight and carrying capacity. Many states restrict the total weight of highway-using trucks (truck and load) to as little as 30 tons (27 metric tons). For jobs where trucks remain on site, such as at dams and some highway construction areas, trucks with a carrying capacity of 50 tons (45 metric tons) are common and some capable of carrying loads in excess of 100 tons (90 metric tons) are in use. A 100-ton (90-metric-ton) rear-dump truck is shown in **Fig. 6**. Wagons towed by a rubber-tired prime mover are also used for hauling dirt. These commonly have bottom dumps which permit spreading dirt as the vehicle moves. In special cases side-dump trucks are also used.

Conveyors, while not commonly used on construction jobs for hauling earth and rock great distances, have been used to good advantage on large jobs where obstructions make impractical the passage of trucks. One such conveyor which was utilized on a New Jersey highway job exceeded 2 mi (3.2 km) in length.

Graders. Graders are high-bodied, wheeled vehicles that mount a leveling blade between the front and rear wheels. The principal use is for fine-grading relatively loose and level earth. Commonly considered a maintenance unit, the grader is still an important machine in highway construction. While the configuration of graders has not changed in many years, some models have been built with articulated main frames that permit faster turns of shorter radii and safer operation at the edges of steep slopes.

Pavers. These place, smooth, and compact paving materials. They may be mounted on rubber tires, endless tracks, or flanged wheels. Asphalt pavers embody tamping pads that consolidate the material; concrete pavers use vibrators for the same purpose. Concrete pavers had been required to use forms to contain the material until the advent of the slip-form pavers. These drag their own short forms behind them and consolidate the concrete sufficiently to stand without slumping after removal of the forms. Many high-speed conventional pavers have been produced with highly sophisticated automated control devices that provide extremely accurate and consistent surface elevations.

Drilling equipment. Holes are drilled in rock for wells and for blasting, grouting, and exploring. Drills are classified according to the way in which they penetrate rock, namely, percussion, rotary percussion, and rotary. The first two types are the most common for holes up to 6 in. (15 cm) in diameter and under 40 ft (12 m) in depth. In smaller sizes these drills may be hand-held, but for production work they are mounted on masts which are supported by trucks or, as shown in **Fig. 7**, special tracks mounted on drill rigs. In tunnel work the drills are commonly mounted on platform-supported movable arms or posts that are hydraulically or pneumatically controlled to permit drilling in horizontal or angled positions, with a minimum of effort by the drill operator. The rotary drill is most common in larger sizes, but drills as small as 3 in. (7.5 cm) in diameter are used for coring rock to obtain samples.

Specialized equipment. Among the most common specialized construction equipment are augers, compactors, and pile hammers.

Augers. These are used for drilling wells, dewatering purposes, and cutting holes that can be filled with concrete for foundations. Augers up to 6 ft (1.8 m) in diameter are common.

Compactors. These machines are designed solely to consolidate earth and paving materials to sustain loads greater than those sustained in the uncompacted state. They range in size from small pneumatic hand-held tampers to multiwheeled machines weighing more than 60 tons (50 metric tons). Actual compaction may be achieved by heavily loaded rubber tires or steel rollers. The steel rollers may be solid

Fig. 7. Crawler-mounted drill. (*Gardner-Denver*)

cylinders, or have separate pads or grids, or contain protrusions (sheep-foot roller). Many machines induce a vibratory action into the compacting units so that compaction is achieved by impact force rather than sheer weight.

Pile hammers. These machines are used to install bearing piles for foundations, or sheet piles for cofferdams and retaining walls. The prehistoric pile hammer consisted of a heavy weight lifted by a rope and allowed to drop on top of a pile. This drop hammer is still in use, basically unchanged. More efficient modern hammers are true machines activated by steam, air, oil, hydraulic fluid, or electricty. Conventional hammers contain pistons that are raised by one of these means and then either allowed to fall freely because of gravity (single-acting) or to be driven downward by the same means (double-acting) to impart an impact to the pile. Vibratory hammers have been developed which use electrically activated eccentric cams to vibrate piles into place. Relatively rare are machines that use hydraulic action to install piles.

Road planer. This machine looks like a conventional motor grader, but instead of a blade it carries near its center a horizontal drum that has on its periphery many rows of replaceable hardened steel teeth. As the drum revolves, the teeth pulverize cracked asphalt or decayed concrete pavement to depths of up to 4 in. (10 cm). This permits the placement of a smooth new riding surface on a sound base without raising the road surface elevation, having to raise manhole covers, and reducing the clearances under bridges.

Bore tunneling machine. This is a machine capable of placing water, sewer, or utility pipes accurately for great distances underground. Key to the operation is a series of intermediate hydraulic jacking rings that expand or contract as controlled to permit the movement of any section of pipe independent of the sections before or behind. This independent movement of short sections reduces the friction on the line and therefore the amount of pressure that would be required if the entire pipe were moved from a single push point.

Power plants. Steam is seldom used as a source of power today except in some marine applications and rarely for pile driving. Gasoline and diesel engines of the piston type are the most common source of power for construction machines, with the diesel attaining an increasingly greater prominence for at least two major reasons. First, the size of many construction machines has increased to proportions formerly thought impractical. With this increase in size, the economy of operation and maintenance of the diesel has come to far outweigh its greater initial cost. Second, the increased popularity of the diesel lies in the fact that manufacturers have been able to build lightweight economical diesel engines in very small sizes, thus making practical their application in small compressors, pumps, portable electric power plants, and so on. *See* DIESEL ENGINE.

Electricity is sometimes, though not often, used as a primary source of power for some construction machines, but usually only at the site of large dams and strip-mining operations where mobility is not a primary requirement. Electricity is making its appearance as a secondary source of power on several types of mobile construction machinery, such as trucks and scrapers, which use diesel or gas engines to turn generators that provide power for electric wheels.

A more common type of secondary power, however, is the hydraulic motor which, activated by a gasoline or diesel-powered hydraulic pump, is being used to provide direct power for virtually every movement, including travel, of construction machines.

Some manufacturers have experimented with turbine engines for construction applications. While they are being used with success as primary power sources for large stationary electric power plants on job sites, their practical use in mobile equipment is not evident. *See* CONSTRUCTION ENGINEERING.

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Construction methods

The procedures and techniques utilized during construction. Construction operations are generally classified according to specialized fields. These include preparation of the project site, earthmoving, foundation treatment, steel erection, concrete placement, asphalt paving, and electrical and mechanical installations. Procedures for each of these fields are generally the same, even when applied to different projects, such as buildings, dams, or airports. However, the relative importance of each field is not the same in all cases. For a description of tunnel construction, which involves different procedures, *see* TUNNEL

Preparation of site. This consists of the removal and clearing of all surface structures and growth from the site of the proposed structure. A bulldozer is used for small structures and trees. Larger structures must be dismantled.

Earthmoving. This includes excavation and the placement of earth fill. Excavation follows preparation of the site, and is performed when the existing grade must be brought down to a new elevation. Excavation generally starts with the separate stripping of the organic topsoil, which is later reused for landscaping around the new structure. This also prevents contamination of the nonorganic material which is below the topsoil and which may be required for fill. Excavation may be done by any of several excavators, such as shovels, draglines, clamshells, cranes, and scrapers. For a discussion of their application *see* CONSTRUCTION EQUIPMENT.

Efficient excavation on land requires a dry excavation area, because many soils are unstable when wet

Fig. 1. Steel erection with guy derricks on a high structure. (*Bethlehem Steel Co.*)

and cannot support excavating and hauling equipment. Dewatering becomes a major operation when the excavation lies below the natural water table and intercepts the ground-water flow. When this occurs, dewatering and stabilizing of the soil may be accomplished by trenches, which conduct seepage to a sump from which the water is pumped out. Dewatering and stabilizing of the soil may in other cases be accomplished by wellpoints and electroosmosis. *See* WELLPOINT SYSTEMS.

Some materials, such as rock, cemented gravels, and hard clays, require blasting to loosen or fragment the material. Blast holes are drilled in the material; explosives are then placed in the blast holes and detonated. The quantity of explosives and the blast-hole spacing are dependent upon the type and structure of the rock and the diameter and depth of the blast holes.

After placement of the earth fill, it is almost always compacted to prevent subsequent settlement. Compaction is generally done with sheep's-foot, grid, pneumatic-tired, and vibratory-type rollers, which are towed by tractors over the fill as it is being placed. Hand-held, gasoline-driven rammers are used for compaction close to structures where there is no room for rollers to operate.

Foundation treatment. When subsurface investigation reveals structural defects in the foundation area to be used for a structure, the foundation must be strengthened. Water passages, cavities, fissures, faults, and other defects are filled and strengthened by grouting. Grouting consists of injection of fluid mixtures under pressure. The fluids subsequently solidify in the voids of the strata. Most grouting is done with cement and water mixtures, but other mixture ingredients are asphalt, cement and clay, and precipitating chemicals. *See* FOUNDATIONS.

Steel erection. The construction of a steel structure consists of the assembly at the site of mill-rolled or shop-fabricated steel sections. The steel sections may consist of beams, columns, or small trusses which are joined together by riveting, bolting, or welding. It is more economical to assemble sections of the structure at a fabricating shop rather than in the field, but the size of preassembled units is limited by the capacity of transportation and erection equipment. The crane is the most common type of erection equipment, but when a structure is too high or extensive in area to be erected by a crane, it is necessary to place one or more derricks on the structure to handle the steel (**Fig. 1**). In high structures the derrick must be constantly dismantled and reerected to successively higher levels to raise the structure. For river bridges the steel may be handled by cranes on barges, or, if the bridge is too high, by traveling derricks which ride on the bridge being erected. Cables for long suspension bridges are assembled in place by special equipment that pulls the wire from a reel, set up at one anchorage, across to the opposite anchorage, repeating the operation until the bundle of wires is of the required size.

Concrete construction. Concrete construction consists of several operations: forming, concrete production, placement, and curing. Forming is required to contain and support the fluid concrete within its desired final outline until it solidifies and can support itself. The form is made of timber or steel sections or a combination of both and is held together during the concrete placing by external bracing or internal ties (**Fig. 2**). The forms and ties are designed to withstand the temporary fluid pressure of the concrete.

The usual practice for vertical walls is to leave the forms in position for at least a day after the concrete is placed. They are removed when the concrete has solidified or set. Slip-forming is a method where the form is constantly in motion, just ahead of the level of fresh concrete. The form is lifted upward by means of jacks which are mounted on vertical rods embedded in the concrete and are spaced along the perimeter of the structure. Slip forms are used for high structures such as silos, tanks, or chimneys.

Concrete may be obtained from commercial batch plants which deliver it in mix trucks if the job is close to such a plant, or it may be produced at the job site. Concrete production at the job site requires the erection of a mixing plant, and of cement and aggregate receiving and handling plants. Aggregates are sometimes produced at or near the job site. This requires opening a quarry and erecting processing equipment such as crushers and screens.

Fig. 2. Concrete form. (*Superior Concrete Accesories*)

Concrete is placed by chuting directly from the mix truck, where possible, or from buckets handled by means of cranes or cableways, or it can be pumped into place by special concrete pumps.

Curing of exposed surfaces is required to prevent evaporation of mix water or to replace moisture that does evaporate. The proper balance of water and cement is required to develop full design strength. *See* CONCRETE.

Concrete paving for airports and highways is a fully mechanized operation. Batches of concrete are placed between the road forms from a mix truck or a movable paver, which is a combination mixer and placer. A series of specialized pieces of equipment, which ride on the forms, follow to spread and vibrate the concrete, smooth its surface, cut contraction joints, and apply a curing compound. *See* HIGHWAY ENGINEERING; PAVEMENT.

Asphalt paving. This is an amalgam of crushed aggregate and a bituminous binder. It may be placed on the roadbed in separate operations or mixed in a mix plant and spread at one time on the roadbed. Then the pavement is compacted by rollers.

William Hershleder

Contact aureole

The zone of alteration surrounding a body of igneous rock caused by heat and volatiles given off as the magma crystallized. Changes can be in mineralogy, texture, or elemental and isotopic composition

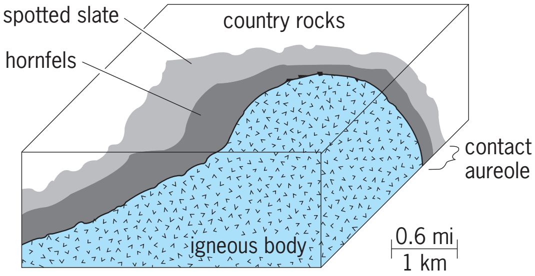

Fig. 1. Zoned contact aureole developed around an igneous body.

of the original enclosing (country or wall) rocks, and progressively increase closer to the igneous contact. The contact aureole is the shell of metamorphosed or metasomatized rock enveloping the igneous body (**Fig. 1**). The ideal contact aureole forms locally around a single magma after it is emplaced.

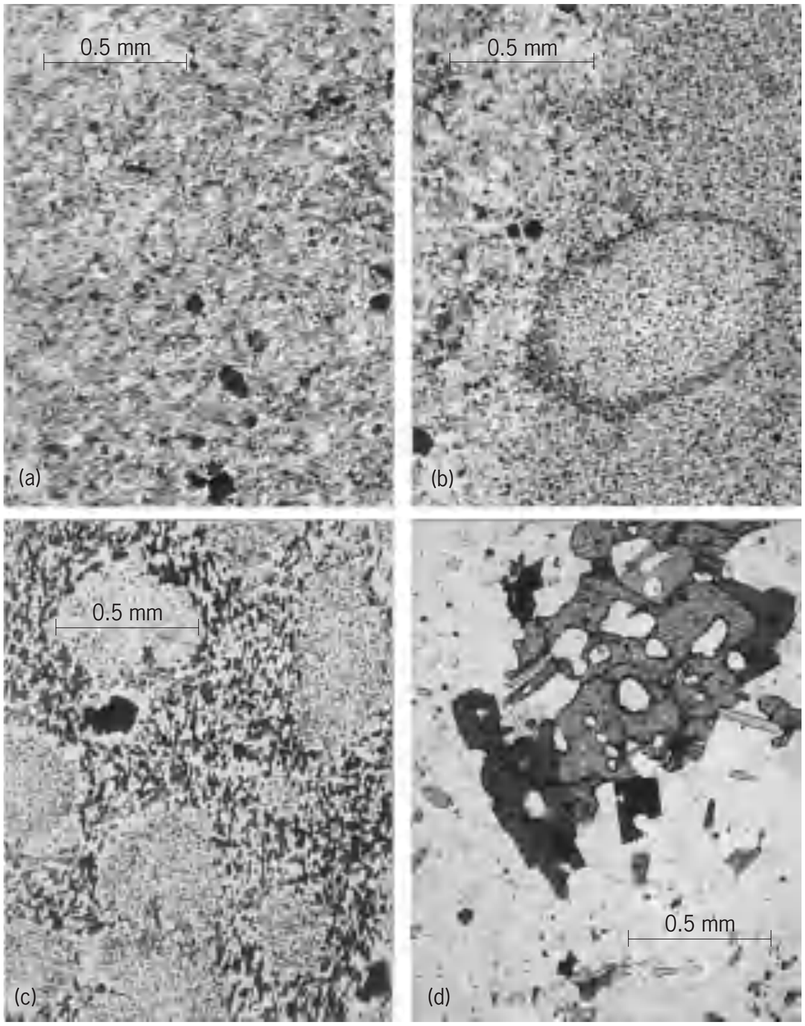

Fig. 2. Microscopic appearance of progressive metamorphism in a contact aureole. (*a*) Original slate country rock comprising chlorite, muscovite, albite, and quartz. (*b*) Spotted slate with the same mineralogy and texture as country rock but with the addition of cordierite plus biotite spots. (*c*) Hornfels with poikiloblastic porphyroblasts of cordierite in a matrix of biotite, muscovite, quartz, and plagioclase. (*d*) Granoblastic hornfels with garnet, biotite, cordierite, alkali feldspar, plagioclase, and quartz.

Metamorphism over a much larger area can result from coalescing of several contact aureoles. This is termed a contact-regional metamorphic aureole and is thought responsible for the regional metamorphism of several mountain areas. Other contact aureoles develop at greater depths and may be physically emplaced to shallower levels along with the igneous body. These are termed dynamothermal aureoles. *See* IGNEOUS ROCKS; MAGMA; METAMORPHIC ROCKS; METAMORPHISM; METASOMATISM; PLUTON.

Extent. The aureole extends from the igneous contact, where the metamorphic effects are the greatest, out into the country rocks to where the temperature or heat energy is insufficient to effect any changes. This temperature lies between 400 and 750°F (200 and 400°C), and actual widths of contact aureoles range from several inches to miles.

Most important in determining the metamorphic intensity and the extent of the aureole are the heat content of the magma and the temperature contrast between the magma and country rock. Initial temperature of the magma depends on its type; metamorphic effects around gabbro magma (∼2200°F or 1200°C) are generally more extensive and intensive than those around granite (∼1400°F or 750°C). Better developed aureoles are found around larger igneous bodies, magmas which were not extensively crystallized before emplacement, and convecting magmas. Under the right circumstances, the highest temperature in the aureole can approach that of the magma. At deeper crustal levels, country rock temperatures increasingly coincide with those of common magmas, and the contact effects are correspondingly reduced until they are indistinguishable from metamorphic changes brought about by normal burial. Thus contact aureoles are most commonly found around shallow igneous bodies where magma temperatures exceed those of the country rock. They are considered to have low-pressure metamorphism, occurring at pressures less than 5 kilobars (500 megapascals), but usually much less. This corresponds to depths of less than 12 mi (20 km).

Factors of heat transfer also affect the extent and intensity of the metamorphism in the contact aureole. Geometry and orientation of the igneous body are important; intense metamorphism occurs at acute corners of the body and wider aureoles occur at the roof of an igneous body, where most heat is escaping, as opposed to the floor. Wider aureoles and less intense metamorphism occur in country rocks with good thermal conductivity. Heat transfer by conduction produces narrower, more regular, aureoles in contrast to heat transfer by fluid convection. Convective heat transport can produce wide or very narrow aureoles depending on the fluid content of the magma, fluid content of the wall rock, permeability of the system, and direction of fluid flow. Dry magmas and impermeable systems tend to have narrow aureoles. Cool fluid from the wall rocks can flow into the magma, cooling it and preventing development of the aureole. Conversely, hot fluid from the magma or wall rock fluid heated by the magma flowing outward can produce an extensive aureole.

Aureoles are most pronounced where wall rocks are easily affected by metamorphism because of their composition, texture, or previous metamorphism. Shale and limestone generally show a more conspicuous metamorphism than does sandstone. Aureoles are best developed in fine-grained and previously unmetamorphosed or weakly metamorphosed rocks; they may not be detected in intensely metamorphosed rocks because minerals of the wall rocks are stable at the conditions imposed upon them by the magma. Heat absorption by energy-consuming reactions will lessen the intensity of metamorphism elsewhere in the aureole. If the rate of heating and subsequent cooling exceeds the rate of recrystallization or reaction in the aureole, metamorphic effects will be reduced.

Rocks. Weakly contact-metamorphosed wall rocks may be only discolored or indurated. Contact aureoles with more intense metamorphism are progressively zoned, with appearance of new textures and minerals toward the igneous body (**Fig. 2**). At the outer edge of the aureole, textural changes include development of scattered aggregates of existing or new minerals, which are larger than the matrix minerals. If the host rock is shale, these recrystallized rocks become spotted slates. Further inward there is sequential appearance of new minerals, more extensive recrystallization, and color changes. Average grain size may increase but is still small, usually less than 0.08 in. (2 mm). Fine grain size in contact metamorphism results from short-duration heating and lack of deformation. Well within the aureole, where new mineral growth and recrystallization is complete, older structures (bedding or schistosity) may be eliminated. Mineral grains tend to become equidimensional with little or no preferred orientation and lack their crystal form in an interlocking mosaic (granoblastic texture); the rock is called a hornfels. The term hornfels is applied in a wide sense to any contact-metamorphosed rock and made specific by mineral or rock compositional modifiers. The massive texture of hornfelses results from the lithostatic or hydrostatic nature of the pressure; directed pressure as in regional metamorphism is absent. However, some hornfelses develop a preferred alignment because of intrusion of the adjacent magma. Hornfelses typically have a few larger mineral grains (porphyroblasts) which can contain abundant inclusions of the smaller matrix minerals (poikiloblastic texture). Adjacent to the igneous contact, melting of the wall rocks can occur. *See* HORNFELS; PORPHYROBLAST; ROCK.

Mineral facies. Contact metamorphism can occur over a wide range of temperatures, pressures, or chemical gradients in rocks of any composition. Thus any mineral assemblage or facies of metamorphic rocks can be found. However, the nature of contact aureoles results in minerals characteristic of low to moderate pressures and moderate to high temperatures usually in common rock types: shales, basalt, limestone, and sandstone. Characteristic minerals developed in shales are andalusite, sillimanite, cordierite, biotite, orthopyroxene, and garnet. At the highest temperatures, tridymite, sanidine, mullite, and pigeonite form; whereas in limestone unusual calcium silicates form, including tilleyite, spurrite, rankinite, larnite, merwinite, akermanite, monticellite, and melilite. *See* FACIES (GEOLOGY).

Chemical alterations. Compositional changes in a contact aureole range from none to great, but as a rule, contact metamorphism entails relatively little change in bulk rock composition. Because metamorphic changes are largely brought about by heat, contact aureoles are often termed thermal aureoles. However, there is a tendency for volatiles (water, carbon dioxide, oxygen) and alkalies (sodium, potassium) to be lost from rocks in the aureole. Stable isotope compositions (oxygen, sulfur) change in response to the thermal gradient and flow of fluids through the rocks. In some cases, volatiles (boron, fluorine, and chlorine) and other elements from the crystallizing magma are gained.

Some wall rock compositions, such as limestone, can be greatly changed and form rocks termed skarn. These contact aureoles are economically important because they often contain ore deposits of iron, copper, tungsten, graphite, zinc, lead, molybdenum, and tin. Conversely, the magma can incorporate material from the wall rocks by assimilation or mixing with any partial melts formed. Mixing results in elemental and isotopic contamination of the magma, crystallization of different minerals from the melt, and hybrid rock types at the margin of the igneous body. *See* ORE AND MINERAL DEPOSITS; PNEUMATOLYSIS; SKARN.

J. Alexander Speer

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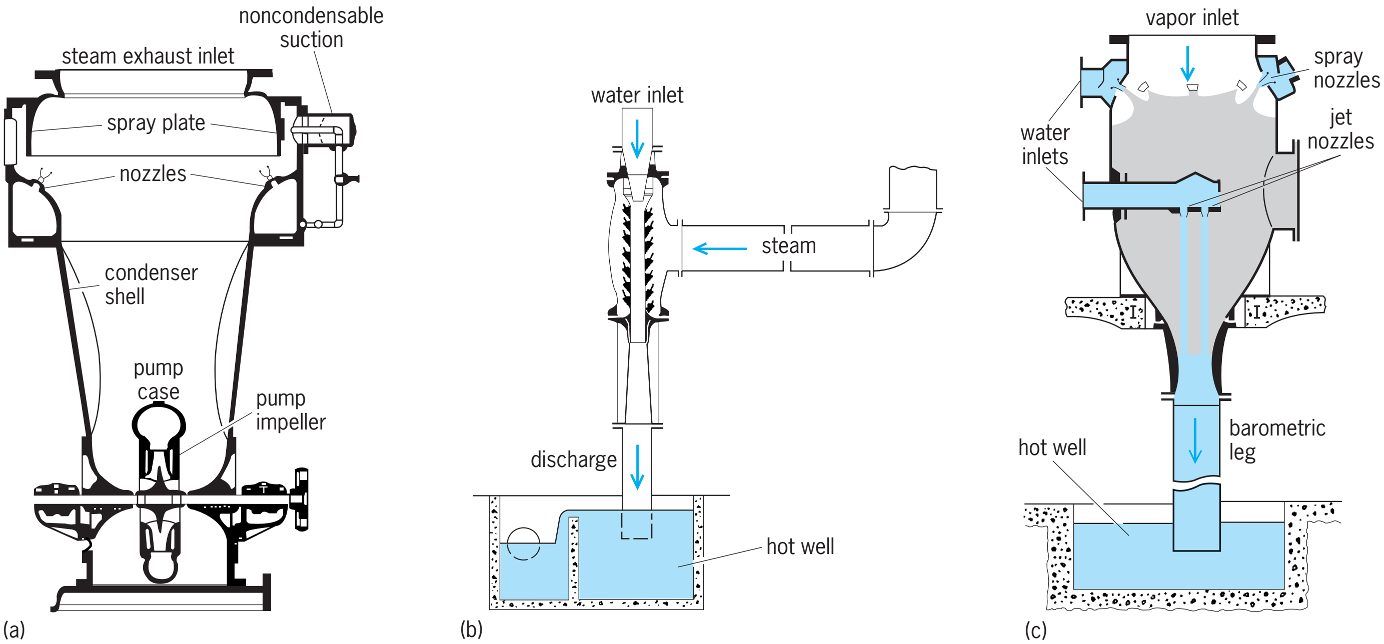
Contact condenser

A device in which a vapor is brought into direct contact with a cooling liquid and condensed by giving up its latent heat to the liquid. In almost all cases the cooling liquid is water, and the condensing vapor is steam. Contact condensers are classified as jet, barometric, and ejector condensers (see **illus.**). In all three types the steam and cooling water are mixed in a condensing chamber and withdrawn together. Noncondensable gases are removed separately from the jet condenser, entrained in the cooling water of the ejector condenser, and removed either separately or entrained in the barometric condenser. The jet condenser requires a pump to remove the mixture of condensate and cooling water and a vacuum breaker to avoid accidental flooding. The barometric condenser is self-draining. The ejector condenser converts the energy of high-velocity injection water



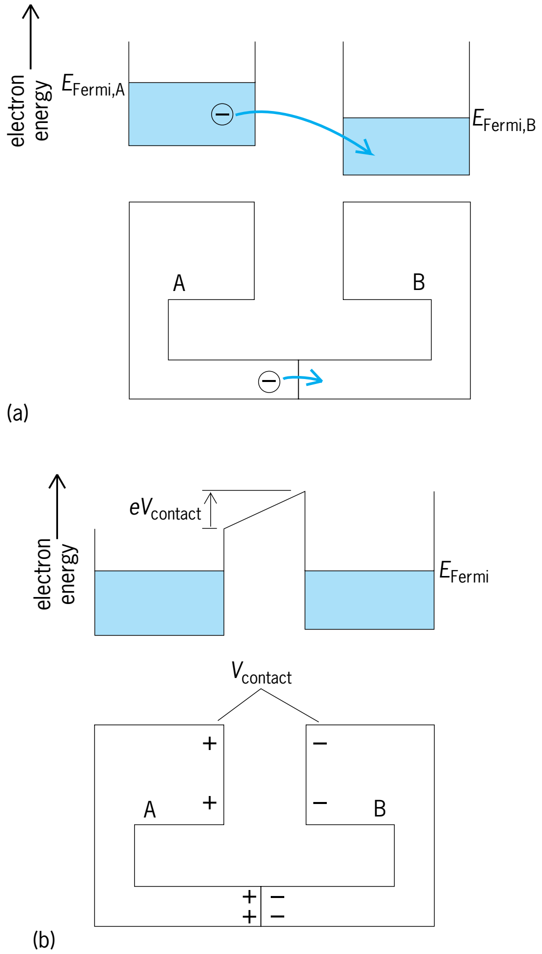
Three basic types of contact condenser: (*a*) low-level jet condenser (*C. H. Wheeler Manufacturing Co.*); (*b*) single-jet ejector condenser; (c) multijet barometric condenser (*Schutte and Koerting Co.*).

to pressure in order to discharge the water, condensate, and noncondensables at atmospheric pressure. *See* VAPOR CONDENSER. Joseph F. Sebald

Contact potential difference

An electrostatic potential that exists between samples of two dissimilar electrically conductive materials (metals or semiconductors with different electron work functions) that have been brought into thermal equilibrium with each other, usually through a physical contact. Although normally measured between two surfaces which are not in contact, this potential is called the contact potential difference. Its origin can be described in terms of the process necessary to bring the samples into equilibrium. Initially it is expected that mobile charge carriers (electrons or holes) will migrate from one sample to the other. If there is a net flow of electrons from material A to material B (see **illus.**), material B will become negatively charged and material A will become positively charged, assuming that they were originally neutral. This process is self limiting because a potential difference between the two samples will develop due to the charge separation and will grow to a value sufficient to stop further motion of the electrons from A to B.

In a metal or a semiconductor, the electrons are distributed in energy such that virtually all of them exist at or below a "sea level" called the Fermi level. When any combination of metals and semiconductors are put into equilibrium with one another, the Fermi levels in all will coincide. The contact potential difference between materials is that value necessary to raise or lower the potential energies of the electrons to produce a common Fermi sea level.



Development of a contact potential as two conductive materials are brought into thermal equilibrium. (*a*) Initial charge transfer. (*b*) Thermal equilibrium. Diagrams show corresponding electron energy distributions. E_{Fermi} = Fermi level; V_{contact} = contact potential difference; e = electron charge.

Since they are then at the same energy, electrons at the Fermi level in either material will have no net force on them, that is, no reason to travel to the other material. Because it causes no net force on the equilibrium distribution of electrons, contact potential difference cannot be directly measured with an ordinary voltmeter. Nevertheless, it profoundly affects the behavior of a number of electronic devices. *See* FREE-ELECTRON THEORY OF METALS; SCHOTTKY BARRIER DIODE; SEMICONDUCTOR; WORK FUNCTION (ELECTRONICS). James E. Nordman

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Continent

A protuberance of the Earth's crustal shell with an area of several million square miles and with sufficient elevation above neighboring depressions (the ocean basins) so that much of it is above sea level.

The term was originally applied to the most extensive continuous land areas of the globe. The great majority of maps now in use imply that the boundaries of continents are their shorelines. From the geological point of view, however, the line of demarcation between a continent and an adjacent ocean basin lies offshore, at distances ranging from a few to several hundred miles, where the gentle slope of the continental shelf changes somewhat abruptly to a steeper declivity. This change occurs at depths ranging from a few to several hundred fathoms (1 fathom = 6 feet) at different places around the periphery of various continents. *See* CONTINENTAL MARGIN.

On such a basis, numerous offshore islands, including the British Isles, Greenland, Borneo, Sumatra, Java, New Guinea, Tasmania, Taiwan (formerly Formosa), Japan, and Sri Lanka (formerly Ceylon), are parts of the nearby continent. Thus, there are six continents: Eurasia (Europe, China, and India are parts of this largest continent), Africa, North America, South America, Australasia (including Australia, Tasmania, and New Guinea), and Antarctica.

All continents have similar structural features but display great variety in detail. Each includes a basement complex (shield) of metamorphosed sedimentary and volcanic rocks of Precambrian age, with associated igneous rocks, mainly granite. Originally formed at considerable depths below the surface, this shield was later exposed by extensive erosion, then largely covered by sediments of Paleozoic, Mesozoic, and Cenozoic age, chiefly marine limestones, shales, and sandstones. In at least one area on each continent, these basement rocks are now at the surface (an example is the Canadian Shield of North America). In some places they have disappeared beneath a sedimentary platform occupying a large fraction of the area of each continent, such as the area in the broad lowland drained by the Mississippi River in the United States. In each continent there are long belts of mountains in which thick masses of sedimentary rocks have been compressed into folds and broken by faults. *See* CONTINENTS, EVOLUTION OF.

Presumably because of the large volume of acidic aluminum-rich granitic rocks beneath the surface of each continent, the velocity of transmission of earthquake vibrations in continental segments of the Earth's crust is slower than in oceanic segments, in which alkaline, iron-rich basaltic rather than granitic rocks are the dominant type. For the same reason the average density of the rocks composing continents is less than that of the rocks beneath the deep-sea floors. *See* EARTHQUAKE.

Continents are the less dense, subaerially exposed portion of the large and not-so-large plates that make up the Earth's lithosphere, or outer shell of rigid rock material. As such, continents together with part of the ocean's floor are intimately joined portions of the lithospheric plates. As plates rip apart and migrate horizontally over the Earth's surface, so too do continents rip apart and migrate, sometimes colliding with other continental segments scores of millions of years later. Mountain systems, such as the Appalachian-Ouachita, the Arbuckle-Wichita, and the Urals systems, are now believed to represent the sutures of former continents attached to their respective plates which collided long ago. The Red Sea and the linear rift-volcano-lakes district of Africa are also believed by many to manifest continental ripping and early continental drifting. Such continental collision and accretion are believed to have occurred throughout most of the Earth's history. *See* AFRICA; ANTARCTICA; ASIA; AUSTRALIA; EARTH, GRAVITY FIELD OF; EUROPE; ISOSTASY; LITHOSPHERE; NORTH AMERICA; PLATE TECTONICS; SEISMOLOGY; SOUTH AMERICA. Donald Lee Johnson

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Continental drift

The concept that the world's continents once formed part of a single mass and have since drifted into their present positions. Although it was outlined by Alfred Wegener in 1912, the idea was not particularly new. Paleontological studies had already demonstrated such strong similarities between the flora and fauna of the southern continents between 300,000,000 and 150,000,000 years ago that a huge supercontinent, Gondwana, containing South America, Africa, India, Australia, and Antarctica, had been proposed. However, Gondwana was thought to be the southern continents linked by land bridges, rather than contiguous units.

Wegener's ideas were almost universally rejected at a meeting of the American Association of Petroleum Geologists in 1928. His evidence and timing were undoubtedly wrong in many instances, and only a few scientists accepted his general concepts and remained sympathetic to the ideas. The fundamental objection was the lack of a suitable mechanism. Studies of the passage of earthquake waves through the Earth had shown that, whereas the core is liquid, the Earth's mantle and crust are solid. It was therefore difficult to find sufficient force to move the continents through the mantle and oceanic crust, and even more difficult to picture them moving without leaving obvious evidence of their passage.

Almost simultaneously with the temporary eclipse of Wegener's theory, Arthur Holmes was considering a mechanism that is still widely accepted. With the knowledge that radioactive minerals occurring within the Earth could result in an internal zone of slippage, Holmes conceived the idea of convective currents within the Earth's mantle which were driven by the radiogenic heat produced by radioactive minerals within the mantle. Since the rates of motion were slow, but vast and inexorable, the Earth appeared solid to the rapid passage of seismic waves, but behaved plastically to such slow motions. This accounted for the apparent discrepancy between the seismic observations and the drift of continents. At that time, Holmes's ideas, like those of Wegener, were largely ignored, as it was no longer thought that continental drift was worthy of further consideration. Nonetheless, several geologists, particularly those living in the Southern Hemisphere, continued to believe the theory and accumulate more data in its support, particularly from the study of the similarities in fossils and rock types on now separated continents.

By the 1950s, convincing evidence had accumulated, with studies of the magnetization of rocks, paleomagnetism, beginning to provide numerical parameters on the past latitude and orientation of the continental blocks. Early work in North America and Europe clearly indicated how these continents had once been contiguous and had since separated. The discovery of the mid-oceanic ridge system also provided more evidence for the geometric matching of continental edges, but the discovery of magnetic anomalies parallel to these ridges and their interpretation in terms of sea-floor spreading finally led to almost universal acceptance of continental drift as a reality. In the 1970s and 1980s, the interest changed from proving the reality of the concept to applying it to the geologic record, leading to a greater understanding of how the Earth has evolved through time. The fundamental change in concept was that not only have the continents drifted, but the continents are merely parts of thicker tectonic plates, comprising both oceanic and continental crust, with 50–300 km (31–186 mi) of the Earth's mantle moving along with them. *See* CONTINENTS, EVOLUTION OF; EARTH, CONVECTION IN; PALEOMAGNETISM; PLATE TECTONICS; GEODYNAMICS.

D. H. Tarling

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Continental margin

The submerged portions of the continental masses on crustal plates, including the continental shelf, the continental slope, and the continental rise. All continental masses have some continental margin, but there is great variety in the size, shape, and geology depending upon the tectonic setting.

The most common settings are the trailing-edge margin and the leading-edge margin. The former is associated with tectonic stability, as exemplified by the Atlantic side of the North American landmass (**Fig. 1**). Here the margin is wide and geologically relatively uncomplicated, with thick sequences of coastal plain to shallow marine strata dipping slightly toward the ocean basin. By contrast, the leading-edge margin (for example, the Pacific side of the United States) is narrow, rugged, and geologically complicated. The global distribution of these widespread continental margin types is controlled by the plate tectonic setting in which the landmass resides. Some major landmasses, such as Australia, are surrounded by wide margins, but most, such as North and South America, have some of both types. *See* PLATE TECTONICS.

Any consideration of the continental margin must include a general understanding of global seal-level history over the past few million years. As glaciers expanded greatly just over 2 million years ago, sea level was lowered more than 300 ft (100 m). The cyclic growth and decay of glaciers during this period caused the shoreline to move from near its present position to near the edge of the present continental shelf on multiple occasions. These sea-level changes had a profound effect on the entire continental margin, particularly the shelf and the rise. During times of glacial advance, the coast was near the shelf edge, causing large volumes of river-borne sediment to flow down the continental slope and pile up on the rise; deltas were poorly developed for lack of place for sediment to accumulate. During times of high sea-level stand similar to the present time, little sediment crossed the shelf and large volumes of riverine sediment accumulated in large fluvial deltas. *See* DELTA.

Continental shelf. This part of the margin is simply an extension of the adjacent landmass. It is characterized by a gentle slope and little relief except for shelf valleys (Fig. 1), which are old rivers that were active during times of low sea level. Because of the great variability in the depth, width, and gradient, it is misleading to give average values for these characteristics. The width ranges from a few kilometers to hundreds of kilometers, with the Florida peninsula being a good example of both. The Atlantic shelf is very narrow, and the Gulf side is very wide. The gradient also ranges, generally between 6 and 22 ft/mi (1 and 4 m/km); it is so gentle that it would not be possible for a person walking over it to detect a change. The outer limit of the shelf shows a distinct change in gradient to the much steeper slope. This change may occur at depths of less than 300 ft (100 m) or up to nearly 1000 ft (300 m).

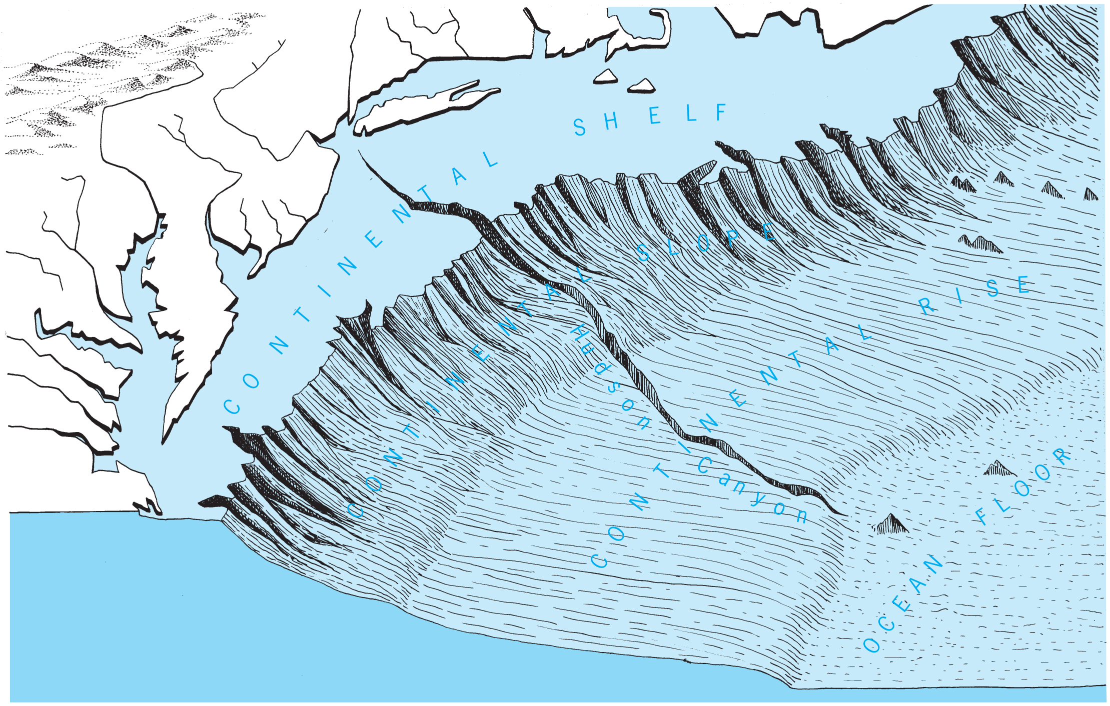

Fig. 1. Continental margin off the northeastern United States.

Unfortunately, legal definitions typically use depth limits to define the shelf for economic purposes without paying attention to the geologic or geomorphic boundaries. The shelf environment may include complete seas, such as the North Sea between Great Britain and Europe.

The modern continental shelf is covered with a combination of Holocene sediments that were deposited as sea level rose over the last 18,000 years, when the last extensive glaciers melted, and older sediments that have yet to be covered. The outer one-half to two-thirds of the shelf has relict sediments that were deposited in coastal environments when sea level was lower, and that were drowned without being buried when sea level rose rapidly in the early Holocene. Intense storms and burrowing organisms can rework these outer shelf sediments into palimpsest sediments. The inner shelf is covered with Holocene sand and mud in thicknesses that vary depending upon sediment flux from the adjacent continent. The shelf also supports an abundant and diverse benthic community that includes both epifauna and infauna. The numerous grazers, burrowers, and filter feeders rework sediment and extract it from suspension. Fecal pellets are a significant part of continental sediments. *See* HOLOCENE; MARINE SEDIMENTS.

Continental slope and rise. The outer continental margin includes the relatively steep slope and the rise that accumulates at the base of the slope (Fig. 1). This continental material has the same general composition as the landmass. Although the slope is steep relative to the shelf and rise, it has an average gradient of only about 4.5° but the range is from less than 2° to more that 40°. The very gentle gradients are areas of large deltas or fans, and the steep ones are associated with faulted margins. The gradient of the continental rise is generally less than 1°. The slope is dissected by numerous deep and steep-sided submarine canyons. These canyons are conduits for sediment transported in various sediment gravity modes to the continental rise. Some have continuations across the shelf where former rivers were located during low stands of sea level. These canyons may also extend across at least part of the rise. During low stands of sea level the rise received great quantities of sediment in rapid rates of accumulation as rivers dumped their loads near the shelf-slope break, whereas sediment supply is now relatively slow. *See* FAULT AND FAULT STRUCTURES; SUBMARINE CANYON.

The sediments carried by sediment gravity processes have a wide range in grain size, from mud to gravel. They accumulated in strata with a wide range of thickness, partly related to their grain size and partly to the volume of sediment introduced. Most of these units display graded bedding, a decreasing-upward grain-size trend.

In addition to sediment gravity processes supplying sediment to the slope and particularly to the continental rise, there are two other sources of sediments for these areas. Contour currents that flow parallel to bathymetric contours carry and deposit sediment along the outer continental margin. These contourites may be hundreds of meters thick. The other sediment supplied to this region is in the form of the tests of planktonic organisms that fall through the water column and accumulate slowly. They include both calcium carbonate (calcite and aragonite) from foraminifera and coccolithophores, and silicon dioxide (opal) from diatoms and radiolaria.

Continental borderland. The leading-edge continental margin that is commonly associated with a crustal plate boundary displays a very different geology, geomorphology, and bathymetry than the outer continental margin. In this type there is no distinct shelf, slope, and rise. Like the trailing-edge margin, the leading-edge margin exhibits the same characteristics as the adjacent landmass, in this case a structurally complex geology with numerous fault basins and high relief. The borderland is narrow and overall steep. Its geomorphology consists of numerous local basins that receive sediment through numerous submarine canyons. The canyons commonly extend nearly to the beach; there is no shelf as such. Because much of the sediment is trapped in these basins, there is only a modest rise accumulation adjacent to the ocean floor. The best example of this type of continental margin is adjacent to southern California (**Fig. 2**), where dozens of fault-bounded basins exist. These basins range from being essentially filled with sediment to having considerable accommodation space.

Resources. The continental margin contains a vast amount and array of natural resources, most of which are being harvested. The primary fishing grounds around the globe are in shelf waters. The Grand Banks off northeastern North America and the North Sea adjacent to Europe are among the most heavily fished. There are also many mineral resources that are taken from shelf sediments, including heavy minerals that are sources of titanium, phosphate, and even placer gold. Important commodities such as sand, gravel, and shell are also taken in large quantities from the inner shelf. Salt domes that underlie the shelf, especially in the northern Gulf of Mexico, provide salt and sulfur.

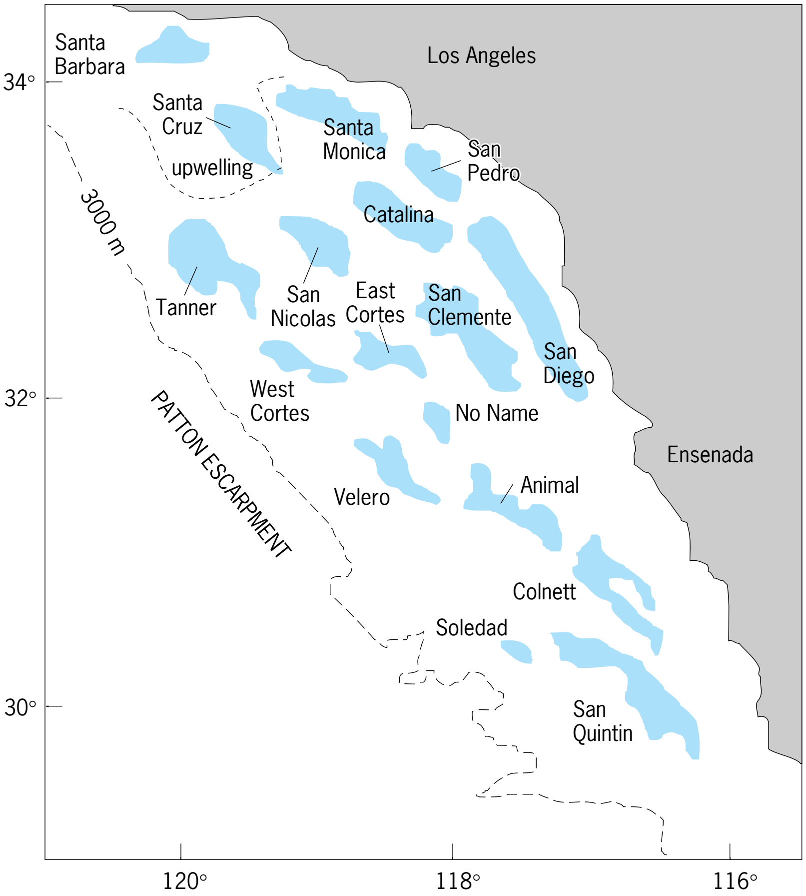

Fig. 2. California continental borderland, showing the outlines of the major basins. Upwelling is centered in the area south of the northern Channel Islands and extends south to 33°N latitude. (*After D. S. Gorsline, J. Sediment. Petrol., 48:1056, 1978*)

Probably the most important resource obtained from the continental margin is petroleum, in the form of both oil and gas. Production is extremely high in some places, ranging from the deltas at the coast across the entire shelf and onto the outer margin, and reserves are high. *See* MARINE GEOLOGY; OIL AND GAS, OFFSHORE.

Richard A. Davis, Jr.

Shelf circulation. Shelf circulation is the pattern of flow over continental shelves. An important part of this pattern is any exchange of water with the deep ocean across the shelf-break and with estuaries or marginal seas at the coast. The circulation transports and distributes materials dissolved or suspended in the water, such as nutrients for marine life, freshwater and fine sediments originating in rivers, and domestic and industrial waste.

Water movements over continental shelves include tidal motions, wind-driven currents, and long-term mean circulation. Tidal currents reverse every half tidal cycle (about 6 h for the usually dominant semidiurnal tide), and water particles undergo back-and-forth excursions due to tides amounting to a few miles. Storms generate currents which persist typically for several days and lead to particle excursions of tens of kilometers. A pattern of long-term mean circulation is characteristic of each major subdivision of the continental shelves. Off the North American east coast, for example, the region of the shelf between the Grand Banks of Newfoundland and Cape Hatteras is characterized by a persistent southwestward drift, always present over the outer portions of the shelf (in water at least 150 ft or 50 m deep). The mean shelf circulation in this area is one leg of a larger oceanic gyre lying offshore (**Fig. 3**). Water particles are eventually swept off the shelf and into a deepwater current adjacent to the Gulf Stream. The coupling of shelf circulation to a more massive deep-ocean boundary current is tighter in some other locations, for example in the South Atlantic Bight, where the Gulf Stream controls outer shelf flow. Along the west coast of North America, the seasonally changing upwelling-downwelling regime is coupled to the weaker boundary currents along the eastern margin of the Pacific Ocean. *See* GULF STREAM.

Important for the exchange of water between a shelf region and the deep ocean are differences in motion between surface and bottom layers. At the ocean surface, the wind is a dominant influence, while at depths greater than about 30 ft (10 m) internal forces determine the intensity and direction of motion. In the east coast example discussed above, the surface layers move significantly offshore over the long term, a consequence of westerly winds, in addition to their general southwestward drift. Over shorter periods they move in whatever direction the wind carries them. The bottom layers move shoreward, to replace the water driven offshore by the wind, transporting saltier, nutrient-rich water from the deep ocean onto the shelf.

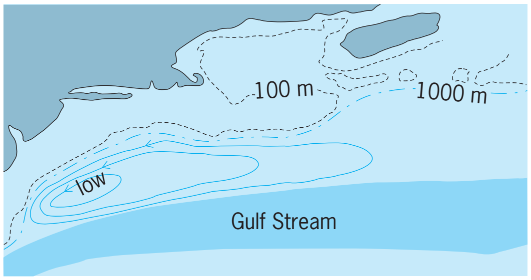

Fig. 3. Deepwater gyre between the Gulf Stream and the North American continent, influencing continental shelf circulation. Georges Bank is at the center of the illustration, separating the Gulf of Maine from deep water, and is subject to intense tidal flow. 1 m = 3.3 ft.

Tidal currents are mainly important for shelf circulation on account of the mixing they cause. While tidal currents are typically 0.6 ft/s (0.2 m/s) in amplitude, they are much stronger in some locations where shallow depth constricts the flow, for example, over Georges Bank where tidal currents are up to 3 ft/s (1 m/s). Currents of this intensity cause strong bottom friction, turbulence, and mixing. Tides on continental shelves are not caused directly by the pull of the Moon and Sun, but propagate in from the deep ocean, where the gravitational attraction of the heavenly bodies acts over a much larger water mass.

The inflow of fresh water from land also contributes to shelf circulation, because such water would tend to spread out on the surface on account of its low density. Rapid nearshore mixing reduces the density contrast, and the Earth's rotation deflects the offshore flow into a shore-parallel direction, leaving the coast to the right. A compensating shoreward flow at depth is deflected in the opposite direction, adding to the complexity of shelf circulation. *See* NEARSHORE PROCESSES; OCEAN CIRCULATION.

G. T. Csanady

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Continents, evolution of

The process that led to the formation of the continents. The Earth's crust is distinctively bimodal in thickness. Oceanic crust is normally about 4 mi (7 km) thick, varying mainly with the temperature of the mantle beneath the sea-floor spreading ridges when the crust was formed. In contrast, the typical 22–25-mi (35–40-km) thickness of continental crust is controlled ultimately—through the agents of erosion, sedimentation, and isostatic adjustment—by sea level. Oceanic crust is formed at spreading ridges, continental crust at subduction zones. Both are recycled to the mantle, but oceanic crust, being less buoyant, is recycled about 30 times faster than continental crust. Consequently, continents, having a mean age of almost 2 billion years and a maximum age of 4 billion years, provide the only directly accessible record spanning most of Earth history. They are, however, structurally more complex than ocean basins because of their great antiquity and weak rheology. *See* EARTH CRUST; MID-OCEANIC RIDGE.

Constructive processes. Subduction zones are the main factories for making continental crust (**Fig. 1**). The primary constructive processes are trench accretion, arc magmatism, and arc-continent collision. Mantle plumes and lithospheric stretching cause secondary magmatic additions to continental crust. *See* LITHOSPHERE; MAGMA; SUBDUCTION ZONES.

Trench accretion. Where an oceanic plate sinks beneath a continental plate or another oceanic plate, sediment scraped off the top of the descending plate accumulates as an accretionary prism at the leading edge of the overriding plate (Fig. 1). Accretionary prisms are bounded by trenches on one side and fore-arc basins on the other. They are best developed at trenches containing thick accumulations of terrigenous sediment, where the off-scraping process is facilitated by high fluid pore pressures in the sediment. Accretionary prisms may also contain slices of pelagic ooze and underlying oceanic crust, volcanic seamounts and their capping atoll reefs, or far-traveled deep-sea fans. They are typically dismembered: accretion does not proceed smoothly because the top of the descending plate is subject to block faulting related to the bending of the plate. The accreted material is dewatered, deformed, and metamorphosed as the accretionary prism grows. Accretionary prisms are rarely active magmatically. Where they intersect spreading ridges, the descending oceanic crust may be hot enough to partially melt at relatively shallow depths. A distinctive suite of sodic granitoid intrusive rocks record such events. Trench accretion is dominantly a process of crustal reworking, not crustal growth, because the bulk of the sediment is derived from the erosion of preexisting crust. *See* ATOLL; REEF.

Arc magmatism. A volcanic arc is a surface manifestation of partial melting near the tip of the mantle wedge above the subducting slab (Fig. 1). Melting in the wedge is induced by the infiltration of aqueous fluids, which lower the temperature required for melting to begin (hydration melting). The fluids are derived from the breakdown of hydrous minerals associated with the subducting oceanic crust. Depth-dependent release of water controls the location of the volcanic front facing the trench, typically 60–70 mi (100–120 km) vertically above the slab. A fertile source of melting in the mantle wedge is maintained by convective flow driven by the viscous drag of the cold descending slab. Although the main source of arc magmas is the mantle wedge, sediment and ablated crust entrained in the slab make subordinate contributions to arc magmas. The

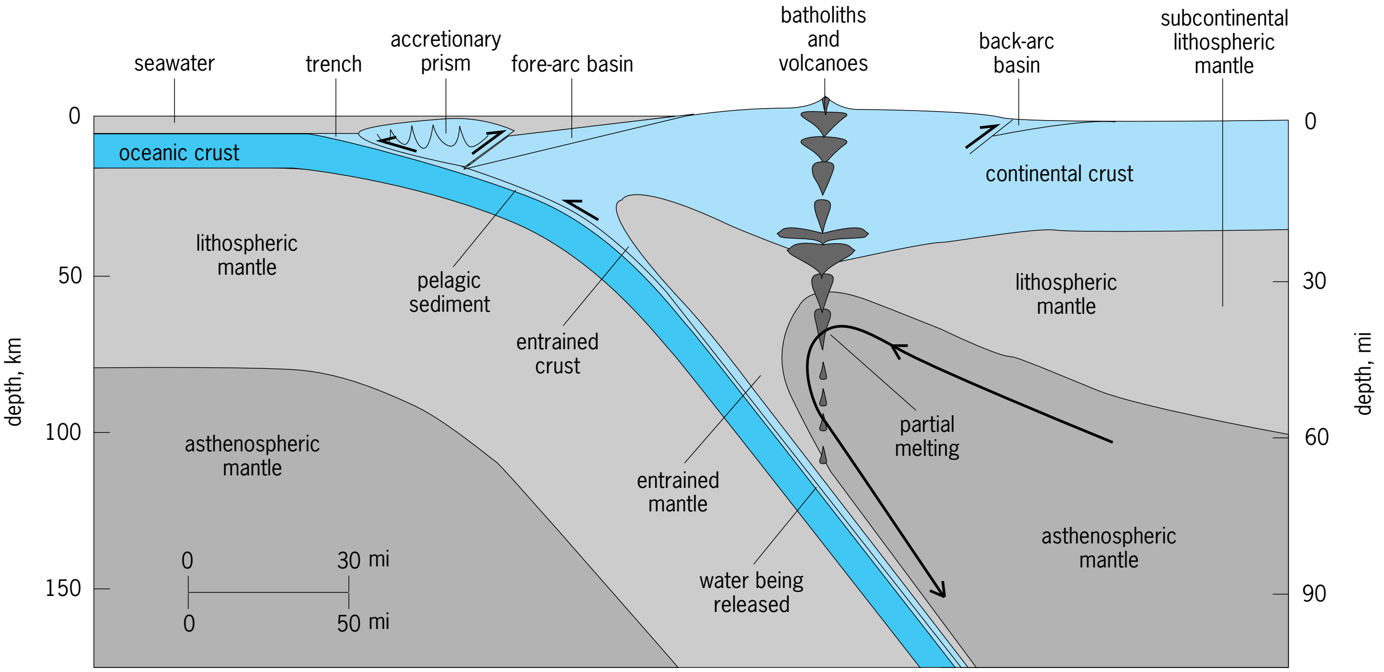

Fig. 1. Recycling of continental crust at a subduction zone. Arrows show direction of movement.

mantle-derived fraction represents new crustal addition. The slab-derived melts serve to speed up (fast-track) the mantle recycling process.

Unlike mid-ocean ridges, magmatic arcs evolve with time because the supply of magma is not balanced by crustal spreading. The crust of volcanic arcs thickens through the addition of new magma. Consequently, the compositions of the magmas evolve as the height of the mantle melting column decreases and the filtering effect of the overlying crust increases. The filtering effect causes crustal differentiation with more buoyantly mobile components concentrating upward. Denser and more refractory components collect in the lower crust. The magmas ingest and assimilate wall rocks and interact with meteoric ground waters, producing hybrid, compositionally diverse, igneous rock suites. Moreover, magmatic arcs are usually the rheologically weakest part of the lithosphere in subduction zones because of their high heat flow. Consequently, they localize tectonic deformation, which generally combines wrenching parallel to the trench (driven by oblique subduction) and extension or compression across the arc (governed by changes in buoyancy of the subducting slab or motion of the upper plate). *See* IGNEOUS ROCKS.

Collisions. Where subduction occurs beneath continental lithosphere, trench accretion and arc magmatism add crust to the continent directly. Continental-type protocrust is also formed at subduction zones (often having complex developmental histories) situated entirely within oceanic lithosphere. Incorporation of such protocrust in a continent is accomplished by arc-continent collision (**Fig. 2**). The reversal of subduction polarity that typically follows arc-continent collision (best exemplified in the modern world by the diachronous collision—a collision progressing from north to south with time—at Taiwan between the Luzon arc of the Philippines and southeast China) is the principal means by which subduction beneath a continent is initiated.

Final closure of an ocean basin results in continent-continent collision, a mainly destructive event. Tectonic crustal thickening produces mountains and greatly accelerated rates of erosion. Much of the resulting sediment is washed off the continent onto deep-sea fans or trenches, and some fraction of that sediment will be subducted. Small crustal gains may be made if the tectonically thickened lithospheric mantle becomes unstable and sinks away. The hotter replacement mantle may partially melt as it rises to take its place (decompression melting), causing small magmatic additions to the already thickened continental crust. *See* BASIN; OROGENY.

Plumes and rifts. Plumes are jets of anomalously hot mantle that partially melts as it reaches the lithosphere, causing the volcanism of Hawaiian-type islands and related seamount chains. Plumes also cause volcanism on continents, for example, Yellowstone in North America. Starting plumes have large heads and relatively small tails through which the plume is maintained. The arrival of starting plume heads at the lithosphere is signaled by continental flood basalt or oceanic plateau volcanism. The largest volumes of melt are generated where lithospheric stretching (upper crustal rifting) occurs in conjunction with a plume. The combination maximizes the potential for decompression melting. In addition to surface volcanism, the melts may pond at or near the base of the crust, causing magmatic underplating. Seamounts and oceanic plateaus are fragmentarily accreted to continents at trenches. *See* BASALT; OCEANIC ISLANDS; SEAMOUNT AND GUYOT; VOLCANOLOGY.

Destructive processes. Subduction zones are sites of continental accretion, but they may also cause

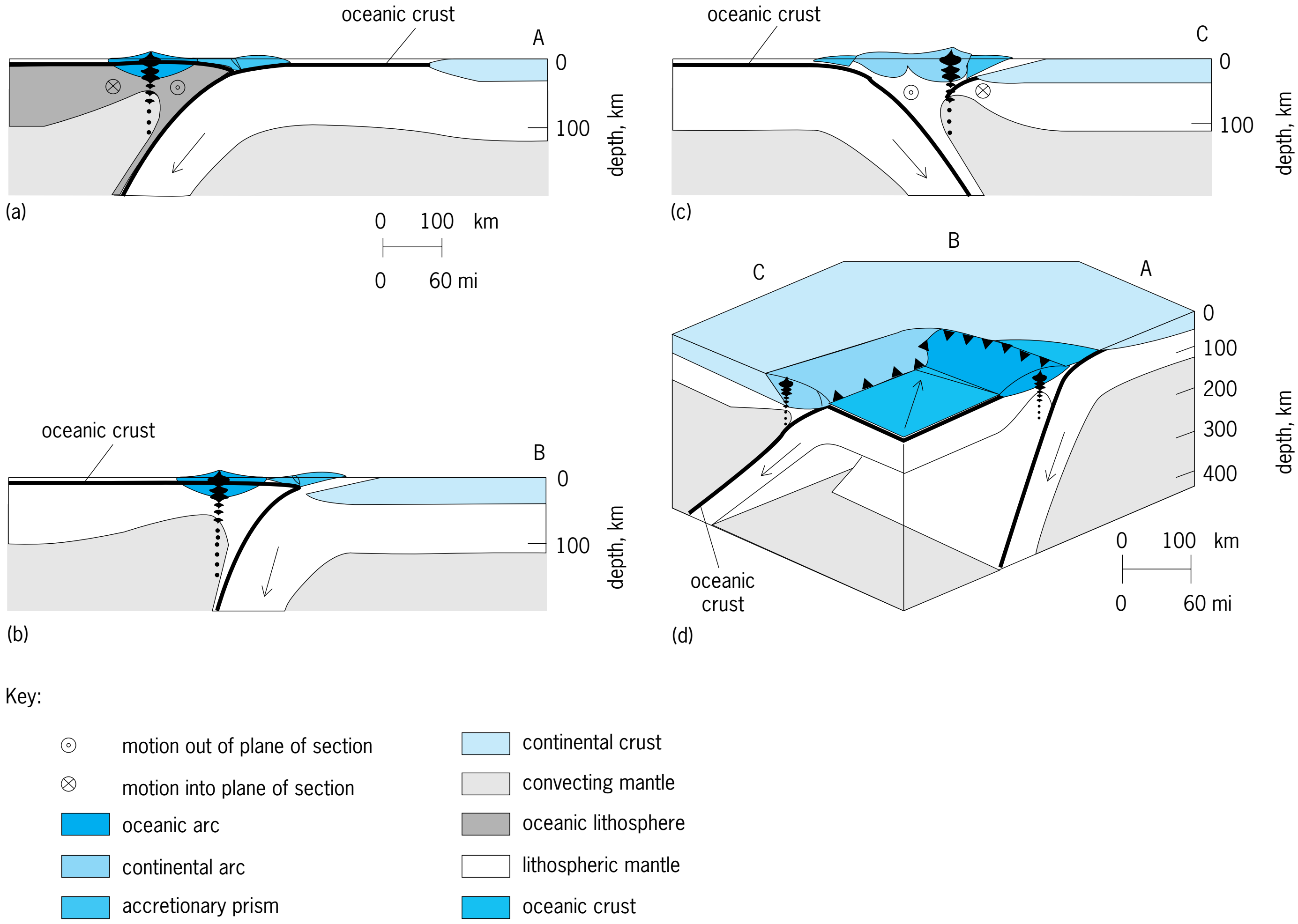

Fig. 2. **Stages of an arc-continent collision; arrows give direction of lithospheric movement. (*a*) Passive continental margin converging with an oceanic arc. (*b*) Arc colliding with continent. (*c*) Subduction polarity reversed and continental arc established. (*d*) General diachrony of the collision.**

destruction of continental crust (Fig. 1). The destructive processes are sediment subduction and subduction ablation. Constructive and destructive processes may be at work simultaneously, and the net balance may swing one way or the other with time. Selective destruction of lower crust may occur in continent-continent collision zones as a result of convective dripping of tectonically thickened lithosphere.

Sediment subduction. Accretionary prisms are poorly developed or lacking where trenches receive only very sparse amounts of terrigenous sediment. In such cases, pelagic oozes are subducted along with the oceanic crust. Even at subduction zones with well-developed accretionary prisms, some of the pelagic and terrigenous sediments disappears beneath the deformation front of the prism. Some is accreted structurally to the base of the prism, and some is transferred to the magmatic arc by melting. Some escapes melting and sinks deeply into the mantle, where it constitutes an isotopically recognizable component in the source of plume basalts. Sediment subduction, being fed by surface erosion, preferentially destroys the upper crust.

Subduction ablation. It is postulated that crust and lithospheric mantle from the overriding plate may become entrained in the subducting slab, causing tectonic ablation. Like subducted sediment, ablated crust is potentially capable of melting as it passes beneath the convecting mantle wedge. Unlike subducted sediment, ablated material may include lower crust and lithospheric mantle as well as upper crust. The ablation flux is quantitatively unknown.

Continental drip. Where continental lithosphere is tectonically thickened, cold lithospheric mantle is forced downward into hotter convecting mantle. Lithospheric thickening generates lateral thermal gradients, which drive mantle convection. The thickened lithospheric mantle is therefore unstable and may drip away. The missing lithospheric mantle is replaced by hotter asthenospheric mantle, causing melting and surface uplift. Lower crust may be entrained in the drip if it has been transformed to eclogite (a high-density rock chemically equivalent to basalt but composed of garnet and pyroxene) under the load of the tectonically thickened crust. Unlike sediment subduction, upper crust is not lost by dripping; and unlike subduction ablation, continental drips are not susceptible to hydration melting. Drips may sink deeply into the mantle; this view is based on the recognition of distinctive chemical and isotopic signatures of subcontinental lithospheric mantle in plume basalts. *See* ASTHENOSPHERE; ECLOGITE.

Continents and Earth history. The oldest surviving crust on Earth was formed 4 billion years ago. The absence of crust older than 4 billion years is attributed to recycling associated with the early high-impact flux inferred from the dated cratered surface of the Moon. Since the impact flux waned, processes that construct and destroy continental crust have adjusted to slow cooling and convective slowing of the mantle. The estimated magnitude of the secular change in mean upper-mantle temperature since 4 billion years ago is on the order of 360°F (200°C). This is comparable in magnitude to regional temperature variations in the upper mantle at the present time. In effect, mantle plumes in the present simulate more general conditions that prevailed in the early Earth. Furthermore, processes limited to the earlier or later parts of Earth history should be only those that operate in anomalous situations. This reasoning is consistent with empirical comparisons of continental crust of different ages. The basic forms and scales of continental accretion as well as those of continental fragmentation and collision appear to have changed remarkably little over geologic time. *See* MOON.

Oldest crustal relics. Areas of crust between 3.5 and 4 billion years old are small (less than 390 mi^2 or 1000 km^2), and there is nothing extraordinary about the rock suites they contain. Their isotopic characteristics and variability are striking. They show that the contemporaneous mantle was very heterogeneous, containing different sectors strongly depleted in some crustal components and strongly enriched in others. The crust was also heterogeneous and included sectors having long crustal residence times (greater than 200 million years) as well as newly formed sectors. These observations suggest that abundant continental-type crust already existed and that it was subject to vigorous recycling. However, these inferences are widely disputed. *See* ROCK AGE DETERMINATION.

Early juvenile crust. Juvenile crust, in a strict temporal sense, is continental crust recently separated from the mantle. In the broader nontemporal sense used here, it is continental crust not strongly modified by postaccretionary tectonism. Coherent areas up to 1550 mi (2500 km) in diameter of juvenile crust older than 2 billion years are exposed in Precambrian shields. Although rocks and structures typical of accretionary prisms, magmatic arcs, and fore-arc and back-arc basins abound, some systematic differences in comparison with geological younger juvenile crust are evident. The relative abundance of certain sodic granitoid suites in old shields implies a secular decline in the importance of slab (crustal) melting relative to wedge (mantle) melting in subduction zones. Komatiites (extremely hot, magnesium-rich, lava flows) are essentially confined to old shields and are interpreted as representing mantle-plume volcanism in the early Earth. Conversely, blueschists (rocks metamorphosed at high pressure and low temperature) are unknown in old shields. They are products of extremely rapid burial and exhumation in subduction zones having severely depressed geothermal gradients. Blueschists could not have survived even slightly increased geothermal gradients. These and other observations are consistent with the estimated cooling of the Earth and consequent adjustments in the tectonic regime. *See* BLUESCHIST; PRECAMBRIAN.

Cratons and mantle roots. Areas of juvenile crust older than about 2 billion years tend to be rheologically stiffer than younger areas. Such strong blocks are called cratons. Most have survived several rounds of continental fragmentation and collision, their margins battered by repeated openings and closing of ocean basins. Mantle tomography (three-dimensional mantle thermal structure inferred from velocity variations of earthquake-generated seismic waves) shows that cratons are underlain by anomalously cold mantle corresponding to lithosphere more than twice the approximately 60-mi (100-km) thickness of mature oceanic or noncratonic continental lithosphere. The mantle roots must be chemically distinct because, given that cratons tend to have neutral or even positive buoyancy, a low intrinsic density is required to offset the density increase due to thermal contraction. *See* COMPUTERIZED TOMOGRAPHY; CONTINENTAL MARGIN.

Conveniently, rock samples of mantle roots (peridotites) have been delivered to the surface as inclusions in diamond-bearing subvolcanic pipes. The inclusions have appropriate densities and are composed of residual mantle material from which high degrees of partial melt were driven. A class of associated inclusions, called eclogites, consists of rocks corresponding compositionally to oceanic crust but metamorphosed under mantle depth conditions. Isotopic studies reveal that the eclogite inclusions are samples of ancient oceanic crust subducted billions of years ago to depths exceeding 90 mi [150 km (into the diamond stability field)]. There they remained, fixed within drifting lithospheric plates, until fired volcanically to the surface in relatively recent times. If the peridotite and eclogite inclusions are cogenetic, the former should also have originated at seafloor spreading ridges billions of years ago. *See* DIAMOND; PERIDOTITE.

When the Earth was hotter, greater degrees of melting at oceanic spreading ridges (comparable to modern spreading ridges situated above mantle plumes, for example, Iceland) would have generated oceanic lithosphere characterized by thick (greater than 12 mi or 20 km) crust and highly depleted mantle. Such lithosphere might not sink deeply upon subduction because of the buoyancy of the thick crust and because the removal of melt actually lowers the density of the residual mantle. Accordingly, it is postulated that cratonic mantle roots are composed of buoyantly subducted slabs of highly depleted oceanic lithosphere. The presence of mantle roots would have increased the survivability of cratons: they would have been less susceptible to tectonic thickening and destruction by sediment subduction. Therefore, noncratonic continents may have existed on the young Earth but were selectively destroyed.

Continental growth. The mean age of extant continental crust is about 2 billion years. The primary mode in crustal abundance by geologic age is at 2.7 billion years, and perhaps half of all extant crust formed between 1.5 and 3 billion years ago. The conventional interpretation is that there was little continental crust following the period of high impact flux and that continental growth was slow at first, then rose to a peak 2–3 billion years ago, after which it slowly tapered off. An alternative interpretation, however, holds that the volume of continental crust has been in a near steady state since the impact flux waned. The present age distribution is explained by assuming a secular decline in the rate of crustal recycling, presumably modulated by the decreasing vigor of mantle convection as the Earth cooled. The difference in interpretation hinges on the importance assigned to recycling of continental crust. In crustal growth models, there is little crust older than 3 billion years, because little was formed. In steady-state models, much crust was formed early on but little of it survives. The steady-state interpretation is consistent with isotopic data showing that the oldest crustal relics contain highly evolved as well as juvenile components, and that the contemporaneous mantle was also heterogeneous and included strongly depleted regions. Furthermore, the near steady-state alternative is supported by comparative planetology, which indicates that for the hot young mantle not to be thoroughly differentiated by near-surface melting is physically implausible. *See* CONTINENTAL DRIFT; EARTH; EARTH, AGE OF; EARTH, CONVECTION IN; FAULT AND FAULT STRUCTURES; GEOPHYSICS; MARINE GEOLOGY; PLATE TECTONICS; SEISMOLOGY. Paul Hoffman

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Continuous-wave radar

A radar in which the transmitter output is uninterrupted, in contrast to pulse radar, where the output consists of short pulses. Among the advantages of continuous-wave (CW) radar is its ability to measure velocity with extreme accuracy by means of the Doppler shift in the frequency of the echo. The detected, reflected wave is shifted in frequency by an amount which is a function of the relative velocity between the target and the transmitter-receiver. Range data are extracted from the change in Doppler frequency with time. *See* DOPPLER RADAR.

In order to measure the range of targets, some form of frequency modulation (FM) of the continuous-wave output must be used. In one very effective form of modulation, the carrier frequency of the transmitted signal is varied at a uniform rate. Range is determined by comparing the frequency of the echo with that of the transmitter, the difference being proportional to the range of the target that produced the echo. Systems in which this is done are known as FM-CW radars. *See* FREQUENCY MODULATION.

A modified form of FM-CW radar employs long, but not continuous, transmission. This might be regarded as the same as transmitting extremely long pulses on an FM carrier. Systems of this type are referred to as pulse compression radars.

An FM-CW radar used in the radio-proximity fuses of missiles generates functions of the Doppler signal envelope that have identifiable characteristics at certain ranges. The amplitude of the received FM-CW signal is used to determine when the missile has attained the proper altitude. Then the generated functions tell when the missile has arrived at the desired point of burst. Three triangular-wave modulators can be used to enhance the accuracy of an FM-CW radar fusing system.

In advanced short-range air defense radar (ASHORAD) a coded continuous-wave signal reflected from the target is fed to a tapped delay line, where a predetermined delay between adjacent taps is used to establish the range.

Design objectives. Design objectives for continuous-wave radar include protecting the receiver from the transmitter output and close-by return echoes when a single antenna is used; resolving side-lobe ambiguity; resolving range ambiguity; distinguishing between approaching and receding targets; eliminating noise and clutter; simultaneously measuring both target range and velocity; determining the shapes of targets; handling multiple targets; measuring target acceleration; communicating with targets; and increasing the received signal-to-noise ratio.

Receiver protection. One disadvantage of continuous—wave radar is that when a single antenna is used for both reception and transmission it is difficult to protect the receiver against the transmitter because, in contrast to pulse radar, both are on all the time. Use of isolation circuitry gives the receiver protection from a transmitter output up to 200 W. Use of magnetically biased yttrium-iron-garnet (YIG) provides three tuned, tandem-connected power-limiter stages in one X-band FM-CW radar. *See* FERRIMAGNETIC GARNETS.

In continuous-wave surveillance radars where wide bandwidth is required to meet range and range-rate measurement requirements despite clutter and other interfering environments, the transmitter output can be coded by pseudorandom binary signals that vary with range. This is an ideal waveform for permitting range measurements, retaining a capability for range-rate measurements, and rejecting the transmitter output and other nearby echoes.

Side-lobe ambiguity. The problem of distinguishing between echoes from the main lobe and those from the side lobes has been addressed by providing a demodulated range response that has one polarity for the main-lobe echoes and the opposite polarity for side-lobe echoes.

Side-lobe ambiguity is removed in an FM-CW radar fusing system in which the reflected signal is compared with a sample of the continuous-wave output in a pair of FM discriminators displaced from each other in the frequency domain. Thresholding circuits determine in which half of which discriminator the difference frequency signal is concentrated.

Side-lobe ambiguity in the range response of an FM-CW radar can be resolved when a periodic modulation frequency is reflected from a target and combined with a sample of the transmitted signal. Selected harmonics of the combination signal are processed to develop a main-lobe response of one polarity with all side lobes of the opposite polarity.

Range ambiguity. This ambiguity results from reception of echoes from targets beyond the range of interest and of second-time-around echoes. It can be resolved by range gates that make the radar insensitive to targets beyond the range of interest or by filters that put limits on range. Resolution of range ambiguity is very important in radars for personnel surveillance.

Directional ambiguity. To distinguish between approaching and receding targets, a continuous wave beamed by a radar is sampled continuously but delivers an output voltage only when the distance to the target is changing significantly. The voltage is positive if the target is closing, and negative if it is receding.

Noise and clutter. Suppression of noise, clutter, chaff, and jamming has received a great deal of attention. In one approach, a fixed pair of amplitude-modulation (AM) sidebands is added and used to null out the noise.

Echo signal analyzers can be selectively adjusted for a certain moving-target size so that small targets are not detected. A series of digital range cells can be defined such that each cell represents the minimum allowable distance between two reflective points on a target. The radar also can be adaptively adjusted to attend to a desired average signal level.

Use of digitally controlled voltage-tunable radio-frequency generators permits frequency jumping to avoid jamming or spoofing. Pseudorandom-noise-modulated continuous-wave radar can be used to establish perimeter surveillance in a heavily foliaged environment. Pseudorandomly coded continuous-wave radar can also be used to detect targets in the presence of clutter. *See* ELECTRICAL NOISE; ELECTRONIC WARFARE.

Range and velocity sensing. Several techniques are used to obtain simultaneous measurements of range and velocity. One involves transmitting sidebands of linearly increasing and decreasing frequency or using triangular modulation, and comparing the difference between transmitted and received frequencies with the difference between the received frequency and the transmitted frequency delayed by a period of time proportional to the range of the target. Phase-shift keying by a pseudorandom code also permits simultaneous measurement of range and velocity. *See* MODULATION.

A double-sideband linear FM radar obtains simultaneous range and Doppler measurements. Waveforms of both increasing and decreasing frequency are transmitted simultaneously and combined coherently to give an output that is a measure of the target's radial velocity. The received signals are processed separately to obtain range information.

Target shape. Millimeter-wave FM-CW radar can be used to determine the shape of a target. These radars operate at frequencies in excess of 90 GHz. They often use Gunn oscillators as the source. *See* MICROWAVE SOLID-STATE DEVICES.

French and Russian research suggests that in some applications it may be necessary to use space diversity in which two beams illuminate the target in order to compensate for nonlinearities in frequency scanning.

The dependence of radar cross section on transmitted frequency over a wide bandwidth can be used to make the signal amplitude scintillate so that target characteristics can be determined.

Rapid discontinuous fluctuations in the scattering from a moving multielement target is known as the intermittent-contact RADAM (radar detection of agitated metals) effect. This effect is observed in the contact between the drive sprocket and the tread of a tank and can be used to define signatures of various kinds of fighting vehicles.

Multiple targets. Discrete Fourier analysis of the video heterodyne (beat) signals using a digital computer permits multiple-target handling and achieves good resolution between approaching and receding targets. *See* SPECTRUM ANALYZER.

Target acceleration. An indication of the acceleration of a target can be obtained by double subtraction and delay of the returned signal.

Communicating with the target. In radar missile guidance, homing beacons, and identification–friend-or-foe, it is necessary to communicate with the target. This can be done by interrupting the range beat frequency at short intervals near its peak excursion and transmitting AM signals to the illuminated target.

Signal-to-noise ratio. The signal-to-noise ratio can be improved by digitizing the beat frequency signals. Moreover, compressing the received signals to a sine-squared shape can increase the signal level more than 20 decibels. *See* SIGNAL-TO-NOISE RATIO.

Applications. Applications of continuous-wave radar include missile guidance; detection of hostile targets; terrain clearance indication and ground surveillance; laser radar systems; atmospheric studies; automobile safety; surveillance of personnel; ice studies; remote sensing; and reproduction of the shape of a patient's pulse.

Missile guidance. The principal use of continuous-wave radar is in short-range missile guidance. Typically the missile's course is tracked from the ground while the missile is simultaneously illuminated. Continuous-wave radar, in some cases the same radar, can be used for both tracking and illumination, although it is more common for pulse Doppler radar to be used for tracking.

Advances in the design of phased-array antennas have led to pulse Doppler radar becoming more attractive than continuous-wave radar even for illumination. However, at least one system allows the operator to select either continuous-wave or pulse Doppler radar for illumination.

Illumination radar is for target acquisition. Two signals are of interest. One, the directly received illumination of the missile, is called the rear signal. The other, the signal reflected from the target, is called the front signal. The front signal is shifted in frequency as the missile closes with the target. This shift occurs because of the Doppler effect. The shift, and therefore the range to the target, is obtained by coherently detecting the front signal against the rear signal. In an active guidance system, detection is performed on board the missile. Semiactive missile guidance is more frequently used, and in this system the signals are relayed over a data link for processing at the ground station.

A late version of the MPQ-34 tracking and acquisition radar for the Hawk ground-to-air missile incorporates the choice of either continuous-wave or pulse Doppler radar illumination. The ability of continuous-wave radar to discriminate against clutter made it attractive in this system, which was intended to be used against low-flying aircraft.

Pulsed tracking radar with continuous-wave acquisition radar is used with the Sparrow air-to-air missile system and with the Tartar shipborne missile system.

A miss-distance indicator (MDI) is a special application of continuous-wave radar. It uses radio-frequency signals to determine the relative velocity between two objects, the time of intercept when the distance will be a minimum, and the actual value of that minimum distance. With the availability of real-time intercept information, a prior determination of guidance parameters that will produce a direct hit can be made. *See* GUIDANCE SYSTEMS; GUIDED MISSILE.

Detection of hostile targets. Modulated continuous-wave radar has been used to detect hostile military vehicles and personnel.

The Navy MK-92 fire-control system uses a linear FM-CW radar with multiple resonant filters.

An FM-CW naval radar operating at 95.6 GHz uses pseudorandom-coded phase-shift keying, digital signal processing, and microprocessor-controlled azimuth and elevation scanning. It can display the shape, range, velocity, and direction of vessels. *See* NAVAL ARMAMENT.

In the United States, Canada, and the United Kingdom, there has been interest in continuous-wave radar for detecting nonmetallic mines. One radar operates between 2 and 4 GHz and can detect plastic objects buried in 10 in. (25 cm) of wet sand.

Terrain surveillance. One of the first uses of FM continuous-wave radar was in terrain clearance indicators or radar altimeters. Today intruder aircraft and air-breathing missiles obtain continuous guidance from that kind of equipment. *See* ALTIMETER.

The ability of side-looking radar on reconnaissance aircraft and Earth-observation satellites to resolve targets has been enhanced by the use of synthetic-aperture radar. Although this technique usually requires a huge data rate and great processing complexity, special-purpose processors have been used to extract useful data economically. Such a processor on the *Seasat 1* was able to determine the direction of ocean wave from 800 mi (1300 km) up. *See* REMOTE SENSING.

Earth surveillance has been hampered by some radar reflection phenomena, notably foreshadowing, which distorts distance; layover, which tends to fill in depressions; and shadow, which obscures features. These problems place limiting requirements on the size and contrast of images needed for successful interpretation. These limitations can be partially overcome by training radargrammetrists with simulators.

Laser radar systems. An experimental modulated continuous-wave laser radar was built to track low-flying airborne targets from the ground. The system can determine both range and the rate at which the range is changing. An advantage of this system is its extreme precision. The divergence of the beam is less than 1 milliradian. The transmitter is a carbon dioxide laser operating at a wavelength of 10.6 micrometers. The infrared carrier is frequency-modulated with 10-MHz excursions occurring at a frequency of 1 kHz. *See* LASER.

Atmospheric studies. The ability of FM-CW radar to measure distance and velocity despite smoke, dust, and thermal gradients makes it attractive for many industrial automatic control applications. The Naval Ocean Systems Center uses S-band continuous-wave radar to update refractive index profiles of the troposphere. This work forms the basis for radio interception and over-the-horizon targeting. In France, continuous-wave radar has been used to measure the electron temperatures in the ionosphere. The National Oceanic and Atmospheric Administration (NOAA) has used continuous-wave radar to measure wind in clear air.

Automobile safety. An experimental continuous-wave radar which exploits the Doppler principle has been developed for use in automobiles. The radar can anticipate a crash when an obstacle is 30 ft (10 m) away in order to deploy air-cushion-type passive restraints. It can sense obstacles 500 ft (150 m) away to govern automatic braking and headway control. The source of carrier power is an X-band Gunn-type solid-state oscillator.

Surveillance of personnel. A variant of continuous-wave radar is used to illuminate persons under surveillance by techniques employing semiconductor tracer diodes. These devices are secreted on or implanted in the subject's body without his or her knowledge, or else concealed in objects that are to be protected against theft. Despite the fact that pulsed X-band sources could provide the needed power levels more conveniently, the requirement to reduce clutter makes it desirable to use continuous-wave power.

These techniques are also used to sweep premises to discover clandestine listening devices and to guard protected locations against the introduction of concealed tape recorders.

Implementation of tracer-diode surveillance utilizes a single carrier frequency and looks for reflections of the third harmonic as evidence that the person sought has been acquired by the beam. The surveillance operations have been carried out from fixed posts, vans, and low-flying aircraft.

An improved version makes use of two carrier frequencies for illumination and depends upon coherent detection of the third and fourth harmonics of the sum and difference frequencies to signify acquisition of the target. *See* ELECTRONIC LISTENING DEVICES.

Other applications. In Finland, a continuous-wave radar operating between 1 and 1.8 GHz has been used to measure ice and frost thickness in lakes and bogs. Continuous-wave radars operating at 1.5 and from 8 to 18 GHz have been used to discriminate among different types of Arctic Sea ice.

Continuous-wave radar has been used in the Netherlands to discriminate among different types of vegetation, crops, and bare soils.

With its antenna placed over a patient's wrist artery, continuous-wave radar has been shown to be able to reproduce the shape of the arterial pulse. *See* RADAR.

John M. Carroll

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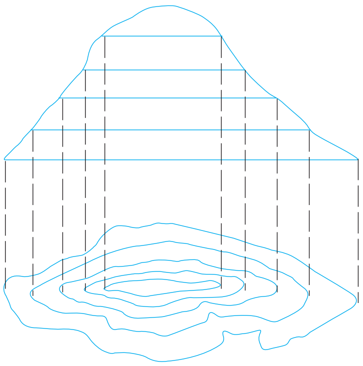
Contour

The locus of points of equal elevation used in topographic mapping. Contour lines represent a uniform series of elevations, the difference in elevation between adjacent lines being the contour interval of the given map. Thus, contours represent the shape of terrain on the flat map surface (see **illus.**). Closely spaced contours indicate steep ground; sparseness or absence of contours indicates gentle slope or flat ground. Contours do not cross each other unless there is an overhang. *See* TOPOGRAPHIC SURVEYING AND MAPPING.

In ground-survey procedures the horizontal positions and elevation of numerous points are observed. Points on the elevations chosen for contouring are then located by interpolation, and each contour is sketched by connecting the points found for its elevation. *See* SURVEYING.

In photogrammetric mapping with a stereoplotting instrument, the operator sets the plotting table at the chosen contour elevation; the elevation is "hunted" by shifting the table until a floating dot appears to touch the stereoscopic image; the operator then lowers the plotting pencil and traces the contour by keeping the floating dot in apparent touch with the image. *See* CARTOGRAPHY; PHOTOGRAMMETRY.



Contour representation; vertical projection indicates the profile of the elevation as it relates to the spacing of the contours.

Robert H. Dodds

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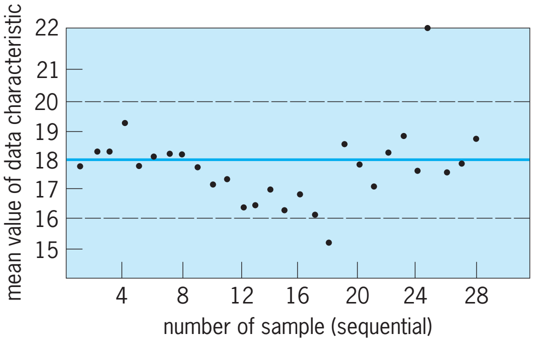
Control chart

A graphical technique for determining whether a process is or is not in a state of statistical control. Being in statistical control means that the extent of variation of the output of the process does not exceed that which is expected on the basis of the natural statistical variability of the process. Several main types of control charts are used, based on the nature of the process and on the intended use of the data.

Every process has some inherent variability due to random factors over which there is no control and which cannot be eliminated economically. For instance, in a metal fabrication process random factors may include the distribution of impurities and structural faults among the metal molecules, vibrations of the fabrication equipment, fluctuations in the power supply that affect the speed and torque of the equipment, and variations in the operator performance from one cycle to the next. The inherent variability of the process is the aggregate result of many individual causes, each having a small impact.

The control chart technique is applicable to processes that produce a stream of discrete output units. Control charts are designed to detect excessive variability due to specific assignable causes that can be corrected. Assignable causes result in relatively large variations, and they usually can be identified and economically removed. Examples of assignable causes of variations that may occur in the example of metal fabrication include a substandard batch of raw material, a machine malfunction, and an untrained or poorly motivated operator.

A control chart is a two-dimensional plot of the evolution of the process over time. The horizontal dimension represents time, with samples displayed in chronological order, such that the earliest sample taken appears on the left and each newly acquired sample is plotted to the right. The vertical dimension represents the value of the sample statistic, which might be the sample mean, range, or standard deviation in the case of measurement by variables, or in the case of measurement by attributes, the number of nonconforming units, the fraction nonconforming,



Control chart, showing changes in average of process.

the number of nonconformities, or the average number of nonconformities per unit.

Typically a control chart includes three parallel horizontal lines (see **illustration**): a center line and two control limits. The centerline (CL) intersects the vertical dimension at a value that represents the level of the process under stable conditions (natural variability only). The process level might be based on a given standard or, if no standard is available, on the current level of the process calculated as the average of an initial set of samples. The two lines above and below the centerline are called the upper control limit (UCL) and lower control limit (LCL) respectively, and they both denote the normal range of variation for the sample statistic. The control limits intersect the vertical axis such that if only the natural variability of the process is present, then the probability of a sample point falling outside the control limits and causing a false alarm is very small. Typically, control limits are located at three standard deviations from the centerline on both sides. This results in a probability of a false alarm being equal to 0.0027.

The principle of operation of control charts is rather simple and consists of five general steps:

1. Samples are drawn from the process output at regular intervals.

2. A statistic is calculated from the observed values of the units in the sample; a statistic is a mathematical function computed on the basis of the values of the observations in the sample.

3. The value of the statistic is charted over time; any points falling outside the control limits or any other nonrandom pattern of points indicate that there has been a change in the process, either its setting or its variability.

4. If such change is detected, the process is stopped and an investigation is conducted to determine the causes for the change.

5. Once the causes of the change have been ascertained and any required corrective action has been taken, the process is resumed.

The main benefit of control charts is to provide a visual means to identify conditions where the process level or variation has changed due to an assignable cause and consequently is no longer in a state of statistical control. The visual patterns that indicate either the out-of-control state or some other condition that requires attention are known as outliers, runs of points, low variability, trends, cycles, and mixtures. *See* CONTROL SYSTEMS; QUALITY CONTROL; STATISTICAL PROCESS CONTROL.

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Control system stability

The well-behavedness of the output of a control system in response to either external inputs or internal excitations. Several definitions of stability are in use, each being appropriate to a different application. The objective of stability theory is to obtain information concerning the behavior of a control system without actually solving the equations that describe the system.

Stability theory can be applied in a wide variety of disciplines, such as engineering, mathematics, physics, biology, and economics.

A few examples illustrate such stability theory: (1) The classical problem studied by the Soviet mathematician A. M. Lyapunov was the stability of the solar system. The objective was to determine the ultimate behavior of the trajectories of the various planets, in particular whether they would all spiral into the Sun, fly off into space, or do something else. (2) In digital filters, it is sometimes possible to encounter limit cycles, that is, round off errors that do not decay, perhaps due to the finite word length of the operations. It has been experimentally observed that certain configurations and certain coefficient values never exhibit limit cycles, and a mathematical explanation of this phenomenon would be useful. (3) A voltage source is connected to an electronic circuit containing resistors, capacitors, and operational amplifiers. For a broad but prespecified class of voltage excitations, it would be useful to know whether the resulting current will eventually decay to zero. (4) In a plasma laboratory, a scheme is proposed for confining the plasma to a specified cylindrical region; it would be useful to know whether the proposed scheme will work. (5) A model is developed for the spread of an infectious disease within a population, and it would be useful to be able to determine how the number of survivors is affected by various parameters of the model. *See* ELECTRIC FILTER; NUCLEAR FUSION.

As shown by the discussion below, stability theory encompasses systems described by a wide variety of models. Thus the equations governing the system may be linear or nonlinear; they may be difference equations or differential equations; they may be ordinary, partial, or functional differential equations; finally, they may be difference equations in more than one parameter. This article deals chiefly with differential equations; the theory for other types of equations is similar in concept, though not in detail.

Routh, Hurwitz, and related tests. Consider a system whose transfer function is of the form given by Eq. (1), where $\hat{n}$ and $\hat{d}$ are polynomials and s denotes

$$\hat{h}(s) = \frac{\hat{n}(s)}{\hat{d}(s)} \tag{1}$$

the variable of Laplace transformation. Such a system exhibits a bounded response to every bounded excitation if and only if the following two conditions hold: (1) $\hat{h}$ is proper, that is, the degree of the polynomial $\hat{n}$ is less than or equal to that of $\hat{d}$; (2) all poles of $\hat{h}$, that is, all zeros of the polynomial $\hat{d}$, must have negative real parts. (A polynomial satisfying these conditions is called a strictly Hurwitz polynomial.) Given a transfer function $\hat{h}$, inspection will verify whether or not the first condition is satisfied, but the second condition is harder to verify. In particular, it would be useful to determine whether or not all zeros of $\hat{d}$ have negative real parts (that is, whether or not $\hat{d}$ is strictly Hurwitz) without actually computing these zeros. The various tests described below are addressed to this problem. *See* LAPLACE TRANSFORM.

Routh test. Suppose the polynomial $\hat{d}$ is of the form given by Eq. (2), where it may be supposed, with-

$$\hat{d}(s) = d_m s^m + d_{m-1} s^{m-1} + \cdots + d_1 s + d_0 \tag{2}$$

out loss of generality, that $d_m > 0$. The Routh test is based on forming the ratio of the even part of $\hat{d}$ over the odd part of $\hat{d}$ (or vice versa), and then carrying out a continued fraction expansion. To illustrate, suppose $m = 2k$ is an even number; then $\hat{d}_{\text{even}}(s)$ and $\hat{d}_{\text{odd}}(s)$ are defined by Eqs. (3) and (4). Then the ratio $\hat{d}_{\text{even}}(s)/\hat{d}_{\text{odd}}(s)$ is expressed in the form given by Eq. (5). [If m is odd, $\hat{d}_{\text{odd}}(s)/\hat{d}_{\text{even}}(s)$ this form.] The

$$\hat{d}_{\text{even}}(s) = \sum_{i=0}^{k} d_{2i} s^{2i} \tag{3}$$

$$\hat{d}_{\text{odd}}(s) = \sum_{i=0}^{k-1} d_{2i} +{}_1 s^{2i+1} \tag{4}$$

$$\frac{\hat{d}_{\text{even}}(s)}{\hat{d}_{\text{odd}}(s)} = b_m s + \cfrac{1}{b_{m-1} s + \cfrac{1}{\cdots + \cfrac{1}{b_1 s}}} \tag{5}$$

basis of the Routh test is in the following fact: $\hat{d}$ is a strictly Hurwitz polynomial if and only if (1) it is possible to completely carry out the continued fraction expansion in Eq. (5), and (2) all the constants $b_m, \ldots, b_1$ are positive. The test also furnishes one additional piece of information. Suppose that the expansion in Eq. (5) is completed, but not all the b_i's are positive. (Then of course $\hat{d}$ is not strictly Hurwitz.) Under these conditions, if none of the b_i's is zero, then the number of zeros of $\hat{d}$ with positive real part is equal to the number of negative b_i's.

Though the above is the theoretical basis of the Routh test, this is not the manner in which the test is actually carried out. To perform the test in an efficient manner, an array is set up, called the Routh array, as shown in Eq. (6), for the case that m is even,

$$\begin{array}{l|lllll}
s^m & d_m & d_{m-2} & \cdots & d_2 & d_0 \\
s^{m-1} & d_{m-1} & d_{m-3} & \cdots & d_1 & \\
s^{m-2} & a_{m-2,1} & a_{m-2,2} & \cdots & a_{m-2,k} & \\
\cdot & & & & & \\
\cdot & & & & & \\
\cdot & & & & & \\
s^1 & a_{1,1} & & & & \\
s^0 & a_{0,1} & & & &
\end{array} \tag{6}$$

and the entries in the array are recursively defined by Eq. (7). With reference to Eq. (5), it can be shown

$$a_{i,j} = a_{i+2,j+1} - \frac{a_{i+2,1} \cdot a_{i+1,j+1}}{a_{i+1,1}} \tag{7}$$

that the b_i's are given by Eq. (8). Hence the Routh

$$b_i = a_{i,1}/a_{i-1,1} \qquad i = m, \ldots, 1 \tag{8}$$

test can be concisely stated as follows: The polynomial $\hat{d}$ is strictly Hurwitz if and only if all the entries in the first column of the Routh array are positive. Now suppose d is not strictly Hurwitz, but none of the entries in the first column of the Routh array is zero. Then the number of zeros of $\hat{d}$ with positive real part is equal to the number of sign changes in the first column of the Routh array.

Hurwitz test. The Routh test is frequently misnamed the Routh-Hurwitz test. Actually the Hurwitz test is different from the Routh test, though they are equivalent in the sense that they both give the same information. The Hurwitz test is as follows: Given a polynomial $\hat{d}$ of the form in Eq. (2), construct the $m \times m$ matrix **H** given by Eq. (9), and let $\Delta_1, \ldots, \Delta_m$ denote

$$\mathbf{H} = \begin{bmatrix}
d_{m-1} & d_{m-3} & \cdots & 0 & 0 & \cdots & 0 \\
d_m & d_{m-2} & \cdots & & & & \\
0 & d_{m-1} & d_{m-3} & \cdots & & & \\
0 & d_m & d_{m-2} & \cdots & & & \\
\cdot & & & & & & \\
\cdot & & & & & & \\
\cdot & & & & & & \\
0 & 0 & \cdots & & & d_3 & d_1 \\
0 & 0 & \cdots & & & d_2 & d_0
\end{bmatrix} \tag{9}$$

the leading principal minors of **H**. (That is, Δ_i is the determinant of the matrix consisting of the entries in **H** that belong to both the first i rows and the first i columns.) Then $\hat{d}$ is a strictly Hurwitz polynomial if and only if $\Delta_i > 0$ for all i. If $\hat{d}$ is not strictly Hurwitz but none of the Δ_i's is zero, then the number of zeros of $\hat{d}$ with positive real part is equal to the number of negative Δ_i's. *See* DETERMINANT.

The relationship between the Hurwitz determinants and the first column of the Routh array is given by Eq. (10), where $\Delta_0 = 1$.

$$a_{i,1} = \Delta_{m-i}/\Delta_{m-i-1} \qquad i = 1, \ldots, m-1 \tag{10}$$

Liénard-Chipart test. Given a polynomial $\hat{d}$ of the form in Eq. (5), a necessary but by no means sufficient condition for $\hat{d}$ to be strictly Hurwitz is that all the coefficients d_i be positive. In this case, it is possible to somewhat simplify the Hurwitz test. In particular, if $d_i > 0$ for all i, then $\hat{d}$ is strictly Hurwitz if and only if either of the equivalent conditions (11) and (12) is satisfied. This simplification is known as the Liénard-Chipart test.

$$\Delta_1 > 0, \Delta_3 > 0, \Delta_5 > 0, \ldots \tag{11}$$

$$\Delta_2 > 0, \Delta_4 > 0, \Delta_6 > 0, \ldots \tag{12}$$

Tests for zeros all of magnitude less than 1. In analyzing the stability of sampled-data control systems, digital filters, and so forth, it is desirable to determine not whether all zeros of $\hat{d}$ have negative real parts, buy whether all zeros of $\hat{d}$ have magnitude less than 1. One means of doing so is by using the bilinear transformation defined by Eq. (13), which maps the inte-

$$s = \frac{v+1}{v-1} \tag{13}$$

rior of the unit circle in the s plane into the left half of the v plane. Thus, all zeros of $\hat{d}$ in the form (2) have magnitude less than 1 if and only if the associated polynomial given by Eq. (14) is strictly Hurwitz. This

$$p(v) = \sum_{i=0}^{m} d_i (v+1)^i (v-1)^{m-i} \tag{14}$$

can be determined using the tests described above.

However, there are many tests that can be applied directly to the polynomial $\hat{d}$ without requiring any transformation. One of these is the Schur-Cohn test: Let $\hat{d}(s)$ be a polynomial of the form in Eq. and define the determinants Δ_i by Eq. (15) Δ_i is the determinant of a $2i \times 2i$ matrix. The Schur-Cohn test states that all zeros of $\hat{d}$ have magnitude less than 1 if and only if $(-1)^i\Delta_i > 0$ for all i, that is Δ_i positive for even i and negative for odd i.

$$\Delta_i = \left|\begin{array}{ccccc|cccc}
d_0 & 0 & 0 & \cdots & 0 & d_m & d_{m-1} & \cdots & d_{m-i+1} \\
d_1 & d_0 & 0 & \cdots & 0 & 0 & d_m & \cdots & d_{m-i+2} \\
d_2 & d_1 & d_0 & \cdots & 0 & 0 & 0 & \cdots & d_{m-i+3} \\
\cdot & & & & & \cdot & & & \\
\cdot & & & & & \cdot & & & \\
\cdot & & & & & \cdot & & & \\
d_{i-1} & d_{i-2} & d_{i-3} & \cdots & d_0 & 0 & 0 & \cdots & d_m \\
\hline
d_m & 0 & 0 & \cdots & 0 & d_0 & d_1 & \cdots & d_{i-1} \\
d_{m-1} & d_m & 0 & \cdots & 0 & 0 & d_0 & \cdots & d_{i-2} \\
\cdot & & & & & \cdot & & & \\
\cdot & & & & & \cdot & & & \\
\cdot & & & & & \cdot & & & \\
d_{m-i+1} & d_{m-i+2} & & \cdots & d_m & 0 & 0 & \cdots & d_0
\end{array}\right| \tag{15}$$

The theoretical advantage of the Schur-Cohn test is that it can be used (with slight modifications) even if the coefficients d_i are complex. However, in practical situations, the coefficients d_i are all real, in which case it is possible to simplify the Schur-Cohn test. The Jury-Blanchard test is as follows: Given a polynomial $\hat{d}$ in the form of Eq. (2), define an array of elements $a_{i,j,}$ $i = 0$ to $m = 2, j = 0$ to $(m - i)$, by the rules of Eqs. (16) and (17). With these definitions, all zeros of

$$a_{0,j} = d_j \qquad j = 0, \ \ldots, m \tag{16}$$

$$a_{i,j} = \begin{vmatrix} a_{i-1,0} & a_{i-1,m-i-j} \\ a_{i-1,m-i} & a_{i-1,j} \end{vmatrix} \tag{17}$$

$\hat{d}$ have magnitude less than 1 if and only if conditions (18) and (19) are satisfied.

$$\hat{d}(1) > 0 \quad (-1)^m \hat{d}(-1) > 0 \quad |d_0| > |d_m| \tag{18}$$

$$|a_{i,0}| > |a_{i,m-i}| \ \text{ for } i = 1 \text{ to } m-2 \tag{19}$$

Nyquist, circle, and Popov criteria. The Nyquist criterion provides a necessary and sufficient condition for the stability of a broad class of linear, time-invariant systems. The criterion can be stated at various levels of generality, and what is given below is one of the simplest versions.

Nyquist plot. Consider a feedback system of the form shown in **Fig. 1**, where the forward element has a transfer function $\hat{g}(s)$ and the feedback contains a constant gain k. It is assumed that the transfer function consists of the sum of three terms, in the form of Eq. (20), where g_0 is a constant; $\hat{g}_a(s)$ is the Laplace

$$\hat{g}(s) = g_0 + \hat{g}_a(s) + \hat{g}_b(s) \tag{20}$$

transform of an absolutely integrable function, that is, Eq. (21) is valid, and $\hat{g}_b(s)$ is a proper rational

$$\hat{g}_a(s) = \mathcal{L}[g_a(t)] \qquad \text{where} \int_0^\infty |g_a(t)|\, dt \text{ is finite} \tag{21}$$

function. Under these conditions, it is possible to determine whether or not the closed-loop system

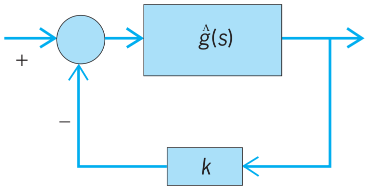

Fig. 1. Feedback system with feedback containing a constant gain *k*.

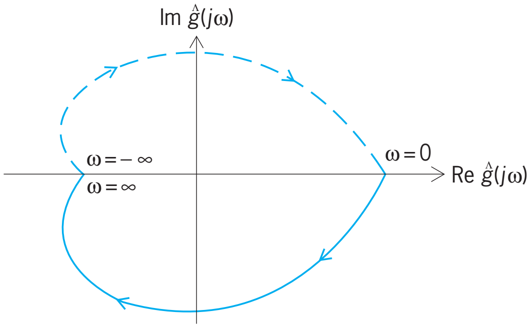

Fig. 2. Nyquist plot of a transfer function $\hat{g}$.

is stable by examining only the behavior of $\hat{g}(j\omega)$, where $j = \sqrt{-1}$ and the frequency parameter ω is allowed to vary along the real axis from $-\infty$ to ∞.

The plot of the real part of $\hat{g}(j\omega)$ versus the imaginary part of $\hat{g}(j\omega)$, as the frequency parameter ω varies from $-\infty$ to ∞, is called the Nyquist plot of $\hat{g}$ (**Fig. 2**). Since $\hat{g}(-j\omega)$ is the complex conjugate of $\hat{g}(j\omega)$, the plot as ω varies from 0 to $-\infty$ is the mirror image, about the real axis, of the plot as ω varies from 0 to ∞.

It sometimes happens that $\hat{g}$ has some poles on the imaginary axis, in which case $\hat{g}(j\omega)$ may be undefined for certain values of ω. In such cases, it is necessary to indent the $j\omega$ axis around the poles of $\hat{g}(j\omega)$, as shown in **Fig. 3**.

Nyquist criterion. With these conventions, the Nyquist criterion can be stated as follows: The system of Fig. 1 is stable if and only if (1) the Nyquist plot of $\hat{g}(j\omega)$ does not intersect the critical point $-(1/k) + j0$, and (2) as ω increases from $-\infty$ to ∞, the Nyquist plot encircles the critical point exactly μ times in the counterclockwise direction, where μ is the number of poles of $\hat{g}$ with positive real parts.

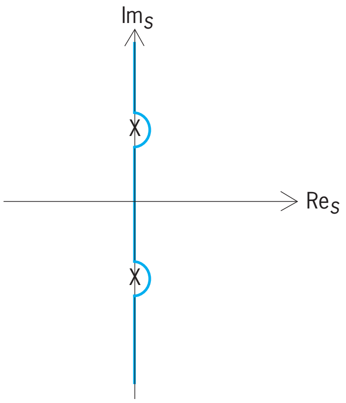

Fig. 3. Modification of Laplace transformation variable to avoid poles of the transfer function $\hat{g}$.

Several advantages of the Nyquist criterion are immediately apparent. (1) It is based on the behavior of $\hat{g}(j\omega)$, which can be readily obtained by frequency response measurements. (2) Since $\hat{g}$ is not required to be a rational function of s (only $\hat{g}_b$ is required to be rational), the criterion is applicable to systems containing transmission lines, time delays, and so forth. (3) For a given transfer function $\hat{g}$, one can readily calculate the range of values of k that result in a stable closed-loop system. (4) Even if the system of Fig. 1 is unstable, it can easily be determined what sort of "compensation" is needed to make the system stable.

Circle criterion. Now consider the system of **Fig. 4**, which is similar to that of Fig. 1, except that the constant gain k has been replaced by a time-varying gain $k(t)$. The assumptions on $\hat{g}(s)$ are the same as before.

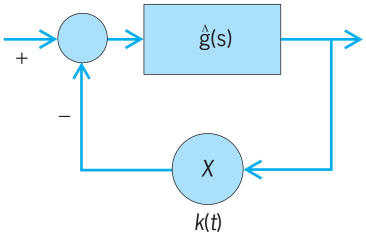

Fig. 4. Feedback system with feedback containing a time-varying gain *k*(*t*).

The circle criterion gives sufficient conditions for the stability of such a system, and can be stated as follows: Suppose the gain $k(t)$ varies in the range $[\alpha,\beta]$, that is, $\alpha \le k(t) \le \beta$ for all t. Let $D(\alpha,\beta)$ denote the critical disk, which passes through $-1/\alpha + j0$ and $-1/\beta + j0$, and is centered on the real axis. Under these conditions, the system of Fig. 4 is stable if one of the following conditions, as appropriate, holds:

Case 1: $0 < \alpha < \beta$. The Nyquist plot of $\hat{g}(j\omega)$ does not intersect the critical disk $D(\alpha,\beta)$ and encircles it in the counterclockwise direction exactly μ times (**Fig. 5**).

Case 2: $0 = \alpha < \beta$. The Nyquist plot of $\hat{g}(j\omega)$ lies in the half-plane Re $\hat{g}(j\omega) < 1/\beta$.

Case 3: $\alpha < 0 < \beta$. The Nyquist plot of $\hat{g}(j\omega)$ is contained within the critical disk $D(\alpha,\beta)$.

Case 4: $\alpha < \beta < 0$. Replace $\hat{g}$ by $-\hat{g}$, α by $-\beta$, β by $-\alpha$, and apply case 1 (since $0 < -\beta < -\alpha$).

The circle criterion shares the same advantages as the Nyquist criterion. In addition, if $\alpha \to \beta$, so that the time-varying gain $k(t)$ approaches a constant gain β, then the critical disk in the circle criterion shrinks to the critical point of the Nyquist criterion.

Popov criterion. Finally, consider the system shown in **Fig. 6**, wherein the feedback contains a memoryless nonlinear element N. Suppose the graph of the nonlinearity lies in the sector $[0,k]$, that is, between the horizontal axis and a line of slope k through the origin (**Fig. 7**). Finally, suppose $\hat{g}(s)$ is strictly proper and that all poles of $\hat{g}$ have negative real parts. The Popov criterion gives a sufficient condition for the stability of such a system.

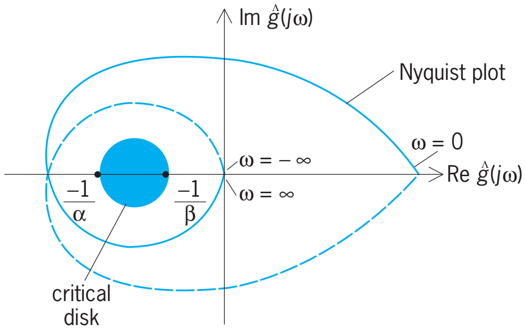

Fig. 5. Circle criterion for $0 < \alpha < \beta$. The Nyquist plot does not intersect the critical disk and encircles it in the counterclockwise direction exactly μ times, where μ is the number of poles of $\hat{g}$ with positive real parts.

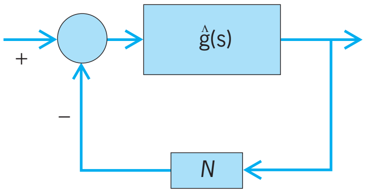

Fig. 6. Feedback system with feedback containing a memoryless nonlinear element *N*.

It states that the system of Fig. 6 is stable, provided one can find a number $q \geq 0$ and a number $\delta > 0$ such that inequality (22) is satisfied.

$$\text{Re}\,[(1 + j\omega q)\hat{g}(j\omega)] + 1/k \geq \delta > 0 \quad \text{for all } \omega \tag{22}$$

The criterion (22) can also be given a graphical interpretation by means of a plot of Re $\hat{g}(j\omega)$ versus ω a Im $\hat{g}(j\omega)$, called a Popov plot (**Fig. 8**). It is only necessary to do the plot for $\omega \geq 0$, since both Re $\hat{g}(j\omega)$ and ω Im $\hat{g}(j\omega)$ are even functions of ω. The inequality (22) states that it is possible to draw a line of slope $1/q$ through the point $1/k + j0$ in such a way that the Popov plot of $\hat{g}(j\omega)$ lies strictly to the right of this line (Fig. 8).

Lyapunov theory. This can be used to analyze the behavior of the solutions of the vector differential equation (23), corresponding to various initial conditions $\mathbf{x}(t_0) = \mathbf{x}_0$ without actually solving the differential equation (23).

$$\dot{\mathbf{x}}(t) = \mathbf{f}(t, \mathbf{x}(t)) \tag{23}$$

The form of Eq. (23) is quite general, and is referred to as the set of state equations for a system; it is distinguished by the fact that the system under study is described by a set of first-order differential equations. The form of Eq. (23) is sufficiently general that any set of coupled ordinary differential equations, of any order, can be equivalently expressed in this form. To simplify the exposition, only the case where the time *t* does not explicitly appear in the state equations will be discussed, that is, where the state equations are of the form of Eq. (24).

$$\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}(t)) \tag{24}$$

See DIFFERENTIAL EQUATION; LINEAR SYSTEM ANALYSIS.

Equilibrium. An important concept for the system of Eq. (23) is that of an equilibrium. A vector $\mathbf{x}_0$ is called an equilibrium of the system of Eq. (24) if Eq. (25)

$$\mathbf{f}(\mathbf{x}_0) = \mathbf{0} \tag{25}$$

is satisfied. Equivalently, if $\mathbf{x}_0$ is an equilibrium of Eq. (24), then the solution of Eq. (24) corresponding to the initial condition $\mathbf{x}(0) = \mathbf{x}_0$ is $\mathbf{x}(t) = \mathbf{x}_0$ for all $t \geq 0$.

Asymptotic stability. There are many distinct concepts of "stability" in Lyapunov theory, each of them suitable for a different application, and only one of them will be discussed here. Suppose $\mathbf{x} = \mathbf{0}$ is an equilibrium of Eq. (24) [that is, $\mathbf{f}(\mathbf{0}) = \mathbf{0}$], and let $\mathbf{x}(t,\mathbf{x}_0)$ denote the solution of Eq. (24), corresponding to the initial condition $\mathbf{x}(0) = \mathbf{x}_0$. Finally, let the norm of the vector $\mathbf{x}$ be defined by Eq. (26). Then $\mathbf{0}$ is called

$$|\mathbf{x}| = \left(\sum_i x_i^2\right)^{1/2} \tag{26}$$

an asymptotically stable equilibrium of Eq. (24) if the following two conditions are satisfied: (1) There is a number $\delta_0 > 0$ such that $|\mathbf{x}(t,\mathbf{x}_0)|$ is bounded as a function of *t* whenever $|x_0| < \delta_0$. Moreover, the function ϕ defined by Eq. (27) is continuous at $r = 0$.

$$\phi(r) = \sup_{|\mathbf{x}_0| \leq r} \sup_{t \geq 0} |\mathbf{x}(t, \mathbf{x}_0)| \tag{27}$$

(2) There is a number $\delta_1 > 0$ $|\mathbf{x}(t,\mathbf{x}_0)| \to 0$ as $t \to \infty$, whenever $|\mathbf{x}_0| < \phi_1$.

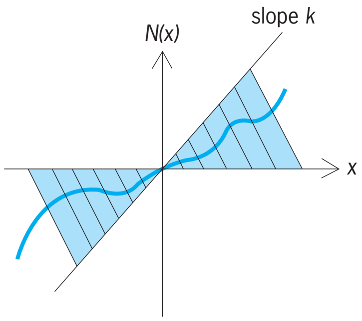

Fig. 7. Graph of nonlinear element *N*.

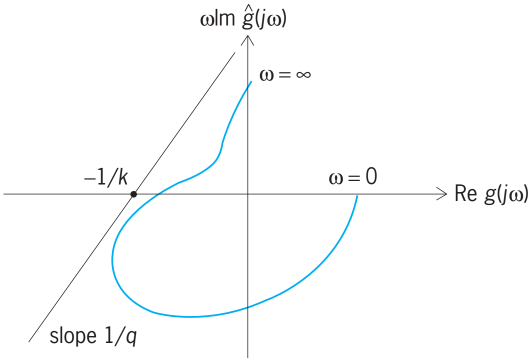

Fig. 8. Popov plot of a transfer function $\hat{g}$.

Basically, condition (1) states that, whenever the magnitude of the initial condition is sufficiently small ($|\mathbf{x}_0| < \delta_0$), small perturbations in the initial condition produce small perturbations in the corresponding solution. Condition (2) states that there is a domain of attraction (the sphere of radius δ_1) such that, whenever the initial condition belongs to this domain, the corresponding solution approaches **0** as $t \to \infty$.

Linear systems. In the case of a linear system, Eq. (28), where $\mathbf{x}(t)$ is an $m \times 1$ vector and **a** is

$$\dot{\mathbf{x}}(t) = \mathbf{A}\mathbf{x}(t) \tag{28}$$

an $m \times m$ matrix, the equilibrium $\mathbf{x} = \mathbf{0}$ stable if and only if all eigenvalues of **A** have negative real parts, that is, the characteristic polynomial $\phi(s) = \det(s\mathbf{I} - \mathbf{A})$ is strictly Hurwitz. Moreover, if $\mathbf{x} = \mathbf{0}$ is asymptotically stable, then the domain of attraction is the entire state space, that is, $|\mathbf{x}(t,\mathbf{x}_0)| \to 0$ as $t \to \infty$ for every $\mathbf{x}_0$.

A test that can be used to determine whether or not all eigenvalues of **A** have negative real parts (that is, whether **A** is a Hurwitz matrix), without actually computing them, is summarized in the following theorem:

Given an $m \times m$ matrix **A**, the following three conditions are equivalent: (1) All eigenvalues of **A** have negative real parts. (2) For some symmetric positive definite matrix **Q**, Eq. (29) has a unique solution **P**;

$$\mathbf{A}^{\mathrm{T}}\mathbf{P} + \mathbf{P}\mathbf{A} = -\mathbf{Q} \tag{29}$$

moreover, this solution is symmetric and positive definite. (3) For every symmetric positive definite matrix **Q**, Eq. (29) has a unique solution for **P**, and this solution is positive definite.

Thus the testing procedure is as follows: Given a matrix **A**, select a symmetric positive definite matrix **Q** arbitrarily, and solve Eq. (29) [known as the Lyapunov matrix equation] for **P**. If a unique **P** cannot be found, or if the unique **P** is not positive definite, then **A** is not a Hurwitz matrix; if there is a unique **P** satisfying Eq. (29) and this **P** is positive definite, the **A** is a Hurwitz matrix. The test also provides additional information: If Eq. (29) has a unique solution for **P**, then the number of negative eigenvalues of **P** equals the number of eigenvalues of **A** having positive real part. *See* EIGENFUNCTION; MATRIX THEORY.

Nonlinear systems. To analyze the nonlinear system of Eq. (24), two general methods are available, namely the direct and indirect methods of Lyapunov. The indirect method is based on expanding $\mathbf{f}(\mathbf{x})$ in a Taylor series around the point $\mathbf{x} = \mathbf{0}$. Specifically, let **A** be defined by Eq. (30). Since $\mathbf{f}(\mathbf{0}) = \mathbf{0}$ by assumptions, Eq. (31) follows. Lyapunov's indirect method is

$$\mathbf{A} = \frac{\partial \mathbf{f}}{\partial \mathbf{x}} \bigg|_{\mathrm{x}=0} \tag{30}$$

$$\mathbf{f}(\mathbf{x}) = \mathbf{A}\mathbf{x} + \text{higher} - \text{order terms in } \mathbf{x} \tag{31}$$

based on the following fact: If **A** is strictly Hurwitz, then $\mathbf{x} = \mathbf{0}$ is an asymptotically stable equilibrium of the nonlinear system of Eq. (24); if **A** has some eigenvalues with positive real parts, then $\mathbf{x} = \mathbf{0}$ is an unstable equilibrium of Eq. (24).

The direct method of Lyapunov is based on constructing an energylike function $v(\mathbf{x})$, known as a Lyapunov function, whose value decreases along the solution trajectories of Eq. (24). The actual details are somewhat complex, but the direct method provides a very powerful tool for analyzing nonlinear systems. *See* NONLINEAR CONTROL THEORY.

Advanced methods. The techniques described here have been extended to systems governed by partial or even functional differential equations, as well as to multidimensional systems (for example, two-dimensional digital filters). In addition, advanced mathematical techniques such as functional analysis and differential geometry have been applied to stability problems. *See* CONTROL SYSTEMS. M. Vidyasagar

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Control systems

Interconnections of components forming system configurations which will provide a desired system response as time progresses. The steering of an automobile is a familiar example. The driver observes the position of the car relative to the desired location and makes corrections by turning the steering wheel. The car responds by changing direction, and the driver attempts to decrease the error between the desired and actual course of travel. In this case, the controlled output is the automobile's direction of travel, and the control system includes the driver, the automobile, and the road surface. The control engineer attempts to design a steering control mechanism which will provide a desired response for the automobile's direction control. Different steering designs and automobile designs result in rapid responses, as in the case of sports cars, or relatively slow and comfortable responses, as in the case of large autos with power steering.

Open- and closed-loop control. The basis for analysis of a control system is the foundation provided by linear system theory, which assumes a cause-effect relationship for the components of a system. A component or process to be controlled can be represented by a block. Each block possesses an input (cause) and output (effect). The input-output relation represents the cause-and-effect relationship of the process, which in turn represents a processing of the input signal to provide an output signal variable, often with power amplification. An open-loop control system utilizes a controller or control actuator in order to obtain the desired response (**Fig. 1**). *See* BLOCK DIAGRAM.

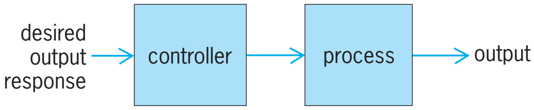

Fig. 1. Open-loop control system.

A closed-loop control system utilizes an additional measure of the actual output in order to compare the actual output with the desired output response (**Fig. 2**). A standard definition of a feedback control system is a control system which tends to maintain a prescribed relationship of one system variable to another by comparing functions of these variables and using the difference as a means of control. In the case of the driver steering an automobile, the driver visually measures and compares the actual location of the car with the desired location. The driver then serves as the controller, turning the steering wheel. The process represents the dynamics of the steering mechanism and the automobile response.

A feedback control system often uses a function of a prescribed relationship between the output and reference input to control the process. Often, the difference between the output of the process under control and the reference input is amplified and used to control the process so that the difference is continually reduced. The feedback concept has been the foundation for control system analysis and design.

Because of the increasing complexity of the system under control and the interest in achieving optimum performance, the importance of control system engineering has grown over the years. Furthermore, as the systems become more complex, the interrelationship of many controlled variables must be considered in the control scheme.

History of automatic control. The first automatic feedback controller used in an industrial process was James Watt's flyball governor (1769) for controlling the speed of a steam engine. Prior to World War II, one main impetus for the use of feedback control in the United States was the development of the telephone system and electronic feedback amplifiers. The frequency domain was used primarily to describe the operation of the feedback amplifiers in terms of bandwidth and other frequency variables. In contrast, the Russian theory, which was dominated by mathematicians, tended to utilize a time-domain formulation using differential equations.

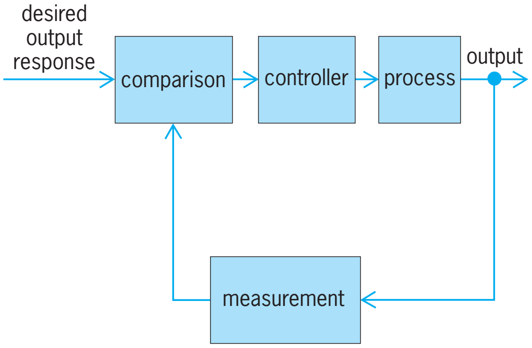

Fig. 2. Closed-loop control system.

A large impetus to the theory and practice of automatic control occurred during World War II, when it became necessary to design and construct automatic airplane pilots, gun-positioning systems, radar antenna control systems, and other military systems based on the feedback control approach. The complexity and expected performance of these military systems necessitated an extension of the available control techniques and fostered interest in control systems and the development of new insights and methods.

Frequency-domain techniques continued to dominate the field of control following World War II, with the increased use of the Laplace transform and the complex frequency plane. During the 1950s, the utilization of both analog and digital computers for control components became possible. These new controlling elements possessed an ability to calculate rapidly and accurately, which was formerly not available to the control engineer. Digital process control computers are employed especially for process control systems in which many variables are measured and controlled simultaneously by the computer. *See* ANALOG COMPUTER; DIGITAL COMPUTER; PROCESS CONTROL.

With the advent of the space age, it became necessary to design complex, highly accurate control systems for missiles and space probes. Furthermore, the necessity to minimize the weight of satellites and to control them very accurately spawned the important field of optimal control. It appears that control engineering must consider both the time-domain and the frequency-domain approaches simultaneously in the analysis and design of control systems. *See* GUIDANCE SYSTEMS; OPTIMAL CONTROL THEORY; SPACE NAVIGATION AND GUIDANCE.

Applications. Familiar control systems have the basic closed-loop configuration as shown earlier. For example, a refrigerator has a temperature setting for desired temperature, a thermostat to measure the actual temperature and the error, and a compressor motor for power amplification. Other examples in the home are the oven, furnace, and water heater. In industry, there are controls for speed, process temperature and pressure, position, thickness, composition, and quality, among many others.

In order to provide a mass transportation system for modern urban areas, a large, complex, high-speed system is necessary. Automatic control is necessary in order to maintain a constant flow of trains and to ensure comfortable deceleration and braking conditions at stations (**Fig. 3**). A measurement of the distance from the station and the speed of the train is used to determine the error signal and therefore the braking signal. *See* RAILROAD CONTROL SYSTEMS.

The electric power industry is primarily interested in energy conversion, control, and distribution. It is critical that computer control be increasingly applied to the power industry in order to improve

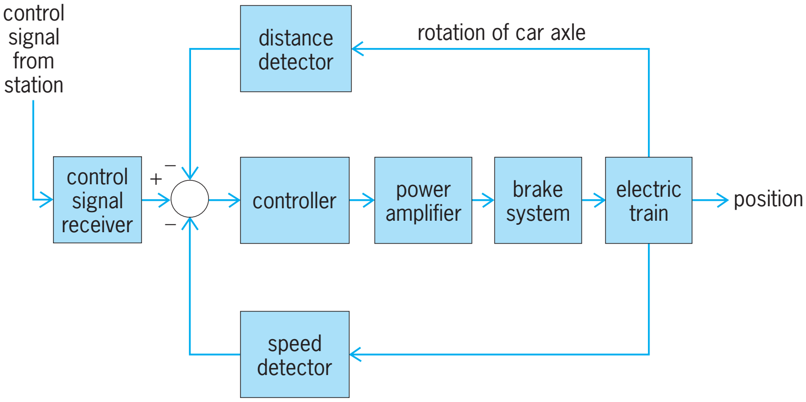

Fig. 3. Train-brake control system.

the efficiency of use of energy resources. Also, the control of power plants for minimum waste emission has become increasingly important. The modern large-capacity plants which exceed several hundred megawatts require automatic control systems which account for the interrelationship of the process variables and the optimum power production. It is common to have as many as 90 or more manipulated variables under coordinated control. Computer controls are also used to control energy use in industry and stabilize and connect loads evenly to gain fuel economy.

Feedback control concepts have been applied to automatic warehousing and inventory control and to the automatic control of agriculture systems (farms). Automatic control of wind turbine generators, solar heating and cooling, and automobile engine performance are other important examples.

Also, there have been many applications of control system theory to biomedical experimentation, diagnosis, prosthetics, and biological control systems. The control systems under consideration range from the cellular level to the central nervous system and include temperature regulation and neurological, respiratory, and cardiovascular control. Most physiological control systems are closed-loop systems. However, they involve not one controller but rather control loop within control loop, forming a hierarchy of systems. The modeling of the structure of biological processes confronts the analyst with a high-order model and a complex structure. Prosthetic devices are designed to provide automatically controlled aids to the disabled. An artificial hand that uses force feedback signals and is controlled by the amputee's bioelectric control signals is an example. *See* MATHEMATICAL BIOLOGY; PROSTHESIS.

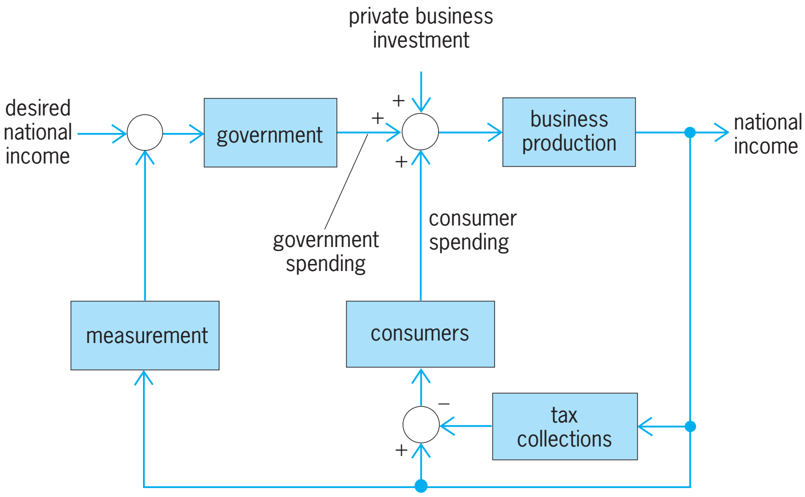

Fig. 4. Feedback control system model of the United States economy.

Finally, it has become of interest to attempt to model the feedback processes prevalent in the social, economic, and political spheres. This approach is undeveloped but appears to have a reasonable future. A simple lumped model of the national-income feedback control system is shown in **Fig. 4**. This type of model helps the analyst to understand the effects of government control—granted its existence—and the dynamic effects of government spending. Of course, many other loops not shown also exist. This type of political or social feedback model, while usually nonrigorous, does impart information and understanding. *See* SYSTEMS ANALYSIS; SYSTEMS ENGINEERING.

Analysis using the Laplace transform. In order to understand a complex control system, it is necessary to analyze the relationships between the system variables and to obtain a quantitative mathematical model of the system. Since the systems under consideration are dynamic in nature, the descriptive equations are usually differential equations. Furthermore, if these equations can be linearized, then the Laplace transform can be utilized in order to simplify the method of solution. In practice, the complexity of systems and incomplete knowledge of the relevant factors necessitate the introduction of assumptions concerning the system operation. Therefore, it is often useful to consider the physical system, delineate some necessary assumptions, and linearize the system. Then, by using the physical laws describing the linear equivalent system, one can obtain a set of linear differential equations. Finally, utilizing mathematical tools, such as the Laplace transform, a solution describing the operation of the system is obtained. In summary, the approach to dynamic system problems can be listed as follows: (1) define the system and its components; (2) formulate the mathematical model and list the necessary assumptions; (3) write the differential equations describing the model; (4) solve the equations for the desired output variables; (5) examine the solutions and the assumptions; and then (6) reanalyze or design. *See* DIFFERENTIAL EQUATION.

The Laplace transform of a function f of time t is given by Eq. (1), where s is a complex variable

$$F(s) = \mathcal{L}\{f(t)\} = \int_0^\infty f(t)e^{-st}dt \qquad (1)$$

related to the frequency ω by the equations $s = \sigma + j\omega$ (where $j = \sqrt{-1}$). The analysis thus takes place in the frequency domain. The inverse Laplace

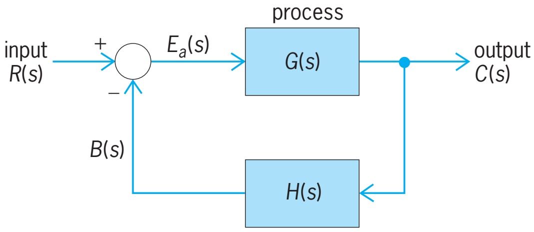

Fig. 5. Negative-feedback control system.

transformation is usually obtained by a partial fraction expansion. *See* LAPLACE TRANSFORM.

The transfer function of a linear system is the ratio of the Laplace transform of the output variable to the Laplace transform of the input variable with all initial conditions assumed to be zero. The block diagram of a negative-feedback control system is shown in **Fig. 5**. The transfer function $G(s)$ of the process is given by Eq. (2).

$$\frac{C(s)}{E_a(s)} = G(s) \tag{2}$$

The transfer function of the closed-loop system can be obtained by the algebraic manipulation of the system equations. The error, $E_a(s)$, is given by Eq. (3), and the output is given by Eq. (4).

$$E_a(s) = R(s) - B(s) = R(s) - H(s)C(s) \tag{3}$$

$$C(s) = G(s)E_a(s) = G(s)[R(s) - H(s)C(s)] \tag{4}$$

Solving for $C(s)$, Eq. (5) is obtained, and therefore $C(s)$ is given by Eq. (6).

$$C(s)[1 + G(s)H(s)] = G(s)R(s) \tag{5}$$

$$C(s) = \frac{G(s)}{1 + G(s)H(s)}R(s) \tag{6}$$

The closed-loop transfer function $T(s) = C(s)/R(s)$ is given by Eq. (7), and the error is then given by Eq. (8).

$$\frac{C(s)}{R(s)} = T(s) = \frac{G(s)}{1 + G(s)H(s)} \tag{7}$$

$$E_a(s) = \frac{1}{1 + G(s)H(s)}R(s) \tag{8}$$

It is clear that in order to reduce the error, the magnitude of $[1 + G(s)H(s)]$ must be greater than 1 over the range of s under consideration.

Advantages of feedback control. The addition of feedback to a control system results in several important advantages.

Reduction in sensitivity. A process, represented by the transfer function $G(s)$, whatever its nature, is subject to a changing environment, aging, ignorance of the exact values of the process parameters, and other natural factors which affect a control process. In the open-loop system, all these errors and changes result in a changing and inaccurate output. However, a closed-loop system senses the change in the output due to the process changes and attempts to correct the output. The sensitivity of a control system to parameter variations is of prime importance. A primary advantage of a closed-loop feedback control system is its ability to reduce the system's sensitivity.

For the closed-loop case, if $G(s)H(s)$ is much greater than 1 for all complex frequencies of interest, then from Eq. (6) one obtains Eq. (9). That is,

$$C(s) = \frac{1}{H(s)}R(s) \tag{9}$$

the output is affected only by $H(s)$, which may be constant. If $H(s) = 1$, the desired result is obtained; that is, the output is equal to the input. However, this approach cannot be used for all control systems because the requirement that $G(s)H(s)$ be much greater than 1 may cause the system response to be highly oscillatory and even unstable. But the fact that an increase in the magnitude of the loop transfer function $G(s)H(s)$ results in a reduction of the effect of $G(s)$ on the output is an exceedingly useful concept. Therefore, the first advantage of a feedback system is that the effect of the variation of the parameters of the process, $G(s)$, is reduced.

Control of transient response. One of the most important characteristics of control systems is their transient response, which often must be adjusted until it is satisfactory. If an open-loop control system does not provide a satisfactory response, then the process, $G(s)$, must be replaced with a suitable process. By contrast, a closed-loop system can often be adjusted to yield the desired response by adjusting the feedback loop parameters. It is often possible to alter the response of an open-loop system by inserting a suitable cascade filter, $G_1(s)$, preceding the process, $G(s)$. Then it is necessary to design the cascade transfer function $G_1(s)G(s)$ so that the resulting transfer function provides the desired transient response. Therefore, the second advantage of feedback control is control of the transient response of the system.

Reduction of effects of disturbance. The third most important effect of feedback in a control system is the control and partial elimination of the effect of disturbance signals. Many control systems are subject to extraneous disturbance signals which cause the system to provide an inaccurate output. Electronic amplifiers have inherent noise generated within the integrated circuits or transistors, radar antennas are subjected to wind gusts, and many systems generate unwanted distortion signals due to nonlinear elements. Feedback systems have the beneficial aspect that the effect of distortion, noise, and unwanted disturbances can be effectively reduced.

As a specific example of a system with an unwanted disturbance, consider the speed control system for a steel rolling mill. Rolls passing steel through are subject to large load changes or disturbances. As a steel bar approaches the rolls, the rolls turn unloaded. However, when the bar engages in the rolls, the load on the rolls increases immediately to a large value. This loading effect can be approximated by a step change of disturbance torque.

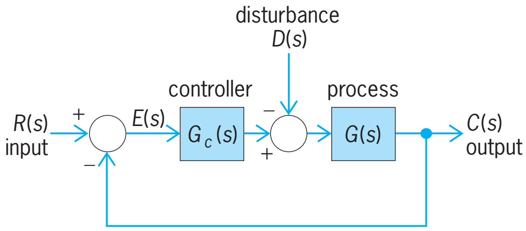

Fig. 6. Feedback control system with a disturbance.

The block diagram of a feedback control system with a disturbance, $D(s)$, is shown in **Fig. 6**, where $H(s) = 1$. Then the output, $C(s)$, may be shown to be given by Eq. (10) when the input, $R(s)$, is set to zero.

$$C(s) = \frac{-G(s)D(s)}{1 + G_c(s)G(s)} \qquad (10)$$

Then if $G_c(s)G(s)$ is much greater than one over the range of s, the approximate result given by Eq. (11)

$$C(s) \simeq -\frac{1}{G_c(s)}D(s) \qquad (11)$$

is obtained. Therefore, if $G_c(s)$ is made sufficiently large, the effect of the disturbance can be decreased by closed-loop feedback.

Reduction of steady-state error. The reduction of the steady-state error of a control system is another advantage of feedback control.

The error of the closed-loop system when $H(s) = 1$ is given by Eq. (12). The steady-state error can be

$$E(s) = \frac{1}{1 + G(s)}R(s) \qquad (12)$$

calculated by using the final-value theorem which is given by Eq. (13), where $e(t)$ is the error variable in

$$\lim_{t\to\infty} e(t) = \lim_{s\to 0} sE(s) \qquad (13)$$

the time domain. Therefore, using a unit step input as comparable input, Eq. (14) is obtained for the closed-

$$e(\infty) = \lim_{s\to 0} s\left(\frac{1}{1 + G(s)}\right)\left(\frac{1}{s}\right) = \frac{1}{1 + G(0)} \qquad (14)$$

loop system. The value of $G(s)$ when $s = 0$ is often called the dc gain and is normally greater than 1. Therefore, the open-loop system will usually have a steady-state error of significant magnitude. By contrast, the closed-loop system with a reasonably large dc-loop gain $G(0)H(0)$ will have a small steady-state error.

Costs of feedback control. While the addition of feedback to a control system results in the advantages outlined above, it is natural that these advantages have an attendant cost.

Increased complexity. The cost of feedback is first manifested in the increased number of components and the complexity of the system. In order to add the feedback, it is necessary to consider several feedback components, of which the measurement component (sensor) is the key component. The sensor is often the most expensive component in a control system. Furthermore, the sensor introduces noise and inaccuracies into the system.

Loss of gain. The second cost of feedback is the loss of gain. For example, in a single-loop system, the open-loop gain is $G(s)$ and is reduced to $G(s)/[1 + G(s)]$ in a unity negative-feedback system. The reduction in closed-loop gain is $1/[1 + G(s)]$ which is exactly the factor that reduces the sensitivity of the system to parameter variations and disturbances. Usually, there is open-loop gain to spare, and one is more than willing to trade it for increased control of the system response.

However, it is the gain of the input-output transmittance that is reduced. The control system does possess a substantial power gain which is fully utilized in the closed-loop system.

Possibility of instability. Finally, a cost of feedback is the introduction of the possibility of instability. While the open-loop system is stable, the closed-loop system may not be always stable.

Necessity of considering problems. The addition of feedback to dynamic systems results in several additional problems for the designer. However, for most cases, the advantages far outweigh the disadvantages, and a feedback system is utilized. Therefore, it is necessary to consider the additional complexity and the problem of stability when designing a control system.

It is desired that the output of the system $C(s)$ equal the input $R(s)$. However, one might ask, "Why not simply set the transfer function $G(s) = C(s)/R(s)$ equal to 1?" The answer to this question is that the process (or plant) $G(s)$ was necessary in order to provide the desired output; that is, the transfer function $G(s)$ represents a real process and possesses dynamics which cannot be neglected. To set $G(s)$ equal to 1 implies that the output is directly connected to the input. However, it must be recalled that a specific output, such as temperature, shaft rotation, or engine speed, is desired, while the input might be a potentiometer setting or a voltage. The process $G(s)$ is necessary in order to provide the physical process between $R(s)$ and $C(s)$. Therefore, a transfer function $G(s) = 1$ is unrealizable, and a practical transfer function must be adopted.

State variables and the time-domain. A useful approach to the analysis and design of feedback systems was outlined above. The Laplace transform was utilized to transform the differential equations representing the system into an algebraic equation expressed in terms of the complex variable, s. Utilizing this algebraic equation, a transfer function representation of the input-output relationship was obtained. The Laplace transform approach, carried out in terms of the complex variable s and accomplished in the frequency domain, is extremely useful; it is and will remain one of the primary tools of the control engineer. However, the limitations of the frequency-domain techniques and the attractiveness of the time-domain approach require a reconsideration of the time-domain formulation of the equations representing control systems.

The frequency-domain techniques are limited in applicability to linear, time-invariant systems.

Furthermore, they are particularly limited in their usefulness for multivariable control systems because of the emphasis on the input-output relationship of transfer functions. By contrast, the time-domain techniques may be readily utilized for nonlinear, time-varying, and multivariable systems. A time-varying control system is a system for which one or more of the parameters of the system may vary as a function of time. For example, the mass of a missile varies as a function of time as the fuel is expended during flight. A multivariable system is a system with several input and output signals. Furthermore, the solution of a time-domain formulation of a control system problem is facilitated by the availability and ease of use of digital and analog computers.

Definition of state variables. The time-domain analysis and design of control systems utilizes the concept of the state of a system. The state of a system is a set of numbers such that the knowledge of these numbers and the input functions will, with the equations describing the dynamics, provide the future state and output of the system. For a dynamic system, the state of a system is described in terms of a set of state variables $[x_1(t), x_2(t), \ldots, x_n(t)]$. The state variables determine the future behavior of a system when the present state of the system and the excitation signals are known. A set of state variables $(x_1, x_2, \ldots, x_n)$ is a set such that knowledge of the initial values of the state variables $[x_1(t_0), x_2(t_0), \ldots, x_n(t_0)]$ at the initial time t_0, and of the input signals $u_1(t)$ and $u_2(t)$ for times t greater than t_0, suffices to determine the future values of the output and state variables. *See* LINEAR SYSTEM ANALYSIS.

A simple example of a state variable is the state of an on-off light switch. The switch can be in either the on or off position, and thus the state of the switch can assume one of two possible values. Thus if the present state (position) of the switch is known at t_0 and if an input is applied, the future value of the state of the element can be determined.

Example of dynamic system. The concept of a set of state variables which represent a dynamic system can be illustrated in terms of the spring-mass-damper system shown in **Fig. 7**. The number of state variables chosen to represent this system should be as few as possible in order to avoid redundant state variables.

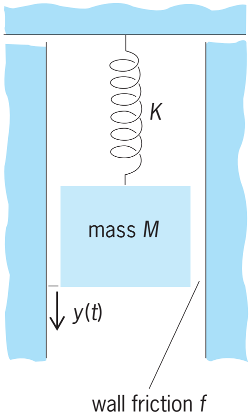

Fig. 7. **Spring-and-mass system with wall friction.**

A set of state variables sufficient to describe this system is the position $y(t)$ and the velocity of the mass. Therefore, a set of state variables is defined as (x_1,x_2), given by Eqs. (15).

$$x_1(t) = y(t) \qquad x_2(t) = \frac{dy(t)}{dt} \tag{15}$$

The differential equation describing the behavior of the system is usually written as Eq. (16), where M

$$M\frac{d^2y}{dt^2} + f\frac{dy}{dt} + Ky = u(t) \tag{16}$$

is the mass, K is the force constant of the spring, and the coefficient f determines the frictional force exerted by the wall. In order to write Eq. (16) in terms of the state variables, one substitutes the definition of the state variables and obtains Eq. (17). Therefore,

$$M\frac{dx_2}{dt} + fx_2 + Kx_1 = u(t) \tag{17}$$

the differential equations which describe the behavior of the spring-mass-damper system may be written as a set of two first-order differential equations, Eqs. (18) and (19). This set of differential equations

$$\frac{dx_1}{dt} = x_2 \tag{18}$$

$$\frac{dx_2}{dt} = \frac{-f}{M}x_2 - \frac{K}{M}x_1 + \frac{1}{M}u \tag{19}$$

describes the behavior of the state of the system in terms of the rate of change of each state variable.

Matrix differential equation. The state of a system is described by the set of first-order differential equations written in terms of the state variables $(x_1, x_2, \ldots, x_n)$. These first-order differential equations may be written in general form as Eqs. (20), where $\dot{x} = dx/dt$.

$$\begin{aligned}
\dot{x}_1 &= a_{11}x_1 + a_{12}x_2 + \cdots \\
&\qquad + a_{1n}x_n + b_{11}u_1 + \cdots + b_{1m}u_m \\
\dot{x}_2 &= a_{21}x_1 + a_{22}x_2 + \cdots \\
&\qquad + a_{2n}x_n + b_{21}u_1 + \cdots + b_{2m}u_m \\
&\ \cdot \\
&\ \cdot \\
&\ \cdot \\
\dot{x}_n &= a_{n1}x_1 + a_{n2}x_2 + \cdots \\
&\qquad + a_{nn}x_n + b_{n1}u_1 + \cdots + b_{nn}u_m
\end{aligned} \tag{20}$$

Thus this set of simultaneous differential equations may be written in matrix form. The column matrix consisting of the state variables is called the state vector and is written as Eq. (21), where the boldface indicates a matrix. The matrix of input signals

$$\mathbf{x} = \begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_n \end{bmatrix} \tag{21}$$

is defined as **u**. Then the system may be represented by the compact notation of the system vector differential equation as Eq. (22). The matrix **A** is an

$$\dot{\mathbf{x}} = \mathbf{Ax} + \mathbf{Bu} \tag{22}$$

$n \times n$ square matrix, and **B** is an $n \times m$ matrix. The vector matrix differential equation relates the rate of change of the state of the system to the state of the system and the input signals. In general, the outputs of a linear system may be related to the state variables and the input signals by the vector matrix equation (23), where **c** is the set of output signals expressed in

$$\mathbf{c} = \mathbf{Dx} + \mathbf{Hu} \tag{23}$$

column vector form. *See* MATRIX CALCULUS; MATRIX THEORY.

The solution of the matrix differential equation uses the matrix exponential given by Eq. (24). The

$$\phi(t) = e^{\mathbf{A}t} \tag{24}$$

matrix exponential function describes the unforced response of the system and is called the fundamental or transition matrix $\phi(t)$. Therefore, the solution may be written as Eq. (25).

$$\mathbf{x}(t) = \phi(t)\mathbf{x}(0) + \int_0^t \phi(t-\tau)\mathbf{Bu}(\tau)\,d\tau \tag{25}$$

The solution to the unforced system (that is, when $u = 0$) is given simply by Eq. (26). Hence, in order to

$$\begin{bmatrix} x_1(t) \\ x_2(t) \\ \cdot \\ \cdot \\ \cdot \\ x_n(t) \end{bmatrix} = \begin{bmatrix} \phi_{11}(t) & \cdots & \phi_{1n}(t) \\ \phi_{21}(t) & \cdots & \phi_{2n}(t) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \phi_{n1}(t) & \cdots & \phi_{nn}(t) \end{bmatrix} \begin{bmatrix} x_1(0) \\ x_2(0) \\ \cdot \\ \cdot \\ \cdot \\ x_n(0) \end{bmatrix} \tag{26}$$

determine the transition matrix, all initial conditions are set to zero except for one state variable, and the output of each state variable is evaluated. That is, the term $\phi_{ij}(t)$ is the response of the ith state variable due to an initial condition on the jth state variable when there are zero initial conditions on all the other states. The time-domain approach may be used to investigate the performance of a control system as well as to design improved systems.

Time response. The time response of a second-order feedback control system (**Fig. 8**) is illustrative of the normal range of response of a control system. The transfer function of the process of such a system has the general form $G(s) = K/s(s+p)$, where K is the gain of the process, and the transfer function contains a pole at the origin of the s-plane and one pole at $s = -p$. The response to a unit step input will be determined. The closed-loop output is given by Eq. (27). Utilizing a generalized notation, Eq. (27) may be rewritten as Eq. (28),

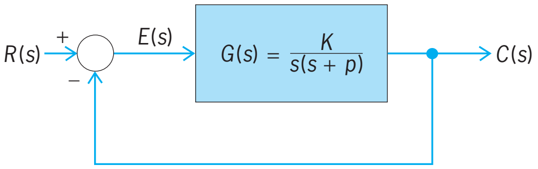

Fig. 8. Closed-loop second-order control system.

$$C(s) = \frac{G(s)}{1+G(s)}R(s) = \frac{K}{s^2+ps+K}R(s) \tag{27}$$

$$C(s) = \frac{\omega_n^2}{s^2 + 2\zeta\omega_n^2 + \omega_n^2}R(s) \tag{28}$$

where ω_n is the natural frequency and ζ is called the damping ratio. With a unit step input, this becomes Eq. (29), for which the transient output is given by Eq. (30), where $\beta = \sqrt[2]{1-\zeta^2}$ and $\phi = \tan^{-1}\beta/\zeta$.

$$C(s) = \frac{\omega_n^2}{s(s^2 + 2\zeta\omega_n s + \omega_n^2)} \tag{29}$$

$$c(t) = 1 - \frac{1}{\beta}e^{-\zeta\omega}n^t \sin(\omega_n t + \theta) \tag{30}$$

The transient response of this second-order system for various values of the damping ratio ζ is shown in **Fig. 9**. As ζ decreases, the overshoot of the response increases. It is usually desired to have a rapid response to a step input while minimizing the overshoot.

Standard performance measures are usually defined in terms of the step response of a system (**Fig. 10**). The swiftness of the response is measured by the rise time T_r and the peak time T_p. For underdamped systems with an overshoot, the 0–100% rise time is a useful index.

The similarity with which the actual response matches the step input is measured by the percent overshoot and settling time T_s. The percent overshoot, P.O., is defined by Eq. (31) for a unit step input,

$$\text{P.O.} = \frac{M_{p_t} - 1}{1} \times 100\% \tag{31}$$

where M_{pt} is the peak value of the time response. The settling time T_s is defined as the time required for the system to settle within a certain percentage δ of the input amplitude. This band of $\pm\delta$ is shown in Fig. 10. For the second-order system with a closed-loop damping constant ω_n, the response remains within 2% after four time constants τ, Eq. (32). There-

$$T_s = 4\tau = \frac{4}{\zeta\omega_n} \tag{32}$$

fore, the settling time is defined as four time constants of the dominant response. Finally, the steady-state error of the system may be measured on the step response of the system as shown in Fig. 10. *See* TIME CONSTANT.

Stability of closed-loop systems. The transient response of a feedback control system is of primary interest and must be investigated. A very important characteristic of the transient performance of a system is the stability of the system. A stable system is defined as a system with a bounded system response. That is, if the system is subjected to a bounded input

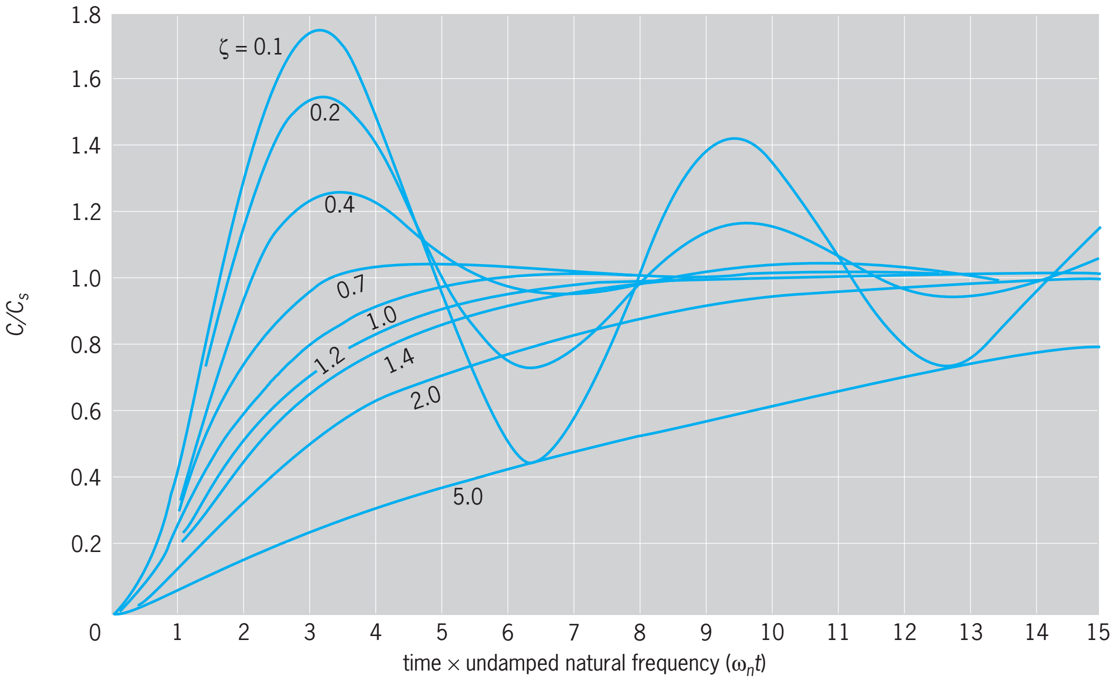

Fig. 9. Response of a second-order system to a step input. C = output at time t; C_s = output when time t is ∞.

or disturbance and the response is bounded in magnitude, the system is said to be stable.

The concept of stability can be illustrated by considering a right circular cone placed on a plane horizontal surface. If the cone is resting on its base and is tipped slightly, it returns to its original equilibrium position. This position and response is said to be stable. If the cone rests on its side and is displaced slightly, it rolls with no tendency to leave the position on its side. This position is designated as neutral stability. On the other hand, if the cone is placed on its tip and released, it falls onto its side. This position is said to be unstable.

The stability of a dynamic system is defined in a similar manner. The response to a displacement, or initial condition, will result in either a decreasing, neutral, or increasing response. Specifically, it follows from the definition of stability that a linear system is stable if and only if the absolute value of its response to an impulse input $g(t)$, integrated over an infinite range, is finite.

There are three general approaches to determining the stability of a system: (1) the s-plane approach, (2) the frequency-plane ($j\omega$) approach, and (3) the time-domain approach. Only the first will be considered here.

The stability requirement of a linear system may be defined in terms of the location of the poles in the closed-loop system transfer function, which may be written as Eq. (33), where $q(s) = \Delta(s)$ is the characteristic polynomial whose roots are the poles of the closed-loop system. The output response for an impulse function input is then given by Eq. (34),

$$T(s) = \frac{p(s)}{q(s)} = \frac{K\prod_{i=1}^{M}(s+z_i)}{S^N\prod_{k=1}^{Q}(s+\sigma_k)\prod_{m=1}^{R}[s^2+2\alpha_m s+(\alpha_m^2+\omega_m^2)]} \tag{33}$$

$$c(t) = \sum_{k=1}^{Q} A_k e^{-\sigma} k^t + \sum_{m=1}^{R} B_m \left(\frac{1}{\omega_m}\right) e^{-\alpha} m^t \sin \omega_m^t \tag{34}$$

when $N = 0$. It follows from Eq. (34) that the poles in the left-hand portion of the s plane result in a decreasing response for disturbance inputs. Similarly, poles on the imaginary axis (the $j\omega$ axis) and in the

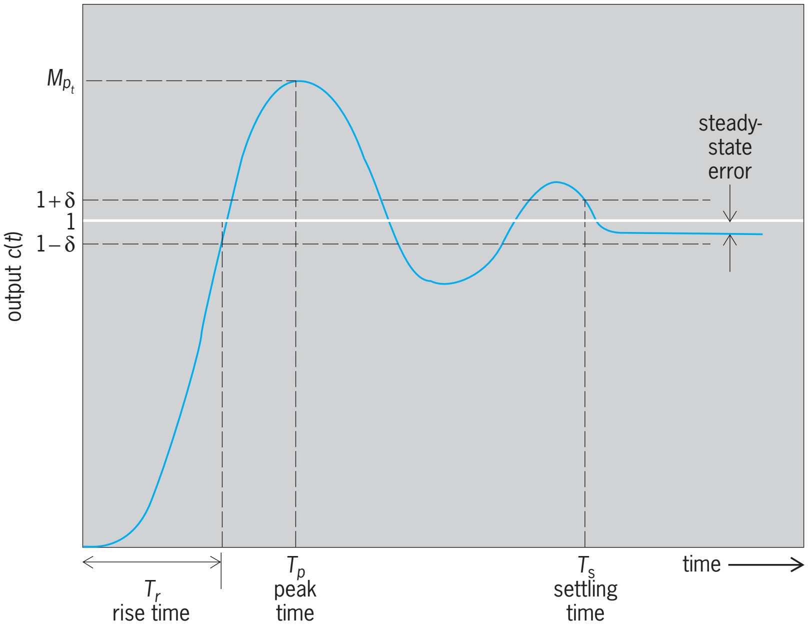

Fig. 10. Step response of a control system.

right-hand plane result in a neutral and an increasing response, respectively, for a disturbance input. Clearly, in order to obtain a bounded response, the poles of the closed-loop system must be in the left-hand portion of the *s* plane. Thus, a necessary and sufficient condition that a feedback system be stable is that all the poles of the system transfer function have negative real parts.

Therefore, one can ascertain the stability of a feedback control system by determining the roots of the characteristic polynomial $q(s)$. A method for determining whether any of the roots of $q(s)$ lie in the right half of the *s* plane, and thereby ascertaining the stability of the system, was developed independently by A. Hurwitz and E. J. Routh, in the late 1800s. *See* CONTROL SYSTEM STABILITY.

Design and compensation. The performance of a feedback control system is of primary importance. A suitable control system is stable and results in an acceptable response to input commands, is less sensitive to the system parameter changes, results in a minimum steady-state error for input commands, and finally, is able to eliminate the effect of undesirable disturbances. A feedback control system that provides an optimum performance without any necessary adjustments is rare indeed. Usually one finds it necessary to compromise among the many conflicting and demanding specifications and to adjust the system parameters to provide a suitable and acceptable performance when it is not possible to obtain all the desired optimum specifications.

As discussed above, it is often possible to adjust the system parameters in order to provide the desired system response. However, it is often not possible to simply adjust a system parameter and thus obtain the desired performance. Rather, the scheme or plan of the system must be reexamined, and a new design or plan must be obtained which results in a suitable system. Thus, the design of a control system is concerned with the arrangement, or the plan, of the system structure and the selection of suitable components and parameters. For example, if one desires a set of performance measures to be less than some specified values, one often encounters a conflicting set of requirements. If these two performance requirements cannot be relaxed, the system must be altered in some way. The alteration or adjustment of a control system, in order to make up for deficiencies and inadequacies and provide a suitable performance, is called compensation.

In redesigning a control system in order to alter the system response, an additional component or device is inserted within the structure of the feedback system to equalize or compensate for the performance deficiency. The compensating device may be an electric, mechanical, hydraulic, pneumatic, or other type of device or network, and is often called a compensator. An electric circuit serves as a compensator in many control systems. The transfer function of the compensator is designated as $G_c(s) = E_{out}(s)/E_{in}(s)$, and the compensator may be placed in a suitable location within the structure of the system. The system when the compensator is placed in the forward path is illustrated in **Fig. 11**.

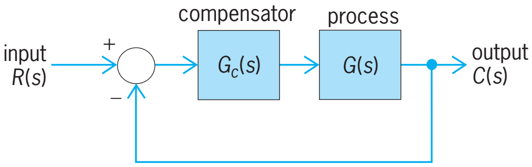

Fig. 11. Cascade compensator in a feedback system.

The performance of a system may be specified by requiring a certain peak time T_p, maximum overshoot, and settling time for a step input. Furthermore, it is usually necessary to specify the maximum allowable steady-state error for several test signal inputs and disturbance inputs. These performance specifications may be defined in terms of the desirable location of the poles and zeros of the closed-loop system transfer function, $T(s)$. Thus, the performance of a control system may be described in terms of frequency-domain performance measures.

The time-domain method, expressed in terms of state variables, may also be utilized to design a suitable compensation scheme for a control system. Typically, one is interested in controlling the system with a control signal $u(t)$, which is a function of several measurable state variables. Then one develops a state-variable controller which operates on the information available in measured form. This type of system compensation is quite useful for system optimization.

Quite often, in practice, the best and simplest way to improve the performance of a control system is to alter, if possible, the process itself. That is, if the system designer is able to specify and alter the design of the process which is represented by the transfer function $G(s)$, then the performance of the system may be readily improved. For example, in order to improve the transient behavior of a servomechanism position controller, one can often choose a better motor for the system. In the case of an airplane control system, one might be able to alter the aerodynamic design of the airplane and thus improve the flight transient characteristics. However, often the process is fixed and unalterable or has been altered as much as is possible and is still found to result in an unsatisfactory performance. Then the addition of compensation networks becomes useful for improving the performance of the system. In the following discussion, it will be assumed that the process has been improved as much as possible and that the $G(s)$ representing the process is unalterable.

Digital computer control systems. The use of a digital computer as a compensator device grew after 1970 as the price and reliability of digital computers improved dramatically. A block diagram of a single-loop digital control system is shown in **Fig. 12**. The digital computer in this system configuration receives the input and output and performs calculations in order to provide an output $u^*(t)$. It may

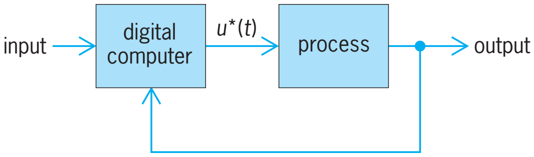

Fig. 12. Digital computer control system.

be programmed to provide an output $u^*(t)$, so that the performance of the process is near or equal to that desired. Many computers are able to receive and manipulate several inputs, so a digital computer control system can often be a multivariable system. *See* DIGITAL COMPUTER; DIGITAL CONTROL.

Within a computer control system, the digital computer receives and operates on signals in digital (numerical) form, as contrasted to continuous signals. The measurement data are converted from analog form to digital form by means of a converter. After the digital computer has processed the inputs, it provides an output in digital form. This output is then converted to analog form through the use of a digital-to-analog converter. *See* ANALOG-TO-DIGITAL CONVERTER; DIGITAL-TO-ANALOG CONVERTER.

Automatic handling equipment for home, school, and industry is particularly useful for hazardous, repetitious, dull, or simple tasks. Machines that automatically load and unload, cut, weld, or cast are used by industry in order to obtain accuracy, safety, economy, and productivity.

Robots are programmable computers integrated with machines. They often substitute for human labor in specific repeated tasks. Some devices even have anthropomorphic mechanisms, including what might be recognized as mechanical arms, wrists, and hands. Robots may be used extensively in space exploration and assembly as well as for various industrial applications. *See* ROBOTICS. Richard C. Dorf

Modeling and simulation. The design of feedback control systems generally assumes that a mathematical model of the system to be controlled is available. The model may have been obtained experimentally by applying test input signals and measuring the response, or analytically by utilizing the laws of physics to derive the equations representing the system. The model would generally be expressed either as a differential equation relating the system's input and output signals or as a transfer function in the complex Laplace variable $s = \sigma + j\omega$ for the special case where the system is linear. The values of the coefficients in the differential equation or transfer function would be functions of the physical quantities in the system. The form of the compensator used in the feedback control system to make it respond satisfactorily to inputs, as well as to possess sufficient stability, would depend on the model for the system being controlled.

At several stages in the control system design process, it is desirable to use a simulation of the control system. Simulation refers in general to the process of numerically representing the equations that describe the system on a digital computer. This allows the designer to analyze the performance of the control system relative to the specifications, and indicates how the design should be modified in order to make its performance more acceptable. Analog computers, although still available for simulation, are now less used than digital computers. Simulation on a computer (analog or digital) permits the system to be analyzed without expending the time and the cost of constructing a physical model, or of testing the system itself. The risk of damage to the equipment by an incorrectly designed compensator is also reduced considerably.

System modeling. When models for physical systems are derived analytically, the equations are developed by applying the appropriate conservation laws. For an electrical system, Kirchhoff's current and voltage laws may be used to model the relationships between variables. For mechanical systems, Newton's second law of motion or Lagrange's equations may be used. An example is the spring-mass damper system of Fig. 7, and the variables and parameters of this simple example. The sum of the applied and reactive forces from the spring, mass, and damper is equal to zero. The reactive forces are given in Eqs. (35)–(37), where

$$F_k = K(y) \quad \text{for spring} \qquad (35)$$

$$F_m = M(\ddot{y}) \quad \text{for mass} \qquad (36)$$

$$F_f = f(\dot{y}) \quad \text{for damper (wall friction)} \qquad (37)$$

the dots over the variables represent differentiation with respect to time. The model for this mechanical system, expressed as a second-order differential equation, becomes, through use of Newton's law, Eq. (16), where $u(t)$ is the total applied force.

Equation (16) is often not convenient in form for control system design. The model of this linear system may be expressed either in state-variable form or as a transfer function. In state-variable form, an nth-order differential equation is expressed as n first-order differential equations. For the model of Equation (16), the state variables $x_1 = y$ and $x_2 = \dot{y}$ and input variable u can be defined. The system model's state equations then become Eq. (38). The output equation for this model is Eq. (39).

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -(K/M) & -(f/M) \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} + \begin{bmatrix} 0 \\ (1/M) \end{bmatrix} u \qquad (38)$$

$$y = [1 \quad 0] \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} + [0]\, u \qquad (39)$$

In order to develop the transfer-function model for this system, the Laplace transform is taken of Eq. (16) under the assumption that all initial conditions are zero. This yields Eq. (40). The transfer function is

$$(Ms^2 + fs + K)Y(s) = U(s) \qquad (40)$$

defined as the ratio of the Laplace transform of the output to the Laplace transform of the input with zero initial conditions. Equation (37) thus provides the transfer function, Eq. (41).

$$\frac{Y(s)}{U(s)} = \frac{(1/M)}{s^2 + (f/M)s + (K/M)} \tag{41}$$

Comparison of Eqs. (16), (38), and (41) shows that the coefficients in the various model forms are related to the component parameters in the physical system. For simple systems, such as that in Fig. 7, the state equation or transfer-function models can be developed by inspecting the original differential equation.

In order to model a system experimentally, certain input test signals are chosen and applied to the system, and the output is measured. Perhaps the most common set of input signals for this purpose is composed of sinusoids of various frequencies. Each input signal is of the form given in Eq. (42) for some value

$$u(t) = \sin(\omega t) \tag{42}$$

of angular frequency ω. The input signals are applied singly to the system until a steady-state condition is reached at the output, which will be of the form given in Eq. (43). Therefore, the ratio of the mag-

$$y(t) = A(\omega)\sin[\omega t + \theta(\omega)] \tag{43}$$

nitudes of output to input signal is $A(\omega)$, and the phase shift of the output relative to the input is $\theta(\omega)$. The plots of $A(\omega)$ and $\theta(\omega)$ versus ω are called Bode plots. Generally, $20\log_{10}[A(\omega)]$ is plotted rather than $A(\omega)$, thereby expressing the magnitude ratio in decibels (dB). From known rules of constructing Bode plots, the transfer function for the system can be obtained from the experimental results. To obtain the best plots for developing the transfer function, the frequencies chosen for the input signals should be evenly spaced on a logarithmic scale. **Figure 13** shows the magnitude plot for a particular system. The circles are the values of magnitude ratio that would be determined experimentally if the corresponding sinusoidal frequencies were input to the system. The curve represents the actual magnitude.

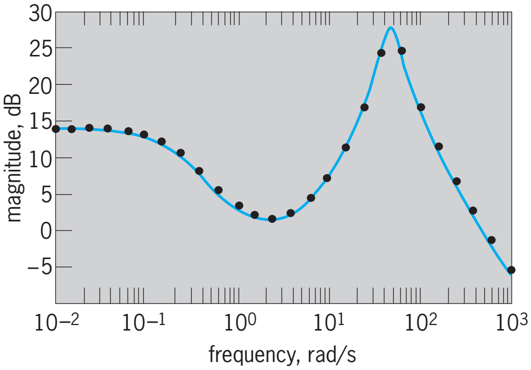

Fig. 13. Frequency domain magnitude for an experimentally determined model.

Equation (44) gives the transfer function for this system.

$$\begin{aligned} G(s) &= \frac{500(s+1)(s+5)}{(s+0.2)(s^2+20s+2500)} \\ &= \frac{5(1+s)(1+s/5)}{(1+s/0.2)[1+s/125+(s/50)^2]} \end{aligned} \tag{44}$$

The second form of $G(s)$ shows how the transfer function can be obtained from the plot. The dc (zero-frequency) gain in the plot is 14 dB $= 20\log_{10}(5)$. The plot starts to curve down near a pole of the transfer function and curves up near a zero. Underdamped complex poles cause an overshoot in the curve, with a sharper peak for less damping. The quadratic factor in the denominator of Eq. (44) corresponds to an undamped natural frequency $\omega_n = 50$ rad/s and a damping ratio $\zeta = 0.2$. The slopes of the Bode magnitude curve change by integral multiples of ±20 dB per decade as poles or zeros are encountered.

Care must be taken in determining a system model experimentally. The amplitude of the input signal must be so chosen that the system response remains linear throughout the experiment. Feedback loops must not be broken if the open-loop system has unstable poles.

System simulation. Simulation is used to evaluate the performance of both open- and closed-loop systems. With simulation on a digital computer, either the continuous-time equations forming the mathematical model may be converted into a discrete-time state equation or difference equation, or they may be solved directly by numerical integration. In any case, a sampling period T must be chosen small enough for the important dynamics of the continuous-time system to be reproduced. In converting to a discrete-time system, a rule of thumb is to choose T so that the highest-frequency components of the original system are sampled five to ten times per period. In using numerical integration, T must be so chosen that the products of T with each of the poles of the system all lie inside the region of absolute stability for the particular integration operator used.

If the system model is given in the state-variable form shown in Eqs. (45), then the discrete-time

$$\begin{aligned} \dot{x}(t) &= Ax(t) + Bu(t) \\ y(t) &= Cx(t) + Du(t) \end{aligned} \tag{45}$$

model which can be used for simulation is given by Eqs. (46) and (47). Here k takes on values

$$x[(k+1)T] = \Phi x(kT) + \Psi u(kT) \tag{46}$$

$$y(kT) = Cx(kT) + Du(kT) \tag{47}$$

[0, 1, 2, ...] and the matrices in Eq. (46) are defined by Eqs. (48) assuming that $u(t)$ is constant in

$$\Phi = e^{AT} \qquad \psi = \int_0^T e^{A\tau} B\, d\tau \tag{48}$$

the interval from kT to $(k+1)T$. Equations (46) and (47) can be solved for the output at each discrete point in time kT.

If the simulation is to be performed as an nth-order difference equation, the system model is expressed in the form of a discrete-time transfer function through the use of the Z transform, as shown in Eq. (49). In this form, the sample period T is implicit

$$\frac{Y(z)}{U(z)} = \frac{b_m z^m + b_{m-1} z^{m-1} + \cdots + b_1 z + b_0}{z^n + a_{n-1} z^{n-1} + \cdots + a_1 z + a_0} \tag{49}$$

in the values of the a_i and b_i coefficients. The solution for the output $y(kT)$ is given by Eq. (50). The

$$\begin{aligned} y(kT) = {} & -a_{n-1} y[(k-1)T] - \cdots \\ & - a_1 y[(k-n+1)T] - a_0 y[(k-n)T] \\ & + b_m u[(k+m-n)T] + \cdots \\ & + b_1 u[(k-n+1)T] + b_0 u[(k-n)T] \end{aligned} \tag{50}$$

output is generated recursively as a sum of previous values of the output and present (if $n = m$) and past values of the input.

If the simulation is to be performed by numerical integration, the continuous-time state model of Eq. (45) is used, along with the selected integration operator. Many computer installations have software which can provide highly accurate solutions to linear or nonlinear differential equations. *See* NUMERICAL ANALYSIS; SIMULATION. Guy O. Beale

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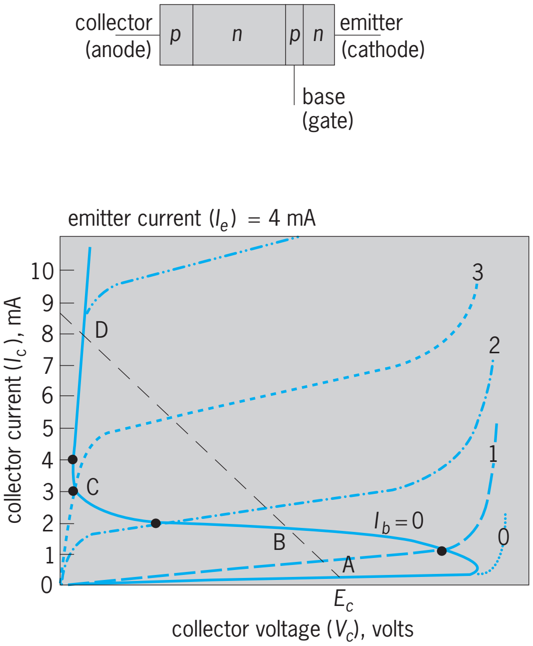
Controlled rectifier

A three-terminal semiconductor junction device with four regions of alternating conductivity type (*pnpn*), also called a thyristor. This switching device has a characteristic such that, once it conducts, the voltage in the circuit in which it conducts must drop below a threshold before the controlled rectifier regains control. Such devices are useful as high-current switches and may be used to drive electromagnets and relays.

The principle of operation can be understood by referring to the **illustration**. The central junction is reverse-biased (positive collector, grounded emitter). The wide n region between collector and base regions prevents holes injected at the collector junction from reaching the collector-to-base barrier by diffusion. The junction between emitter and base is the emitter. When operated as a normal transistor, this device shows a rapid increase of current gain of α (equal to I_c/I_e) with collector current. This effect may be due to a field-induced increase of transport efficiency across the floating n region, or to increased avalanching in the high-field barrier region, or to increased injection efficiency at the two forward-biased junctions, or to a combination of these phenomena.



Controlled rectifier diagram and characteristics.

With a floating-base region ($I_b = 0$), the device is a two-terminal device and collector current I_c must equal emitter current I_e.

By selecting the points on the illustrated characteristics where $I_c = I_e$, the characteristic for the base current $I_b = 0$ is shown as the heavy curve with the negative-resistance characteristic. This characteristic will be found in any transistor which shows an integrated α increasing from below unity at low collector currents to above unity at high collector currents.

If this device is operated as a three-terminal device, the switching between the nonconducting and conducting states can be controlled by the base. If in the grounded-emitter case the collector is biased to $+E_c$ as shown, the device will remain at point A until the base is pulsed positive by at least enough current to carry the emitter current to point B. At this point α exceeds unity and the device will spontaneously switch to point D in the conducting state. To reset the unit, either the emitter must be cut off or the collector voltage must be reduced so that the load line falls below the valley point C. The current of point C is called the holding current. Either of these results can be achieved by appropriate pulses on the base. Modern terminology usually refers to the rectifier terminals as anode and cathode and to the control terminal as the gate. *See* SEMICONDUCTOR RECTIFIER.

Overall current gain α may be maintained below unity for low anode-cathode currents by designing the junction between the anode and the floating *n* region and the junction between the gate and the cathode so each has a low-current injection efficiency below 0.5. For further discussion of four-layer devices *see* TRANSISTOR Lloyd P. Hunter

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Controlled/living radical polymerization

A synthetic method which avoids the premature termination of growing radicals and produces polymers with precise compositions, architectures, and functionalities.

Free-radical polymerization is used extensively in industry for the synthesis of a variety of polymeric materials. Its widespread use is due to its compatibility with many functional groups, its tolerance toward water and acidic media, and its simplicity. Free-radical polymerization routinely is done under various conditions and processes, including bulk, solution, or aqueous environments, and is now the leading industrial method for producing vinyl polymers and copolymers. *See* COPOLYMER; FREE RADICAL; POLYMER; POLYMERIZATION; POLYVINYL RESINS.

In spite of its utility, free-radical polymerization is considered unsuitable for the synthesis of polymers with precise compositions, architectures, and functionalities. This is because of the very limited lifetime of the propagating free-radical species (typically 0.1 to 10 s), which suffer from the propensity to undergo diffusion-controlled termination by recombination or disproportionation (**Fig. 1**), unlike growing ionic species which inherently repel each other. The polymers obtained by free-radical means are therefore generally ill defined and polydisperse (wide molecular-weight distribution), with only limited control over molecular weight or architecture.

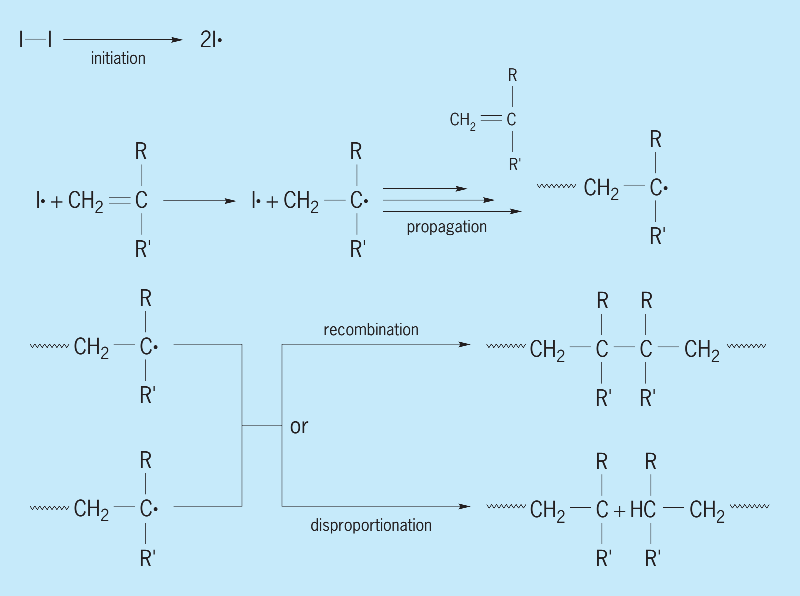

Fig. 1. Free-radical polymerization.

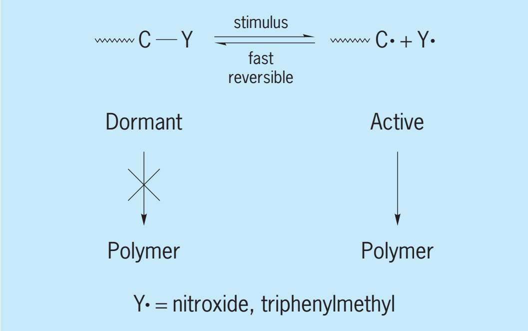

Fig. 2. Active and dormant radical equilibrium.

Until recently, the only option for efficiently controlling the structure and architecture of vinyl polymers was ionic or coordination polymerizations, which do not suffer from irreversible chain-terminating (deactivating) reactions and are known as "living" polymerizations. Unfortunately, living ionic polymerizations are of limited scope since they require stringent purity conditions as well as the total absence of water and oxygen, and are generally incompatible with monomers with functional groups. The necessity to overcome these limitations fueled the development of a new polymerization procedure that would exhibit all characteristic features of regular free-radical polymerization, as well as "living" character, similar to ionic polymerizations.

When addressing this challenge, the primary difficulty was to find a way to avoid the premature termination of the growing radicals. The idea that eventually predominated was to lower the instantaneous concentration of growing radicals by trapping them in a large reservoir of covalent, dormant species and establish a fast equilibrium between the latter and a minute concentration of active, growing radical species. If such a dynamic equilibrium could be established, the probability for spontaneous bimolecular radical termination would be minimized, and all chains would be given an equal opportunity to grow through constant interconversion between their active and dormant forms (**Fig. 2**). Another interesting outcome would be a nearly uniform molecular weight, as determined by the ratio of the concentrations of converted monomer to that of the dormant species (or the initiator). First conceptualized by T. Otsu in 1982, this seminal idea has given birth to the field of controlled/living radical polymerization, which has grown explosively.

Characterized by different mechanisms and chemicals involved, three main methods (by far the most studied) of control of radical polymerization are (1) nitroxide-mediated radical polymerization (NMP), (2) atom transfer radical polymerization (ATRP), and (3) reversible addition-fragmentation chain transfer (RAFT) polymerization.

Nitroxide-mediated radical polymerization. Nitroxides are stable free radicals that are generally used in organic chemistry to trap transient radicals. They react at diffusion-controlled rates with carbon-centered radicals and are known not to initiate polymerization. Taking advantage of these features, M. K. Georges and coworkers used the commercially available nitroxide, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), to trap growing polymer chains and demonstrated that the trapping process is reversible when the temperature range is appropriately chosen. The mechanism of control involves the reversible termination of growing radicals by TEMPO, which functions as a counter radical. Samples of polystyrene exhibiting narrow molecular-weight distributions could be obtained by heating styrene at 123°C (253°F) in the presence of TEMPO and a free-radical initiator. However, the reversible radical capping by TEMPO could not be used for most monomers other than styrene, since most other vinyl monomers showed a total incompatibility with this kind of nitroxide. Anticipating that the structure of the stable radical used to trap the growing radicals must play a crucial role in the success or failure of such living radical polymerization, Y. Gnanou and P. Tordo designed a more effective nitroxide to extend the scope of NMP. They developed a α-hydrogen-bearing nitroxide, namely *N-tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide [DEPN], which is of slightly lower stability than TEMPO and whose main characteristics is to give alkoxyamines with much weaker C—O bonds than TEMPO. Not only could styrene be polymerized at faster rates and under living conditions in the presence of DEPN and a radical initiator, but also the polymerization of acrylates, acrylamides, and more recently methacrylates were found to be living in the presence of DEPN (**Fig. 3**). *See* POLYACRYLATE RESIN; POLYSTYRENE.

In a similar approach, C. Hawker and coworkers developed unimolecular alkoxyamines based on 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO), another α-hydrogen-bearing nitroxide, and used these as initiators and controlling agents for the living polymerization of the above monomers, as well as for acrylonitrile, butadiene, and so others. The beauty of nitroxide-mediated radical polymerization lies in the fact that the amount of terminated chains eventually formed is exactly equal to the excess nitroxide produced by the system to minimize termination reactions. H. Fischer conceptualized this remarkable phenomenon and called it the persistent radical effect. To minimize the amount of terminated chains to a level lower than that determined by the system, the nitroxide can be used in excess with respect to the initiator.

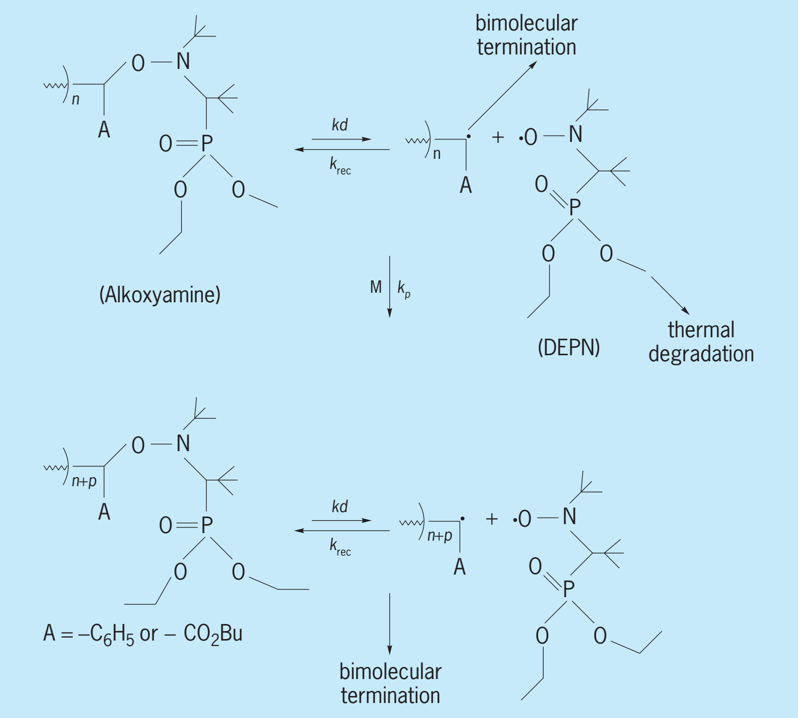

Fig. 3. Nitroxide-mediated radical polymerization of styrene or butylacrylate.

Atom transfer radical polymerization (ATRP). Discovered by K. Matyjaszewski in 1995, atom transfer radical polymerization entails a reversible one-electron oxidation of a transition metal, abstracting a halogen from an organic halide (RX), thus generating a radical species ($R^{\bullet}$) that can attack an unsaturated compound ($CH_2{=}CHR'$) and further propagate ($R{-}[CH_2{-}CHR']_n{-}CH_2{-}C^{\circ}HR'$), followed by a one-electron reduction of the now oxidized metal, transferring its halogen to the growing chain ($R{-}[CH_2{-}CHR']_n{-}CH_2{-}C^{\circ}HR'$), and thus producing ($R{-}[CH_2{-}CHR']_n{-}CH_2{-}CHR'{-}X$) as a dormant species. Such halide abstraction (k_{act}) and subsequent transfer (k_{deact}) occur repeatedly, and polymer chains grow between each activation/deactivation cycle (**Fig. 4**).

Provided the latter process is rapid, all the chains can grow uniformly. The oxidized metal complexes $X\text{-}M_t^{n+1}$ generated by activation of the dormant alkyl halides behave like persistent radicals and therefore reduce the stationary concentration of growing radicals, minimizing the extent of termination. Like nitroxide-mediated radical polymerization, atom transfer radical polymerization is under the control of the persistent radical effect, which means that a successful atom transfer radical polymerization contains a small amount of terminated chains. Also in 1995, M. Sawamoto independently described metal-catalyzed living radical polymerization (MCRP), which appeared to exhibit the same

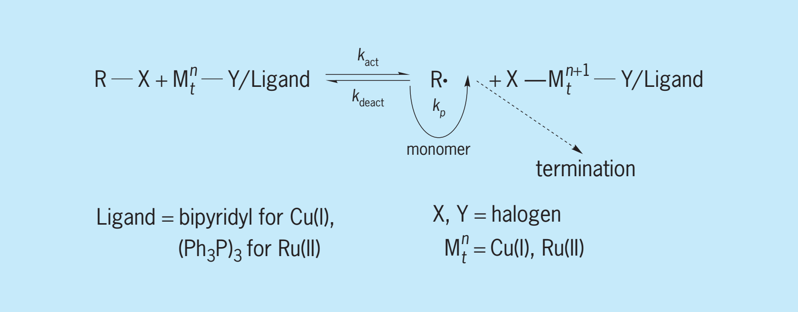

Fig. 4. Atom transfer radical polymerization.

mechanism as that of atom transfer radical polymerization. The initiating systems for both methodologies consist of a transition-metal/ligand complex and an initiator (typically an activated alkyl halide), the role of the former being to generate radical species from the latter by the above mechanism. In choosing the appropriate metal/ligand catalyst for controlling the polymerization, four criteria are critical: (1) the metal center must have at least two accessible oxidation states separated by one electron, (2) it must exhibit affinity toward halogen, (3) the coordination sphere around the metal must be able to accommodate the halogen upon oxidation, and (4) the ligand must form a strong complex with the metal. On these grounds, Matyjaszewski proposed copper(I)bromide associated with a variety of nitrogen-based ligands as the atom transfer radical polymerization catalysts, and Sawamoto associated Ru(II) with phosphine and other ligands as metal-catalyzed living radical polymerization catalysts. As demonstrated by its extensive use in the synthesis of polymers with precise composition and architecture, atom transfer radical polymerization is superior to metal-catalyzed living radical polymerization by its versatility and cost. *See* LIGAND.

Reversible addition-fragmentation chain transfer (RAFT) polymerization. In 1998, E. Rizzardo described a new method for controlling free-radical polymerization that involved the use of thiocarbonylthio compounds reacting by reversible addition-fragmentation transfer (RAFT) with the growing radicals. The effectiveness of these RAFT reagents, mirrored in chain-transfer constants Ctr larger than 1, depends on the nature of their (Z) and (R) groups, Z determining their reactivity toward entering radicals and R its aptitude for fragmentation. The key step in a successful RAFT process is the chain transfer of growing radicals to the RAFT reagent and the subsequent formation of the intermediate radical. The latter then undergoes fragmentation, releasing a radical ($R^\bullet$) which can initiate polymerization. The entering polymer chain now carries a terminal [S═C(Z)S—] moiety and is transformed into a dormant species. After total consumption of the thiocarbonylthio compound, an equilibrium is established between the dormant thiocarbonylthio-carrying chains and active ones, producing a polymer with narrow polydispersity (**Fig. 5**), for large C_{tr} values of the thiocarbonylthio compound.

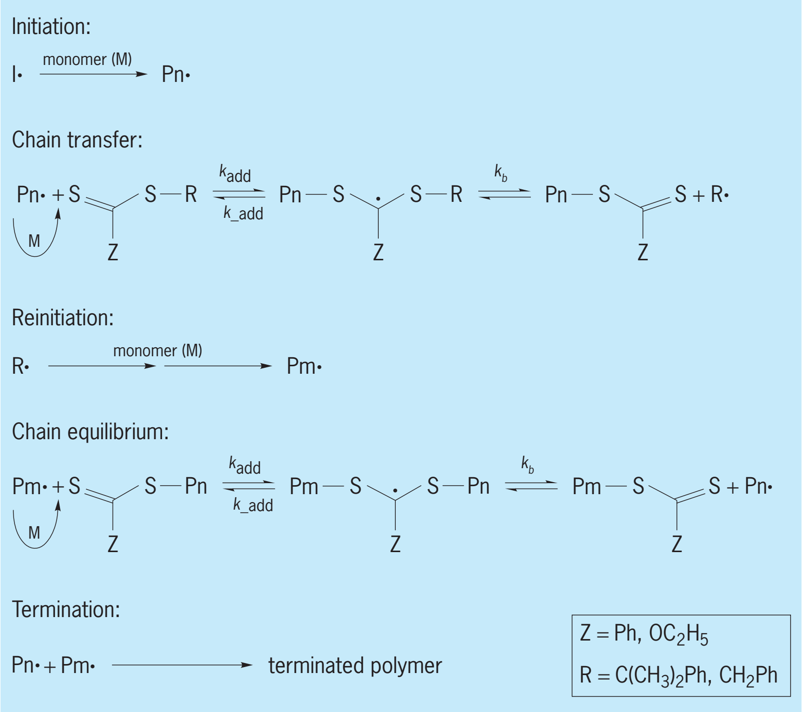

Fig. 5. RAFT polymerization.

The molecular weight is given by the ratio of monomer to thiocarbonylthio compound, and the amount of terminated chains correspond to that of the radical initiator used to trigger the polymerization. The main advantage of RAFT over nitroxide-mediated radical polymerization and atom transfer radical polymerization is its applicability to a wider range of monomers, including functional ones such as acrylic acid or those carrying an electron-donating substituent such as vinyl acetate. D. Charmot of Rhodia Recherches, France, showed that xanthates, which are also thiocarbonylthio compounds, are excellent RAFT reagents for vinyl acetate and analogues, and termed its invention MADIX for macromolecular design via interchange of xanthates.

Application. The three methodologies of controlling free-radical polymerization have their merits and limitations. ATRP is easy to carry out but it cannot be used with certain functional monomers and requires a tedious metal-removal step, whereas RAFT or NMP can be applied to functional and nonfunctional monomers but their controlling agents may necessitate complex synthesis.

With the advent of NMP, ATRP, and RAFT, novel polymeric materials—many of which are totally original and exhibit precise composition such as block and gradient copolymers and complex topology such as star-, comb-, and dendrimer-like polymers—can be obtained under the conditions of regular free-radical polymerization. This paves the way for tremendous opportunities in bio- and nanotechnologies and other high-tech areas. **Yves Gnanou; Daniel Taton**

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Conulariida

A group of extinct invertebrate organisms normally having an elongate, four-sided pyramidal exoskeleton of calcium phosphate composition. Due to poor preservation of key biological structures, the evolutionary affinities and classification of conulariids are uncertain; however, they are often regarded as an unusual group of cnidarians.

Morphology. The conulariid exoskeleton has an aperture at the widest end, and tapers to a closed, slightly rounded apex. The apex is rarely observed in fossils (**Fig. 1***a*). Usually the apical end of the exoskeleton is broken, revealing an internal, slightly bowed partition called the apical wall. Specimens typically range in size from 1 to 30 cm (0.4 to 12 in.). Externally, each of the four sides or faces is crossed by numerous pairs of transverse, curved ridges that meet at a distinct longitudinal midline. On the inside of the exoskeleton, the midline may be represented by a carina, or ridge. Ridges are formed through thickenings of phosphatic skeletal layers (sometimes called rods), and they probably conferred structural strength to an otherwise rather flexible integument. The external surface commonly shows other features such as nodes and small crests. Adjacent sides meet at a longitudinal groove called a corner groove.

Conulariids were evidently attached epibenthic (ocean-bottom-dwelling) organisms. In rare circumstances, the attachment structure, an elongate organic (probably proteinaceous) stalk (Fig. 1*b*), is preserved. The stalk sheaths the apical end of the exoskeleton.

The conulariid exoskeleton was pliable. In shales, they are often found compacted, and in storm bed deposits, they are sometimes oddly bent. Often the faces are bent inward at the aperture (**Fig. 2***b*), and this is interpreted as a taphonomic (postmortem) phenomenon.

Classification. Conulariids are problematic fossils and comprise more than 400 species that are assigned to about 50 genera. Not all these species and genera are undisputed members of the group, however. Because of the rather simple pyramidal or conical morphology of conulariids, it is possible that some fossils have been erroneously categorized. In general, the evolutionary affinities of conulariids and their position within the Linnaean classification system are uncertain because key biological structures were not preserved as fossils. Because of their skeletal shape or composition, at various times they have been classified as worms, mollusks, cnidarians, chordate relatives, and representatives of an extinct phylum. The majority opinion is that these fossils represent an unusual group of cnidarians. The main characters supporting this view include a four-sided symmetry and the presence of a carina along the inside of each side's midline that resembles one of the four interradial septa formed by the ectoderm that divides the enteron (alimentary canal) of a scyphozoan (jellyfish). The pattern of ridge distribution and the phosphatic composition of the conulariid exoskeleton tend to argue against a cnidarian affinity, but not unequivocally. Preserved soft parts of conulariids include an elongate gut tract and various internal ovoid-shaped organs but do not include tentacles. *See* CNIDARIA.

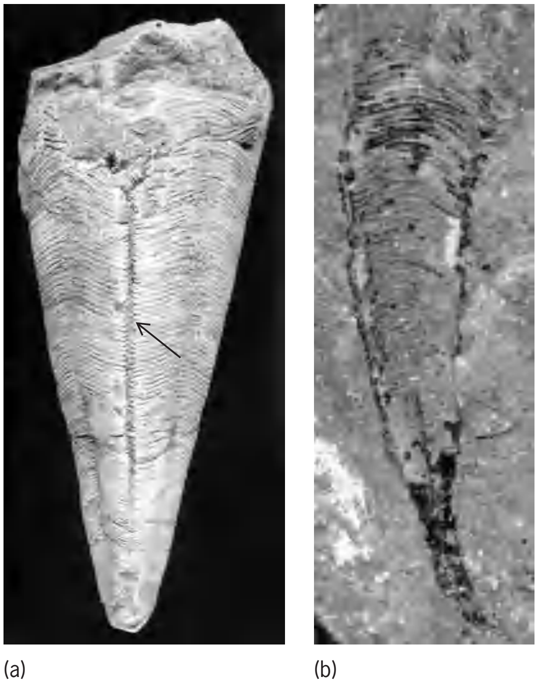
(a) (b)

Fig. 1. Conulariid morphology. (*a*) *Paraconularia byblis*, a well-preserved specimen in siderite (iron carbonate) from the Carboniferous (Mississippian) of Ohio showing two adjacent sides meeting at a deep corner groove (arrow). Ridges along each side meet at a subtle longitudinal midline. Length of specimen: 13 cm (5.1 in.). (*b*) Specimen of *Paraconularia chesterensis* from the Carboniferous (Mississippian) of British Columbia showing attachment stalk (black) extending from the apical end. Length of specimen: 26 mm (1 in.).

Geologic occurrence, paleoecology, and taphonomy. Conulariid fossils are known from marine strata of all continents except Antarctica. In most shale, limestone, and sandstone deposits, articulated conulariids are uncommon to rare. There are notable exceptions, however. Dark, organic-rich shales representing low-oxygen (dysaerobic or exaerobic) environments in the Carboniferous of Kansas and Missouri yield hundreds of specimens per square meter along some bedding planes. Concretions composed of siderite (iron carbonate) in the Carboniferous of Ohio and Kentucky, as well as concretions composed of phosphate in the Carboniferous of Kansas and silica in the Devonian of Bolivia, also yield large numbers of specimens. Normally, deposits rich in conulariid remains have biotas of low overall diversity. Clusters of conulariids (Fig. 2*a*) are a common occurrence. In such circumstances, individuals are usually of approximately the same size. This suggests that the clusters originated from either a spat-fall of larvae or perhaps from asexual budding of a single progenitor.

Following death, conulariid exoskeletons disarticulated into small pieces of integument or even

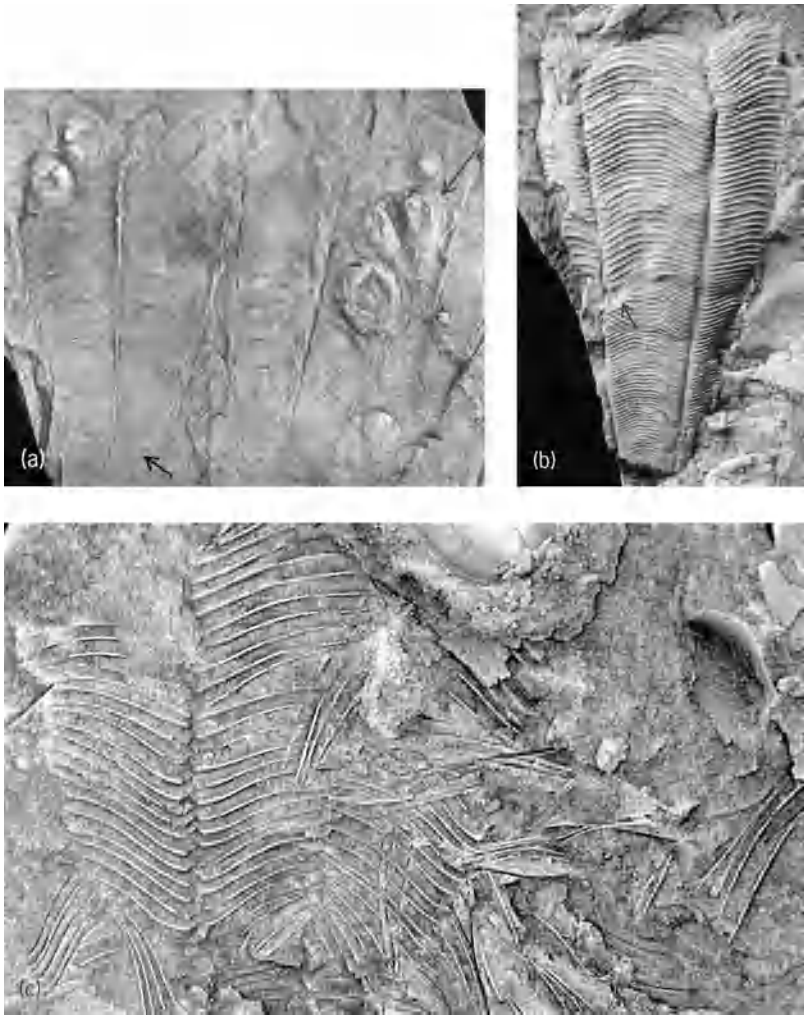

Fig. 2. Conulariid paleoecology and taphonomy. (*a*) Cluster of *Conularia congregata* compacted in shale from the Devonian of New York. The specimens show apical walls (lower arrow), indicating detachment from, or nonpreservation of, their attachment stalks. The conulariids are encrusted by round shells of inarticulate brachiopods (upper arrow). Length of large specimen at left: 6 cm (2.4 in.). (*b*) *Paraconularia chesterensis*, a specimen compacted in shale from the Carboniferous (Mississippian) of Indiana showing one complete, exposed face flanked by two partly exposed sides. Pairs of ridges meeting at the longitudinal midline are exposed on the complete face. At the aperture, the faces have been folded inwardly. A healed bite mark, marked by broken ridges and scar tissue, is present about midway down the left side of the specimen (arrow). Length of specimen: 8 cm (3.1 in.). (*c*) *Paraconularia subulata* from the Carboniferous (Mississippian) of Ohio in mostly disarticulated condition showing fragments of integument (especially at left) and thin, scattered rods. Average length of rods: 3.6 mm (0.14 in.).

into individual rods (Fig. 2*c*). Injuries, both sublethal (Fig. 2*b*) and lethal, inflicted by carnivores such as cephalopods and sharks, have been recorded in conulariids, sometimes in large numbers of specimens from an individual locality. Predation must have led to the breakage of conulariid exoskeletons and may account, in part, for the low numbers of articulated specimens in numerous deposits.

Conulariid skeletons, both in life and afterward, often served as attachment sites for other marine organisms. Inarticulate brachiopods (Fig. 2*a*), edrioasteroid echinoderms, sponges, and other animals have been observed attached to conulariid exoskeletons. *See* FOSSIL; PALEOECOLOGY; TAPHONOMY.

Evolutionary history. Conulariids are a relatively small group that have a stratigraphic range through much of the Paleozoic and the lowermost Mesozoic. Small phosphatic fossils that are usually classified as conulariids occur in the lower part of the Cambrian. These fossils, which include hexaconulariids and hexangulaconulariids, if they are phylogenetically related to Ordovician and younger conulariids, differ from these later examples in having small size (typically less than 1 cm in length) and in having a variable number of faces, instead of just four sides. Some fossils from the Neoproterozoic (Ediacaran Period) have been questionably interpreted as close relatives of conulariids, and even as possible ancestral taxa.

Undisputed conulariids occur in the upper part of the Cambrian but do not become a significant part of fossil assemblages until the Middle Ordovician. Peak diversity was apparently reached in the Devonian through Carboniferous. Conulariids became nearly extinct at the end of the Permian, and barely recovered in the Early Mesozoic. They are represented in the Triassic by only one known genus. *See* ANIMAL EVOLUTION; GEOLOGIC TIME SCALE.

Loren E. Babcock

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Convection (heat)

The transfer of thermal energy by actual physical movement from one location to another of a substance in which thermal energy is stored. A familiar example is the free or forced movement of warm air throughout a room to provide heating. Technically, convection denotes the nonradiant heat exchange between a surface and a fluid flowing over it. Although heat flow by conduction also occurs in this process, the controlling feature is the energy transfer by flow of the fluid—hence the name convection. Convection is one of the three basic methods of heat transfer, the other two being conduction and radiation. *See* CONDUCTION (HEAT); HEAT RADIATION; HEAT TRANSFER.

Natural convection. This mode of energy transfer is exemplified by the cooling of a vertical surface in a large quiescent body of air at temperature t_∞. The lower-density air next to a hot vertical surface moves upward because of the buoyant force of the higher-density cool air farther away from the surface

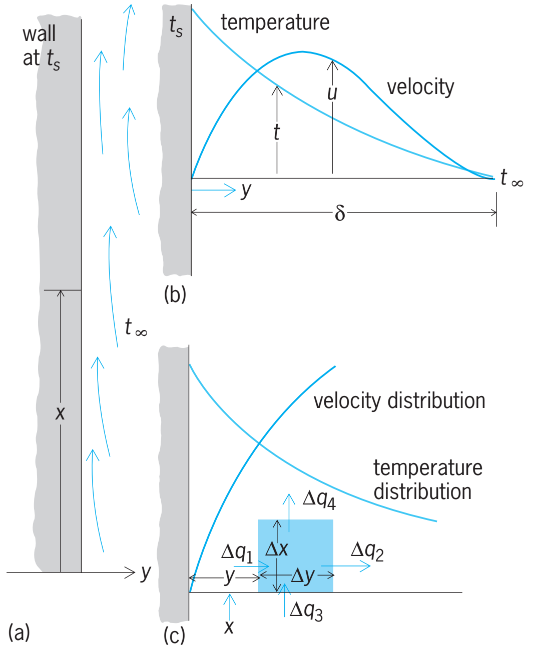

Fig. 1. Temperature and velocity distributions in air near a heated vertical surface. (*a*) Upward movement of hot air. (*b*) Distributions at arbitrary vertical location. The distance δ is that distance at which the velocity and the temperature reach ambient surrounding conditions. (*c*) Distributions in boundary layer.

(**Fig. 1*a***). At any arbitrary vertical location x, the velocity parallel to the surface will increase from zero at the surface to a maximum, and then decrease to zero as ambient surrounding conditions are reached (Fig. 1*b*). In contrast, the temperature of the air decreases from the heated wall value to the surrounding air temperature. These temperature and velocity distributions are clearly interrelated, and the distances from the wall through which they exist are coincident because, when the temperature approaches that of the surrounding air, the density difference causing the upward flow approaches zero.

The region in which these velocity and temperature changes occur is called the boundary layer. Because velocity and temperature gradients both approach zero at the outer edge, there will be no heat flow out of the boundary layer by conduction or convection. *See* BOUNDARY-LAYER FLOW.

An accounting of all of the energy streams entering and leaving a small volume in the boundary layer (Fig. 1*c*) during steady-state conditions yields Eq. (1),

$$\kappa\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}\right)=\rho c_p\left(u\frac{\partial t}{\partial x}+v\frac{\partial t}{\partial y}\right) \qquad (1)$$

where κ, ρ, and c_p are the thermal conductivity, the mass density, and specific heat at constant pressure of the air, and u and v are the velocity components in the x and y directions, respectively. Equation (1) states that the net energy conducted into the element equals the increase in energy of the fluid leaving (convected) over what it had entering.

Very close to the surface, the velocity components u and v both approach 0, and the partial derivatives $\partial^2 t/\partial x^2$ and $\partial t/\partial x$ also approach 0. Therefore, the heat transfer from the wall must be by conduction through a thin layer of air which is effectively stationary relative to the surface. Thus, Eq. (2) is obtained,

$$q=-\kappa\left.\frac{\partial t}{\partial y}\right|_{y\to 0} \qquad (2)$$

where q is the time rate of heat flow per unit of surface area through an infinitesimally thin layer of air. At a very small distance from the surface, the velocity becomes finite and some of the energy conducted normal to the surface is convected parallel to it. This process causes the temperature gradient to decrease, eventually to zero. The solution of a problem requires simultaneous determination of the velocity and temperature distributions throughout the boundary layer. From this, the temperature gradient at the wall and the rate of heat flow can be computed.

The effect of energy leaving a surface and remaining in the boundary layer is (1) a gradual increase in temperature of the air in this layer as it moves upward, and (2) diffusion of energy farther from the surface, entraining more air in (thickening) the boundary layer. This effect can be visualized with interference photographs (**Figs. 2** and **3*a***), where the interference fringes indicate lines of constant temperature (isotherms).

Forced convection. If air is blown across a cylinder (Fig. 3*b*), the boundary layer on the forward half of the cylinder will become so thin that it is not possible to resolve the isotherms within it. Although the natural convection forces are still present in this latter case, they are clearly negligible compared with the imposed forces. The process of energy transfer from the heated surface to the air is not, however, different from that described for natural convection. The major distinguishing feature is that the maximum fluid velocity is at the outer edge of the boundary layer. This difference in velocity profile and the higher velocities provide more fluid near the surface to carry along the heat conducted normal to the surface. Consequently, boundary layers are very thin.

The properties of a fluid which influence its heat-convecting ability are the dynamic viscosity μ, heat capacity at constant pressure c_p, and thermal conductivity κ. These combine in a single significant property in the form $\mu c_p/\kappa = \mu/(\kappa/c_p)$, which is the ratio of the fluid viscosity to the quotient of its heat-conducting and heat-storage capacities. With proper units, this ratio is dimensionless and is called the Prandtl number, N_{Pr}. For air N_{Pr} is approximately 1. Fluids such as oils have values greater than 100. Liquid metals, for which $N_{\mathrm{Pr}} \sim 0.01$, are particularly effective for convective heat-transfer applications. *See* FLUIDS.

Heat-transfer coefficient. The convective heat-transfer coefficient h is a unit conductance used for

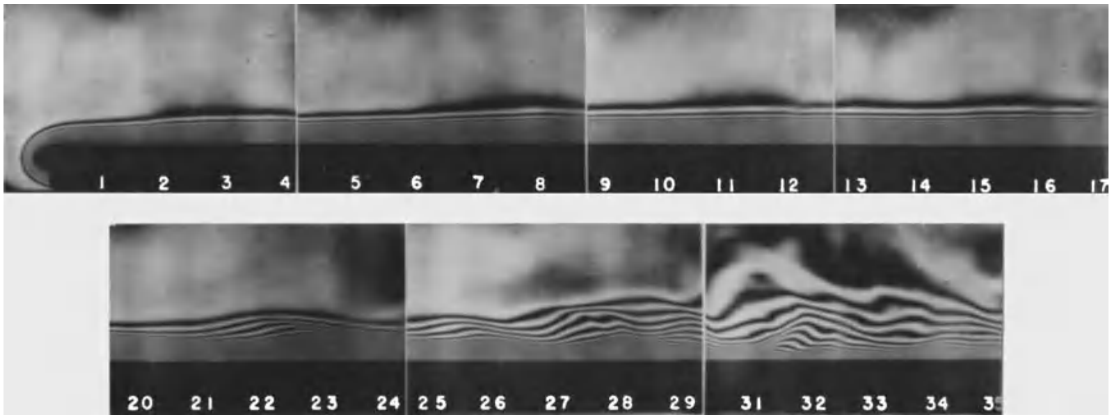

Fig. 2. **Laminar and turbulent convection along a vertical plate, as revealed by interference photographs. Interference fringes indicate lines of constant temperature (isotherms). (*Courtesy of E. R. G. Eckert and E. Soehngen*)**

calculation of convection heat transfer. It was introduced by Isaac Newton and, until the mechanism of convection was properly interpreted, was thought to be a characteristic of the fluid flowing. To describe quantitatively the cooling of objects in air, Newton suggested Eq. (3). This equation, known

$$q = hA(t_{\text{surface}} - t_{\text{fluid}}) \qquad (3)$$

as Newton's law of cooling, is really a definition of h. By comparison with Eq. (2), this coefficient can be seen to be proportional to the slope of the fluid temperature distribution right at the surface, and the thermal conductivity κ of the fluid. Metric units are W/(m^2)(°C); common engineering units are Btu/(h)(ft^2)(°F).

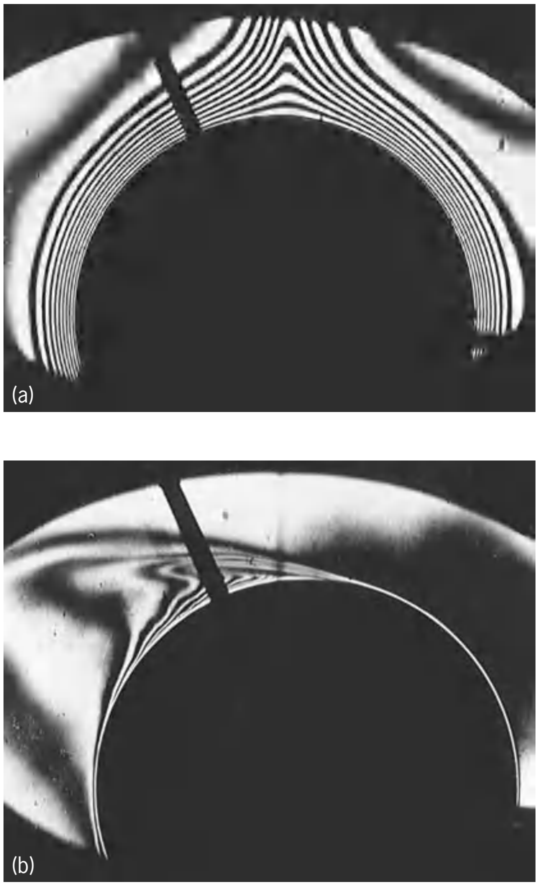

Fig. 3. **Interference photographs of isotherms around a heated horizontal cylinder 4 in. (10 cm) in diameter. (*a*) Cylinder in still air. The outer broad fringe indicates the approximate edge of the boundary layer, which is about $^3/_4$ in. (2 cm). (*b*) Cylinder normal to a 33-ft/s (10-m/s) airstream. The boundary layer on the forward half of the cylinder is so thin that the isotherms cannot be resolved. (*Courtesy of D. L. Doughty and W. H. Giedt*)**

Local and average coefficients. As the fluid in the heated or cooled boundary layer moves along an isothermal surface, it gradually approaches the temperature of the surface. This causes the temperature gradient in the fluid at the surface (and the rate of heat transfer) to decrease in the direction of flow. Taking, for example, an airstream at 104°F (40°C) moving at 50 ft/s (15 m/s) over a flat plate at 68°F (20°C), the local heat-transfer coefficient h_x decreases in 1 ft (0.3 m) to about one-fifth of its leading-edge value. For practical calculations, an average heat-transfer coefficient h is more useful. It is obtained by integrating h_x over the heat-transfer surface and dividing by the surface area. For this system, h is a function of the plate length l, κ, μ, ρ, and u_∞ of the fluid. For comparing geometrically similar systems involving different fluids, dimensional analysis shows that the specific properties can be combined into dimensionless parameters, conveniently reducing the number of independent variables. For the flat plate, these are the Nusselt number, $N_{\text{Nu}} = hl/\kappa$, the Reynolds number, $N_{\text{Re}} = lu_\infty\rho/\mu$, and the Prandtl number, N_{Pr}. For example, it can be shown that in this case Eq. (4) holds. In the case of free convection, the

$$N_{\text{Nu}} = 0.664 N_{\text{Pr}}^{1/3} \sqrt{N_{\text{Re}}} \qquad (4)$$

Grashof number, $N_{\text{Gr}} = \beta g l^3\,\Delta t/\nu^2$ (where β is the coefficient of thermal expansion, and $\nu = \mu/\rho$), replaces the Reynolds number. The product of N_{Gr} and N_{Pr} is known as the Rayleigh number (N_{Ra}), and is used in correlating free convection transfer. Other dimensionless numbers pertinent to convection include the Stanton number, $N_{\mathrm{St}} = h/\rho u c_p = N_{\mathrm{Nu}}/N_{\mathrm{Re}}N_{\mathrm{Pr}}$, which is related to the skin-friction coefficient. *See* DIMENSIONAL ANALYSIS; REYNOLDS NUMBER.

Turbulent flow. Heat convection in turbulent flow is interpreted similarly to that in laminar flow, which has been implied in the above discussion. Rates of heat transfer are higher for comparable velocities, however, because the fluctuating velocity components of the fluid in a turbulent flow stream provide a macroscopic exchange mechanism which greatly increases the transport of energy normal to the main flow direction. For example, if free-stream turbulence caused the boundary-layer flow in the example above to be turbulent, the heat-transfer rate would be about 2.5 times higher. Because of the complexity of this type of flow, most of the information regarding heat transfer has been obtained experimentally. Such results, combined with dimensional analysis, have yielded useful design equations, typical of which is Eq. (5), for predicting the heat transfer in a pipe,

$$\frac{hd}{\kappa} = 0.023\left(\frac{du}{\nu}\right)^{0.8}\left(\frac{\mu c_p}{\kappa}\right)^{0.4} \qquad (5)$$

where d is the pipe diameter.

An illustration of the controlling effect of fluid flow on convective heat transfer is provided by measurements of the local variation around a bluff body such as a cylinder normal to an airstream of velocity u_∞. Major changes occur in the streamline pattern as u_∞ is increased from very low to high values (**Fig. 4**). At very low velocities the flow at the edge of the boundary layer is slowed to zero as it approaches the forward stagnation point. It accelarates as it flows around the cylinder to a maximum at an angle from the stagnation point $\theta = 90^\circ$, and then decelerates to zero at the rear. As the free-stream velocity is increased, the flow separates from the surface before reaching $\theta = 180^\circ$ (Fig. 4*a*). With further increase the separation point moves farther forward (Fig. 4*b*). When the Reynolds number, $N_{\mathrm{Re}} = Du_\infty\rho/\mu$ (where D is the cyclinder diameter), reaches about 1×10^5 (Fig. 4*c*), the flow in the boundary layer around $\theta = 90^\circ$ becomes turbulent. Thus, the boundary can remain attached to the surface longer and the separation point moves toward the rear (Fig. 4*d*). This change may be delayed until N_{Re} reaches as high as 5×10^5 in a low-turbulence-level airstream.

Dramatic changes in the local rate of heat transfer are produced by these changes in the flow. For $N_{\mathrm{Re}} \geq 140{,}000$, the local heat transfer rises rapidly from a minimum around $\theta = 90^\circ$ to a maximum and then decreases to a second minimum around 140°. This variation is due to the change to turbulent flow before separation on the rear of the cyclinder occurs. *See* LAMINAR FLOW; TURBULENT FLOW.

Condensation and boiling. Condensation and boiling are important phase-change processes involving heat release or absorption. Because vapor and liquid movement are present, the energy transfer is basically by convection. Local and average heat-transfer coefficients are determined and used in the Newton cooling-law equation for calculating heat rates which include the effects of the latent heat of vaporization.

Condensation. Consider a saturated or superheated vapor of a single substance in some region. When it comes in contact with a surface maintained at a temperature lower than the saturation temperature, heat flow results from the vapor, releasing its latent heat and condensing on the surface. The condensation process may proceed in two more or less

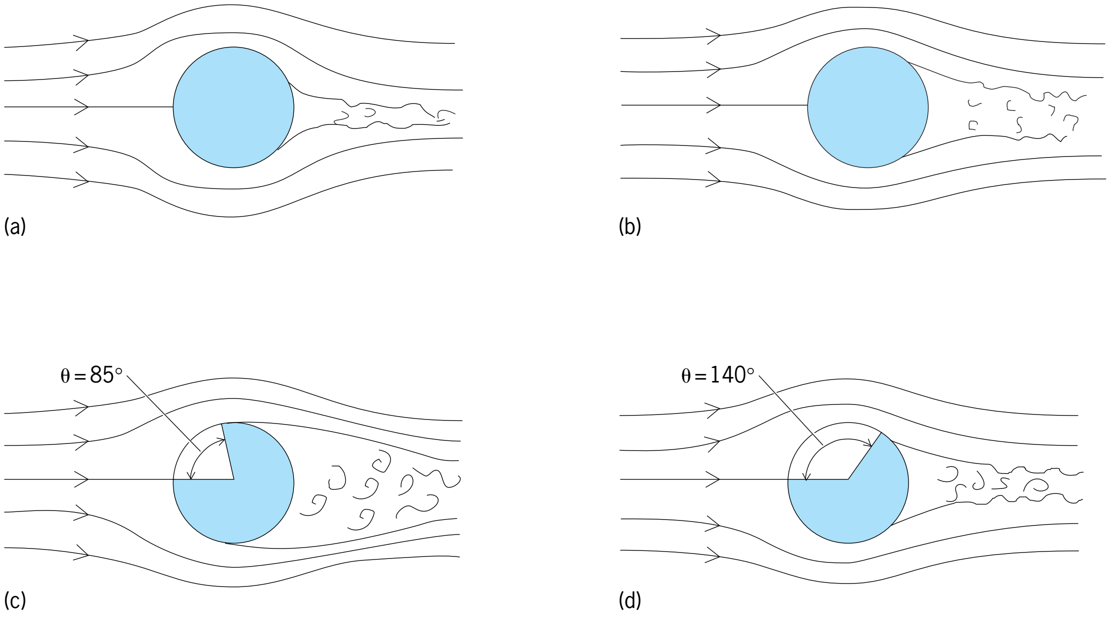

Fig. 4. Streamlines in flow past a cylinder normal to flow at increasing values of the flow velocity (expressed in terms of the Reynolds number, N_{Re}). (*a*) $N_{\mathrm{Re}} \approx 10$. (*b*) $N_{\mathrm{Re}} \approx 10^4$. (*c*) $N_{\mathrm{Re}} \leq 1 \times 10^5$. (*d*) $N_{\mathrm{Re}} \geq 1.5 \times 10^5$.

distinct ways. If there are no impurities in the vapor or on the surface (which need not be smooth), the condensate will form a continuous liquid film. If, however, such contaminants as fatty acids or mercaptans are present, the vapor will condense in small droplets. These droplets increase in size until their weight causes them to run down the surface. In doing so, they sweep the surface free for formation of new droplets. For the same temperature difference between the vapor and surface, heat transfer with dropwise condensation may be 15–20 times greater than filmwise condensation. The dropwise type is therefore very desirable, but conditions under which it will occur are not predictable, and designs are limited to systems for which experimental results are available.

Boiling. In boiling, results indicate the existence of several regimes. The important independent variable is the temperature difference Δt between the hot surface and the fluid relatively far from the surface. For values of Δt up to approximately 10°F (6°C), the liquid is being superheated by natural convection, and q/A is proportional to $\Delta t^{5/4}$. With further increase in Δt, bubbles form at active nuclei on the heated surface. These bubbles break away and rise through the pool, their stirring action causing the heat transfer to be much above that due to natural convection. This phenomenon is called nucleate boiling, and q/A varies as Δt^3 to Δt^4. When the rate of bubble formation becomes so rapid that the bubbles cannot get away before they tend to merge, a vapor film begins to form, through which heat must flow by conduction. The rate of heating then decreases with Δt until complete film boiling is reached and heat flows by radiation and conduction through the film.

The high heat rates which occur during boiling make it a very effective means of absorbing the energy capable of being released in furnaces and nuclear reactors. The high heat rates are also one reason why the vapor power-generating cycles have been successful.

Warren H. Giedt

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Convective instability

A state of fluid flow in which the distribution of body forces along the direction of the net body force is unstable and will thus break down. Fluid flows are subject to a variety of instabilities, which may be broadly viewed as the means by which relatively simple flows become more complex. Instabilities are an important step in the transition between smooth and turbulent flow, and in the atmosphere they are responsible for phenomena ranging from thunderstorms to low- and high-pressure systems. Meteorologists and oceanographers divide instabilities into two broad classes: convective and dynamic. *See* DYNAMIC INSTABILITY.

In the broadest terms, convective instabilities arise when the displacement of a small parcel of fluid causes a force on that parcel which is in the same direction as the displacement. The parcel of fluid will then continue to accelerate away from its initial position, and the fluid is said to be unstable. In most geophysical flows, the convective motions that result from convective instabilities operate very quickly compared with the processes acting to destabilize the fluid; the result is that such fluids seem to be nearly neutrally stable to convection.

Types. The simplest type of convective instability arises when a fluid is heated from below or cooled from above. This heating and cooling result in a temperature distribution as shown in **Fig. 1**; here a small chunk of fluid at temperature T_3 is shown displaced upward. If it conserves its original temperature, it will be warmer than its environment at the same altitude and will accelerate upward, since warm air is less dense than cold air. The parcel is said to be positively buoyant. Warm air rises and cold air sinks; thus a fluid whose temperature decreases with altitude is convectively unstable, while one in which the temperature increases with height is convectively stable. A fluid at constant temperature is said to be convectively neutral. *See* ARCHIMEDES' PRINCIPLE.

The above description assumes that density depends on temperature alone and that density is conserved in parcels of fluid, so that when the parcels are displaced their density does not change. However, in the Earth's atmosphere, neither of these assumptions is true. In the first place, the density of air depends on pressure and on the amount of water vapor in the air, in addition to temperature. Second, the density will change when the parcel is displaced because both its pressure and its temperature will change. Because of these conditions it is convenient to define a quantity known as virtual potential temperature (θ_v) that is conserved and reflects the actual density of

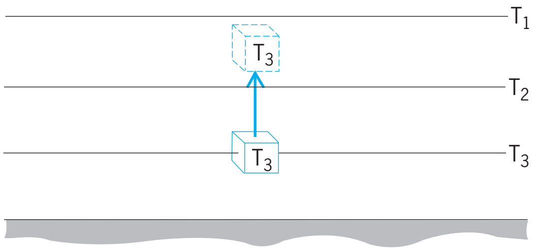

Fig. 1. Diagram showing temperature decreasing upward in a fluid and convective instability. When a small parcel of fluid is displaced upward from its initial position (solid-line box) to a new position (dashed-line box), it will be warmer than its environment and will continue to accelerate upward. T denotes temperature, with T_3 the highest and T_1 the lowest.

air. This quantity is given by Eq. (1), where T is the

$$\theta_v \equiv T\left(\frac{1+(r/0.622)}{1+r}\right)\left(\frac{1000}{p}\right)^{0.287} \qquad (1)$$

temperature in kelvins, p is the pressure in millibars, and r is the number of grams of water vapor in each gram of dry air. When θ_v decreases with height in the atmosphere, it is convectively unstable, while θ_v increasing with height denotes stability.

Over the tropical oceans, the θ_v of air adjacent to the sea surface is continually increased by addition of both heat and water vapor from the ocean, while at higher levels θ_v is decreased by cooling due to radiation to space. The result is that a layer roughly 1600 ft (500 m) deep is continually convecting. The convection is so efficient that this layer of the atmosphere is kept very close to a state of convective neutrality. Measurements show that θ_v is constant with height in this layer to within measurement error. A similar situation prevails over land during the day, when the land is heated by the Sun, but at night the land cools and the air becomes convectively stable (θ_v increases with height).

In the oceans, density is a function of pressure, temperature, and salinity; convection there is driven by cooling of the ocean surface by evaporation of water into the atmosphere and by direct loss of heat when the air is colder than the water. It is also driven by salinity changes resulting from precipitation and evaporation. In many regions of the ocean, a convectively driven layer exists near the surface in analogy with the atmospheric convective layer. This oceanic mixed layer is also nearly neutral to convection.

Convective instabilities are also responsible for convection in the Earth's mantle, which among other things drives the motion of the plates, and for many of the motions of gases within other planets and in stars.

Convective motions. Experiments have been performed to determine what kind of motions result from convective instability. Typically these experiments use a fluid contained between two parallel, horizontal plates maintained at constant temperature, with the lower plate warmer than the upper plate. If the temperature difference is small, the viscosity of the fluid prevents convection from occurring. As the temperature difference is increased beyond a critical value, convection begins as steady overturning cells whose width is roughly equal to the distance between the plates. When the temperature difference is increased further, the cells begin to oscillate and eventually the flow becomes chaotic. Variations on this experiment include one in which the flux of heat, rather than the temperature, is fixed at the parallel plates. In this case, the cells tend to be much broader than they are deep.

Virtually all convection in nature is well into the chaotic regime determined by experiments, and yet natural convection is often organized in distinctive patterns. In the atmosphere, these include long rows of clouds known as cloud streets and regular hexagonal arrays of clouds whose width can be more than 50 times their depth. The reason for this is as yet unknown. Little is known about the organization of convecting fluid in the Earth's mantle, which determines the motion of the plates that make up the Earth's crust. Convection on the Sun is also known to be organized in clumps called granules; these are in turn organized in larger clumps, or supergranules.

Moist convection. In the atmosphere, convection is complicated by the phase changes of water substance. When water vapor condenses into the liquid waterdroplets that make up clouds, for example, the heat that was used to evaporate the water in the first place is released, making the air warmer than it would otherwise be. Conversely, when rain evaporates it takes up heat and makes the air cooler. In addition to these effects, suspended condensate (that is, cloud, rain, snow, hail, and so forth) adds directly to the effective density of the air. All of these effects make moist convection, which produces cumulus clouds and thunderstorms and is considerably more exotic than dry convection.

The criterion for convective instability of moist atmospheres has been the subject of much research. A basic tool for examining the stability of moist atmospheres is the thermodynamic diagram, an example of which is presented in **Fig. 2**. This diagram has pressure on the vertical coordinate, and temperature increases downward and to the right. (Since pressure

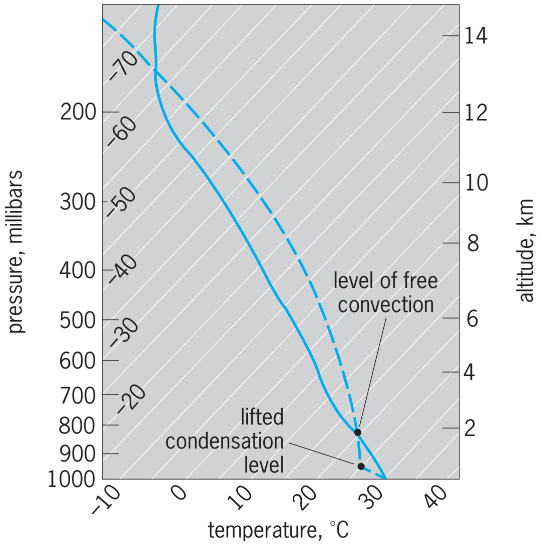

Fig. 2. Thermodynamic diagram with height on the vertical coordinate (with pressure decreasing upward), while temperature increases downward and to the right. The solid line shows an example of temperature measured at various levels in the atmosphere, typically by an ascending instrumented balloon. The broken line shows the temperature that a parcel would have if lifted from near the surface. At the lifted condensation level, water vapor begins to condense, and the parcel cools less rapidly above this point. At the level of free convection, it becomes warmer than its environment and would ascend freely above this point. 1 millibar = 10^2 pascals. 1 km = 0.6 mi. °F = (°C × 1.8) + 32.

decreases with height in the atmosphere, the vertical coordinate also represents height.) The temperature of air measured from an ascending balloon has been plotted as the solid line on this diagram. The thermodynamic diagram may contain various sets of background curves that permit a determination of the temperature of a parcel of air lifted from any point on the sounding. For example, the broken line shows the temperature a parcel of air would have if it were lifted from near the surface. At first, its temperature decreases rapidly with height, since the first law of thermodynamics states that temperature must fall with pressure. Then, when it reaches the lifted condensation level, water vapor begins to condense into cloud, releasing heat, and the temperature does not fall as fast with height.

In the example shown in Fig. 2, the lifted parcel has about the same temperature as the surrounding atmosphere up to its lifted condensation level, reflecting the neutral stability of the layer of air next to the surface. But if the parcel is displaced beyond its level of free convection, it will be warmer than its environment and will accelerate upward. This type of atmosphere is said to be conditionally unstable; that is, it is stable unless near-surface parcels are forcibly displaced beyond their level of free convection. Such an atmosphere will not spontaneously convect, and thus the amount of conditional instability can build up to large values until something triggers convection. The result is severe thunderstorms and sometimes tornadoes. This situation is common in the plains of North America in spring. *See* THUNDERSTORM; TORNADO.

It was formerly believed that the tropical atmosphere is conditionally unstable, but convective stability that is assessed by using thermodynamic diagrams like the one in Fig. 2 omits an important contribution to density: the weight of suspended condensate such as rain, snow, and cloud. When this is included, the tropical atmosphere is nearly neutrally stable to parcels of air displaced upward from near the surface. It is maintained in such a state by the nearly continuous activity of moist convection, which takes the form of cumulus clouds and thunderstorms. In this sense, the whole depth of the tropical troposphere (a layer of air extending up to about 7 mi or 12 km altitude in the tropics) exists in a convectively adjusted state in analogy with the layer near the surface, which has constant θ_v. *See* TROPICAL METEOROLOGY.

Convective instability may be driven by centrifugal as well as by gravitational forces. This is illustrated in **Fig. 3**, which shows the distribution of angular momentum per unit mass (M) in a rotating cylinder of fluid. This angular momentum is defined by expression (2), where r is the radius from the center

$$M \equiv rV \tag{2}$$

and V is the velocity of the fluid rotating about the center. If a ring of fluid centered about the axis of the cylinder is displaced radially inward or outward, it conserves its angular momentum. For example, as the ring of fluid in Fig. 3 is displaced outward, its angular momentum is less than that of the surrounding fluid, and the laws of physics can be used to demonstrate that since the centrifugal force on that fluid is less than on the surrounding fluid, it will accelerate inward. The fluid is then said to be centrifugally stable. A corollary to Archimedes' law states that a fluid with low M tends to sink toward the axis of rotation, while fluid with high M rises away from the axis. A fluid whose angular momentum increases outward is centrifugally stable, while a fluid with M decreasing outward is unstable. The nature of this instability is much like that of thermal convection, and this, too, is a type of convective instability. *See* ANGULAR MOMENTUM.

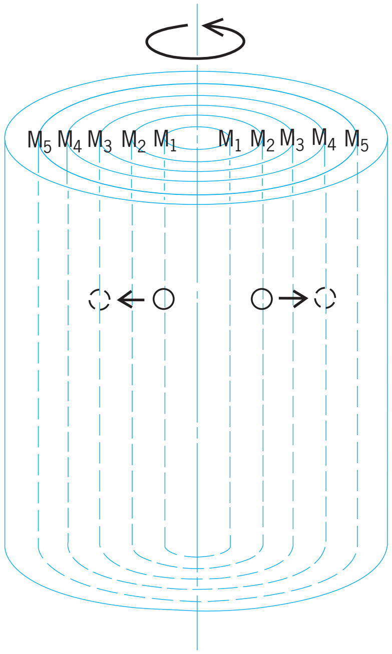

Fig. 3. Diagram of a cylinder of rotating fluid with an angular momentum per unit mass, *M*, which in this case increases outward from the axis (M_1, M_2, M_3, and so forth denote increasing values of *M*). This arrangement is centrifugally stable, since a ring of fluid (solid-line circle) displaced outward to a new position (broken-line circle) will have less centrifugal force acting on it than on its environment; it will therefore accelerate inward toward its initial position.

In the atmosphere, it is possible to have a combination of centrifugal and buoyant convection. It turns out that the criterion for this to happen is that parcels displaced upward along angular momentum surfaces must become positively buoyant. These surfaces are usually sloped in the atmosphere because of the increase with height of atmospheric winds. Convection that results from this combined instability (which is also known as symmetric instability) is also generally sloped and is thus called slantwise convection. This form of convection results in bands of rain and snow embedded in winter storms; these bands may be hundreds of miles wide and as much as 600 mi (1000 km) long. The concept of convective neutrality applies here as well, as measurements made by flying instrumented aircraft along angular momentum surfaces show that parcels displaced along them are almost neutrally buoyant. *See* ATMOSPHERE; ATMOSPHERIC GENERAL CIRCULATION; FLUID FLOW; PRECIPITATION (METEOROLOGY); STORM.

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Converter

A device for processing alternating-current (ac) or direct-current (dc) power to provide a different electrical waveform. The term converter denotes a mechanism for either processing ac power into dc power (rectifier) or deriving power with an ac waveform from dc (inverter). Some converters serve both functions, others only one. *See* RECTIFIER.

Historically, converters were needed to accommodate various needs to match characteristics of the supply voltage. For example, dc motors, which in principle could be connected directly to early dc distribution systems, required a rectifier for operation with ac supplies. *See* DIRECT-CURRENT MOTOR.

While ac has been universally adopted for power distribution and consequently is the standard power supply for industrial, commercial, and domestic purposes, the range of demands for conversion far exceeds the occasional rectifier load. Converters are used for such applications as (1) rectification from ac to supply electrochemical processes with large controlled levels of direct current; (2) rectification of ac to dc followed by inversion to a controlled frequency of ac to supply variable-speed ac motors; (3) interfacing dc power sources (such as fuel cells and photoelectric devices) to ac distribution systems; (4) production of dc from ac power for subway and streetcar systems, and for controlled dc voltage for speed-control of dc motors in numerous industrial applications; and (5) transmission of dc electric power between rectifier stations and inverter stations within ac generation and transmission networks. *See* DIRECT-CURRENT TRANSMISSION.

These are a few examples of the need for converters to be versatile, controllable, and able to handle a wide range of power levels. Furthermore, emphasis on long-term cost of power losses has drawn attention to the efficiency of converters and the ability to contribute to the overall efficiency of their loads. For example, it can be economically advantageous to recapture the kinetic energy of some mechanical loads, which are subject to frequent stops and starts, through a converter power reversal back to the supply (regeneration) rather than losing it as heat in friction braking. This increases operating efficiency in such applications as electric vehicles and steel rolling mills.

Converter development has been furthered by advances in power semiconductors and microprocessors for their control. Beyond the basic converter action, there may be control of voltage, current, power, reactive power, and frequency at the converter output terminals. *See* MICROPROCESSOR.

Types. Until the advent of power semiconductors, converter action was achieved either by rotary converters or mercury-arc valves. In a rotary converter, an electric motor drives a generator. For example, a dc motor drives an ac generator to provide ac voltage at a chosen frequency. The mercury-arc valve is a unidirectional switching device which relies on ionization between a pool of mercury and an anode. Later developments permitted the timing of the start of conduction to be controlled by a grid between the mercury and the anode. Some of the modern semiconductor circuits have evolved from mercury-arc technology.

The introduction of the thyristor (silicon-controlled rectifier) in the 1960s had an immediate effect on converter applications because of its ruggedness, reliability, and compactness. As a controlled, unidirectional, solid-state switch, it replaced mercury-arc devices with ratings in the kilowatt range and, through series–parallel combinations, at high power levels. Power semiconductor devices for converter circuits include (1) thyristors, controlled unidirectional switches that, once conducting, have no capability to suppress current; (2) triacs, thyristor devices with bidirectional control of conduction; (3) gate turn-off devices with the properties of thyristors and the further capability of suppressing current; and (4) power transistors, high-power transistors operating in the switching mode, somewhat similar in properties to gate turn-off devices.

Thyristors are available with ratings from a few watts up to the capability of withstanding several kilovolts and conducting several kiloamperes. All the devices incorporate one or more gates, that is,

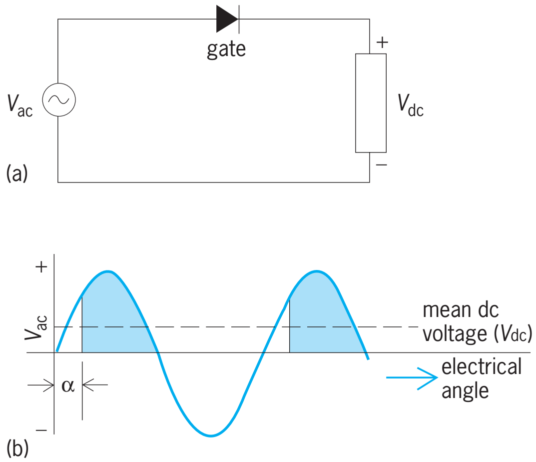

Fig. 1. Thyristor half-wave rectifier. (*a*) Circuit. (*b*) Voltage waveforms. Shaded areas indicate nonsmooth dc output waveform.

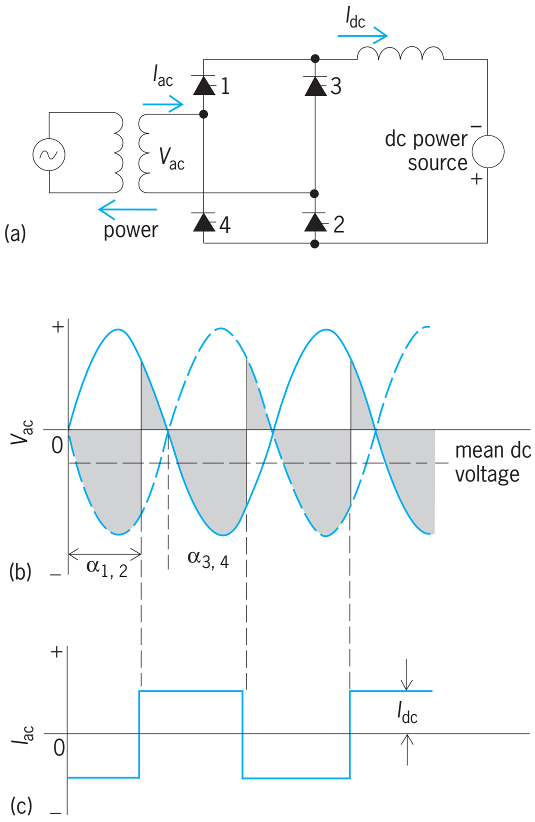

Fig. 2. Inverter operation by thyristor full-wave bridge. (*a*) Circuit. (*b*) Voltage waveforms. Shaded areas indicate nonsmooth dc waveform with negative mean value. (*c*) Current waveform.

low-power input connections to permit point-on-wave control of turn-on relative to the waveform of applied voltage. *See* SEMICONDUCTOR RECTIFIER.

Circuits. Of the many different converter circuits, three types are described.

Half-wave rectifier. The thyristor in the controlled half-wave rectifier (**Fig. 1***a*) conducts on parts of the positive half-cycles of the ac supply to provide a mean dc voltage across the load. Conduction is delayed by the variable control angle α resulting in the nonsmooth dc waveform shown (Fig. 1*b*). In practice, the dc component in the supply current tends to cause saturation problems in supply transformers.

Full-wave circuit. A full-wave circuit (**Fig. 2***a*) has a bidirectional current in the ac supply transformer. Thyristors 1 and 2 are gated together and then, in turn, dc-side current is transferred to thyristors 3 and 4 to provide the negative half-cycle of ac current. The inductor provides some smoothing of the dc waveform. By delaying gating by more than 90 electrical degrees while providing a dc power source (Fig. 2*b*), the sign of the mean dc voltage is reversed so that the circuit now inverts dc power into the ac supply. The ac system must provide an existing ac voltage waveform sufficient to naturally allow the thyristors to turn on and off in the conducting sequence. The ac current waveform is not sinusoidal (Fig. 2*c*); ac filters may be added to reduce the harmonic content. *See* COMMUTATION; ELECTRIC FILTER.

The above examples are called bridge circuits. Inversion into an ac system that does not contain an ac voltage source requires a circuit that either develops internal reverse voltages to turn off thyristors or uses gate turn-off devices. Other types include the cycloconverter which synthesizes a lower frequency from an ac waveform, and the pulse-width-modulated converter which processes a waveform into a series of segments that are recombined into the desired waveform. *See* PULSE MODULATION.

Three-phase bridge. Three-phase ac/dc converters are often used in industrial applications. Very high-power versions are used in power transmission systems.

Converters at the terminal stations of the dc transmission system either rectify three-phase ac voltages to dc or invert the dc voltage to feed power into the adjacent ac system. A three-phase converter bridge is made up of six thyristor valves conducting in sequence as numbered 1, 2, . . . , 6 in **Fig. 3***a*. Bridges are usually connected in series pairs, as shown. The 30° ac phase difference between the converter-side voltages of the wye/wye and the wye/delta converter transformers permits a conduction sequence 1, 1′, 2, 2′, . . . , 6, 6′. This is called 12-pulse operation and gives a smoother dc waveform and less ac harmonic currents.

Each valve is made up of many thyristors in series together with additional components to aid in the voltage sharing between individual thyristors (Fig. 3 *b*). Valves are often combined into single units, such as the quadrivalve in Fig. 3*a*.

Converters range from low-power applications, such as the power supply in a television, up to thousands of megawatts in dc power transmission. *See* ALTERNATING CURRENT; DIRECT CURRENT. John Reeve

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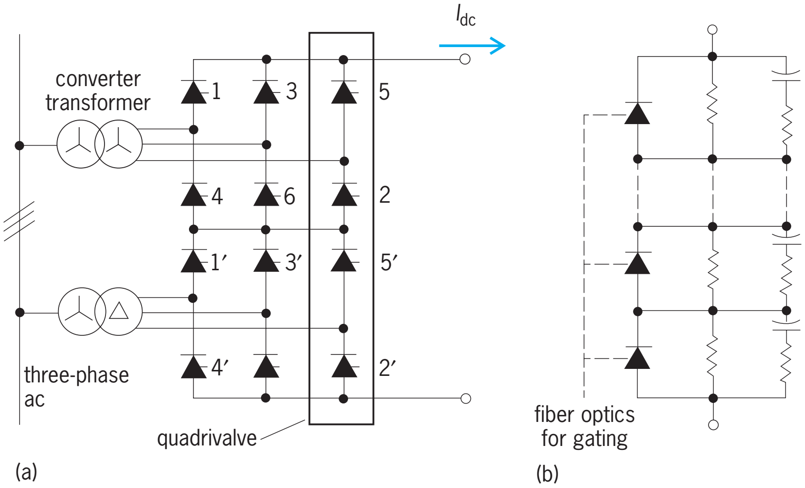

Fig. 3. Converter for dc power transmission. (*a*) Circuit of 12-pulse converter. (*b*) Thyristor valve.

Conveyor

A horizontal, inclined, declined, or vertical machine for moving or transporting bulk materials, packages, or objects in a path predetermined by the design of the device and having points of loading and discharge fixed or selective. Included in this category are skip hoist and vertical reciprocating and inclined reciprocating conveyors; but in the strictest sense this category does not include those devices known as industrial trucks, tractors and trailers, cranes, hoists, monorail cranes, power and hand shovels or scoops, bucket drag lines, platform elevators, or highway or rail vehicles. The more usual basic types of conveyors and their normal, rather than exceptional, operating characteristics

Normal operating characteristics of typical conveyors

	Paths						Typical products											Bulk Materials							
Conveyor Type	horizontal	declined	inclined	vertical	straight	curved	cases, boxes, etc.	barrels and kegs	drums	textile bags	paper bags	bottles and jars	cans	small parts	food products	lumber, pipe, etc.	towing trucks	free flowing	sluggish	dry	wet	cold	hot	nonabrasive	abrasive
GRAVITY CONVEYORS																									
Sliding friction																									
Skid		X			X			X	X																
Chute		X			X	X	X			X	X				X			X		X		X	X	X	
Spiral chute		X				X	X			X	X				X										
Rolling friction																									
Wheel	X	X			X	X	X				X					X									
Roller	X	X			X	X	X	X	X							X									
Spiral wheel		X				X	X																		
Spiral roller		X				X	X	X	X																
POWERED CONVEYORS																									
Continuous belt																									
Fabic	X	X	X		X		X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X
Flexible tube with zipper	X	X	X	X	X	X												X		X		X	X	X	X
Steel band	X	X	X		X		X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X
Woven or flat wire	X	X	X		X																				
Linked rod	X	X	X		X	X																			
Live roller (drive)																									
Flat belt	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X									
V belt	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X									
Sprocket	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X									
Chain																									
Apron (slat)	X	X	X		X		X	X	X	X	X														
Free roller	X	X	X		X		X	X	X																
Pan	X	X	X		X								X	X	X										
Pusher bar	X	X	X		X		X																		
Hinged plate	X	X	X										X	X	X										
Flat top plate	X				X	X						X	X												
Bucket[*]	X	X	X	X	X													X		X	X	X	X	X	X
Flight	X	X	X	X	X													X		X		X	X	X	
Drag chain																									
Plain links with lugs	X	X	X		X	X	X		X				X			X									
Overhead trolley[†]	X	X	X		X												X								
Infloor trolley	X				X												X								
Cable																									
Overhead trolley[†]	X	X	X		X																				
Table-mounted trolley	X	X	X																						
Cableway[‡]	X	X	X		X																				
Spiral (screw)	X	X	X	X	X													X	X	X	X	X	X	X	X
Vertical																									
Rigid arm				X	X		X	X	X	X	X														
Pendant carriage				X	X		X	X	X	X	X														
Pneumatic																									
Tube (with carriers)	X	X	X	X	X	X								X											
Pressure or suction	X	X	X	X	X	X												X		X		X	X	X	X
Vibrating	X	X	X	X	X													X		X		X	X	X	X

[*] Some bucket conveyors may use endless rubber belts.
[†] Most products or bulk materials can be conveyed by selection of attachments to the trolleys.
[‡] Cableways or serial tramways are used primarily for cross-country conveying of coal, ashes, lumber, and similar products used in construction.

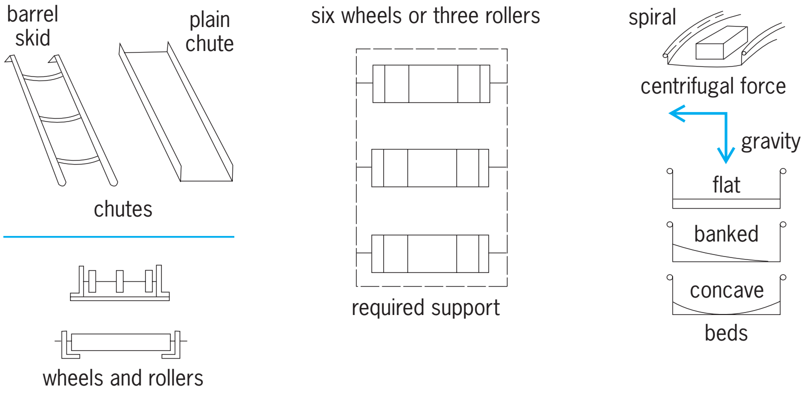

Fig. 1. Elements used in gravity conveyors.

are shown in the **table**. *See* BULK-HANDLING MACHINES.

Gravity conveyors. The economical means for lowering articles and materials is by gravity conveyors. Chutes depend upon sliding friction to control the rate of descent; wheel and roller conveyors use rolling friction for this purpose (**Fig. 1**).

With a body resting on a declined plane, friction *F* opposes component *P* parallel to the surface of the plane of weight *W* of the body. When the angle of elevation equals the angle of repose, the body is just about to start sliding, or to express it another way, when the inclination of the plane equals the angle of repose, *F* equals *P*. In this position the tangent of the angle of repose equals the coefficient of friction. For metal on metal the coefficient of friction is 0.15 to 0.25, and for wood on metal it is 0.2 to 0.6, which is why steel tote boxes slide more readily on metal chutes than do wooden cases.

When the body is a smooth-surfaced container and the inclined plane is replaced by rollers, the rollers are spaced so that at least three rollers support the smallest container to be conveyed; then each roller supports one-third the weight of the load. Component *P* of the weight *W* which acts downward and parallel to the inclination of the plane produces a turning moment *Pr* about the roller's axle, where *r* is the radius of the roller. As the inclination of the conveyor is increased, *P* increases until, at the point where rolling is about to start, *Pr* equals *Fr*. In this case, however, the force of friction is made up of the friction between the contacting surfaces and the friction in the bearings of the rollers. The mass of a tubular roller is concentrated near its circumference; hence rollers have greater starting inertia than wheels, but after they have started rolling, they have a flywheel effect that tends to keep products in motion, especially when packages follow each other in close succession. Inclination (or declination) is expressed as the number of inches of rise or fall per foot of conveyor or per 5-ft (1.5-m) or 10-ft (3-m) length.

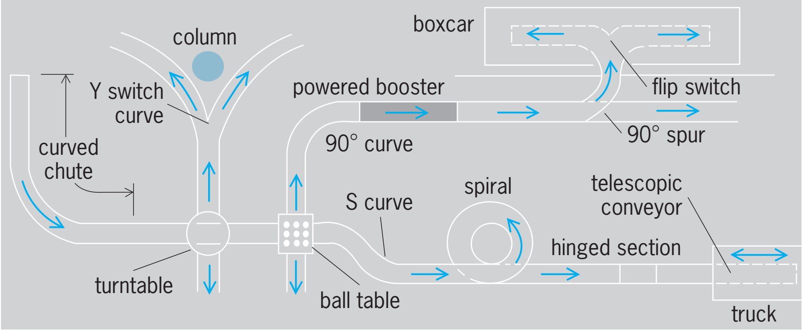

Fig. 2. Gravity components for conveyor lines.

Gravity chutes. Gravity chutes may be made straight or curved and are fabricated from sheet metal or wood, the latter being sometimes covered with canvas to prevent slivering. The bed of the chute can be shaped to accommodate the products to be handled. In spiral chutes centrifugal force is the second controlling factor. When bodies on a spiral move too fast, they are thrown out toward a guard rail, and contact with the rail increases the friction thereby causing the bodies to slow down somewhat and settle back into the center of the runway and continue their descent at a controlled rate. Spirals with roller beds or wheels provide smooth descent of an article and tend to maintain the position of the article in its original starting position. Rollers may be of metal, wood, or plastic and can be arranged in an optimum position, depending upon the articles to be carried.

Changes in direction can be effected by turntables, ball transfer tables, or gradual S curves (**Fig. 2**). Generally speaking, wheel-type conveyors are less expensive than the roller varieties; however, the latter can withstand severer service. For successful use of wheeled conveyors, the conveyed article must have a smooth and firm riding surface.

Chain conveyors. There are three basic types of chain conveyors: (1) those that support the product being conveyed, (2) those that carry actuating elements between the two chains, and (3) those that operate overhead or are set into the floor (**Fig. 3**).

In the sliding chain conveyor either plain links or links with such special attachments as lugs are made up into the conveyors to handle cases, cans, pipes, and other similar products.

Slats or apron conveyors are fitted with slats of wood or metal, either flat or in special shapes, between two power chains. The slats handle such freight as barrels, drums, and crates. With the addition of cleats these conveyors carry articles up steep inclines. In this type of conveyor the article rides on the top strand of the slats.

Push-bar conveyors are a variation of the slat conveyor, in which two endless chains are cross-connected at intervals by pusher bars which propel the load along a stationary bed or trough of the conveyor.

Powered conveyors. Gravity conveyors are limited to use in conditions where the material is to be lowered in elevation. The horizontal conveying distance capabilities of the gravity conveyor depend on the difference in elevation and the angle of sliding or rolling friction of the material to be conveyed.

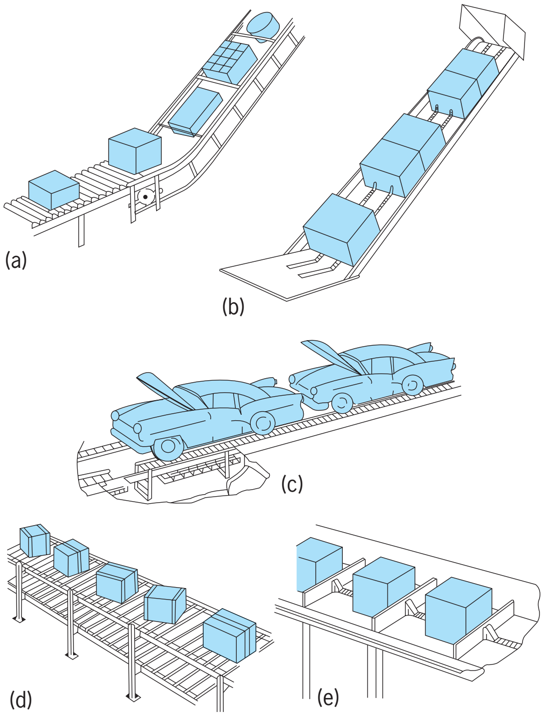

Fig. 3. Five examples of the basic types of chain conveyors. (*a*) Push-bar conveyor. (*b*) Twin chains carrying cartons. (*c*) Heavy-duty plates for assembly conveyor. (*d*) Apron or slat conveyor to carry miscellaneous articles. (e) Push-bar or cleat conveyor. (*After Conveyor Equipment Manufacturers Association*, *Conveyor Terms and Definitions*, *3d ed*., *1966*)

To move loads on level or inclined paths, or declining paths that exceed the angle of sliding or rolling friction of the particular material to be conveyed, powered conveyors must be employed. The following are various types of powered conveyors.

Belt conveyors. Loads are moved on a level or inclined path by means of power-driven belts. Belt conveyors with rough-top belts make possible inclines up to 28°; cleated belts are limited on degree of incline only by the position of the center of gravity of the conveyed item.

Essential components of belt conveyors in addition to the belt itself are (1) a bed, which may be a combination bed and frame; (2) end rollers; (3) a take-up to adjust belt tension as it varies with age and atmospheric conditions; and (4) a power unit (**Fig. 4**). The bed of a fabric belt conveyor may be wood, or more usually flat or concave sheet metal; or it may be made up of rollers. The former are called slide beds, the latter roller beds. Slide beds provide quiet, smooth conveying, but they require more power than roller beds. The two end rollers are mounted in antifriction bearings with provision for lubrication.

Where the tail roller is mounted in adjustable end arms to provide take-up, the length of the conveyor is not constant. Where this feature is objectionable, automatic gravity, screw, or spring take-ups can be used. Another required adjustment is provided by mounting the rollers so that their bearings can be shifted slightly either forward or backward to train the belt to run true.

Belts can be powered in several ways. A gear-head motor can be connected directly to the head roller, or the drive may be through a chain and sprockets. These arrangements necessitate placing the drive outside the frame. When this is undesirable, one of two drives can be located under the frame. Power units usually provide fixed or variable speeds from a few feet per minute to over 50 ft/min (15 m/min); 50 ft/min is usual with package conveyors. Normally $^1/_4$-hp (190-W) motors powers these units, but there are other, more powerful motors which are available for heavier duty.

Powered package conveyors can be combined in various ways to meet specific conditions. Powered curves are used, but wheel and roller sections are more usually employed to change direction. Inclined belt conveyors usually have a hump at the upper end to reduce the slapping by packages on the belt as they move from inclined to horizontal travel (**Fig. 5**). Cleats can be used, but they complicate the feeding of packages onto the line and require special construction features so that the cleats can pass around pulleys and be properly supported on the return portion of the conveying cycle.

Metal belts made of woven and flat wire, linked rods, and steel bands are engineered to make up conveyors, which are essentially the same as fabric belt conveyors. For example, woven wire belts can be driven by pulleys and these may be lagged, that is, covered with a material to improve traction.

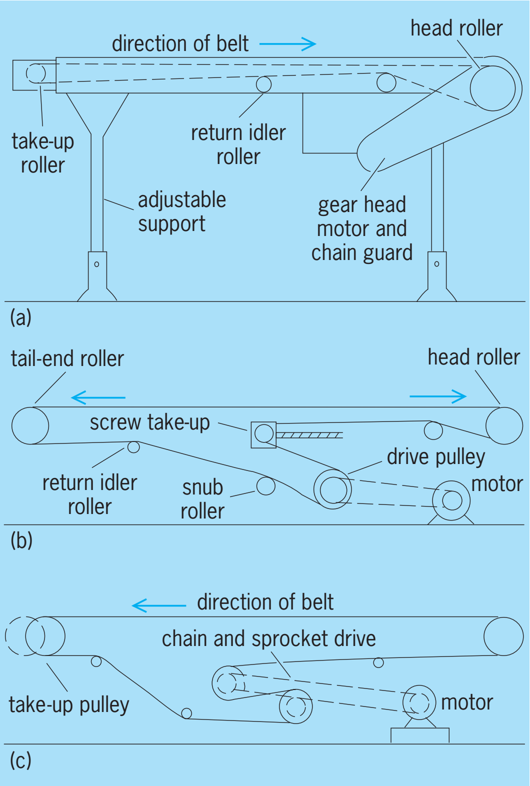

Fig. 4. Diagrams of three driven-belt conveyors. (*a*) Components of a fabric belt conveyor. (*b*) Wrap drive. (*c*) Tandem drive.

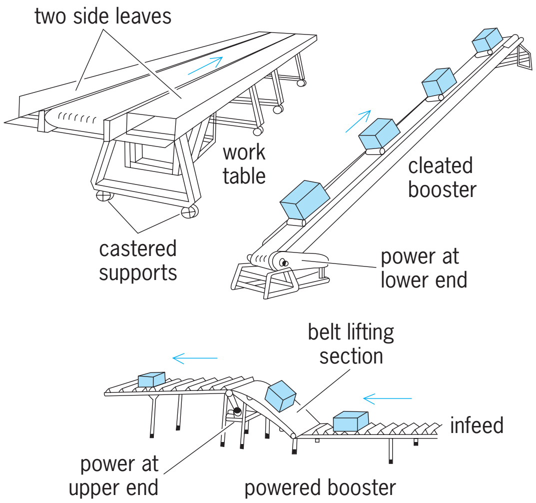

Fig. 5. Fabric belt conveyors.

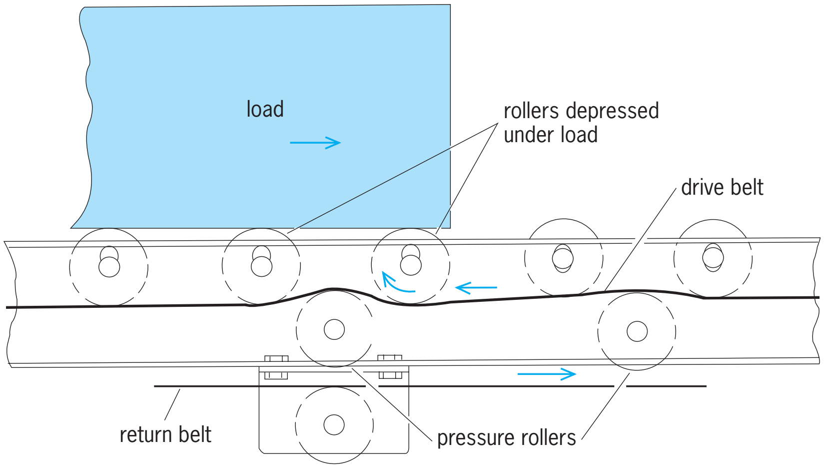

Fig. 6. Live rollers provide power for gravity curves.

Contact with the drive pulley can be increased by snubbing with small-diameter idler pulleys which guide the belt to increase the angle of contact. Flat wire, linked rod, and woven wire belts with chain edges are driven positively by pulleys with sprocket teeth or by true sprockets. Steel band conveyors are driven by pulleys with unusually large diameters. Other components are similar to those used in fabric belt conveyors but are more rugged in construction to handle the heavier carriers and to meet the more exacting conditions under which metal belts operate. Metal belts are used, for example, in high-temperature operations such as baking, annealing, brazing, and heat-treating.

The choice of a belt for a given situation depends on the effect of the belt's surface on the product, amount of drainage required, and similar factors.

Live-roller conveyors. Objects are moved over series of rollers by the application of power to all or some of the rollers. The power-transmitting medium is usually belting or chain. In one arrangement a belt drive running under and in contact with the rollers turns them to propel the load forward (**Fig. 6**). In another variation small sprockets are attached to the ends of some or all of the roller shafts, the sprockets being powered by a chain drive.

Arthur M. Perrin

Vibrating conveyors. These mechanical devices are designed to move bulk materials along a horizontal, or almost horizontal, path in a controlled system (**Fig. 7**). They can be used to simply transport material from one point to another or to perform various functions en route, such as cooling, drying, blending, metering, spreading, and, by installing a screen, scalping or dedusting.

They can be fed by a belt conveyor or, more commonly, used to provide a precisely controlled outlet from a bin, hopper, or chute. In all cases they have the ability to take a vertical flow of material and change the direction of movement up to 90° with only a small change in the handling level.

A vibrating conveyor basically consists of a base or reaction mass and a driven mass connected to each other by springs. The base is excited by a power source such as an electromagnetic or electromechanical drive. A trough or pan forms part of the driven mass and serves as the material carrying surface. In operation, the trough is moved alternately forward and up, then down and back. This causes the conveyed material to move along the trough surface in a series of short hops.

Amplitude or frequency of vibration can be adjusted to control conveyor speed and output. Electromagnetic conveyors operating at 3600 vibrations per minute with a low amplitude [a displacement of 0.09 in. (0.2 cm), for example], provide a gentle motion to the conveyed product and are frequently used to handle fragile or friable materials. Electromechanical conveyors normally operate at a lower frequency but a much higher amplitude [a displacement of 0.5 in. (1.2 cm), for example], which results in rougher handling of the product but greatly

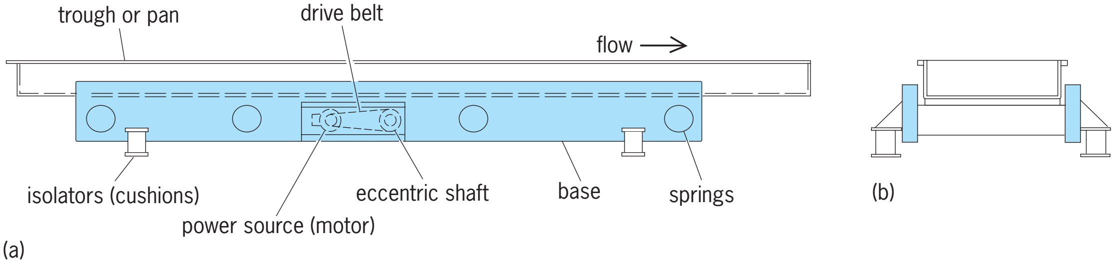

Fig. 7. Vibrating conveyor. (*a*) Side view. (*b*) End view.

increased capacity. The volume of material which can be handled ranges from a few pounds per hour up to thousands of pounds per hour. *See* VIBRATION MACHINE. R. F. Merwin

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Cooling tower

A tower- or buildinglike device in which atmospheric air (the heat receiver) circulates in direct or indirect contact with warmer water (the heat source) and the water is thereby cooled. A cooling tower may serve as the heat sink in a conventional thermodynamic process, such as refrigeration or steam power generation, or it may be used in any process in which water is used as the vehicle for heat removal, and when it is convenient or desirable to make final heat rejection to atmospheric air. Water, acting as the heat-transfer fluid, gives up heat to atmospheric air, and thus cooled, is recirculated through the system, affording economical operation of the process.

Basic types. Two basic types of cooling towers are commonly used. One transfers the heat from warmer water to cooler air mainly by an evaporation heat-transfer process and is known as the evaporative or wet cooling tower. The other transfers the heat from warmer water to cooler air by a sensible heat-transfer process and is known as the nonevaporative or dry cooling tower. These two basic types are sometimes combined, with the two cooling processes generally used in parallel or separately, and are then known as wet-dry cooling towers.

Cooling process. With the evaporative process, the warmer water is brought into direct contact with the cooler air. When the air enters the cooling tower, its moisture content is generally less than saturation; it emerges at a higher temperature and with a moisture content at or approaching saturation. Evaporative cooling takes place even when the incoming air is saturated, because as the air temperature is increased in the process of absorbing sensible heat from the water, there is also an increase in its capacity for holding water, and evaporation continues. The evaporative process accounts for about 65–75% of the total heat transferred; the remainder is transferred by the sensible heat-transfer process.

The wet-bulb temperature of the incoming air is the theoretical limit of cooling. Cooling the water to within 5 to 20°F (−15 to −6.7°C) above wet-bulb temperature represents good practice. The amount of water evaporated is relatively small. Approximately 1000 Btu (1055 kilojoules) is required to vaporize 1 lb (0.45 kg) of water at cooling tower operating temperatures. This represents a loss in water of approximately 0.75% of the water circulated for each 10°F (6°C) cooling, taking into account the normal proportions of cooling by the combined evaporative and sensible heat-transfer processes. Drift losses may be as low as 0.01–0.05% of the water flow to the tower (recent performance of 0.001% has been achieved) and must be added to the loss of water by evaporation and losses from blowdown to account for the water lost from the system. Blowdown quantity is a function of makeup water quality, but it may be determined by regulations concerning its disposal. Its quality is usually expressed in terms of the allowable concentration of dissolved solids in the circulating cooling water and may vary from two to six concentrations with respect to the dissolved solids content of the cooling water makeup.

With the nonevaporative process, the warmer water is separated from the cooler air by means of thin metal walls, usually tubes of circular cross section, but sometimes of elliptical cross section. Because of the low heat-transfer rates from a surface to air at atmospheric pressure, the air side of the tube is made with an extended surface in the form of fins of various geometries. The heat-transfer surface is usually arranged with two or more passes on the water side and a single pass, cross flow, on the air side. Sensible heat transfer through the tube walls and from the extended surface is responsible for all of the heat given up by the water and absorbed by the cooling air. The water temperature is reduced, and the air temperature increased. The nonevaporative cooling tower may also be used as an air-cooled vapor condenser and is commonly employed as such for condensing steam. The steam is condensed within the tubes at a substantially constant temperature, giving up its latent heat of vaporization to the cooling air, which in turn is increasing in temperature. The theoretical limit of cooling is the temperature of the incoming air. Good practice is to design nonevaporative cooling towers to cool the warm circulating water to within 25 to 35°F (14 to 20°C) of the entering air temperature or to condense steam at a similar temperature difference with respect to the incoming air. Makeup to the system is to compensate for leakage only, and there is no blowdown requirement or drift loss.

With the combined evaporative-nonevaporative process, the heat-absorbing capacity of the system is divided between the two types of cooling towers, which are selected in some predetermined proportion and usually arranged so that adjustments can be made to suit operating conditions within definite limits. The two systems, evaporative and nonevaporative, are combined in a unit with the water flow arranged in a series relationship passing through the dry tower component first and the wet tower second. The airflow through the towers is in a parallel-flow relationship, with the discharge air from the two sections mixing before being expelled from the system. Since the evaporative process is employed as one portion of the cooling system, drift, makeup, and blowdown are characteristics of the combined evaporative-nonevaporative cooling tower system,

Fig. 1. Counterflow natural-draft cooling tower at Trojan Power Plant in Spokane, Washington. (*Research–Cottrell*)

generally to a lesser degree than in the conventional evaporative cooling towers.

Of the three general types of cooling towers, the evaporative tower as a heat sink has the greatest thermal efficiency but consumes the most water and has the largest visible vapor plume. When mechanical-draft cooling tower modules are arranged in a row, ground fogging can occur. This can be eliminated by using natural-draft towers, and can be significantly reduced with modularized mechanical-draft towers when they are arranged in circular fashion.

The nonevaporative cooling tower is the least efficient type, but it can operate with practically no consumption of water and can be located almost anywhere. It has no vapor plume.

The combined evaporative-nonevaporative cooling tower has a thermal efficiency somewhere between that of the evaporative and nonevaporative cooling towers. Most are of the mechanical-draft type, and the vapor plume is mitigated by mixing the dry warm air leaving the nonevaporative section of the tower with the warm saturated air leaving the evaporative section of the tower. This retards the cooling of the plume to atmospheric temperature; visible vapor is reduced and may be entirely eliminated. This tower has the advantage of flexibility in operation; it can accommodate variations in available makeup water or be adjusted to atmospheric conditions so that vapor plume formation and ground fogging can be reduced.

Evaporative cooling towers. Evaporative cooling towers are classified according to the means employed for producing air circulation through them: atmospheric, natural draft, and mechanical draft.

Atmospheric cooling. Some towers depend upon natural wind currents blowing through them in a substantially horizontal direction for their air supply. Louvers on all sides prevent water from being blown out of these atmospheric cooling towers, and allow air to enter and leave independently of wind direction. Generally, these towers are located broadside to prevailing winds for maximum sustained airflow.

Thermal performance varies greatly because it is a function of wind direction and velocity as well as wet- and dry-bulb temperatures. The normal loading of atmospheric towers is about 1–2 gal/min (3.7–7.5 liters/min) of cooling water per square foot of cross section. They require considerable unobstructed surrounding ground space in addition to their cross-sectional area to operate properly. Because they need more area per unit of cooling than other types of towers, they are usually limited to small sizes.

Natural draft. Other cooling towers depend for their air supply upon the natural convection of air flowing upward and in contact with the water to be cooled. Essentially, natural-draft cooling towers are chimneylike structures with a heat-transfer section installed in their lower portion, directly above an annular air inlet in a counterflow relationship with the cooling air (**Fig. 1**), or with the heat-transfer section circumscribing the base of the tower in a cross-flow relationship with the cooling airflow (**Fig. 2**). Sensible heat absorbed by the air in passing over the water to be cooled increases the air temperature and its vapor content and thereby reduces its density so that the air is forced upward and out of the tower by the surrounding heavier atmosphere. The flow of air through the tower varies according to the difference in specific weights of the ambient air and the air leaving the heat-transfer surfaces. Since the difference in

Fig. 2. Cross-flow mechanical-draft cooling towers. (*Marley Co.*)

specific weights generally increases in cold weather, the airflow through the cooling tower also increases, and the relative performance improves in reference to equivalent constant-airflow towers.

Normal loading of a natural-draft tower is 2–4 gal/(min)(ft^2) [1.4–2.7 liters/(s)(m^2)] of ground-level cross section. The natural-drafting cooling tower does not require as much unobstructed surrounding space as the atmospheric cooling tower does, and is generally suited for both medium and large installations. The natural-draft cooling tower was first commonly used in Europe. Then a number of large installations were built in the United States, with single units 385 ft (117 m) in diameter by 492 ft (150 m) high capable of absorbing the heat rejected from an 1100-MW light-water-reactor steam electric power plant.

Mechanical draft. In cooling towers that depend upon fans for their air supply, the fans may be arranged to produce either a forced or an induced draft. Induced-draft designs are more commonly used than forced-draft designs because of the lower initial cost, improved air-water contact, and less air recirculation (**Fig. 3**). With controlled airflow, the capacity of the mechanical-draft tower can be adjusted for economic operation in relation to heat load and in consideration of ambient conditions.

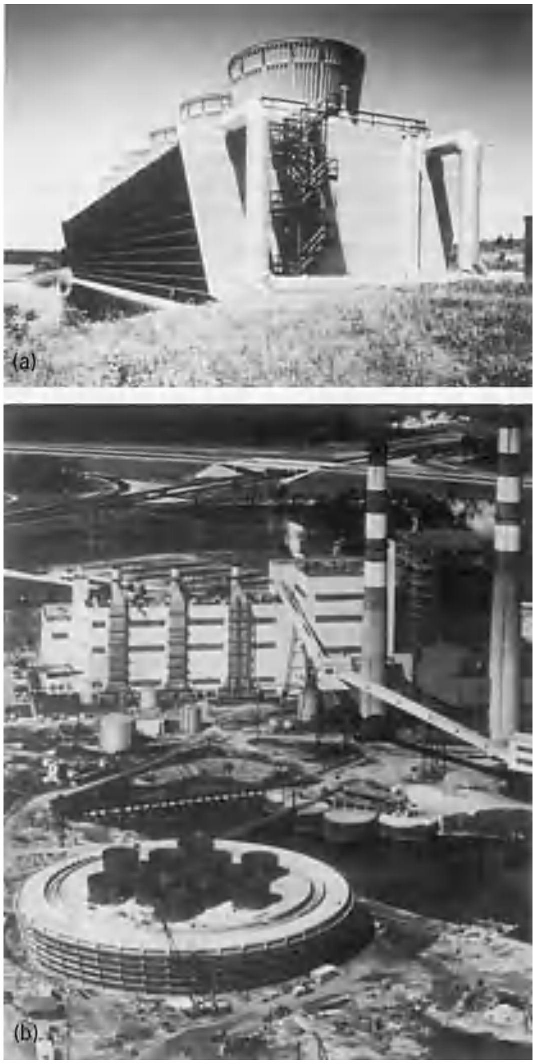

Fig. 3. Mechanical-draft cooling towers. (*a*) Conventional rectangular cross-flow evaporative induced-draft type; (*b*) circular evaporative induced-draft type. (*Marley Co.*)

Normal loading of a mechanical-draft cooling tower is 2–6 gal/(min)(ft^2) [1.4–4.1 liters/(s)(m^2)] of cross section. The mechanical-draft tower requires less unobstructed surrounding space to obtain adequate air supply than the atmospheric cooling tower needs; however, it requires more surrounding space than the natural-draft towers do. This type of tower is suitable for both large and small installations.

Nonevaporative cooling towers. Nonevaporative cooling towers are classified as air-cooled condensers and as air-cooled heat exchangers, and are further classified by the means used for producing air circulation through them. *See* HEAT EXCHANGER; VAPOR CONDENSER.

Air-cooled condensers and heat exchangers. Two basic types of nonevaporative cooling towers are in general use for power plant or process cooling. One type uses an air-cooled steam surface condenser as the means for transferring the heat rejected from the cycle to atmospheric cooling air. The other uses an air-cooled heat exchanger for this purpose. Heat is transferred from the air-cooled condenser, or from the air-cooled heat exchanger to the cooling air, by convection as sensible heat.

Nonevaporative cooling towers have been used for cooling small steam electric power plants since the 1930s. They have been used for process cooling since 1940; a complete refinery was cooled by the process in 1958. The nonevaporative cooling tower was formerly used almost exclusively with large steam electric power plants in Europe. Interest in this type of tower gradually increased in the United States, and a 330-MW plant in Wyoming using nonevaporative cooling towers was completed in the late 1970s.

The primary advantage of nonevaporative cooling towers is that of flexibility of plant siting. There is seldom a direct economic advantage associated with the use of nonevaporative cooling tower systems in the normal context of power plant economics. They are the least efficient of the cooling systems used as heat sinks.

Cooling airflow. Each of the two basic nonevaporative cooling tower systems may be further classified with respect to type of cooling airflow. Both types of towers, the direct-condensing type and the heat-exchanger type, can be built as natural-draft or as mechanical-draft tower systems.

Design. The heat-transfer sections are constructed as tube bundles, with finned tubes arranged in banks two to five rows deep. The tubes are in a parallel relationship with each other and are spaced at a pitch slightly greater than the outside fin diameter, either in an in-line or a staggered pattern. For each section, two headers are used, with the tube ends secured in each. The headers may be of pipe or of a box-shaped cross section and are usually made of steel. The bundles are secured in an open metal frame.

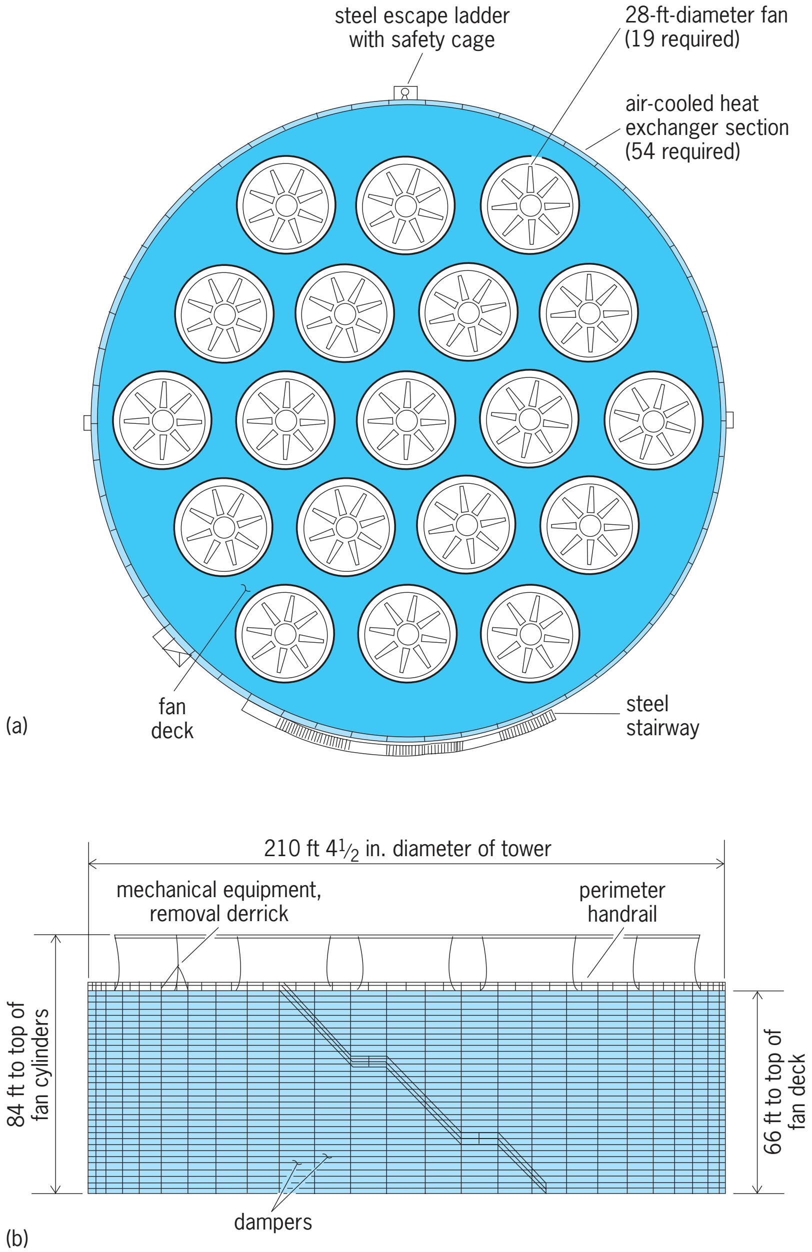

Fig. 4. Multifan circular nonevaporative tower. (*a*) Plan. (*b*) Elevation. 1 ft = 0.3 m; 1 in. = 2.5 cm. (*Marley Co.*)

The assembled tube bundles may be arranged in a V shape, with either horizontal or inclined tubes, or in an A shape, with the same tube arrangement. A similar arrangement may be used with vertical tube bundles. Generally, inclined tubes are shorter than horizontal ones. The inclined-tube arrangement is best suited to condensing vapor, the horizontal-tube arrangement best for heat-exchanger design. The A-shaped bundles are usually used with forced-draft airflow, the V-shaped bundles with induced-draft airflow. With natural-draft nonevaporative cooling towers there is no distinction made as to A- or V-shaped tube bundle arrangement; the bundles are arranged in a deck above the open circumference at the bottom of the tower, in a manner similar in principle to that used in the counterflow natural-draft evaporative cooling tower (Fig. 1). A natural-draft cooling tower with a vertical arrangement of tube bundles has been built, but this type of structure is not generally used.

Modularization of the bundle sections has become general practice with larger units; an installation of a circular module-type unit is shown in **Fig. 4**.

Combined evaporative-nonevaporative towers. The combination evaporative-nonevaporative cooling tower is arranged so that the water to be cooled first passes through a nonevaporative cooling section which is much the same as the tube bundle sections used with nonevaporative cooling towers of the heat-exchanger type. The hot water first passes through these heat exchangers, which are mounted directly above the evaporative cooling tower sections; the water leaving the nonevaporative section flows by force of gravity over the evaporative section.

Fig. 5. Wet-dry cooling tower at Atlantic Richfield Company. (*Marley Co.*)

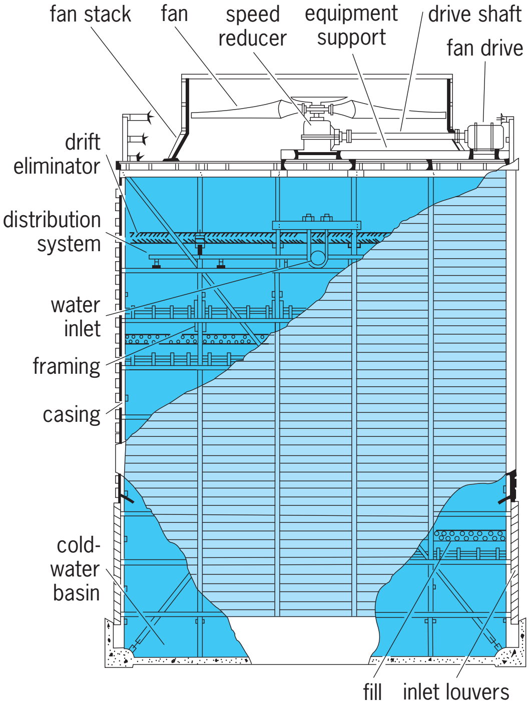

Fig. 6. Induced-draft counterflow cooling tower, showing the component parts.

The cooling air is divided into two parallel flow streams, one passing through the nonevaporative section, the other through the evaporative section to a common plenum chamber upstream of the induced-draft fans. There the two airflow streams are combined and discharged upward to the atmosphere by the fans. A typical cooling tower of this type is shown in **Fig. 5**.

In most applications of wet-dry cooling towers attempts are made to balance vapor plume suppression and the esthetics of a low silhouette in comparison with that of the natural-draft evaporative cooling tower. In some instances, these cooling towers are used in order to take advantage of the lower heat-sink temperature attainable with evaporative cooling when an adequate water supply is available, and to allow the plant to continue to operate, at reduced efficiency, when water for cooling is in short supply.

The more important components of evaporative cooling towers are the supporting structure, casing, cold-water basin, distribution system, drift eliminators, filling and louvers, discharge stack, and fans (mechanical-draft towers only). The counterflow type is shown in **Fig. 6**; the cross-flow type is shown in **Fig. 7**.

Treated wood, especially Douglas-fir, is the common material for atmospheric and small mechanical-draft cooling towers. It is used for structural framing, casing, louvers, and drift eliminators. Wood is commonly used as filler material for small towers. Plastics and asbestos cement are replacing wood to some degree in small towers and almost completely in large towers where fireproof materials are generally required. Framing and casings of reinforced concrete, and louvers of metal, usually aluminum, are generally used for large power plant installations. Fasteners for securing small parts are usually made of bronze, copper-nickel, stainless steel, and galvanized steel. Distribution systems may be in the form of piping, in galvanized steel, or fiber glass–reinforced plastics; and they may be equipped with spray nozzles of noncorrosive material, in the form of troughs and weirs, or made of wood, plastic, or reinforced concrete. Structural framing may also be made of galvanized or plastic-coated structural steel shapes. Natural-draft cooling towers, especially in large sizes, are made of reinforced concrete. The cold-water basins for ground-mounted towers are usually made of concrete; wood or steel is usually used for roof-mounted towers. Fan blades are made of corrosion-resistant

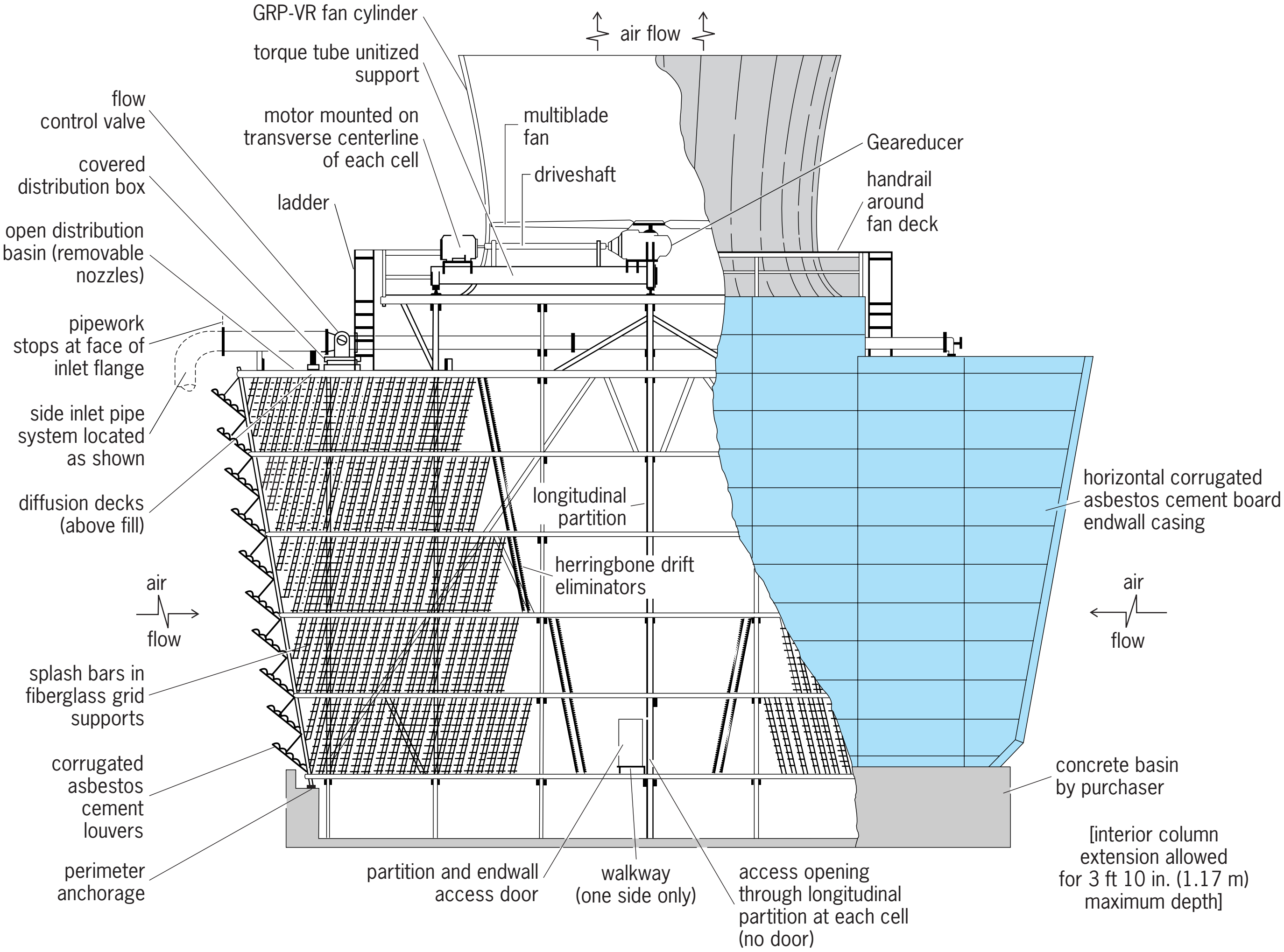

Fig. 7. Transverse cross section of a cross-flow evaporative cooling tower.

material such as monel, stainless steel, or aluminum; but most commonly fiber glass–reinforced plastic is used for fan blades.

The heat-transfer tubes used with nonevaporative cooling towers are of an extended-surface type usually with circumferential fins on the air side (outside). The tubes are usually circular in cross section, although elliptical tubes are sometimes used. Commonly used tube materials are galvanized carbon steel, ferritic stainless steel, and various copper alloys. They are usually made with wrapped aluminum fins, but steel fins are commonly used with carbon steel tubes and galvanized. Most designs employ a ratio of outside to inside surface of 20:25. Outside-diameter sizes range $^3/_4$–$1^1/_2$ in. (19–38 mm).

Tube bundles are made with tube banks two to five rows deep. The tubes are in parallel relationship with each other and secured in headers, either of steel pipe or of weld-fabricated steel box headers. The tube bundle assemblies are mounted in steel frames which are supported by structural steel framework. The bundle assemblies may be arranged in a V pattern, requiring fans of the induced-draft type, or in an A pattern, requiring fans of the forced-draft type (**Fig. 8**). Fans and louvers are similar to those described for evaporative cooling towers.

Nonevaporative cooling towers may also be used with natural airflow. In this case, the tube bundles are usually mounted on a deck within the tower and just above the top of the circumferential supporting structure for the tower. In this application, the tower has no cold-water basin, but otherwise it is identical with the natural-draft tower used for evaporative cooling with respect to materials of construction and design.

Performance. The performance of an evaporative cooling tower may be described by the generally accepted equation of F. Merkel, as shown below,

$$\frac{KaV}{L} = \int_{T2}^{T1} \frac{dT}{h'' - h}$$

where a = water-air contact area, ft^2/ft^3; h = enthalpy of entering air, Btu/lb; h'' = enthalpy of leaving air, Btu/lb; K = diffusion coefficient, lb/(ft^2)(h); L = water flow rate, lb/(h)(ft^2); T = water temperature, °F; T_1 = inlet water temperature, °F; T_2 = outlet water temperature, °F; and V = effective volume of tower, ft^3/ft^2 of ground area. The Merkel equation is usually performed graphically, by Simpson's rule, or with a suitable computer program. *See* PERFORMANCE RATING.

The performance of a nonevaporative cooling tower may be described by the generally accepted equation of Fourier for steady-state unidirectional heat transfer, using the classical summation of resistances formula with correction of the logarithmic temperature difference for cross-counterflow design in order to calculate the overall heat transfer. It is usual practice to reference the overall heat-transfer coefficient to the outside (finned) tube surface.

Evaluation of cooling tower performance is based on cooling of a specified quantity of water through a given range and to a specified temperature approach

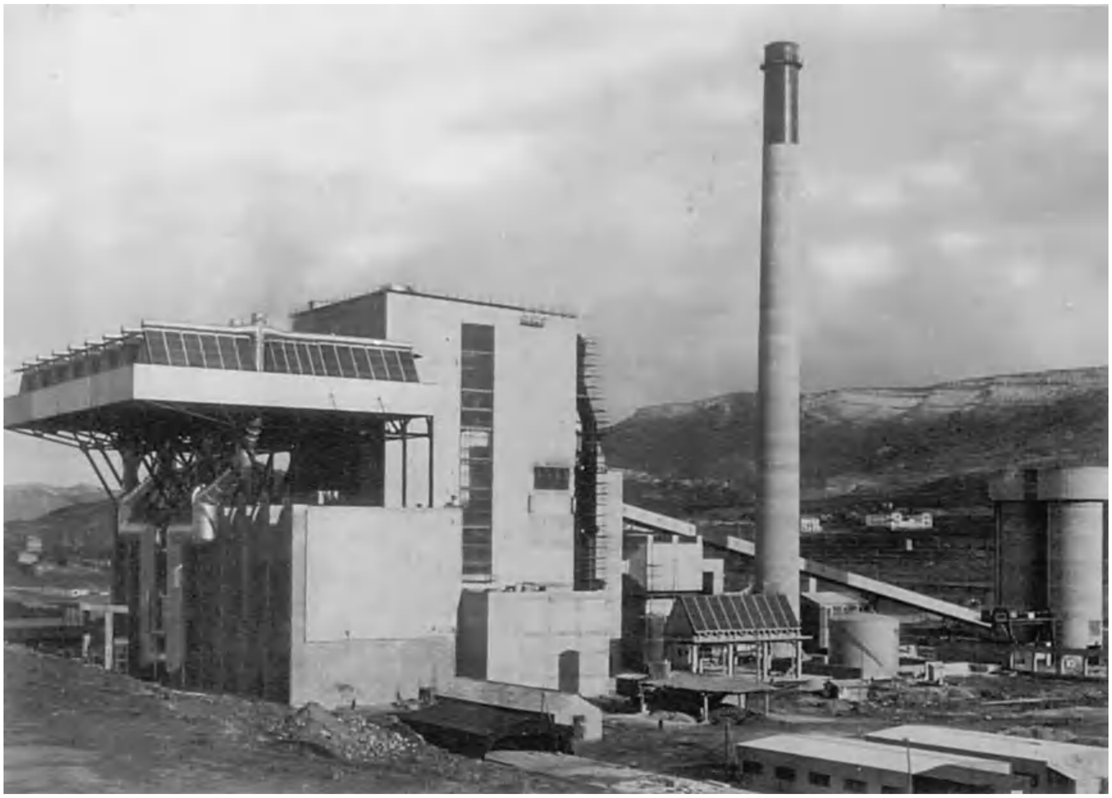

Fig. 8. Nonevaporative cooling tower, Utrillas, Spain. (*GEA*)

to the wet-bulb or dry-bulb temperature for which the tower is designed. Because exact design conditions are rarely experienced in operation, estimated performance curves are frequently prepared for a specific installation. These provide a means for comparing the measured performance with design conditions. Joseph F. Sebald

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Coordinate systems

Schemes for locating points in a given space by means of numerical quantities specified with respect to some frame of reference. These quantities are the coordinates of a point. To each set of coordinates there corresponds just one point in any coordinate system, but there are useful coordinate systems in which to a given point there may correspond more than one set of coordinates.

A coordinate system is a mathematical language that is used to describe geometrical objects analytically; that is, if the coordinates of a set of points are known, their relationships and the properties of figures determined by them can be obtained by numerical calculations instead of by other descriptions. It is the province of analytic geometry, aided chiefly by calculus, to investigate the means for these calculations.

The most familiar spaces are the plane and the three-dimensional euclidean space. In the latter a point P is determined by three coordinates (x, y, z). The totality of points for which x has a fixed value constitutes a surface. The same is true for y and z so that through P there are three coordinate surfaces. The totality of points for which x and y are fixed is a curve and through each point there are three coordinate lines. If these lines are all straight, the system of coordinates is said to be rectilinear. If some or all of the coordinate lines are not straight, the system is curvilinear. If the angles between the coordinate lines at each point are right angles, the system is rectangular.

Cartesian coordinate system. This is one of the simplest and most useful systems of coordinates. It is constructed by choosing a point O designated as the origin. Through it three intersecting directed lines OX, OY, OZ, the coordinate axes, are constructed. The coordinates of a point P are x, the distance of P from the plane YOZ measured parallel to OX, and y and z, which are determined similarly (**Fig. 1**). In this system the coordinate lines through P are straight lines respectively parallel to the three coordinate axes. Usually the three axes are taken to be mutually perpendicular, in which case the system is a rectangular cartesian one. Obviously a similar construction can be made in the plane, in which case a point has two coordinates (x, y). It is this system that is used in the construction of graphs and charts of various data, whether observed or computed.

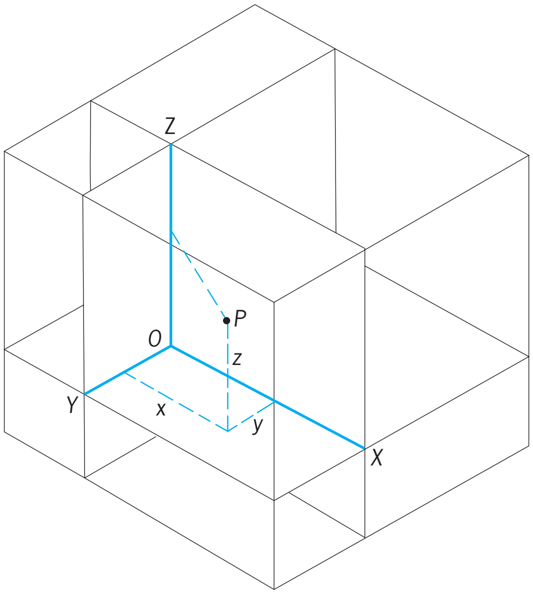


Fig. 1. Cartesian coordinate system.

Polar coordinate system. This system is constructed in the plane by choosing a point O called the pole and through it a directed straight line, the initial line. A point P is located by specifying the directed distance OP and the angle through which the initial line must be turned to coincide with OP in position and direction (**Fig. 2**). The coordinates of P are (r, θ). The radius vector r is the directed line OP, and the vectorial angle θ is the angle through which the initial line was turned, + if turned counterclockwise, − if clockwise. To each pair of values (r,θ) there corresponds just one point, but any point has an endless number of sets of coordinates. The coordinate lines in this case are radial lines through the pole (θ =

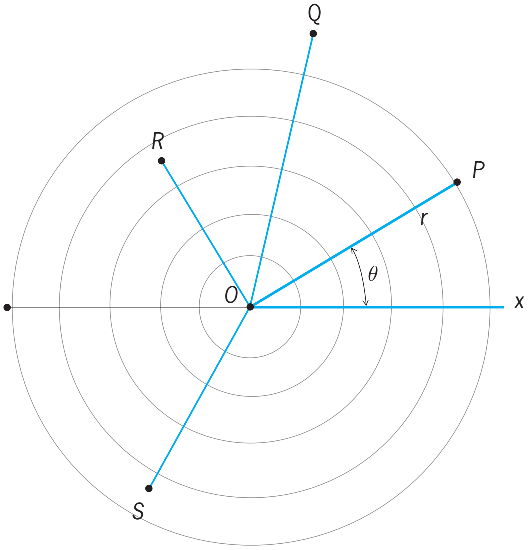


Fig. 2. Polar coordinate system.

constant) and concentric circles with center at the pole (r = constant). In spite of this lack of unique reciprocity between points and their coordinates, the polar system is useful in the study of spirals and rotations and in the investigation of motions under the action of central forces such as those of planets and comets.

Spherical coordinates. In three-dimensional euclidean space this system of coordinates is constructed by choosing a plane and in it constructing a polar coordinate system. At the pole O a polar axis OZ is constructed at right angles to the chosen plane. A point P, not on OZ, and OZ determine a plane. The spherical coordinates of P are then the directed distance OP denoted by ρ, the angle θ through which the initial line is turned to lie in ZOP and the angle $\phi = ZOP$ (**Fig. 3**). The coordinate lines are radial lines through O (θ and ϕ constant), meridian circles (ρ and ϕ constant), and circles of latitude (ρ and θ constant). This is an example of a curvilinear rectangle coordinate system. It is used in locating stars, in the study of spherical waves, and in problems in which there is spherical symmetry.

Cylindrical coordinates. These are constructed by choosing a plane with a pole O, an initial line in it, and a polar axis OZ, as in spherical coordinates. A point P is projected onto the chosen plane. The cylindrical coordinates of P are (r, θ, z) where r and θ are the polar coordinates of Q and $z = QP$ (Fig. 3). This is also a curvilinear rectangular system, the coordinate lines being mutually perpendicular. This system is used in problems of fluid flow and in others in which there is axial symmetry.

What has been done above in the plane and in euclidean space of three dimensions can be extended to curved spaces of any number dimensions. For a space S of n dimensions with some known geometrical or physical properties, a coordinate system in which a point has coordinates $(u_1, u_2, \ldots, u_n)$ is chosen. The coordinate lines are curves along which only one coordinate varies. When the known properties of S are expressed in terms of these coordinates, it is then the province of differential geometry to investigate their consequences. *See* DIFFERENTIAL GEOMETRY.

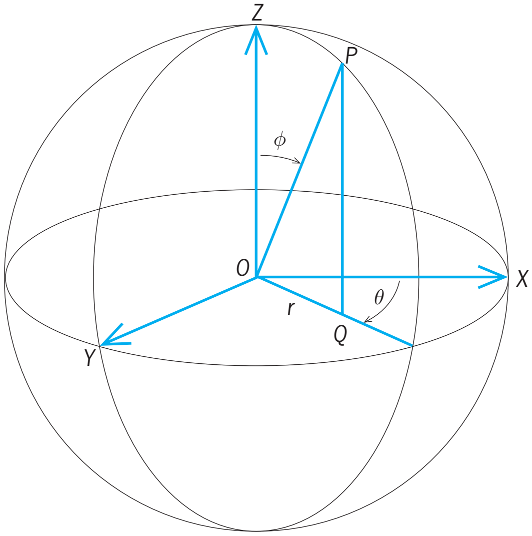


Fig. 3. Spherical coordinate system.

Transformation of coordinates. By means of a system of equations the description of a geometrical object in one coordinate system may be translated into an equivalent description in another coordinate system. Thus in a given space of n dimensions if there is a coordinate system A in which a general point P has coordinates $(u_1, u_2, \ldots, u_n)$ and a coordinate system B in which P has the coordinates $(v_1, v_2, \ldots, v_n)$, the transformation from system A to system B is the set of equations $u_i = f_i(v_1, v_2, \ldots, v_n)$, for $i = 1, 2, \ldots, n$, which expresses each u in terms of the v's. These functions are obtainable from the relation between the two coordinate systems. They are not completely arbitrary, for they must be single-valued, independent, and such that if in the B system P has another set of coordinates, say $(v'_1, v'_2, \ldots, v'_n)$, then $f_i(v_1, v_2, \ldots, v_n) = f_i(v'_1, v'_2, \ldots, v'_n)$. Then if a geometrical locus in the space S is described by one or more equations of the form $F(u_1, u_2, \ldots, u_n) = 0$ in system A, the equivalent description in system B is one or more of the equations of the form

$$F[f_1(v), f_2(v), \ldots, f_n(v)] = 0$$

Other geometrical objects such as vectors and areas have more complicated laws of transformation, but each such law is expressible in terms of the equations of transformation. As remarked above, a coordinate system is a mathematical language; a transformation of coordinates plays the role of a dictionary that translates from one language to another.

The most important transformations of coordinates are between rectangular cartesian coordinate systems. One such set of coordinate axes is obtainable from another by a translation (in the physical sense) and a rotation. Consider a coordinate system A with coordinate axes OX, OY, OZ, and coordinates of a point $P(x,y,z)$. System B *is* obtained by moving the axes without turning to a point O' with coordinates (a, b, c). The new axes are $O'X'$, $O'Y'$, $O'Z'$ and the coordinates of P in this system are (x', y', z'); then the equations of transformation are $x = x' + a$, $y = y' + b$, $z = z' + c$. If the new system is obtained from A by a rotation of the coordinate axes, let $\alpha_1, \alpha_2, \alpha_3; \beta_1, \beta_2, \beta_3; \gamma_1, \gamma_2, \gamma_3$ be the angles which the new axes OX', OY', OZ' make with the original axes (only three of these angles are independent); then the equations of transformation are

$$x = x' \cos\alpha_1 + y' \cos\beta_1 + z' \cos\gamma_1$$

$$y = x' \cos\alpha_2 + y' \cos\beta_2 + z' \cos\gamma_2$$

$$z = x' \cos\alpha_3 + y' \cos\beta_3 + z' \cos\gamma_3$$

The equations of transformation may be differently interpreted. The equations of transformation make the point P of coordinates (x, y, z), in the same coordinate system, correspond to a point P' of coordinates (x', y', z'). This constitutes a mapping of the space upon itself which maps a figure into some other figure. In applications one usually seeks a mapping that carries some pertinent loci into simpler loci while preserving some relevant properties. *See* ANALYTIC GEOMETRY; BARYCENTRIC CALCULUS; CALCULUS; CONFORMAL MAPPING; CURVE FITTING; SPHERICAL HARMONICS.

Morris S. Knebelman

Coordination chemistry

A field which, in its broadest usage, is acid-base chemistry as defined by G. N. Lewis. However, the term coordination chemistry is generally used to describe the chemistry of metals and metal ions in their interactions with other molecules or ions. For example, reactions (1)–(3) show Lewis acid-base-type reactions, which result in the formation of coordinate covalent bonds.

$$\mathrm{Mg^{2+} + 6H_2O \rightarrow Mg(H_2O)_6^{2+}} \qquad (1)$$

$$\mathrm{Ni + 4CO \rightarrow Ni(CO)_4} \qquad (2)$$

$$\mathrm{Fe^{2+} + 6CN^- \rightarrow Fe(CN)_6^{4-}} \qquad (3)$$

The products formed are coordination complex ions or compounds, and this area of chemistry is known as coordination chemistry.

It follows that coordination complex ions or compounds are ions or compounds that contain a central metal atom or ion and a group of ions or molecules bonded to it. Such an ion or compound tends to retain its identity, even in solution, although partial dissociation may occur. The charge on the coordinated species may be positive, zero, or negative, depending on the charges carried by the central atom and the coordinated groups. These groups are called ligands, and the total number of ligands bound to the central metal atom is called the coordination number. Other names commonly used for these compounds include complex compounds, complex ions, Werner complexes, coordinated complexes, chelate compounds, or simply complexes. *See* ACID AND BASE; CHELATION; COORDINATION COMPLEXES.

Experimental observations as early as the middle of the eighteenth century reported the isolation of coordination compounds. During that time and for the following 150 years, the valence theory could not adequately account for such materials. As a result, they were referred to as complex compounds, a term which is still in common usage, but not for the same reason. The correct interpretation of these compounds was finally given by Alfred Werner in 1893. He introduced the concept of residual or secondary valence, and suggested that elements have this type of valence in addition to their normal or primary valence. Thus, platinum(IV) has a normal valence of 4 but a secondary valence or coordination number of 6. This then led to the formulation of $\mathrm{PtCl_4 \cdot 6NH_3}$ as $\mathrm{[Pt(NH_3)_6]^{4+}, 4Cl^-}$ and of $\mathrm{PtCl_4 \cdot 5NH_3}$ as $\mathrm{[Pt(NH_3)_5Cl]^{3+}, 3Cl^-}$. The compound with five ammonias has only three ionic chlorides; the fourth is inside the coordination sphere, and therefore is not readily precipitated upon the addition of silver ion. Although the exact nature of the coordinate bond between metal and ligand remains the subject of considerable discussion, it is agreed that the formulations of Werner are essentially correct.

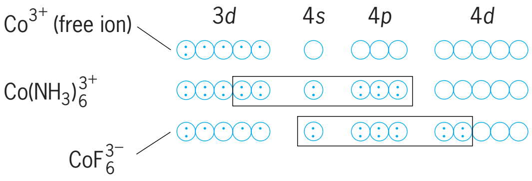


Fig. 1. Cobalt(III) complexes.

Coordinate bond. Three theories have been used to explain the nature of the coordinate bond. These are the valence bond theory, the electrostatic theory, including crystal field corrections, and the molecular orbital theory. Currently, the theory used almost exclusively is the molecular orbital theory. The valence bond theory for metal complexes was developed chiefly by Linus Pauling. This theory considers that the pair of electrons on the ligand enter the hybridized atomic orbitals of the metal and that the bond is essentially covalent. Several of the properties of these substances can be explained on the basis of this theory. For example, cobalt(III) complexes are represented by **Fig. 1**. The orbital hybridization of $\mathrm{Co(NH_3)_6}^{3+}$ is designated as d^2sp^3, and the complex is referred to as an inner orbital complex. Such a representation is consistent with the diamagnetic properties of this cation, for all electrons are paired. The orbital hybridization of $\mathrm{CoF_6}^{3-}$ is designated as sp^3d^2, and it is called an outer orbital complex. This ion is known to be paramagnetic, which is in keeping with the four unpaired electrons in the 3*d* orbitals. The term inner orbital is applied if the *d* orbitals of a lower quantum number than the *s* and *p* orbitals are used in bonding, whereas outer orbital has reference to systems in which the *d* orbitals used have the same quantum number as the *s* and *p* orbitals. *See* ELECTRON CONFIGURATION; MOLECULAR ORBITAL THEORY; QUANTUM NUMBERS.

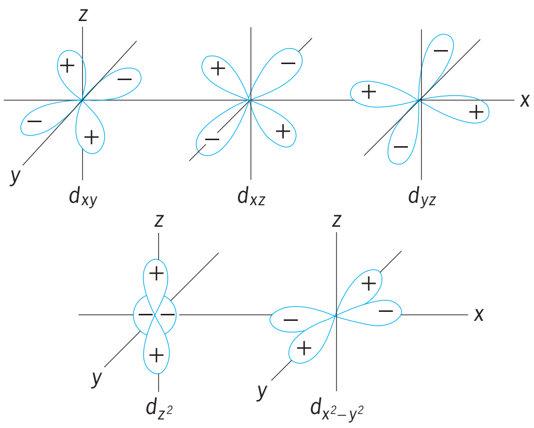


Fig. 2. Orientation of *d* orbitals in space.

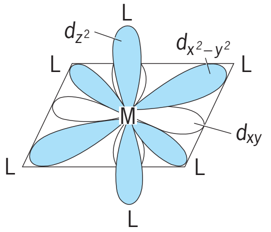


Fig. 3. Spatial orientation of *d* orbitals in coordination complex.

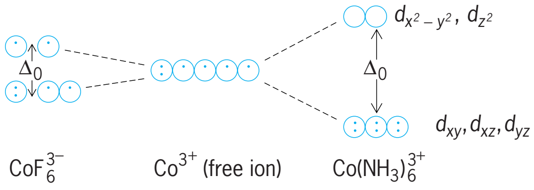


Fig. 4. Cobalt(III) complexes on the basis of crystal field theory.

The electrostatic theory, plus the crystal field theory for the transition metals, assumes that the metal-ligand bond is caused by electrostatic interactions between point charges and dipoles and that there is no sharing of electrons. Physicists have made good use of this theory to explain the properties of ionic crystalline solids, and it has now been extended to the metal complexes. For the nontransition metals, the parameters needed to determine the strength of the metal ligand bond are the charges and sizes of the central ions and the charges, dipole moments, polarizabilities, and sizes of the ligands. In order to give an adequate explanation of the bonding for transition metals, it is also necessary to consider the orientation of the *d* orbitals in space. The five possible spatial configurations are shown in **Fig. 2**. For the gaseous ion M, all five of the *d* orbitals are of equal energy. However, as shown in **Fig. 3**, the $d_{x^2-y^2}$ and d_{z^2} orbitals are pointing directly toward the six ligands at the corners of an octahedron and, because of repulsive interaction with the ligands, are at a higher energy than the d_{xy}, d_{xz}, and d_{yz} orbitals which do not point toward the ligands. *See* LIGAND FIELD THEORY.

Thus, on the basis of the crystal field theory, the cobalt(III) complexes referred to above are designated as in **Fig. 4**. The Co(NH$_3$)$_6^{3+}$ is called a spin-paired, or low-spin, complex, whereas CoF$_6^{3-}$ is called spin-free, or high-spin. This refers to the fact that the electrons are all paired in the former because of the larger crystal field splitting, Δ_0, whereas in the latter, Δ_0 is small, and the electrons are not paired. In addition to explaining the structure and magnetic properties, this theory affords an adequate interpretation of the visible spectra of metal complexes.

The molecular orbital theory assumes that the electrons move in molecular orbitals which extend over all the nuclei of the metal-ligand system. In this manner, it serves to make use of both the valence bond theory and crystal field theory. The molecular orbital theory is therefore the best approximation of the nature of the coordinate bond because it is sufficiently flexible to permit both covalent and ionic bonding as well as the splitting of *d* orbitals into various energy levels. The complexes CoF$_6^{3-}$ and Co(NH$_3$)$_6^{3+}$ can be represented by the molecular orbital energy diagrams shown in **Fig. 5**.

It is apparent from these molecular orbital diagrams that this theory combines the desirable features of both the valence bond and the crystal field theories. The covalent bonding of the valence bond theory appears as the sigma (σ) bonded molecular orbitals, designated here as σ_s, σ_p, and σ_d. Likewise the crystal field splitting (Δ_0) of the crystal field

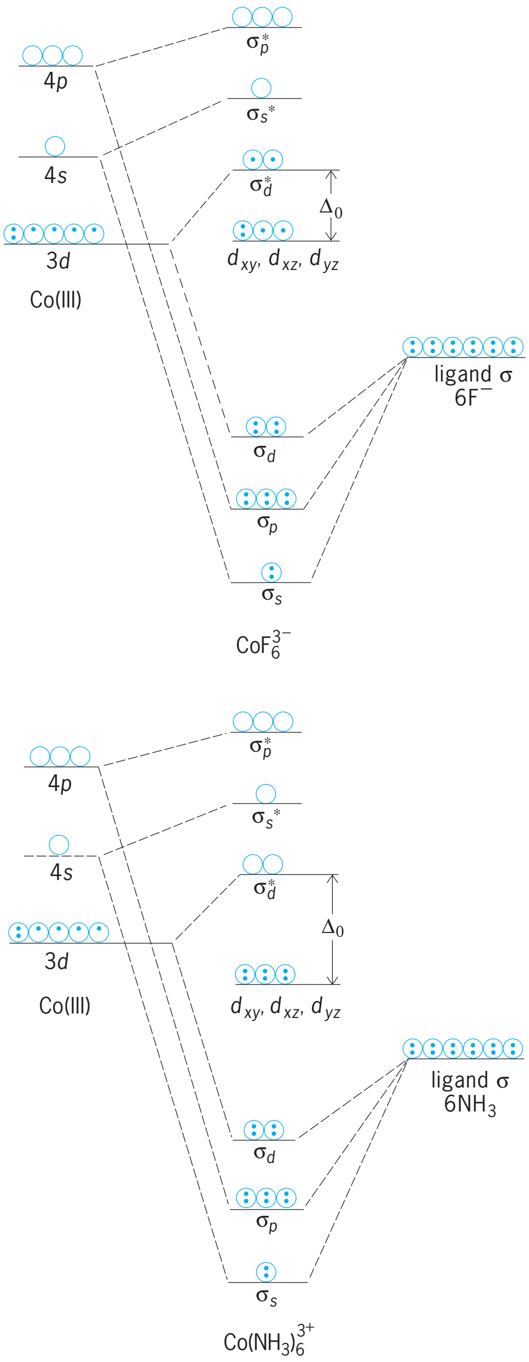
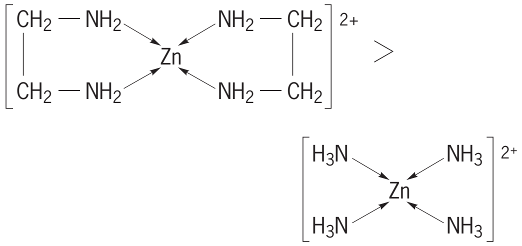


Fig. 5. Cobalt complexes CoF$_6^{3-}$ and Co(NH$_3$)$_6^{3+}$ according to molecular orbital theory.

theory now is the energy difference between the nonbonding d orbitals d_{xy}, d_{xz}, d_{yz} and the antibonding sigma orbital σ_d^*. More complicated molecular orbital diagrams would include the contribution of π bonding in these systems.

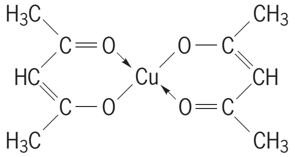
Stability of complexes. The stability of metal complexes depends both on the metal ion and the ligand. There is a great deal of quantitative information on the stability of coordination compounds. These data show that, in general, the stability of metal complexes increases if the central ion increases in charge, decreases in size, and increases in electron affinity. Thus, alkali-metal ions have the least tendency to form complexes, and the highly polarizing transition-metal ions have the greatest tendency. However, even in the least favorable cases of the alkali-metal ions, there is ample evidence that coordination with certain ligands does occur. For the transition-metal ions, it also appears that the electronic configuration of the ion is significant with regard to the stability of its complexes. For example, regardless of the nature of the ligand, the stability of complexes of bivalent transition metals is $\mathrm{Mn} < \mathrm{Fe} < \mathrm{Co} < \mathrm{Ni} > \mathrm{Cu} > \mathrm{Zn}$. This so-called natural order of stability is explained in terms of the crystal field theory, which indicates that a maximum stabilization effect in spin-free complexes is realized with d^8 systems, such as exists in Ni^{2+}. The platinum metals, because of their large polarizing ability, generally form the most stable metal complexes.

Effect of ligand. Several characteristics of the ligand are known to influence the stability of complexes: (1) basicity of the ligand, (2) the number of metal-chelate rings per ligand, (3) the size of the chelate ring, (4) steric effects, (5) resonance effects, and (6) the ligand atom. Since coordination compounds are formed as a result of acid-base reactions where the metal ion is the acid and the ligand is the base, it follows that generally the more basic ligand will tend to form the more stable complex. Much of the available quantitative data on the formation constants of coordination compounds gives a good linear correlation with the base strength of the ligand. It is also known that a polydentate ligand, one attached to the metal ion at more than one point, forms more stable complexes than does an analogous monodentate ligand. For example, ethylenediamine forms more stable complexes than does ammonia, as shown in the following inequality.

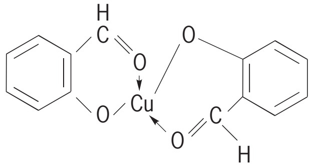


The ethylenediamine complex is referred to as a chelate complex. In general, an increase in the extent of chelation results in an increase in the stability of the complex. Ethylenediaminetetraacetate ion, a sexadentate ligand, is an excellent chelating agent and has found numerous applications as a sequestrant for metal ions. **Figure 6** is the structural formula of the chelate complex of calcium ion and ethylenediaminetetraacetate.

The size of the chelate ring is likewise an important factor. For saturated ligands such as ethylenediamine, five-membered rings are the most stable, whereas six-membered rings are the most stable for chelates containing one or more double bonds, for example (**1**) and (**2**). Examples of smaller and of larger chelate ring systems are known, but these are much less common and less stable. It has been observed that for analogous systems an increase in double bonding in the chelate ring increases the stability of the complex. For ligands of comparable base strengths, the acetylacetonate complexes of type (**1**) are more stable than the salicylaldehyde compounds of type (**2**). There are in effect two double bonds per chelate ring in (**1**) compared to one and a half in (**2**). This same phenomenon is believed to be responsible for the marked stability of the porphyrin complexes such as chlorophyll, hemoglobin, and the phthalocyanine dyes.



(**1**)



(**2**)

Steric factors often have a very large effect on the stability of metal complexes. This is most frequently observed with ligands having a large group attached

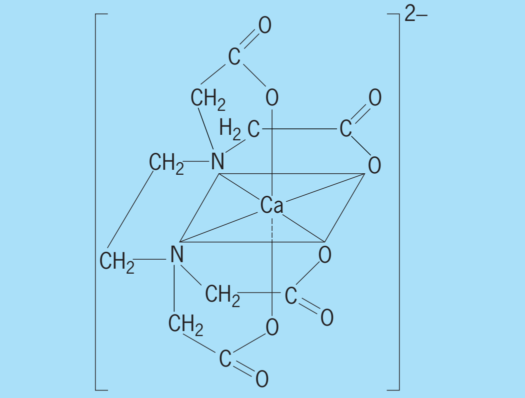


Fig. 6. Structural formula for the chelate complex formed from a calcium ion and ethylenediaminetetraacetate.

to the ligand atom or near it. Thus complexes, of the type shown in **Fig. 7**, with alkyl groups R in the position designated are much less stable than the parent complex where R = H. This results from the steric strain introduced by the size of the alkyl group on or adjacent to the ligand atom. In contrast to this, alkyl substitution at any other position results in the formation of more stable complexes because the ligand becomes more basic, and the bulky group is now removed from a position near the coordination site.

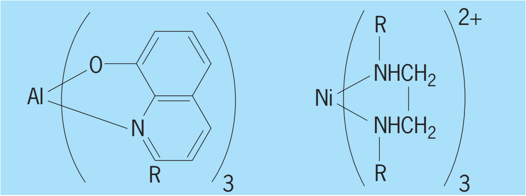


Fig. 7. Structural formulas of metal complexes which are affected by steric factors.

Finally, the ligand atom itself plays a significant role in controlling the stability of metal complexes. For most of the metal ions, the smallest ligand atom with the largest electron density will form the most stable complex. This means that the second period elements form more stable metal-ligand bonds than do other members of the same group, for example, N > P > As > Sb; O > S > Se > Te; F > Cl > Br > I. It is also known that for this same class of metal ions the stability order is N > O > F. These trends are in accord with the coordinate bond strengths expected on the basis of electrostatic interactions. These metal ions and the ligand atoms they prefer are not very polarizable, and are designated as hard Lewis acids and bases, respectively. A different trend in stability is found for a second class of metal ions, for example, Cu(I), Rh(I), Pd(II), Ag(I), Pt(II), and Hg(II). The stability trends observed for these metal ions are N < P > As > Sb, O < S > Se > Te, and F < Cl < Br < I. These metal ions and the ligand atoms they prefer are polarizable, and are designated as soft Lewis acids and bases, respectively. Thus, Pearson has proposed the HSAB theory of acids and bases, which states that hard Lewis acids prefer hard bases and soft Lewis acids prefer soft bases. Since the soft metal ions also have a large number of *d* orbital electrons and the third-period ligand atoms have vacant *d* orbitals, the enhanced stability is attributed to the formation of *dd-π* bonding. This means that the filled *d* orbitals of the metal ion overlap with the empty *d* orbitals of the ligand atom. This is illustrated by **Fig. 8**. This same class of metal ions is the one that forms olefin complexes such as Zeise's salt, K[Pt(CH_2=CH_2)Cl_3]. The stability of these compounds is likewise attributed to *π* bonding.

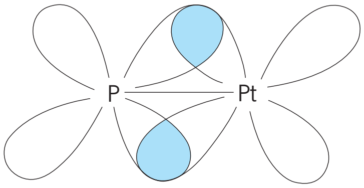


Fig. 8. Overlap of *d* orbitals of platinum with empty *d* orbitals of phosphorus ligand.

Stability and reactivity. Often the most stable complex is also the least reactive or most inert. Therefore, the platinum metal complexes as well as cobalt(III) and chromium(III) complexes are usually very slow to react. However, there are exceptions to this, for instance, the rapid exchange of radiocyanide with the coordinated cyanide in the stable tetracyano complexes $Hg(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$. Several factors, such as the electronic configuration of the central metal ion, its coordination number, and the extent of chelation, all have a marked effect on the rate of reaction of a given compound.

There are sufficient data available to permit a fairly reliable classification for the relative reactivities of six-coordinated systems. Metal complexes are said to be labile if they have reacted completely at room temperature within the time of mixing, such as the instantaneous formation of the deep-blue color of $Cu(NH_3)_4^{2+}$ upon the addition of excess ammonia to $Cu(H_2O)_4^{2+}$. Complexes are designated as being inert if their reactions at room temperature proceed at a detectable rate and have half-lives longer than 2 min. On the basis of such a definition, it is possible to classify the labile complexes as being those of either the outer orbital type, such as CoF_6^{3-}, $Al(C_2O_4)_3^{3-}$, $SnCl_6^{2-}$, $Ni(NH_3)_6^{2+}$, or the inner orbital type with one or more vacant *d* orbitals, such as TiF_6^{2-}, $V(CN)_6^{3-}$, $Mo(SCN)_6^{2-}$. The inert complexes are then the inner orbital type with no vacant *d* orbitals; for example, $Co(NH_3)_6^{3+}$, $Cr(H_2O)_6)_6^{3+}$, $RhCl_6^{3-}$. A similar classification based on the crystal field theory is done in terms of the labile systems being those that are not stabilized greatly by the crystal field.

Reactions of complexes. The reactions referred to above are acid-base reactions, where one basic ligand replaces a less basic ligand coordinated to the acidic metal ion, for example, reaction (4). A reaction of this type is called a nucleophilic substitution reaction and is designated by the symbol S_N. There are at least two fundamentally different pathways conceivable for such a reaction. These are the dissociation and displacement mechanisms which are designated as S_N1 and S_N2, respectively. An S_N1 reaction goes by two-step process, where the first step is a slow unimolecular heterolytic dissociation, reaction (5), followed by the rapid coordination of the entering group, reaction (6). An S_N2 reaction is one involving a bimolecular rate-determining step in

$$Co(NH_3)_5Cl^{2+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + Cl^- \qquad (4)$$

$$Co(NH_3)_5Cl^{2+} \xrightarrow{\text{slow}} Co(NH_3)_5{}^{3+} + Cl^- \qquad (5)$$

$$Co(NH_3)_5{}^{3+} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_5H_2O^{3+} \qquad (6)$$

which one nucleophilic reagent displaces another [reaction (7)]. Examples of both types of substitution are known for the reaction of metal complexes.

$$\mathrm{Co(NH_3)_5Cl^{2+} + H_2O \xrightarrow{slow} H_2O \cdots Co(NH_3)_5 \cdots Cl^{2+} \xrightarrow{fast} Co(NH_3)_5H_2O^{3+} + Cl^-} \qquad (7)$$

The specific reaction just cited, as well as analogous reactions of $Co(NH_3)_4Cl_2^+$ and $Co(NH_3)_4OHCl^+$, appears to proceed by an S_N1 mechanism. However, reactions of platinum(II) complexes are believed to involve an S_N2 process, for example, reaction (8).

$$\mathrm{Pt(NH_3)_3Cl^+ + NO_2^- \xrightarrow{slow} O_2N \cdots Pt(NH_3)_3 \cdots Cl \xrightarrow{fast} Pt(NH_3)_3NO_2^+ + Cl^-} \qquad (8)$$

The symbols AID were introduced in order to better designate the mechanisms of these reactions. A = association and relates to S_N2, where the entering group becomes associated with the complex [slow step of Eq. (8)]; I = interchange and signifies that a group just outside the complex interchanges positions with a ligand on the metal; D = dissociation and relates to S_N1, where the leaving group dissociates away from the complex [Eq. (5)]. In general, I_d is similar to S_N1 and designates a dissociative interchange mechanism, whereas I_a is similar to S_N2 and designates an associative interchange mechanism.

Finally, coordination may have the effect of stabilizing an unusual oxidation state of the coordinated metal. For example, ligands such as CO, CN^-, CNR, 2,2′-bipyridine, and PR_3 are most effective in stabilizing low-valent states. Thus, compounds of the type $Na_2[Fe(CO)_4]$, Na[V(2,2′-bipyridine)$_3$], $K_4[Ni(CN)_4]$, and $Pt(PR_3)_4$ are known where the assigned oxidation states are Fe (2−), V (1−), Ni (0), and Pt (0). It is believed that the low oxidation states in these systems are stabilized by the formation of π-type molecular orbitals between the metal and ligand atoms. If the ligand orbitals are of low energy and vacant, they can accommodate the *d*-orbital electrons of the metal and permit the addition of other electrons leading to the reduction of the complex. In contrast, ligands such as O^{2-}, OH^-, and F^- tend to stabilize high-valence states giving complexes of the type K_2FeO_4, Na_3BiO_4, K_2NiF_6, and K_3CuF_6, where the oxidation states are Fe (6+), Bi (5+), Ni (4+), and Cu (3+). These ligands have no *d* orbitals but only filled *p* orbitals. One explanation for the stabilization of higher-valent states by such ligands is that in these systems the π-type molecular orbitals cannot be formed so the metal electrons are forced into higher-energy antibonding orbitals from which they may be readily removed. *See* CHEMICAL BONDING; MAGNETOCHEMISTRY; SOLID-STATE CHEMISTRY; STEREOCHEMISTRY; SUBSTITUTION REACTION.

Fred Basolo; John L. Burmeister

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Coordination complexes

A group of chemical compounds in which all or a part of the molecular bonding is of the coordinate covalent type.

This article summarizes the different types of compounds that are known and discusses their nomenclature, structure, stereochemistry, and synthesis. For a discussion of the nature of the coordinate bond and the stability and reactivity of complex compounds *see* CHELATION; COORDINATION CHEMISTRY.

Complex compounds contain a central atom or ion and a group of ions or molecules bonded to it. Many simple hydrates, such as $MgCl_2 \cdot 6H_2O$, are best formulated as $[Mg(H_2O)_6]Cl_2$ because it is known that the six molecules of water are bound to the central magnesium ion. Therefore, $[Mg(H_2O)_6]^{2+}$ is a complex ion, and $[Mg(H_2O)_6]Cl_2$ is a complex compound. The charge on this complex ion is 2+, because this is the charge on the magnesium ion and the coordinated water molecules are neutral. However, if the coordinated groups are charged, then the charge on the complex is represented by the sum of the charge on the metal and that of the coordinated ions. See, for example, the progression of charges on the platinum(IV) complexes listed below. Thus the charge is 4+ for $[Pt(NH_3)_6]^{4+}$ because Pt is 4+ and NH_3 is neutral. But the charge is 2− for $[PtCl_6]^{2-}$ because of the 6 Cl^-, that is, $+4 - 6 = -2$ (that is, 2−).

Nomenclature. The metal complex may be a cation, have zero charge, or be an anion, as is exemplified by the following series of complexes:

$[Pt(NH_3)_6]Cl_4$	Hexaammineplatinum(IV) chloride
$[Pt(NH_3)_5Cl]Cl_3$	Chloropentaammine-platinum(IV) chloride
$[Pt(NH_3)_4Cl_2]Cl_2$	Dichlorotetraammine-platinum(IV) chloride
$[Pt(NH_3)_3Cl_3]Cl$	Trichlorotriammine-platinum(IV) chloride
$[Pt(NH_3)_2Cl_4]$	Tetrachlorodiammine-platinum(IV)
$K[Pt(NH_3)Cl_5]$	Potassium pentachloro-ammineplatinate(IV)
$K_2[PtCl_6]$	Potassium hexachloro-platinate(IV)

These compounds are named according to rules set up by the Nomenclature Committee of the International Union of Pure and Applied Chemistry. Some of the rules are the following: (1) Name the cation first as one word followed by the anion as one word. (2) For a cationic complex, name the negative ligands first with an ending of -o, then the neutral ligands, and finally the metal followed by a Roman numeral in parentheses to designate its oxidation state. Neutral ligands are named as the molecule, except that H_2O is aqua and NH_3 is ammine. (3) The prefixes such as di, tri, and tetra are used before simple names such as chloro, aqua, and oxalato. Prefixes such as bis, tris, and tetrakis are used before complex names such as ethylenediamine, 2,2′-bipyridine, and trialkylphosphine. (4) Neutral complexes are named in the same way except that only one word is required. (5) Anionic complexes are also named according to these same rules except that an -ate ending is used. Additional rules are available to name the more complicated compounds, and some of these will be used in the discussion that follows.

Coordination numbers of 2–10 have been observed for different complex compounds. The most common coordination numbers are 6 and 4. Complexes having coordination number 6 generally have an octahedral structure, but may also be trigonal prismatic. Complexes having coordination number 4 are either square planar or tetrahedral. **Table 1** gives examples of complexes having coordination numbers other than 4 or 6.

TABLE 1. Metal complexes with coordination numbers other than 4 or 6

Coord. number	Complex	Structure
2	$[Ag(CN)_2]^-$ $[Ag(NH_3)_2]^+$	Linear
3	$[Cu(PR_3)_2I]$ $[Au(AsR_3)_2I]$	Planar
5	$[Fe(CO)_5]$ [Zn(2,2′,2″-terpyridine)Cl_2]	Trigonal bipyramid
	$[Ni(PR_3)_2Br_3]$ {Pd[*o*-phenylene-bis-(dimethylarsine)]$_2$I}I	Tetragonal pyramid
7	$ZrF_7{}^{3-}$	Pentagonal bipyramid
	$NbF_7{}^{2-}$	Face-centered trigonal prism
	$TaF_7{}^{2-}$	
8	$Mo(CN)_8{}^{4-}$	Dodecahedral
	$TaF_8{}^{3-}$	Archimedean antiprism
9	$Nd(H_2O)_9{}^{3+}$	Face-centered trigonal prism
10	$Cd_2[Mo(CN)_8(H_2O)_2]$	Unknown structure

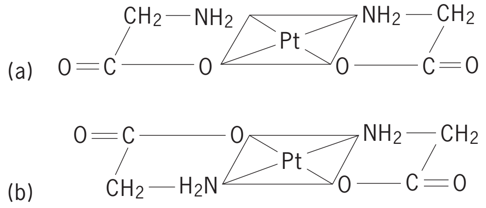


Fig. 1. Structure of (*a*) *cis*-diglycinatoplatinum(II) and (*b*) *trans*-diglycinatoplatinum(II).

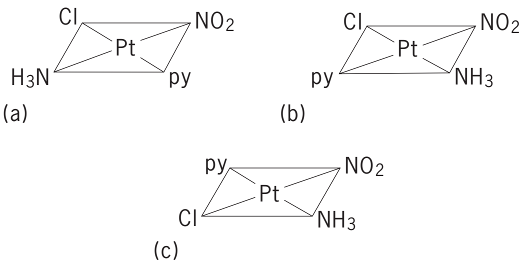


Fig. 2. Isomeric complexes. (*a*) *trans*-Chloropyridine-*trans*-nitroammineplatinum(II). (*b*) *trans*-Chloroammine-*trans*-nitropyridineplatinum(II). (*c*) *trans*-Chloronitro-*trans*-amminepyridineplatinum(II).

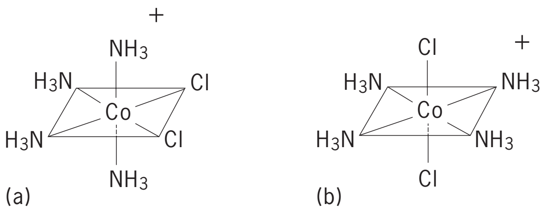


Fig. 3. Structure of (*a*) *cis*-dichlorotetraamminecobalt (III) ion and (*b*) *trans*-dichlorotetraamminecobalt(III) ion.

Structures. Metal complexes exhibit various types of isomerism. In many ways, inorganic stereochemistry is similar to that observed with organic compounds. Geometrical isomers are common among the substitution inert complexes of coordination numbers 4 and 6. Square planar complexes of the type $Pt(NH_3)_2Cl_2$ exist in two forms, cis and trans. Likewise, cis-trans isomers of the $Pt(NH_2CH_2COO)_2$ type have been isolated (**Fig. 1**). It is apparent from the above examples that the isomer with the same ligands or ligand atoms in adjacent positions is called cis, whereas the trans isomer has its like groups in opposite positions. There are also examples of geometrical isomers of complexes containing four different ligands (**Fig. 2**). Although geometrical isomerism of square complexes is most common with platinum(II), it has also been observed with compounds of nickel(II), palladium(II), and gold(III). *See* STEREOCHEMISTRY.

There are many examples of geometrical isomers for 6-coordinated complexes of cobalt(III), chromium(III), and the platinum metals. Most of the examples are of the type $[Co(NH_3)_4Cl_2]^+$ (**Fig. 3**). If three of the ligands differ from the other three, then only two isomers are possible (**Fig. 4**). Similar isomers are obtained with an unsymmetrical bidentate ligand (**Fig. 5**). The complex with 6 different ligands, such as $[Pt(NH_3)(py)(NH_2OH)(Cl)(Br)(NO_2)]$,

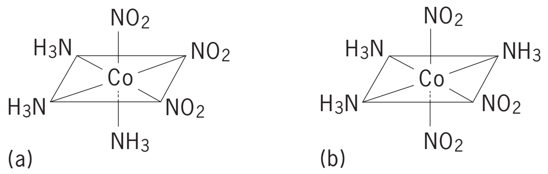


Fig. 4. Structure of (*a*) *cis*- (or facial-) trinitrotriamminecobalt(III) and (*b*) *trans*- (or meridial-) trinitrotriamminecobalt(III).

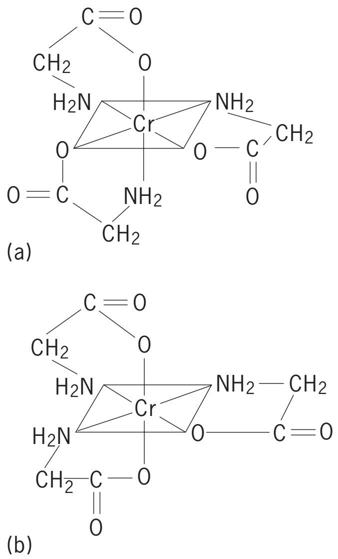


Fig. 5. Structure of (*a*) *fac*-triglycinatochromium(III) and (*b*) *mer*-triglycinatochromium(III).

can exist theoretically in 15 different geometrical forms.

Optical isomerism is also fairly common among these compounds. For example, 4-coordinate tetrahedral complexes containing unsymmetrical bidentate ligands, such as bis(benzoylpyruvato)beryllate (II) ion, have been resolved (**Fig. 6**). Optically active complexes of this type are likewise reported for boron(III) and for zinc(II). Most of the examples of optical activity occur with 6-coordinated systems containing three bidentate ligands, for example, trioxalatorhodiate(III) ion (**Fig. 7**). The resolution of 6-coordinated complexes of this type has been reported for the metal ions Al(III), As(V), Cd(II), Co(III), Cr(III), Ga(III), Ge(IV), Ir(III), Fe(II),(III), Ni(II), Os(II),(III), Pt(IV), Rh(III), Ru(II),(III), Ti(IV), and Zn(II).

The cis isomer of a complex containing two bidentate ligands and two monodentate ligands is asymmetric, and therefore exists in the form of mirror-image isomers, whereas the trans form is symmetrical and cannot be optically active (**Fig. 8**). Since the cis isomer of this type is optically active and the trans isomer is not, the successful resolution of one of the isomers has historically been used as a proof of its cis structure. Other types of isomerism are known for metal complexes (**Table 2**).

Synthesis. The synthesis of metal complexes containing only one kind of ligand generally involves simply the reaction of the metal salt in aqueous solution with an excess of the ligand reagent, reaction (1).

$$[Ni(H_2O)_6](NO_3)_2 + 6NH_3 \longrightarrow [Ni(NH_3)_6](NO_3)_2 + 6H_2O \quad (1)$$

The desired complex salt can then be isolated by removal of water until it crystallizes, or by addition of a water-miscible organic solvent to cause it to separate. Many reactions, such as the one cited above, occur readily at room temperature. For the substitution-inert complexes (those slow to react), prolonged treatment at more drastic conditions is often necessary.

The preparation of geometrical isomers is much more difficult, and in most cases, the approach used

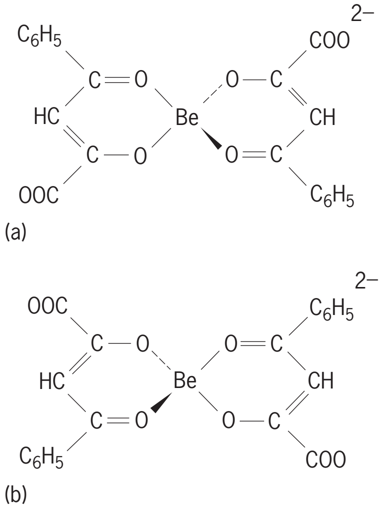


Fig. 6. Optical isomers of bis(benzoylpyruvato)beryllate(II) ion: (*a*) dextro and (*b*) levo.

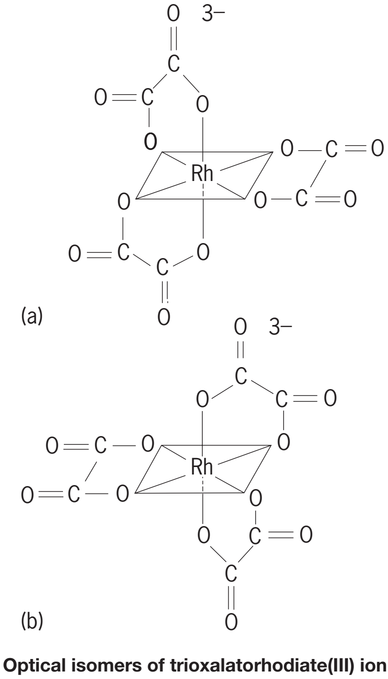


Fig. 7. Optical isomers of trioxalatorhodiate(III) ion: (*a*) lambda and (*b*) delta.

is rather empirical. Generally, reactions yield a mixture of cis-trans products, and these are separated on the basis of their differences in solubility. The trans isomers of platinum(IV) complexes are prepared by the oxidation of the appropriate platinum(II) compound (**Fig. 9**). The cis isomers of cobalt(III) complexes can sometimes be prepared by the reaction of a carbonato complex with the desired acid (**Fig. 10**).

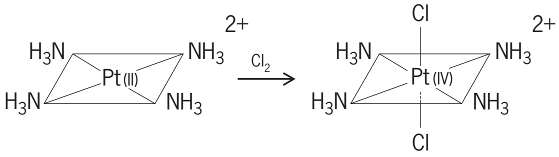


Fig. 9. Reaction in the trans isomer formation of platinum(IV) complexes.

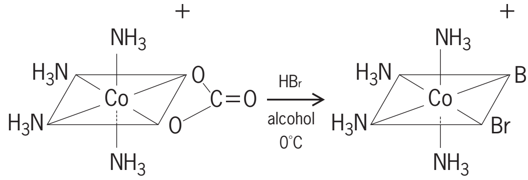


Fig. 10. Cis isomer formation of cobalt(III) complexes.

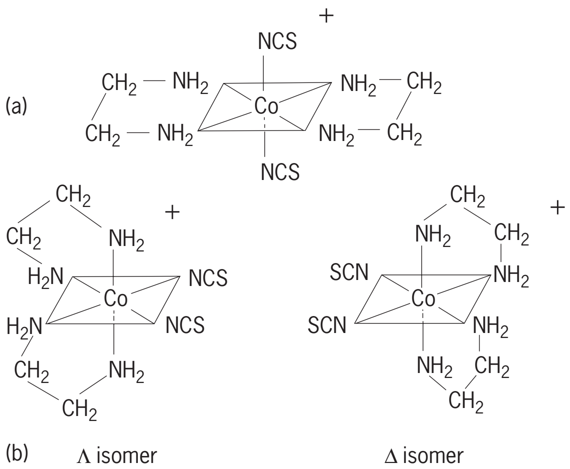
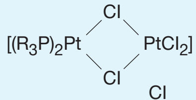
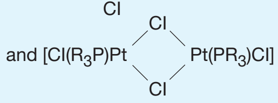


Fig. 8. Symmetric trans form of a complex and asymmetric cis structures. (*a*) *trans*-bis(isothiocyanato) bis(ethylenediamine)cobalt(III) ion. (*b*) Asymmetric forms of lambda, delta; *cis-bis*(isothiocyanato) bis(ethylenediamine) cobalt(III) ion.

TABLE 2. Types of isomerism for complex compounds

Isomerism	Examples
Geometrical	*cis*- and *trans*-$[Pt(NH_3)_2Br_2]$
Optical	Δ-and Ω-$[Ir(NH_2CH_2CH_2NH_2)_3]Cl_3$
Coordination	$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
Coordination position	 $[(R_3P)_2Pt(\mu\text{-}Cl)_2PtCl_2]$  and $[Cl(R_3P)Pt(\mu\text{-}Cl)_2Pt(PR_3)Cl]$
Hydrate	$[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_3 \cdot H_2O$
Ionization	$[Pt(NH_3)_4Cl_2]SO_4$ and $[Pt(NH_3)_4SO_4]Cl_2$
Linkage	$[(NH_3)_5Co—NO_2]SO_4$ and $[(NH_3)_5Co—ONO]SO_4$
Polymerization	$[Co(NH_3)_3(NO_2)_3]$ and $[Co(NH_3)_6][Co(NO_2)_6]$
Conformation	$[Ni(P(C_6H_5)_2CH_2C_6H_5)_2Br_2]$ square-planar and tetrahedral

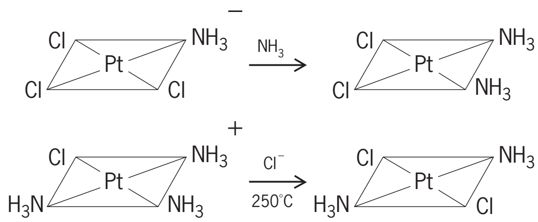


Fig. 11. Cis and trans isomer formation of platinum(II).

The easiest geometric isomers to prepare are those of platinum(II). For example, the cis and the trans isomers of $[Pt(NH_3)_2Cl_2]$ are prepared as shown in reactions (2). The second step in each of these reac-

$$K_2[PtCl_4] + 2NH_3 \longrightarrow cis\text{-}[Pt(NH_3)_2Cl_2] + 2KCl$$
$$[Pt(NH_3)_4]Cl_2 \xrightarrow[(392^\circ F)]{250^\circ C} trans\text{-}[Pt(NH_3)_2Cl_2] + 2NH_3 \qquad (2)$$

tions results in the replacement of the ligand trans to a chloro group (**Fig. 11**). This phenomenon, that a negative ligand often has a greater labilizing effect on a group in the trans position than does a neutral group, for example, $Cl^- > NH_3$, is called the trans effect. Extensive use has been made of this trans effect in the synthesis of desired platinum(II) complexes. The complex *cis*-$[Pt(NH_3)_2Cl_2]$ (Fig. 11) is used as an antitumor drug for certain types of cancer.

Finally, the separation of optical isomers of metal complexes involves techniques similar to those used for organic compounds. The usual procedure is to convert the racemic mixture into diastereoisomers by means of an optically active resolving agent and then to separate the diastereoisomers by fractional crystallization. Nonionic complexes have been resolved by preferential adsorption on optically active quartz or sugars. *See* AMMINE; HYDRATE.

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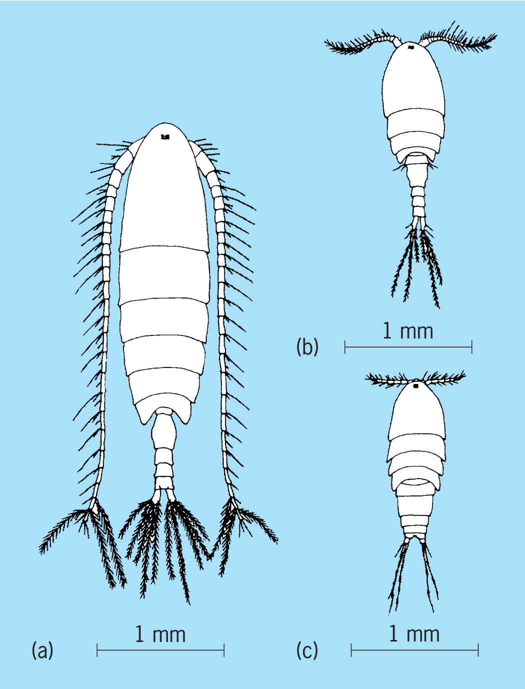
Copepoda

A subclass of Crustacea with eight orders. There are over 6000 species, most of which are free-living in aqueous environments, though many are parasitic or symbiotic with other aquatic animals. The free-living forms are the most abundant of all animals in the sea and directly constitute the main food for vast numbers of fishes, many invertebrates, and also at times for baleen whales.

Structure. The structure of copepods, although similar in basic pattern, varies greatly. In free-living forms the body is composed externally of a series of small chitinous cylinders, or segments, some of which may be more or less fused. The head bears two pairs of antennae. The first antennae are used for stabilizing, retarding sinking, olfactory functioning, and usually in the male for grasping the female. The second antennae are used for creating water currents for food straining and slow locomotion in the Calanoida, and for food grasping in the Cyclopoida and Harpacticoida. The feeding appendages are one pair of mandibles, two pairs of maxillae, and one pair of maxillipeds. During the nauplius larval stage, the second antennae are commonly provided with masticatory hooks for feeding. The thorax, consisting of six segments, bears the swimming feet. The genital aperture occurs on the sixth thoracic segment. The abdomen consists of one to five segments and bears no appendages except a pair of terminal processes known as caudal rami. The sexes are separate and sexual dimorphism is frequently evidenced, especially by modification in the male by one or both of the first antennae for clasping, and in many by marked specialization in the fifth pair of feet for the transfer of spermatophores, or packets of spermatozoa, to the female. Free-living species usually range in size from less than 0.02 in. (0.5 mm) to about 0.4 in. (10 mm) in length. A deep oceanic species, *Bathycalanus sverdrupi,* attains a length of 0.68 in. (17 mm). Some parasitic copepods, such as *Penella,* are greatly elongate, reaching up to 10 in. (250 mm) in length. *See* SEXUAL DIMORPHISM.

Classification. Seven orders of copepods are usually recognized. Three of these, Calanoida, Cyclopoida, and Harpacticoida, are wholly or primarily free-living and because of overwhelming numbers are of greatest general interest. The anatomical differences that set these three apart are, among others, the shape of the body and the position of the movable articulation separating the forebody (metasome) from the hindbody (urosome). In the calanoids and the cyclopoids the urosome is distinctly narrower than the metasome (**illus.** *a* and *b*). In the calanoids the movable articulation falls between the fifth and sixth thoracic segments, whereas in the cyclopoids, it is between the fourth and fifth segments. In the harpacticoids the urosome is commonly not narrow (illus. *c*), and the movable articulation falls between the fourth and fifth thoracic segments. In many harpacticoids there is considerable flexibility also between other segments. The length of the first antennae relative to body length is very useful in distinguishing these three orders. The first antennae in the Calanoida have 20–25 segments, usually extending to or beyond the caudal rami. In the Cyclopoida they have 6–17 segments, extending to the posterior border of the metasome or even the first body segment. In the Harpacticoida they have 5–9 segments, usually not extending to the posterior border of the first body segment. *See* CALANOIDA; CYCLOPOIDA; HARPACTICOIDA.



Free-living copepods. (*a*) *Calanus finmarchicus*, a calanoid. (*b*) *Cyclops*, a cyclopoid. (*c*) *Harpacticus*, a harpacticoid.

In the adult state the remaining orders (Poecilostomatoida, Siphonostomatoida, Monstrilloida, Misophrioida, and Mormonilloida) are parasitic at least part of their lives. Many adult stages are so greatly modified that their crustacean relationship is obscure. Their numbers are relatively small, but they may be conspicuous and important as “fish lice,” burrowing deep into the flesh or feeding externally upon the skin and gills. *See* MISOPHRIOIDA; MONSTRILLOIDA; MORMONILLOIDA; POECILOSTOMATOIDA; SIPHONOSTOMATOIDA.

Life history. The life histories of copepods differ in details, but in nearly all, development takes place from fertilized eggs which are either attached to the genital segment or are cast free in the water. The spermatozoa, transferred to the female genital segment in spermatophores, are stored in spermathecal sacs in the female. Usually one mating suffices for all subsequent eggs laid by the female. A nauplius larva hatches from the egg. This larva usually undergoes five molts in its growth. Most nauplii are self-sustaining, gathering their own food, but some nauplii hatched from yolky eggs are sustained by the yolk through one or more stages. The sixth naupliar stage metamorphoses into the first of six copepodid stages, the last of which is the adult. Only a few life histories have been studied completely. In *Calanus finmarchicus,* a calanoid, a summer brood in boreal waters requires about 2–3 months to reach maturity, but broods produced in the autumn live longer because they winter in deep water as subadults. The number of broods produced is related to latitude, fewer being produced in the far north.

In *Tisbe furcata*, a bottom-living harpacticoid, individual females may live for 70 days, producing 5–10 broods averaging 43 eggs per brood. The young may produce the first batch of eggs in 15 days. Because of their high fecundity and early sexual maturity certain harpacticoids have proved useful for genetic studies.

Habitats. Copepod habitats are extremely varied, but the vast majority of species live in the sea. They are mostly planktonic throughout their lives, some occurring only in coastal waters while others live in the open sea. Many frequent only the upper layers to about 650–1000 ft (200–300 m) depth. Others are bathypelagic at great depths. The harpacticoids, however, are primarily a benthic, or bottom-dwelling, group, though many are truly planktonic. A great many harpacticoid species live upon aquatic vegetation to which they cling with tiny claws. Others are found on the bottom feeding upon detritus. Some are especially adapted by slender wormlike bodies to burrow or creep into the bottom among the grains of sand. There are also many fresh-water copepods living in ponds, lakes, and streams in all parts of the world. Their wide dispersal to isolated bodies of water is probably brought about largely through transport on birds' feet. A few copepods live naturally in damp moss.

Economic biology. The role of copepods in the economy of the sea consists mainly of converting plant into animal substance. Many species are adapted to graze directly upon the chief synthesizers of organic material, the microscopic diatoms and dinoflagellates that constitute the great pasturage of the sea. Some species are predatory on other copepods, fish larvae, and other small animals, such as protozoa. Commonly copepods constitute about 70% of the zooplankton, and at times their numbers are so great as to impart a pinkish color to the sea. They are of sufficient size to be fed upon individually by young fishes and to be filtered from the water by the filtering apparatus (gill rakers) of such fishes as the herring, sardines, and others that require animal protein as food. At higher trophic levels these fishes in turn are, directly or indirectly, food for the more predatory fishes and mammals. *See* MARINE ECOLOGY.

Harry C. Yeatman

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Copolymer

A macromolecule in which two or more types of monomer are incorporated into the polymer chain. This contrasts with a homopolymer, which consists of only one type of monomer. Copolymerization offers the ability to alter the properties of a homopolymer by introducing an appropriately chosen second repeating unit, or to combine the desirable properties of two different homopolymers in a single molecule. The properties of a copolymer depend on the nature of the monomers and their distribution in the chain. Thus, monomers A and B can polymerize randomly (ABBAABA), they can alternate (ABAB), they can form blocks (AAABBB), or one polymer can be grafted onto another polymer (**Fig. 1**). Copolymers can be prepared by all the known methods of polymerization, including addition polymerization of vinyl monomers (by conventional or living free-radical, anionic, cationic, or coordination catalysis), ring-opening polymerization, or condensation polymerization. Copolymers can also be formed by the chemical reaction of functional groups (usually end groups) on the constituent polymer chains. *See* FREE RADICAL; MACROMOLECULAR ENGINEERING; POLYMER; POLYMERIZATION; RING-OPENING POLYMERIZATION.

Statistical copolymers. The simplest method of producing a copolymer is to polymerize a mixture of two (or more) different monomers. Assuming that they are both polymerizable via the same mechanism, the different types of repeat unit will be incorporated into the polymer chain according to their concentration in the monomer feed and their relative reactivities. If the comonomers (A and B) have similar reactivities, a random distribution of the alternative repeat units (BABBAABA) is obtained. If A prefers to add to B and B prefers to add to A, an alternating sequence (ABABABAB) is expected. If A prefers to add to A (and/or B prefers to add to B), one might expect a greater concentration of AAAA or BBBB blocks, or in the extreme case no copolymer at all but a mixture of homopolymers. In reality, the copolymer will have a composition and sequence distribution somewhere between these extremes that can be manipulated by varying the ratio of the comonomers in the feed and by varying the reactivities themselves (for example, by varying the temperature, catalyst, or solvent).

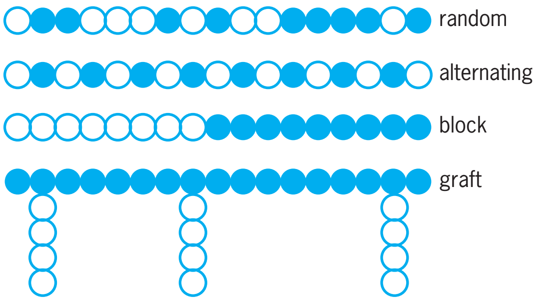

Fig. 1. Different types of copolymers.

Copolymerization models are equations for predicting the composition, sequence distribution, and polymerization kinetics as a function of the monomer feed fractions and a small set of characteristic constants. One of the simplest models is the terminal model. It is assumed that for a given type of polymerization mechanism (radical, anionic, cationic, metallocene-catalyzed, and so on), the reactivity of the propagating species depends only on the nature of its terminal monomer unit. As shown below, there are four types of reaction to consider, with the reacting chains ending in either monomer unit (A* or B*) with each of the comonomers (A or B).

$$\sim\!\sim A^* + \begin{cases} A \xrightarrow{k_{AA}} \sim\!\sim AA^* \\ B \xrightarrow{k_{AB}} \sim\!\sim AB^* \end{cases} \qquad r_A = \frac{k_{AA}}{k_{AB}}$$

$$\sim\!\sim B^* + \begin{cases} A \xrightarrow{k_{BA}} \sim\!\sim BA^* \\ B \xrightarrow{k_{BB}} \sim\!\sim BB^* \end{cases} \qquad r_B = \frac{k_{BB}}{k_{BA}}$$

The reactivity ratios r_A and r_B measure the selectivity of each propagating species toward the alternative monomers, and can be determined experimentally by fitting the terminal model equations to composition or sequence distribution data. Hundreds of reactivity ratios have been measured in this way, and numerous studies have attempted to explain their values in terms of the chemical structure. In recent years, it has been shown that the terminal model rarely holds, and much more complicated copolymerization models are generally required. In radical copolymerization, for instance, models that include additional factors, such as the influence of the penultimate unit of the propagating species, the depropagation reaction, or various types of solvent effects, have been introduced to describe various systems.

Tapered copolymers. An interesting feature of statistical copolymerization is the possibility of composition drift. If the comonomers are consumed at different rates, the comonomer feed ratio will vary through the polymerization process. As a result, the composition of the copolymer will also vary as a function of conversion. In a nonliving process, such as conventional free-radical copolymerization, chains are initiated and grow at different stages of the reaction, resulting in compositional variation among the polymer chains. In contrast, in a living process (such as ionic, coordination-catalyzed, or living free-radical copolymerization) the individual chains are initiated together and continue to grow over the entire polymerization process. As a result, changes in the instantaneous copolymer composition are frozen into the growing polymer chain, and a tapered composition results. For instance, if A is a more reactive monomer, the polymer is initially richer in A; but since monomer A is consumed at a faster rate, the polymer becomes progressively poorer in A. As a result, one end of the polymer chain is richer in A than the other end. Depending on the reactivity ratios and the initial monomer feed fractions, a variety of interesting tapered compositions can be produced. Tapered, or gradient, copolymers have properties that are different from either block copolymers or random copolymers, and are particularly useful as blend compatibilizers and vibration-dampening materials.

Random copolymers. Random copolymers were among the first copolymers produced, and remain to this day among the most commercially important as they offer a means of improving the properties of a homopolymer via the incorporation of a small amount of a second type of repeat unit into the polymer chain. The first commercially important copolymers were developed in Germany in the 1930s, where it was discovered that the properties of synthetic rubber could be markedly improved via the copolymerization of butadiene with small amounts of other monomers. Buna N (now known as nitrile rubber or ABR) is a copolymer of butadiene with acrylonitrile, and combines the elastomeric properties of rubber with the solvent resistance of polyacrylonitrile, while Buna S (now known as SBR) is a copolymer of butadiene with styrene that has improved mechanical properties. Both copolymers continue to find widespread commercial use; in particular, SBR (reinforced with carbon black) is used in vehicle tires and still accounts for approximately 40% of the world market for elastomers. *See* ACRYLONITRILE; CARBON BLACK; POLYACRYLONITRILE RESINS; RUBBER; STYRENE.

Countless other applications for random copolymers exist. Low-density polyethylene is a highly branched homopolymer of ethylene obtained via conventional radical polymerization. Various properties of this homopolymer can be improved through copolymerization with small amounts of other monomers, including vinyl acetate which is used to improve clarity and flexibility for food packaging applications, acrylate or methacrylate monomers which can improve thermal stability for applications in cable insulation and medical packaging, and acrylic or methacrylic acids which offer improved abrasion resistance, flexibility, and adhesion for applications such as packing film and laminates. *See* POLYOLEFIN RESINS.

Emulsions of polymers based on acrylic or methacrylic esters are used extensively in adhesives, caulks, paints, and other surface coatings. A significant number of them are copolymers of acrylic and methacrylic esters, and/or combinations of ester and acid monomers. The copolymer composition is varied to optimize the gloss, adhesion, flexibility, impact strength, and other coating properties. *See* EMULSION POLYMERIZATION.

Alternating copolymers. Alternating copolymers are obtained in a statistical copolymerization if the cross-propagation reactions are very strongly favored over the respective homopolymerizations (that is, r_A and

$r_B \approx 0$). In a radical copolymerization, this will be the case if the comonomers are pairs of strongly electron-accepting and electron-donating monomers (such as styrene with acrylonitrile). Unless both reactivity ratios are exactly zero, the ratio of the comonomers also needs to be finely balanced. Alternating copolymers can also be obtained if just one of the comonomers does not readily homopolymerize (such as SO_2 or maleic anhydride), provided the polymerization is carried out in a large excess of this monomer. Pairs of monomers (such as styrene with methyl methacrylate) that might naturally form random copolymers can sometimes be forced to alternate through complexation of one of the comonomers with a Lewis acid. The complexation alters the reactivity of the propagating species and favors the cross-propagation reaction.

Some commercially important examples of alternating copolymers include the propylene-butadiene elastomer, which has improved mechanical properties and resistance to oxidative degradation compared with polybutadiene, and the vinylidene fluoride–hexafluoroisobutylene copolymer, which has improved abrasion resistance and better processability than the tetrafluoroethylene homopolymer (Teflon®). Copolymers of styrene with 10–40% acrylonitrile (SAN) are also of major commercial significance. Strictly speaking, they are statistical copolymers, with a high alternating tendency that peaks at the 50% copolymer composition. In SAN, the acrylonitrile improves the solvent resistance and tensile strength, compared with polystyrene, and raises the temperature of use. Alternating copolymers of chromophore units and saturated segments are showing promise as tunable electroluminescent devices as, unlike their fully conjugated counterparts (like polyacetylene), the conjugation length is well defined, and the optical properties can be more easily adjusted through variation of the chromophore. *See* CONJUGATION AND HYPERCONJUGATION.

Block copolymers. Copolymers containing block sequences can be prepared in a statistical copolymerization if both of the monomers show a tendency to homo-propagate rather than cross-propagate. However, it is difficult to prepare well-defined block copolymers in this way, since typically one monomer either yields statistical copolymers with blocks of varying length or (if there is no cross-propagation at all) a mixture of homopolymers.

There are three main strategies for preparing true block copolymers. Sequential addition of monomers to a living polymerization is perhaps the simplest method of block copolymer formation, but relies upon the two constituent monomers being polymerizable by the same mechanism. Until recently, this was a limitation, owing to the highly selective nature of ionic and coordination catalysts. However, with the development of controlled radical polymerization, a broader range of block copolymers can now be made. A second, more versatile approach is to prepare the first block as an end-functionalized macroinitiator that is added to the second monomer at a later stage. The advantage of this approach is that it is possible to prepare block copolymers from monomers that would not undergo polymerization via the same mechanism. For instance, step polymers (such as polyesters or polysulfones) can be converted to macroinitiatiors for atom transfer radical polymerization (ATRP) through treatment with 2-bromopropionyl bromide in the presence of pyridine. This introduces bromide end groups that, in conjunction with an appropriate ATRP catalyst, can be used to initiate controlled radical polymerization of styrene or acrylates, resulting in a BAB triblock copolymer. A third approach to preparing block copolymers is to chemically bond the constituent polymer chains as a postpolymerization reaction of functional end groups. *See* CONTROLLED/LIVING RADICAL POLYMERIZATION; POLYESTER RESINS; POLYSULFONE RESINS.

Block copolymers have a wide range of applications. Block copolymers of two otherwise immiscible polymers can function as compatibilizers, while block copolymers of hydrophobic and hydrophilic polymers can self-assemble into stable spherical or cylindrical micelles for use as emulsifiers, dispersants, and even drug delivery devices (**Fig. 2**). Block copolymers of hard (rigid) and soft (flexible) units function as thermoplastic elastomers (**Fig. 3**). *See* MICELLE.

In normal elastomers (such as rubber), the polymer chains are chemically bonded (cross-linked) together to prevent chains from slipping past each other under mechanical stress. This increases the strength of the polymer and allows for rapid recovery after deformation. However, the chemical cross-linking step is irreversible and has to be performed as an additional processing step after fabrication. In the thermoplastic elastomers, the cross-links are not chemical bonds but physical bonds. The hard blocks of these copolymers aggregate together to form rigid domains that act as physical cross-links to keep the rubbery phase in a network structure. At high temperature, the rigid domains melt allowing for reprocessing of the polymer. Thermoplastic elastomers are cheaper to process but offer less resistance to solvents and deformation at high temperatures. As a result, they tend to be used in applications such as wire insulation, footwear, wheels, and adhesives.

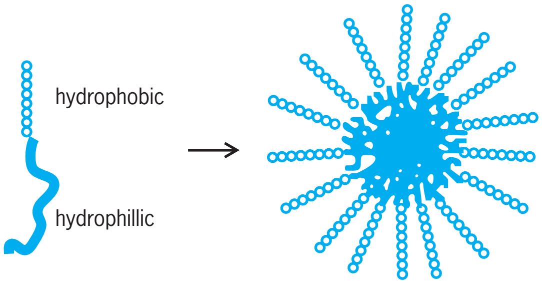

Fig. 2. Micelle formed from block copolymers.

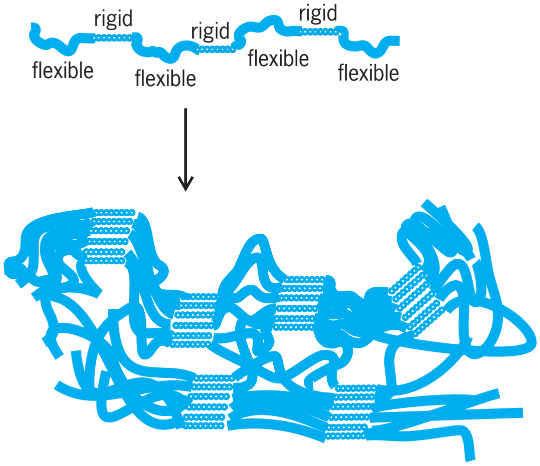

Fig. 3. Thermoplastic elastomer formed from block copolymers.

Graft copolymers. Graft polymers are a type of block copolymer in which one type of polymer chain is chemically attached to the side of the other chain (rather than the chain end). Typically, a single backbone supports several grafts, at either regular or random intervals along the chain. Highly grafted polymers (containing grafts at every repeat unit) are sometimes called bottle-brush polymers, while graft polymers with lower grafting densities are sometimes called comb polymers. *See* BRANCHED POLYMER.

As in the case of block-copolymer formation, grafting offers the possibility of introducing additional favorable properties to a homopolymer (such as improved mechanical properties or adhesion, or special additional functionalities such as antimicrobial action). For example, the impact resistance of polybutadiene (rubber) can be improved by grafting styrene onto it to make high-impact polystyrene, while grafting both styrene and acrylonitrile to make acrylonitrile-butadiene-styrene (ABS) polymers improves solvent resistance. Other commercially important examples include graft copolymers containing acrylic monomers which are used as pressure-sensitive adhesives, self-plasticizing poly(vinyl chloride) [PVC] which is produced by grafting poly(butyl acrylate) onto the PVC backbone, and blend compatibilizers which are obtained by grafting two otherwise immiscible polymers. When copolymers of hydrophilic and hydrophobic blocks are grafted onto a polymer backbone, they can function as unimolecular cylindrical micelles, and are of interest as potential nanoreactors and in drug delivery applications. *See* POLYVINYL RESINS.

Graft copolymers can be prepared using three main strategies: grafting onto, grafting from, and grafting through. In the grafting-onto approach, a preformed polymer with an active end group is attached onto the backbone of another preformed polymer at functional groups along the polymer chain. For example, polystyrene can be chlormethylated via treatment with chloromethyl ether in the presence of a catalyst, and then reacted with living polymeric chains. The grafting-from approach also begins with a polymer backbone but then grows the grafts from initiation sites along this backbone. These sites can be introduced to the backbone during its original preparation, via polymerization or copolymerization of a monomer that contains initiation sites. For example, a graft copolymer can be formed by the copolymerization of propylene with a monomer containing an alkoxyamine functional group. This functional group (which is inert at the temperature of the first polymerization) can then be used to initiate nitroxide-mediated polymerization of styrene in a controlled fashion. Alternatively, one can prepare a normal homopolymer and introduce the initiation sites as a separate reaction. For example, polystyrene can be treated with *N*-bromosuccinimide to brominate the polymer backbone at random intervals; the resulting bromide groups can then act as initiating sites for the polymerization of various vinylic monomers (by ATRP). *See* POLYSTYRENE RESIN.

In the grafting-through approach, one first prepares a macromonomer that is, a polymer with an end group that can be copolymerized with a second monomer. Macromonomers can be prepared using functional initiators or chain terminating agents. For example, polymers containing terminal olefinic bonds [carbon-carbon double bonds ($C{=}C$)] can be prepared in conventional radical polymerization in the presence of a catalytic chain-transfer agent. These monomers can then undergo radical copolymerization with a second olefinic monomer to yield graft copolymer.

Step copolymers. In a step polymerization process, a polymer is formed via the stepwise reaction of two different types of functional groups (such as an acid and an alcohol, or an acid and an amine) on multifunctional monomers. In many instances, the different types of functional groups are located on separate types of monomer (for example, a polyester is often made by reacting a diacid with a dialcohol), and a step homopolymer might be thought of as an alternating copolymer. However, in practice the entire ester linkage is defined as the repeating unit, and the term "copolymer" is reserved for polymers containing different types of repeat units.

As in the case of chain polymerization, statistical copolymers are formed from mixtures of monomers, such as two different types of acid with one or more types of alcohol, or two or more types of amine with one or more types of alcohol. For example, the crystallization and processing rates of poly(ethylene terephthalate) [PET] is improved by copolymerizing ethylene glycol and 1,4-butanediol with dimethyl terephthalate, while flame-retardant polycarbonates can be obtained by copolymerizing bisphenol A and its tetrabromo derivative.

In step polymerization, it is possible to make statistical copolymers not only from a mixture of monomers but also from a mixture of homopolymers. For example, if two different polyesters are heated under vacuum they will transesterify, resulting in the scrambling of their repeat units. Depending on how far the reaction is driven, one can obtain a range of sequence distributions ranging from blocks to fully random copolymers. This scrambling via interchange makes it difficult to synthesize block copolymers from homopolymers containing the same type of functional group. However, as seen above, it is possible to produce block or graft copolymers involving step polymers and various types of chain polymers. One important example is the multiblock copolymers of polyurethanes and butadiene, which function as thermoplastic elastomers. Michelle L. Coote

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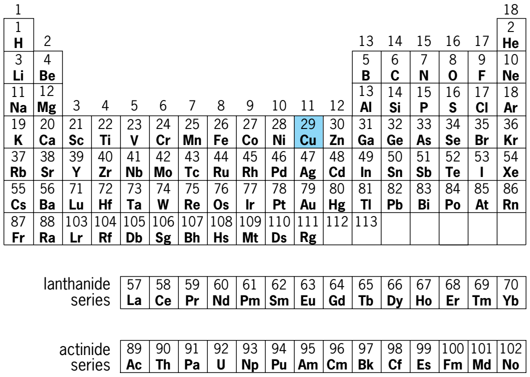
Copper

A chemical element, Cu, atomic number 29, atomic weight 63.546. Copper, a nonferrous metal, is the twentieth most abundant element present in the Earth's crust, at an average level of 68 parts per million (0.22 lb/ton or 0.11 kg/metric ton). Copper metal and copper alloys have considerable technological importance due to their combined electrical, mechanical, and physical properties. The discoveries that mixed-valence Cu(II)/Cu(III) oxides exhibit superconductivity (zero electrical resistance) at temperatures as high as 125 K (−234°F; liquid nitrogen, a cheap coolant, boils at 90 K or −297°F) have generated intense international competition to understand these new materials and to develop technological applications. Although some pure copper metal is present in nature, commercial copper is obtained by reduction of the copper compounds in ores followed by electrolytic refining. The rich chemistry of copper is restricted mostly to the valence states Cu(I) and Cu(II); compounds containing Cu(0), Cu(III), and Cu(IV) are uncommon. Soluble copper salts are potent bacteriocides and algicides at low levels and toxic to humans in large doses. Yet copper is an essential trace element that is present in various metalloproteins required for the survival of plants and animals. *See* COPPER ALLOYS.



Copper is located in the periodic table between nickel and zinc in the first row of transition elements and in the same subgroup as the other so-called coinage metals, silver and gold. The electronic configuration of elemental copper is [$1s^2 2s^2 2p^6 3s^2$] $3d^{10}4s^1$ or [argon]$3d^{10}4s^1$. At first glance, the sole $4s$ electron might suggest chemical similarity to potassium, which has the [argon]$4s^1$ configuration. However, metallic copper, in sharp contrast to metallic potassium, is relatively unreactive. The higher nuclear charge of copper relative to that of potassium is not fully shielded by the 10 additional d electrons, with the result that the copper $4s$ electron has a higher ionization potential than that of potassium (745.5 versus 418.9 kilojoules/mole, respectively). Moreover, the second and third ionization potentials of copper (1958.1 and 3554 J/mole, respectively) are considerably lower than those of potassium, and account for the higher valence-state accessibility associated with transition-metal chemistry as opposed to alkali-metal chemistry. *See* PERIODIC TABLE; TRANSITION ELEMENTS; VALENCE.

Copper is a comparatively heavy metal. The density of the pure solid is 8.96 g/cm^3 (5.18 oz/in.^{3}) at 20°C (68°F). The density of commercial copper varies with method of manufacture, averaging 8.90–8.92 g/cm^3 (5.14–5.16 oz/in.^{3}) in cast refinery shapes, 8.93 g/cm^3 (5.16 oz/in.^{3}) for annealed tough-pitch copper, and 8.94 g/cm^3 (517 oz/in.^{3}) for oxygen-free copper. The density of liquid copper is 8.22 g/cm^3 (4.75 oz/in.^{3}) near the freezing point.

The melting point of copper is 1083.0 $\mp$ 0.1°C (1981.4 $\mp$ 0.2°F). Its normal boiling point is 2595°C (4703°F).

The coefficient of linear expansion of copper is 1.65×10^{-5}/°C at 20°C.

The specific heat of the solid is 0.092 cal/g at 20°C (68°F). The specific heat of liquid copper is 0.112 cal/ g, and of copper in the vapor state about 0.08 cal/g.

The electrical resistivity of copper in the usual volumetric unit, that of a cube measuring 1 cm in each direction, is 1.6730×10^{-6} ohm · cm at 20°C (68°F). Only silver has a greater volumetric conductivity than copper. On a relative basis in which silver is rated 100, copper is 94, aluminum 57, and iron 16.

The mass resistivity of pure copper for a length of 1 m weighing 1 g at 20°C (68°F) is 0.14983 ohm. The conductivity of copper on the mass basis is surpassed by several light metals, notably aluminum. The relative values are 100 for aluminum, 50 for copper, and 44 for silver.

By far the largest use of copper is in the electrical industry, and therefore high electrical conductivity is its most important single property, although for industrial use this property must be accompanied by suitable characteristics in other respects. *See* CONDUCTOR (ELECTRICITY); ELECTRICAL CONDUCTIVITY OF METALS.

Copper-containing proteins provide diverse biochemical functions, including copper uptake and transport (ceruloplasmin), copper storage (metallothionen), protective roles (superoxide dismutase), catalysis of substrate oxygenation (dopamine β-monooxygenase), biosynthesis of connective tissue (lysyl oxidase), terminal oxidases for oxygen metabolism (cytochrome *c* oxidase), oxygen transport (hemocyanin), and electron transfer in photosynthetic pathways (plastocyanin). *See* BIORGANIC CHEMISTRY; ENZYME. Harvey Schugar

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Copper alloys

Solid solutions of one or more metals in copper. Many metals, although not all, alloy with copper to form solid solutions. Some insoluble metals and nonmetals are intentionally added to copper alloy to enhance certain characteristics. Copper alloys form a group of materials of major commercial importance because they are characterized by such useful mechanical properties as high ductility and formability and excellent corrosion resistance. Copper alloys are easily joined by soldering and brazing. Like gold alloys, copper alloys have decorative red, pink, yellow, and white colors. Copper has the second highest electrical and thermal conductivity of any metal. All these factors make copper alloys suitable for a wide variety of products.

Wrought alloys. Copper and zinc melted together in various proportions produce one of the most useful groups of copper alloys, known as the brasses. Six different phases are formed in the complete range of possible compositions. The relationship between composition and phases alpha, beta, gamma, delta, epsilon, and eta are graphically shown in the well-established constitution diagram for the copper-zinc system. Brasses containing 5–40% zinc constitute the largest volume of copper alloys. One important alloy, cartridge brass (70% copper, 30% zinc), has innumerable uses, including cartridge cases, automotive radiator cores and tanks, lighting fixtures, eyelets, rivets, screws, springs, and plumbing products. Tensile strength ranges from 45,000 lb/in.^{2} (310 megapascals) as annealed to 130,000 lb/in.^{2} (900 MPa) for spring temper wire. *See* BRASS; PHASE EQUILIBRIUM.

Lead is added to both copper and the brasses, forming an insoluble phase which improves machinability of the material. Free cutting brass (61% copper, 3% lead, 36% zinc) is the most important alloy in the group. In rod form it has a strength of 50,000–70,000 lb/in.^{2} (340–480 MPa), depending upon temper and size. It is machined into parts on high-speed (10,000 rpm) automatic screw machines for a multiplicity of uses.

Increased strength and corrosion resistance are obtained by adding up to 2% tin or aluminum to various brasses. Admiralty brass (70% copper, 2% aluminum, 0.023% arsenic, 21.97% zinc) are two useful condenser-tube alloys. The presence of phosphorus, antimony, or arsenic effectively inhibits these alloys from dezincification corrosion.

Alloys of copper, nickel, and zinc are called nickel silvers. Typical alloys contain 65% copper, 10–18% nickel, and the remainder zinc. Nickel is added to the copper-zinc alloys primarily because of its influence upon the color of the resulting alloys; color ranges from yellowish-white, to white with a yellowish tinge, to white. Because of their tarnish resistance, these alloys are used for table flatware, zippers, camera parts, costume jewelry, nameplates, and some electrical switch gear.

Copper forms a continuous series of alloys with nickel in all concentrations. The constitution diagram is a simple all alpha-phase system.

Nickel slightly hardens copper, increasing its strength without reducing its ductility. Copper with 10% nickel makes an alloy with a pink cast. More nickel makes the alloy appear white.

Three copper-base alloys containing 10%, 20%, and 30% nickel, with small amounts of manganese and iron added to enhance casting qualities and corrosion resistance, are important commercially. These alloys are known as cupronickels and are well suited for application in industrial and marine installations as condenser and heat-exchanger tubing because of their high corrosion resistance and particular resistance to impingement attack. Heat-exchanger tubes in desalinization plants use the cupronickel 10% alloy.

Copper-tin alloys (3–10% tin), deoxidized with phosphorus, form an important group known as phosphorus bronzes. Tin increases strength, hardness, and corrosion resistance, but at the expense of some workability. These alloys are widely used for springs and screens in papermaking machines.

Silicon (1.5–3.0%), plus smaller amounts of other elements, such as tin, iron, or zinc, increases the strength of copper, making alloys useful for hardware, screws, bolts, and welding rods.

Sulfur (0.35%) and tellurium (0.50%) form insoluble compounds when alloyed with copper, resulting in increased ease of machining.

Precipitation-hardenable alloys. Alloys of copper that can be precipitation-hardened have the common characteristic of a decreasing solid solubility of some phase or constituent with decreasing temperature. Precipitation is a decomposition of a solid solution leading to a new phase of different composition to be found in the matrix. In such alloy systems, cooling at the appropriate rapid rate (quenching) from an equilibrium temperature well within the all-alpha field will preserve the alloy as a single solid solution possessing relatively low hardness, strength, and electrical conductivity.

A second heat treatment (aging) at a lower temperature will cause precipitation of the unstable phase. The process is usually accompanied by an increase in hardness, strength, and electrical conductivity. Some 19 elements form copper-base binary alloys that can be age- or precipitation-hardened. *See* HEAT TREATMENT (METALLURGY).

Two commercially important precipitation-hardenable alloys are beryllium- and chromium-copper. Beryllium-copper (2.0–2.5% beryllium plus cobalt or nickel) can have a strength of 200,000 lb/in.^{2} (1400 MPa) and an electrical conductivity of less than 50% of IACS (International Annealed Copper Standard). Cobalt adds high-temperature stability, and nickel acts as a grain refiner. These alloys find use as springs, diaphragms, and bearing plates and in other applications requiring high strength and resistance to shock and fatigue.

Copper chromium (1% chromium) can have a strength of 80,000 lb/in.^{2} (550 MPa) and an electrical conductivity of 80%. Copper-chromium alloys are used to make resistance-welding electrodes, structural members for electrical switch gear, current-carrying members, and springs.

Copper-nickel, with silicon or phosphorus added, forms another series of precipitation-hardenable alloys. Typical composition is 2% nickel, 0.6% silicon. Strength of 120,000 lb/in.^{2} (830 MPa) can be obtained with high ductility and electrical conductivity of 32% IACS.

Zirconium-copper is included in this group because it responds to heat treatment, although its strength is primarily developed through application of cold deformation or work. Heat treatment restores high electrical conductivity and ductility and increases surface hardness. Tensile strength of 70,000 lb/in.^{2} (500 MPa) coupled with an electrical conductivity of 88% can be developed. Uses are resistance welding wheels and tips, stud bases for transistors and rectifiers, commutators, and electrical switch gear.

Fabrication. Copper alloys have a long history because of their ease of fabrication into utensils and products.

Melting. Alloys are initially prepared by melting the various elements involved in low-frequency induction furnaces. Usually the melt is protected from oxidation by covering it with charcoal. Copper-rich alloys are also deoxidized by adding elements such as phosphorus, lithium, or boron. The melt is usually poured at 100–200°F (38–93°C) above its melting point into oil- and graphite-dressed, water-cooled copper molds of suitable shape. The dressing protects the mold surfaces, produces a reducing gas that aids in the suppression of oxidation, and brings dirt and dross to the molten surface, preventing their inclusion in the casting.

Continuous casting of copper and its alloys is common practice and is accomplished by pouring the melt into the top of an open-end mold as the solidified casting is withdrawn from the bottom. Various mold designs are used, but all use water to cool the mold proper in addition to cooling sprays and tanks of water below the mold. Casting can be performed in either a vertical or a horizontal plane.

Mechanical properties of castings can be affected by such defects as large grain size, directional grain growth, and segregation. Either hot-working of the casting by rolling, forging, piercing, or extrusion, or cold-working by rolling or drawing with necessary intermediate annealing corrects these defects and markedly improves properties.

Processing. Processing varies with alloy, form, and size. Flat products are cast in heavy cakes for initial hot-rolling or in bars for cold-rolling. Copper and lead-free brasses are readily hot-rolled in a single heating from a 9-in. (23-cm) thick cake to a $^1/_2$ in. (1.25-cm) thick slab. Further rolling is done cold with intermediate anneals. Leaded brasses, tin bronzes, and other hot short alloys (alloys that are brittle when heated above red heat) must be cold-rolled from the casting to final size, using intermediate anneals that heat the particular alloy above its recrystallization temperature.

Round copper rods and wire are started by hot-rolling castings (wire bar) in grooved rolls, but most copper alloys are extruded. Both are subsequently reduced in size by cold-rolling, drawing, or both. In extrusion, a billet placed in a press is forced through a lubricated die by a ram.

Tin and tin-lead bronzes which are hot short are continuously cast in rod form and are cold-rolled or drawn to finish sizes using intermediate anneals as necessary.

Copper and high-copper-content lead-free brass tubes are started by hot piercing wherein the solid billet is driven with a helical motion over a rotating mandrel to form a seamless tube. Tubes of most other alloys are formed by extrusion because the alloys do not stand piercing. In extrusion of tube, a mandrel is pushed through a billet forming the inside of the tube, and a ram pushes the billet over the mandrel and through a die to form a seamless tube.

Cast alloys. Copper alloy castings of irregular and complex external and internal shapes can be produced by various casting methods, making possible the use of shapes for superior corrosion resistance, electrical conductivity, good bearing quality, and other attractive properties. High-copper alloys with varying amounts of tin, lead, and zinc account for a large percentage of all copper alloys used in the cast form. Tensile strength ranges from 36,000 to 48,000 lb/in.^{2} (250–330 MPa) depending upon composition and size. Leaded tin-bronzes with 6–10% tin, about 1% lead, and 4% zinc are used for high-grade pressure castings, valve bodies, gears, and ornamental work. Bronzes high in lead and tin (7–25% lead and 5–10% tin) are mostly used for bearings. High tin content is preferred for heavy pressures or shock loading, but lower tin and higher lead for lighter loads, higher speeds, or where lubrication is less certain. A leaded red brass containing 85% copper and 5% each of tin, lead, and zinc is a popular alloy for general use.

High-strength brasses containing 57–63% copper, small percentages of aluminum and iron, and the balance zinc have tensile strengths from 70,000 to 120,000 lb/in.^{2} (490–830 MPa), high hardness, good ductility, and resistance to corrosion. They are used for valve stems and machinery parts requiring high strength and toughness.

Copper alloys containing less than 2% alloying elements are used when relatively high electrical conductivity is needed. Strength of these alloys is usually notably less than that of other cast alloys.

Aluminum bronzes containing 5–10.5% aluminum, small amounts of iron, and the balance copper have high strengths even at elevated temperature, high ductility, and excellent corrosion resistance. The higher-aluminum-content castings can be heat-treated, increasing their strength and hardness. These alloys are used for acid-resisting pump parts, pickling baskets, valve seats and guides, and marine propellers.

Additives impart special characteristics. Manganese is added as an alloying element for high-strength brasses where it forms intermetallic compounds with other elements, such as iron and aluminum. Nickel additions refine cast structures and add toughness, strength, and corrosion resistance. Silicon added to copper forms copper-silicon alloys of high strength and high corrosion resistance in acid media. Beryllium or chromium added to copper forms a series of age- or precipitation-hardenable alloys. Copper-beryllium copper alloys are among the strongest of the copper-base cast materials. *See* ALLOY; COPPER; METAL CASTING; METAL FORMING.

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Copper loss

The power loss caused by the flow of current through copper conductors. When an electric current flows through a copper conductor (or any conductor), some energy is converted to heat. The heat, in turn, causes the operating temperature of the device to rise. This happens in transformers, generators, motors, relays, and transmission lines, and is a principal limitation on the conditions of operation of these devices. Excessive temperature rises lead to equipment failure. *See* CONDUCTOR (ELECTRICITY).

If the resistance R (in ohms) and the current I (in amperes) are both known, the copper loss in watts may be found from the equation $P = I^2R$. An alternative form is to know the voltage across the resistor V (in volts) and to determine the power loss by the equation $P = V^2/R$. V and I are effective values of the voltage and current, respectively. The resistance R varies with both frequency and temperature. *See* ELECTRICAL RESISTANCE.

In electric machines, there are typically constant losses, as well as those that vary with the square of the load, such as the copper loss. Maximum efficiency is obtained when the load is adjusted so as to make the constant and varying losses equal.

Since the discovery of superconductivity in 1911, much effort has been directed toward the development of devices based on superconducting principles, with superconductors replacing the copper coils in electrical devices and systems in order to reduce or eliminate copper loss. Since superconductors have traditionally operated at temperatures close to absolute zero (0 K or −459.67°F), such devices are practical only if the power required to operate the refrigeration equipment is less than the copper loss that is supplanted. In 1986, a ceramic superconductor, lanthanum barium copper oxide, was discovered whose superconducting temperature was 30 K (−406°F), and by 1988 another ceramic, thallium barium calcium copper oxide, was shown to have a superconducting temperature of 125 K (−235°F). The rapid increase of superconducting temperatures has given new hope to the idea of reducing copper loss. However, the process of going from a scientific discovery to technological realization requires solutions to many technical problems as well as complex problems involving economic, reliability, safety, and related considerations. *See* SUPERCONDUCTING DEVICES; WIRING.

Edwin C. Jones, Jr.

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Copper metallurgy

The economic production of pure copper metal, suitable for fabrication and use, from copper ores containing as little as 0.5% Cu. Over 90% of the consumption of primary copper in the Western world is produced from ores containing sulfide minerals (chalcopyrite, $CuFeS_2$; chalcocite, Cu_2S; and bornite, Cu_5FeS_4) that can be economically treated only by pyrometallurgical processes. *See* PYROMETALLURGY, NONFERROUS.

Production. The main processes used in the production of copper from sulfide ores are shown in **Fig. 1**. The mined ore (0.5–2.0% Cu) is finely ground, and then concentrated by flotation to form copper concentrates containing 20–30% Cu. The concentrates are then smelted at high temperatures (about 2280°F or 1250°C) to form a molten mixture of copper and iron sulfides called matte. The molten matte

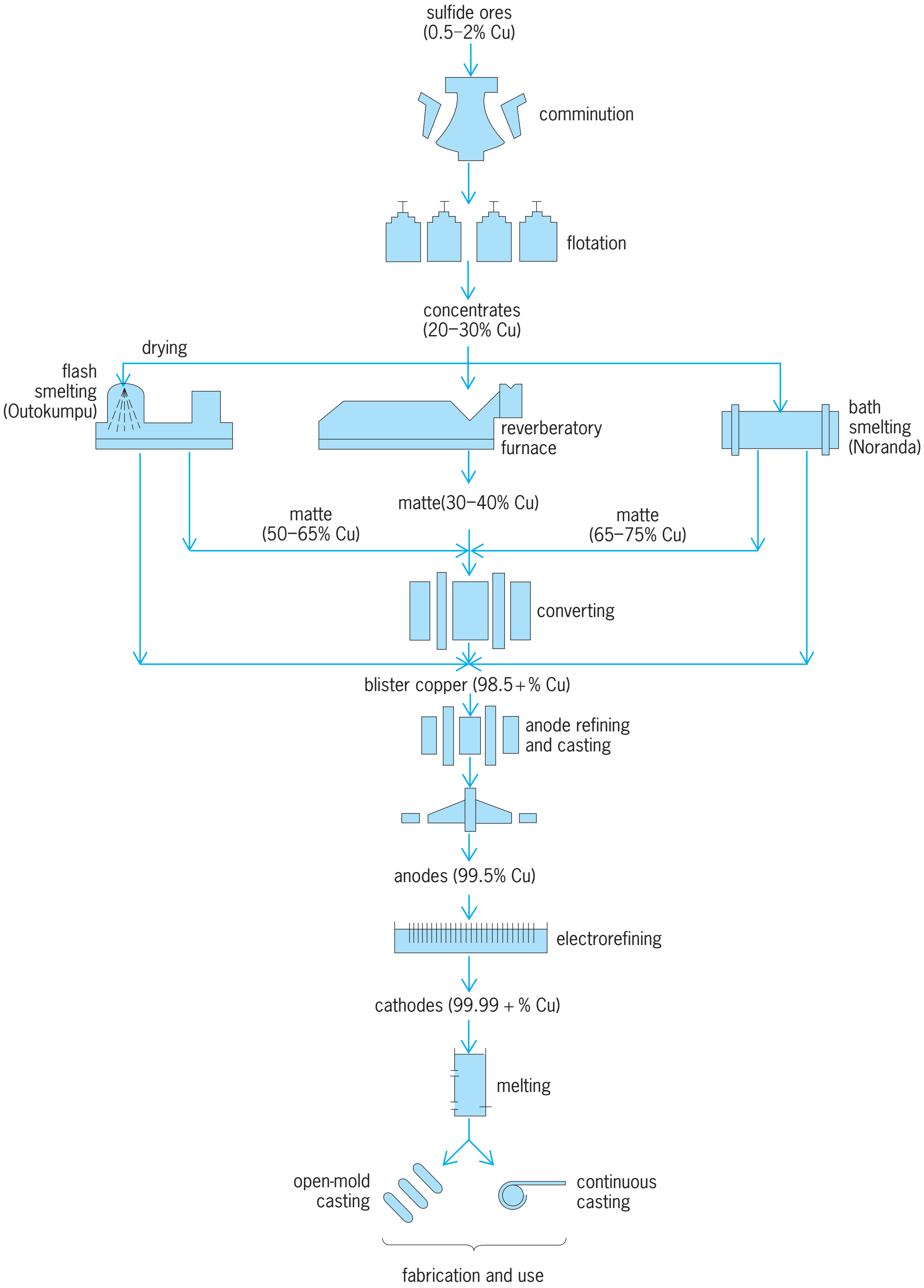

Fig. 1. Flow sheet of copper production from sulfide minerals.

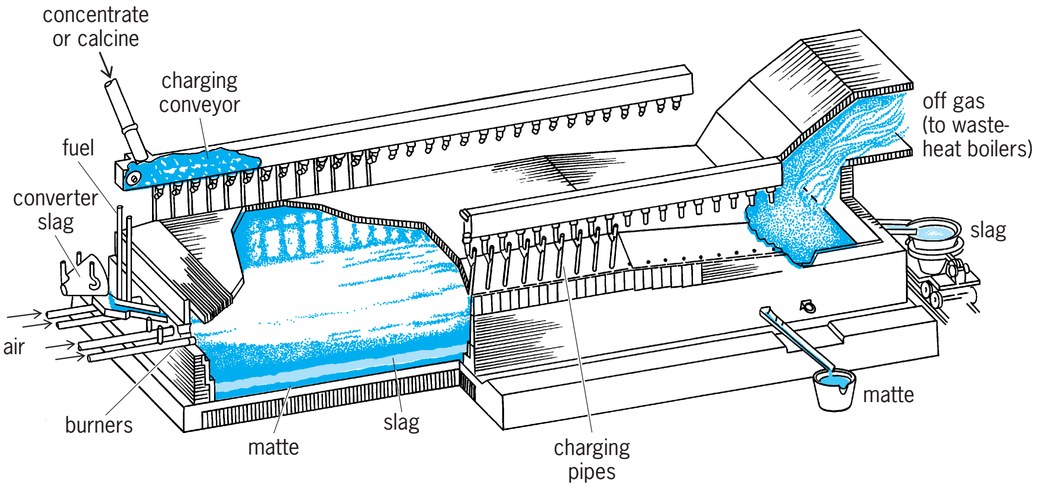

Fig. 2. **Cutaway view of a reverberatory furnace for the production of copper matte from sulfide concentrates or roasted calcines. (*After A. K. Biswas and W. D. Davenport, Extractive Metallurgy of Copper, Pergamon Press, 1980*)**

is converted to blister copper (about 99% Cu) by oxidizing the remaining iron and sulfur. After removing the residual sulfur and oxygen in an anode furnace, copper anodes are cast and then refined electrolytically to produce high-purity cathode copper (99.99% Cu), which is suitable for most uses. *See* ORE DRESSING.

Smelting processes. The reverberatory furnace (**Fig. 2**) is the oldest and most widely used smelting process. It consists of a refractory-lined chamber, typically 100 ft (30 m) long by 30 ft (10 m) wide, into which copper concentrates and silica flux are charged. Fuel-fired burners melt the charge, driving off the labile sulfur by reaction (1). Little iron sulfide is oxidized, so that fuel requirements are high, about 5.4 × 10^6 Btu per ton (6.3 × 10^6 kilojoules per metric ton) of Cu concentrate. Two molten layers are formed in the furnace: an upper layer slag of iron silicate with little copper (≤0.5% Cu); and a lower layer of matte (30–40% Cu), containing most of the original copper value. The slag and matte are drained separately from the furnace through tapholes into ladles. The slag is discarded, while the matte is transferred to the converting step. The sulfur evolved during smelting leaves the furnace in a 1–2% SO_2 gas stream, which is too dilute for economic treatment.

$$2CuFeS_2 \rightarrow Cu_2S \cdot 2FeS(l) + {}^1/_2S_2(g) \qquad (1)$$

The reverberatory furnace cannot meet today's requirements for low-energy consumption and stringent environmental control. Therefore more efficient smelting processes have been developed since the 1960s. These processes use much less energy (typically 0.7–1.8 × 10^6 Btu per ton or 0.8–2.1 × 10^6 kJ per metric ton of Cu concentrate) and produce a strong SO_2 gas stream (10% SO_2) to reduce treatment costs. These processes use oxygen enrichment, and oxidize more iron sulfide to generate more heat and produce mattes with higher copper levels (50–75% Cu). The smelting reaction for these processes can be represented by reaction (2), where

$$2CuFeS_2 + 2\alpha \cdot SiO_2 + (1 + 3\alpha)O_2 \rightarrow$$
$$Cu_2S \cdot 2(1 - \alpha)FeS + 2\alpha \cdot FeO \cdot SiO_2 + (1 + 2\alpha)SO_2 \qquad (2)$$

α is the fraction of FeS reacted (typically, in range $\alpha = 0.5$ to 0.9).

Modern smelting processes fall into two categories: flash smelting (Outokumpu flash smelting furnace) and bath smelting (Noranda process reactor). In flash smelting, dry concentrate is dispersed in an oxidizing gas stream, and the smelting reactions occur very rapidly as the particles fall down a reaction shaft. The molten matte and slag are collected in a hearth, and the SO_2-containing gases exit through an uptake shaft. In bath smelting, moist concentrate is smelted continuously in a molten bath of matte and slag, which is vigorously stirred by the injection of air or oxygen-enriched air. In the Noranda process reactor, the air is injected through tuyeres into a vessel similar to an elongated converter.

Matte converting. The molten matte is converted to blister in Peirce-Smith converters. The converter is a refractory-lined, cylindrical vessel, typically 30 ft (10 m) in length and 13 ft (4 m) in diameter (**Fig. 3**). The converter can be rotated about its axis, and is fitted on one side with a row of about 50 tuyeres through which air is injected. The top of the converter has a large mouth for charging molten matte and removing slag and product copper. Converting is a batch operation; initially several ladles of matte are charged, the air turned on, and the converter rotated until the tuyeres are submerged. The air, bubbling violently through the bath, gradually oxidizes the matte in two stages. In the first or slag-forming stage, iron sulfide is oxidized and fluxed with silica to form a fluid slag by reaction (3). The converter

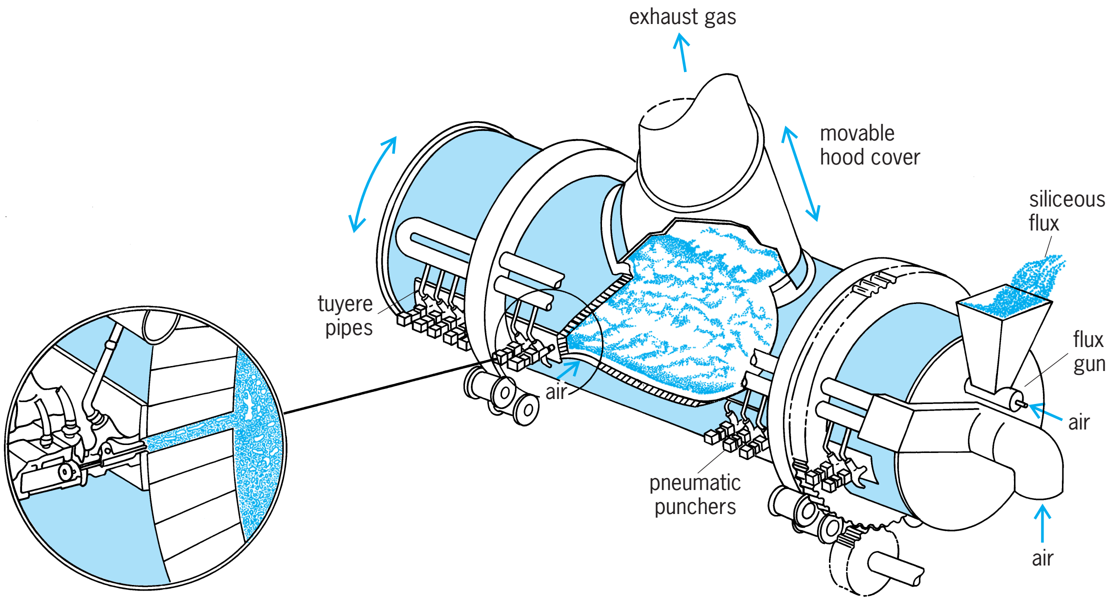

Fig. 3. Cutaway view of a horizontal side-blown Peirce-Smith converter for producing blister copper from matte. (*After A. K. Biswas and W. G. Davenport, Extractive Metallurgy of Copper, Pergamon Press, 1980*)

$$2FeS(l) + 2SiO_2(s) + 3O_2(g) \rightarrow 2FeO \cdot SiO_2(l) + 2SO_2(g) \qquad (3)$$

slag contains some copper (1–5% Cu), and is recycled to the smelting furnace or treated in a separate process. When all the iron has been removed, the remaining copper sulfide is further oxidized to blister copper by reaction (4). The converting process

$$Cu_2S(l) + O_2(g) \rightarrow 2Cu(l) + SO_2(g) \qquad (4)$$

is sufficiently exothermic that no additional fuel is required. The blister copper from the converter is transferred by ladle to the anode furnace, where the residual sulfur and oxygen levels in the copper are reduced further. The copper is then cast into anodes for electrorefining.

Sulfur fixation. Smelting and converting a typical copper concentrate generates over 0.50 ton SO_2 per ton concentrate (0.50 metric ton SO_2 per metric ton concentrate), and the resulting SO_2 emissions must be controlled to meet local environmental standards. This is generally achieved by converting the SO_2 to sulfuric acid in a contact acid plant, as long as the SO_2 concentration exceeds 4% and a viable market for acid exists. If local conditions are favorable, it is also possible to make liquid SO_2 or elemental sulfur from strong SO_2 gases. *See* SULFUR.

Electrorefining. The objective of electrorefining is to remove the remaining impurities in the anode copper (principally As, Bi, Ni, Pb, Sb, and Se) and produce a pure cathode copper (99.99+% Cu). Also, many copper ores contain appreciable amounts of precious metals (Ag, Au, Pt, and so on), which are concentrated into the anode copper during smelting and are recovered as valuable by-products in electrorefining. The impure anodes are suspended alternately with pure copper cathodes in tanks through which an electrolyte of copper sulfate and free sulfuric acid is continuously circulated. When direct current is applied, the copper in the anodes is electrochemically dissolved and then plated as pure copper on the cathodes. Some of the anode impurities, such as arsenic and nickel, are less noble than copper and dissolve in the electrolyte, but they do not plate out at the cathode as long as their concentrations are controlled. The other impurities, such as silver, lead, and selenium, are virtually insoluble in the electrolyte and fall as slimes to the bottom of the tank. These slimes are recovered and processed for eventual recovery of selenium and the precious-metal values. *See* ELECTROCHEMICAL PROCESS; ELECTROMETALLURGY.

Hydrometallurgical processes. Oxidized copper ores are more effectively treated by hydrometallurgical processes. The ore is crushed, ground if necessary, and leached with dilute sulfuric acid, either by percolation through heaps of ore or by agitation in tanks. Copper is recovered from the resulting solution by either cementation or solvent extraction–electrowinning. In cementation, copper is precipitated by contact with scrap iron to form an impure cement copper, which is smelted, then refined. Solvent extraction–electrowinning has become the preferred process. In solvent extraction special organic reagents are used to selectively extract copper from solution. The resulting copper-containing organic phase is then stripped to give a pure and more concentrated aqueous copper solution for electrowinning. Electrowinning is similar to electrorefining except that an inert anode is used and more energy is required. Although electrowon cathode copper is generally not as pure as electrorefined copper, it is still suitable for many applications. *See* HYDROMETALLURGY; SOLVENT EXTRACTION.

Future trends. Considerable progress has been made in improving the efficiency of copper smelting since the 1960s through new process innovations and the use of oxygen in large tonnages. The trend toward the production of higher-matte grades (up to 75% Cu) is expected to continue in order to minimize energy requirements and SO_2-fixation costs. Pyrometallurgical processes will continue to dominate primary copper production, and it is anticipated that the ultimate goal of direct copper production from chalcopyrite concentrates in a single smelting and converting vessel will be achieved. *See* COPPER.

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Copulatory organ

An organ utilized by the male animal for insemination, that is, to deposit spermatozoa directly into the female reproductive tract. Various types of copulatory organs are found among the vertebrates, whereas cloacal apposition occurs in most other vertebrates which lack these structures. Amplexus, or false copulation, is peculiar to amphibians.

In fish, internal fertilization is restricted to certain groups. The pelvic fin of male elasmobranchs and holocephalians is modified for the transmission of sperm and is known as the clasper or clasping organ. A pair of anterior claspers (**Fig. 1***a*) and a frontal clasper which protrudes from the head occur among holocephalians in addition to the modified pelvic clasper of elasmobranchs. The anal fin of teleosts, in which copulation occurs, may be elongated to form a gonopodium. Copulatory organs are lacking in amphibians, even in those in which internal fertilization occurs. Among caecelians, the cloaca of the male is muscular and protrusible; however, it is questionable that this structure is a true copulatory organ. Hemipenes which can be everted during copulation are common to both snakes and lizards; however, these structures lack erectile tissue. Turtles and crocodiles possess a single penis with associated erectile tissue, the corpora cavernosa, which becomes distended with blood. A few species of birds have a penis; among these are the ostriches and anseriforms. The penis is present in all mammals.

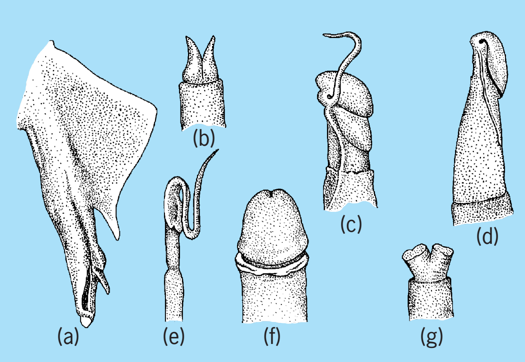

Fig. 1. Vertebrate copulatory organs. (*a*) Clasper of dogfish (*Squalus*). Glans penis of (*b*) opossum, (*c*) ram, (*d*) bull, (*e*) short-tailed shrew, (*f*) man, (*g*) Echidna.

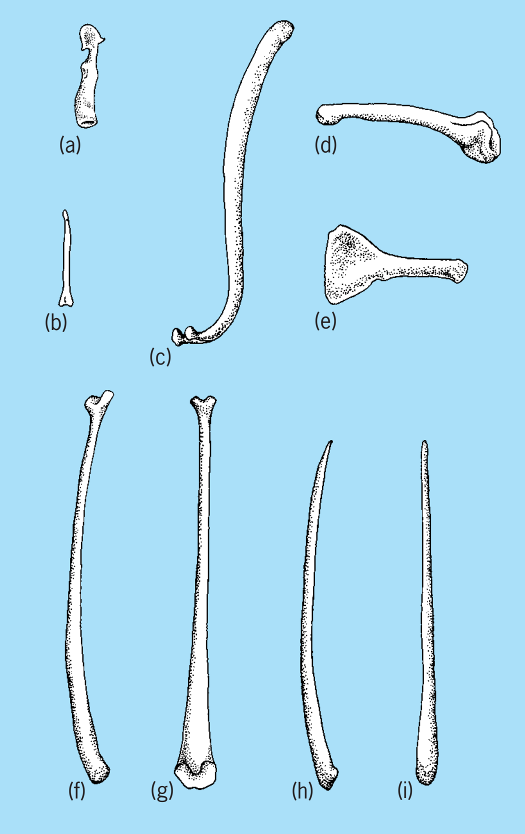

Fig. 2. Bacula of (*a*) fox squirrel, (*b*) cotton mouse, (*c*) otter, (*d*) *Neotoma lepida*, (*e*) *N. micropus*, (*f, g*) *Perognathus hispidus*, showing lateral and ventral views, (*h, i*) *P. baileyi*, showing lateral and ventral views.

This copulatory organ (Fig. 1*b–g*) is variously modified morphologically. Among certain mammals such as rodents, bats, whales, some carnivores, and lower primates, a penis bone, known as the os priapi or baculum (**Fig. 2**), occurs, increasing the rigidity of the penis. *See* FERTILIZATION; PENIS; REPRODUCTIVE SYSTEM.

Charles B. Curtin

Coquina

A calcarenite or clastic limestone whose detrital particles are chiefly fossils, whole or fragmented. The term is most frequently used for an aggregate of large shells more or less cemented by calcite. If the rock consists of fine-sized shell debris, it is called a microcoquina. Encrinite is a microcoquina made up primarily of crinoid fragments (see **illus.**). Some coquinas show little evidence of any transportation by currents; articulated bivalves are preserved in

Coquinoid limestone, encrinite, showing many entire fossils in fine-grained matrix. Note lack of assortment and diversity of types. (*From F. J. Pettijohn, Sedimentary Rocks, 3d ed., Harper and Row, 1949, 1957*)

entirety and the shells are not broken or abraded. *See* LIMESTONE. Raymond Siever

Coraciiformes

A diverse order of land birds found mainly in the tropics. The interrelationships of several families have been disputed, with no resolution. The closest affinities of the coraciiforms may be with other land birds, such as the Piciformes and Passeriformes. *See* PASSERIFORMES; PICIFORMES.

Classification. The Coraciiformes are divided into four suborders and families: Alcedines, including the families Alcedinidae (kingfishers; 91 species; worldwide, but mainly Old World tropics to Australasia), Todidae (todies; five species; West Indies), and Momotidae (motmots; nine species; New World tropics); Meropes, with the single family Meropidae (bee-eaters; 24 species; Old World to Australia, mainly tropics); Coracii, containing the families Coraciidae (rollers; 12 species; Old World to Australia, mainly tropics), Brachypteraciidae (ground-rollers; five species; Madagascar), Leptosomatidae (cuckoo-rollers; one specie; Madagascar); and Bucerotes, with the families Upupidae (hoopoes; one specie; Old World), Phoeniculidae (wood-hoopoes; eight species; Africa) and Bucerotidae (hornbills; 45 species; Old World tropics to New Guinea).

Several of these families, such as the different groups of rollers, are sometimes merged into a single family, and several groups, such as the kingfishers (**Fig. 1**) and hornbills (**Fig. 2**), are divided into subfamilies or even families.

Fossil record. The fossil record of this group of basically forest birds is rather poor; however, there are a number of specimens known that appear to belong to the Coraciiformes. A better picture of the history and relationships of this order may appear once these fossils are better studied. Most interesting is a fossil tody (a group now restricted to the Greater Antilles) from the Oligocene of Wyoming, and a second fossil tody from the Eo-oligocene of France, and a fossil motmot (a group that is now restricted to the American tropics) from the Oligocene of Switzerland. The identification of these fossils as such is controversial, but, if correct, suggests an earlier, broader distribution of several coraciiform families.

Characteristics. Coraciiform birds are characterized by a syndactyl foot in which the three anterior toes are joined at the base, although the cuckoo-rollers have evolved secondarily a zygodactyl foot

Fig. 1. Malachite kingfisher (*Alcedo cristata*), Africa. (*Photo by H. Vannoy Davis; © 2001 California Academy of Sciences*)

Fig. 2. Southern ground hornbill (*Bucorvus leadbeateri*), Masai Mora Game Reserve, Kenya. (*Photo by Gerald and Buff Corsi; © 2002 California Academy of Sciences*)

(in which the toes are arranged two in front and two behind). Most groups are tropical or warm temperate and are brilliantly colored. Except for bee-eaters and wood-hoopoes, coraciiforms are generally solitary. Most temperate species are migratory; the tropical ones are permanent residents. Most coraciiforms feed on insects and other animal prey, including fish; hornbills are omnivorous and some feed mainly on fruit. All nest, either solitarily or in colonies, in holes burrowed in earthen banks or in tree cavities. Wood-hoopoes and bee-eaters have young adults serving as helpers at the nest. The chicks are born naked and cared for by both parents until they can fly. The pair of central tail feathers of most motmots have racquet tips formed by the falling off of more anterior, weakly attached barbs.

Todies, motmots, and one small subfamily of kingfishers are found in the New World, but all other coraciiforms live in the Old World, suggesting the origin of this order in that part of the world. The kingfishers (Fig. 1) are the largest and most diversified family, with many members catching their prey on dry land. The largest and most famous kingfisher is the kookaburra or laughing jackass (*Dacelo novaeguinaea*) of Australia. Rollers are widespread throughout the Old World tropics, but the ground-rollers and the cuckoo-rollers are restricted to Madagascar. Wood-hoopoes are confined to the tropical forests of Africa, while the related hoopoes are widespread throughout Europe and Asia.

The hornbills (Fig. 2) are the largest of the coraciiforms, feed in forests, and are excellent soarers. A number of species possess a large casque on the base of the upper jaw which may serve in courtship or species recognition. The male helmeted hornbill (*Rhinoplax vigil*) of the Malay Peninsula and Indonesia has a solid casque of a thick rhamphotheca (horny covering of the beak) backed by massive bone, making its skull the heaviest of all known Recent birds. Male hornbills seal up the female with her eggs in the nesting cavity in a large tree, and feed her and the chicks until the young birds are ready to fly. During this period, the female undergoes a complete molt. Some species of hornbills are threatened because of habitat destruction, especially the loss of large trees with suitable nesting cavities. *See* AVES.

Walter J. Bock

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Corallimorpharia

An order of cnidarian subclass Hexacorallia commonly known as mushroom anemones. These polyps are morphologically intermediate between members of the hexacorallian orders Scleractinia (corals), with which they share features of internal anatomy, weak musculature, and certain types of nematocysts (intracellular stinging capsules used in food capture and defense), and Actiniaria (anemones), which they resemble in lacking a calcareous skeleton. All three animals have paired, coupled mesenteries that are added around the entire periphery of the polyp. Like Actiniaria and Scleractinia, Corallimorpharia contains some members that are solitary and some that are clonal (reproduce asexually to produce genetically identical individuals that live physically separate from one another); however, by contrast with Scleractinia, Corallimorpharia has no colonial members (clonemates that remain attached to one another). *See* CNIDARIA.

Morphology. There are two distinct morphological variants of corallimorpharians. Members of one group live primarily at high altitudes in shallow water and in deep water (to about 5-km or 3-mi depth) at all latitudes. A typical polyp has a well-defined cylindrical column and an oral disc not much broader than the column. The unbranched tentacles are arranged in radial rows on the disc, and commonly each has a spherical tip (that is, it is capitate). Examples are *Corynactis* (**Fig. 1**), which has a typical oral disc diameter of about 10 mm, and *Corallimorphus*, which may attain a diameter of 100–150 mm (4–6 in.).

In members of the other, primarily tropical, group, the oral disc is much broader than the small column, and the tentacles, which may be arranged in rows or in cycles, can be branched or be mere bumps. Members of this group harbor symbiotic dinoflagellates (zooxanthellae), so they occur only in shallow water. Examples are *Actinotryx* (**Fig. 2**), which may have an oral disc diameter of 20–25 mm (1 in.), and *Amplexidiscus*, the largest corallimorpharian, which can reach an oral disc diameter of 250 mm (10 in.).

Phylogeny. Based on preliminary phylogenetic analyses using both morphological and molecular data, it is likely that the two morphological variants

Fig. 1. *Corynactis californica.* (*Photograph by George Miller*)

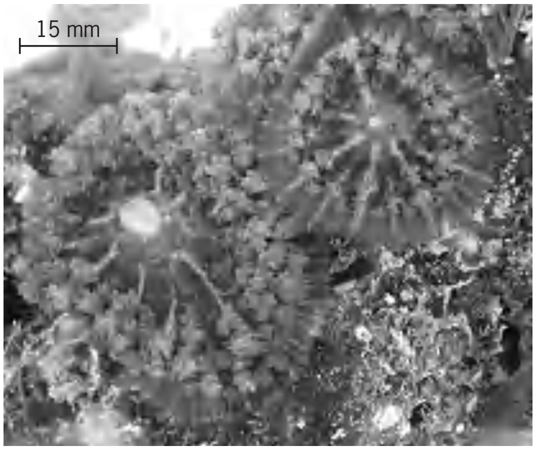

Fig. 2. ***Actinotryx sanctithomae.*** **(*Photograph by Ha-Rim Cha*)**

represent separate evolutionary lineages (that is, are polyphyletic). It seems likely that Corallimorpharia represents at least two taxa, derived independently from different types of scleractinians by loss of the skeleton. Indeed, it may be that corallimorpharians should be considered naked (askeletal) members of the order Scleractinia. Corallimorpharians have no fossil record because the animals lack skeletons. *See* ACTINIARIA; HEXACORALLIA; SCLERACTINIA.

Ecology. Corallimorpharians live in habitats typical of actiniarians and scleractinians. Some species proliferate on stressed coral reefs, attaching to skeletons of dying corals; it is uncertain whether the corallimorpharians merely take advantage of the dead coral skeleton as a substrate on which to grow, but they may kill the corals, for corallimorpharians can aggress toward other cnidarians by extruding their mesenterial filaments (the longitudinal band along the free edge of each mesentery). Like all cnidarians, corallimorpharians eat only animal prey, being opportunistic predators of small animals, such as crustaceans and fishes. The flat, shallow-water species have zooxanthellae, from which they presumably derive photosynthate as well. *See* REEF.

Daphne G. Fautin

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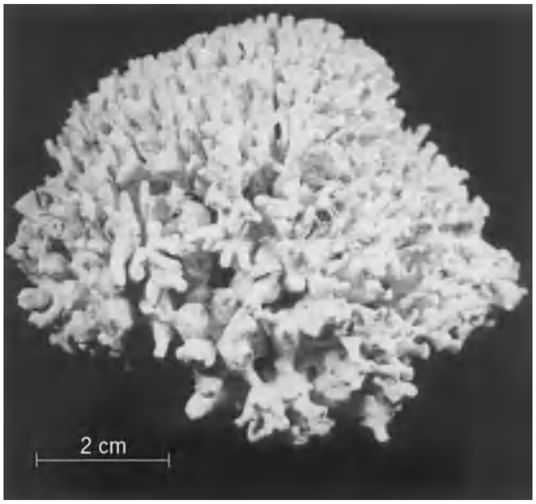
Corallinales

An order of red algae (Rhodophyceae), commonly called coralline algae. Only one family is recognized, the Corallinaceae, which formerly was assigned to the order Cryptonemiales. These algae are distinguished by the impregnation of cell walls with calcite, a form of calcium carbonate, which causes the thallus to be stony or brittle (see **illus.**). The few other red algae that are calcified are much softer than corallines and are impregnated with aragonite, another form of calcium carbonate. Many early biologists (including C. Linnaeus) thought that these plants were related to corals. *See* RHODOPHYCEAE.

Coralline algae, comprising about 40 genera and 500 species, are widespread, abundant, and ecologically important. They are divisible into two groups on the basis of the presence or absence of uncalcified, moderately flexible joints (genicula) between calcified segments (intergenicula). Those with genicula are called articulated coralline algae, while those totally lacking genicula are called nonarticulated or, with reference to their usual habit, crustose coralline algae. The erect portions (fronds) of articulated corallines usually arise from a crustose base. They vary in height from a few millimeters to 30 cm (12 in.) and are pinnately, dichotomously, or proliferously branched. Segments are cylindrical or flattened.

Structure. The most simple nonarticulated coralline algae are individual crusts of varying extent and thickness (to 20 cm or 8 in. thick). These often become confluent and cover large expanses of substrate. Many crusts bear rounded or pointed, branched or unbranched protuberances that can break off and continue to grow as free nodules known collectively as maerl. In some species, only part of the crust is attached to the substrate, the main portion growing free and resembling lichens or bracket fungi. In three genera of nonarticulated corallines, the thallus is ribbonlike, the linear segments being dichotomously branched, dorsiventrally organized, and flexible.

Coralline algae are cytologically similar to other red algae except for calcification of the cell wall. The wall consists of three layers: a thin, uncalcified inner layer; a thick, calcified middle layer; and a thin,



Coralline algae of the Pacific Ocean.

calcified outer layer or middle lamella. The calcite apparently is transported in vesicles from the cell lumen to the outer layers. Growth, which is restricted to uncalcified or decalcified areas or tissues, is usually very slow, especially at sites of low light intensity. Most corallines are perennial.

Reproduction. The life history follows the *Polysiphonia*-type, in which male and female plants alternate with a tetrasporophyte, all three phases being free-living and vegetatively identical or nearly so. Reproductive structures are produced in sunken or elevated chambers (conceptacles) with a roof penetrated by one or many pores. Tetraspores are produced by simultaneous zonate cleavage, a process unique to the order. They are relatively large and in most genera germinate in special patterns of cell division.

Habitat. Coralline algae are exclusively marine, although some species can tolerate a reduction in salinity to 13 parts per thousand. Some species thrive only where light is intense, as at the crest of a coral reef, while others grow only in shaded habitats or in deep water. Most species require constant immersion. Rock is the most common substrate in cold water, with some species preferring particular aspects, such as broad ledges, crevices, cobbles, or pebbles. Other hard substrates include shells, dead coral (the most common substrate in the tropics), and such artifacts as bottles and metal plates. Many corallines are obligate epiphytes, growing on other algae and on seagrasses, and a few overgrow such soft animals as sponges. An inconspicuous layer of corallines often underlies a turf of algae that at first glance appears to be growing directly on rock.

Unlike corals, coralline algae are equally abundant in cold or warm water, occurring from the Arctic to the Antarctic. At high latitudes, crustose corallines pave vast expanses of ocean floor. Along temperate shores, both crustose and articulated corallines are often abundant in tide pools. In areas of rough water, they typically form a broad band in the lowermost intertidal and uppermost subtidal zone. They may dominate deeper sites where herbivores consume fleshy algae. Stands of crustose corallines are made conspicuous by their bright pink or bluish-pink color.

The ecosystem in which coralline algae are most important is the coral reef, where they are primary producers, adding carbon to the ecosystem, adding new material to the reefs, and cementing together other calcareous organisms. They have been engaged in similar activities through the millennia, with modern genera recognizable in limestones at least as old as 150 million years (Jurassic). Paul C. Silva; Richard L. Moe

Fossils. Coralline algae are important frame builders and sediment producers in tropical reefs throughout Cenozoic time. Although scleractinian corals are volumetrically more important in most living reefs, crustose coralline algae are essential binding and cementing agents. Prominent coralline algae of tropical reefs today are *Neogoniolithon, Porolithon*, and *Lithoporella. Mesophyllum* and *Lithothamnium* are mainly cold-water genera, but they do occur in low-latitude regions in deep-water environments.

Coralline algae have a rather complete fossil record consisting of numerous genera and species. The earliest definite representatives of the Corallinaceae appeared in Jurassic time, although fossil forms with similar morphologies are known from late Paleozoic rocks. Coralline algae are some of the more common and widespread skeletal constituents in Cretaceous and Cenozoic marine rocks. *See* ALGAE; ATOLL; REEF.

John L. Wray

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Corbino disk

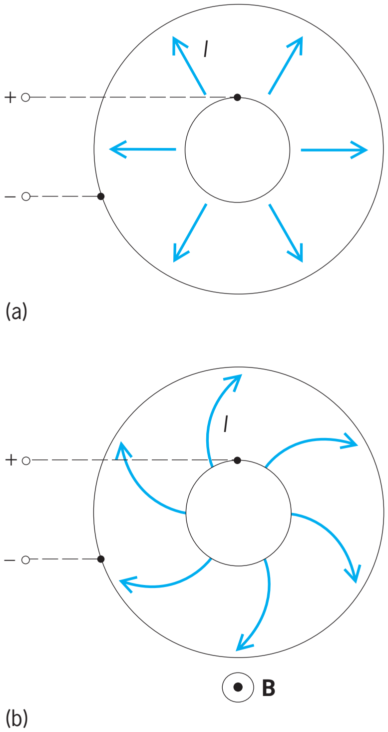
A conducting disk with concentric inner and outer electrical contacts, which can be placed in a magnetic field parallel to its axis. The disk is named after O. M. Corbino, who in 1911 reported magnetoresistance measurements on several metals by using this configuration. In zero applied field the lines of current are simply radial (**illus.** *a*), but in the presence of an axial magnetic field they lengthen by spiraling (illus. *b*). This spiraling occurs because the geometry of the disk is such that the Lorentz force acting on the charge carriers is not counterbalanced by a Hall-effect electric field. The resistance of the disk increases as the field increases, largely as a result of the geometrical magnetoresistance effect associated with the lengthening of the current path.

If B is the magnetic induction, the resistance of the Corbino disk can be expressed by Eq. (1). Here the Hall angle θ is defined by Eq. (2), where ρ_{yx} is

$$R(B) = R(0)(1 + \tan^2\theta)\frac{\rho_{xx}(B)}{\rho_{xx}(0)} \qquad (1)$$

$$\tan\theta = \frac{\rho_{yx}}{\rho_{xx}} = \mu B \qquad (2)$$

the Hall resistivity, ρ_{xx} is the usual resistivity (that is, the resistivity measured on a long wire of the material), and μ is the carrier mobility. For a disk material characterized by high mobility (as is the case for many semiconductors), the factor $1 + \tan^2\theta$, describing the geometrical magnetoresistance effect in Eq. (1), can be very large. The factor $\rho_{xx}(B)/\rho_{xx}(0)$, which measures the intrinsic magnetoresistance, is then relatively much smaller. With conformal mapping methods it is possible to demonstrate that the Corbino disk is equivalent to a very wide or very thin rectangular element of the material in which the Hall voltage is completely shorted and the geometrical magnetoresistance is maximized. Corbino disks have been used only rarely in practical devices



Corbino disk with voltage *V* and current *I* between inner and outer electrodes. (*a*) Current paths are radial in the absence of an applied magnetic field. (*b*) With an axial magnetic induction B directed out of the paper, the current paths become spirals, and the increased path length leads to increased resistance.

since they have a low overall resistance and correspondingly large power dissipation. For background information *see* HALL EFFECT; MAGNETORESISTANCE.

J. F. Herbst

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Cordaitales

An extinct order of the class Pinopsida comprising a natural grouping of Paleozoic forest trees or shrubs that first appeared in the Lower Pennsylvanian. They became an important component of the tropical vegetation during the Middle and Upper Pennsylvanian and diminished during the basal Permian. The Cordaitales were divided into three families, Cordaitaceae, Pityaceae, and Poroxylaceae. However, members of the Pityaceae and Poroxylaceae are now known to be either seed ferns or progymnosperms, so only the Cordaitaceae remain. Detailed information about these prominent Paleozoic gymnosperms comes from impression-compression fossils and sandstone casts. However, coal balls, which are mineral nodules in which the plants are preserved with three-dimensional anatomy, have been essential to establishing whole-plant concepts of cordaitean species. *See* COAL BALLS.

Some of the first fossil plant reconstructions were based on the consistent co-occurrence of plant parts at numerous localities. Reconstructions are based on numerous specimens of anatomically preserved, interconnected organs from single localities. This approach has resulted in several species of cordaitean plants constituting two distinct lineages, characterized by a diversity of life cycle and habitat. For example, although cordaites from mesic environments were tall, slender trees, those that grew in or close to peat-forming swamps were scrambling shrubs and small, possibly mangrovelike trees.

Features. *Mesoxylon* and *Cordaixylon* are cordaitean stem genera that have been expanded to whole-plant concepts. There are some features common to both genera. Cordaitean stems typically have a septate pith, although in some species it is solid (**Fig. 1**). Pith casts typically are 1.6–4 in. (4–10 cm) in diameter and provide evidence of the diaphragms separating the pith cavities. The wood is simple and has the basic structure found in modern Araucarian conifers with radial files of tracheids, mostly uniseriate rays, and no resin canals. Cordaites lack growth rings. Main-stem diameters range from 1.75 in. (4.4 cm) [shrubs] to more than 3 ft (1 m) [trees], with trees attaining heights of up to 100 ft (30 m).

Cordaitean leaves are sessile, are helically arranged, and appear to have been coriaceous and heavily cutinized with acuminate-to-rounded tips (**Fig. 2**). Most leaves are linear, up to 40 in. (100 cm) long and 0.75–2 in. (2–5 cm) wide, with numerous parallel veins but no midrib, much like those of the conifer *Agathis* or the angiosperm *Amaryllis*. However, needle leaves with a single vein are produced in the basal regions of branches in some species. There is no evidence of an abscission layer.

Some trees apparently formed highly branched, shallow root systems similar to many living conifers, while the shrublike forms had numerous

Fig. 1. Cross sections of cordaitean stems with simple wood. Left, *Cordaixylon iowensis* with septate pith. Right, *Mesoxylon priapi* with solid pith. (*Photographs by M. L. Trivett*)

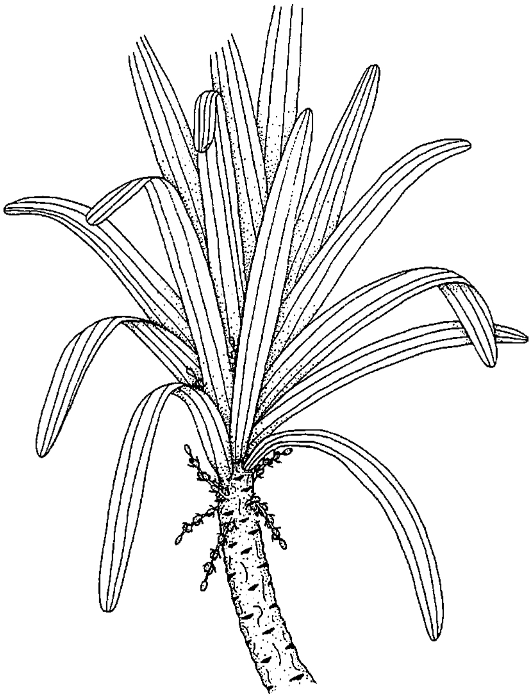

Fig. 2. Shoot of *Cordaixylon dumusum* illustrating strap leaves and nonaxillary *Cordaitanthus*-type cones. (*Courtesy of G. W. Rothwell*)

adventitious roots. Other roots have a combination of aerenchyma, periderm, lenticels, and medullated protosteles reminiscent of the stilt roots of some modern mangrove plants.

Vegetative and fertile branching is almost exclusively axillary. In most species, a single vegetative or fertile branch occurs in the axil of a leaf, although occasionally a vegetative and fertile branch or two fertile branches occur together. In a few species (such as *C. birame*), paired fertile branches are the norm. In others (for example, *C. dumusum*), single fertile branches are borne as nonaxillary, epicormic branches (Fig. 2).

Cordaitean reproductive organs are unisexual compound cones with a bilateral primary axis bearing four ranks of bracts, each subtending a secondary shoot. Secondary axes have numerous helical scale leaves, with some of the apical ones bearing pollen sacs or ovules at their tips.

Features of cauline primary xylem and reproductive structures are important generic characters within the Cordaitales. *Cordaixylon* stems have interconnected cauline strands and leaf traces, while *Mesoxylon* stems lack cauline bundles at the pith margin and have primary xylem present only as leaf traces. *Mesoxylon* cones (*Gothania*) [**Fig. 3**] are larger with more rectangular primary axes than *Cordaixylon* cones (*Cordaitanthus*) [Fig. 2] and produce pollen (*Sullisaccites* or *Felixipollinites*) in a line of pollen sacs. *Cordaixylon* cones produce pollen (*Florinites*) in rings of pollen sacs. *Mesoxylon* ovules (*Mitrospermum*) are winged, and *Cordaixylon* ovules (*Cardiocarpus*) are cordate. *See* FOSSIL SEEDS AND FRUITS.

Growth architecture and ecological interpretations. Integrating depositional information with architectural analyses can provide evidence of plant community structure and ecological partitioning. Delicate organs that show little, if any, transport damage indicate deposition at or near the growth site. Aerial organs of *Mesoxylon priapi* and *C. dumusum* are plentiful. Roots of *C. dumusum* are small but abundant, and *M. priapi* roots are lacking. *Cordaixylon dumusum* is reconstructed as a shrub inhabiting the stressed peat swamp environment, while *M. priapi* trees edged or perhaps grew on hummocks in the swamp. In addition, pollen sacs of *M. priapi* cones matured simultaneously, while those of *C. dumusum* appear to have matured over time, perhaps contributing to its role as a weedy colonizer.

Although most cordaites have leaves uniformly closely spaced, *C. iowensis* leaves are tightly packed in the bud but widely separated on mature stem sections and the pith is disrupted, indicating extensive internodal elongation. Needle leaves develop at the base of some branches. Such features typify rhythmic growth found in many temperate trees, resulting in a somewhat tiered architecture. Although growth rings (evidence of seasonality) are not present, rhythmic growth may have been induced by fluctuating environmental stress. The Cordaitales are an important group in understanding paleocommunity physiognomy, and in determining gymnospermous phylogeny through their relationships to both seed

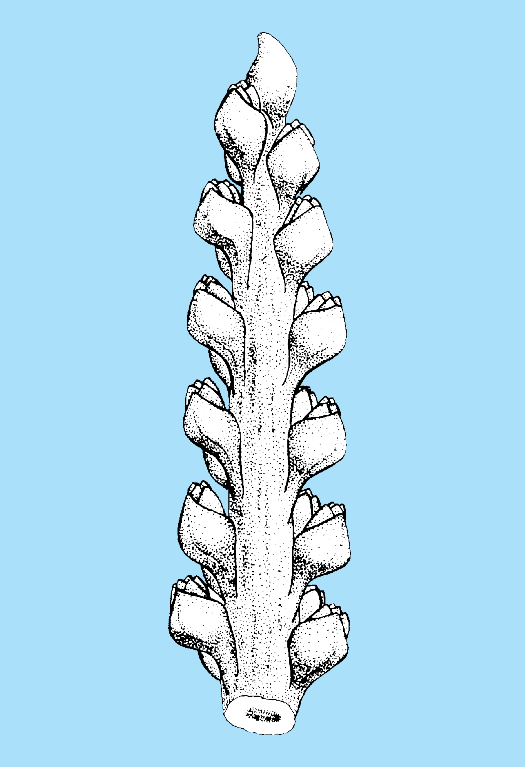

Fig. 3. Compound *Gothania*-type cone of *Mesoxylon priapi* with bracts subtending secondary shoots. (*Courtesy of M. L. Trivett*)

ferns and early conifers. *See* PALEOBOTANY; PINOPHYTA. Mary Louise Trivett

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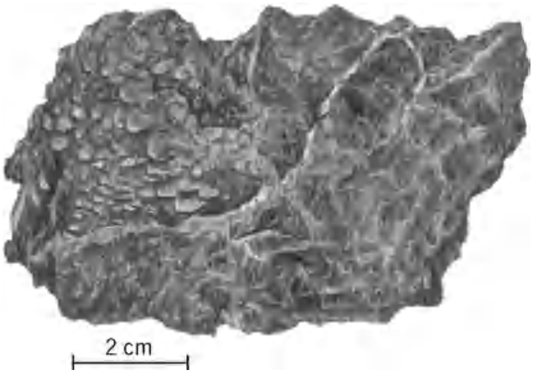
Cordierite

An orthorhombic magnesium aluminosilicate mineral of composition $Mg_2[Al_4Si_5O_{18}]$, $a = 1.710$ nanometers, $b = 0.973$ nm, $c = 0.936$ nm, $Z = 4$, space group *Cccm*. The crystal structure is related to beryl; magnesium is octahedrally coordinated by oxygen atoms, and the tetrahedrally coordinated aluminum and silicon atoms form a pseudohexagonal honeycomb, admitting limited amounts of K^+ and Na^+ ions and water molecules in the open channels. Limited amounts of Fe^{2+} may substitute for Mg^{2+}, and Fe^{3+} for Al^{3+}. The hardness is 7 (Mohs scale), specific gravity 2.6; luster vitreous; cleavage poor; and color greenish-blue, lilac blue, or dark blue, often strongly pleochroic colorless to deep blue (see **illus.**). Transparent pleochroic crystals are used as gem material. The disordered cordierite structure, $Mg_2[(Al,Si)_9O_{18}]$, is called indialite and is hexagonal, space group *P6/mcc*, isotypic with beryl. Osumilite, $KMg_2Al_3\cdot [(Al,Si)_{12}O_{30}]\cdot H_2O$, is also related but has a structure built of double six-membered rings of tetrahedrons. Cordierite, indialite, and osumilite are difficult to distinguish. Pale colored varieties are often misidentified as quartz, since these minerals have many physical properties in common. *See* BERYL; SILICATE MINERALS.

Cordierite possesses unusually low thermal expansion, and synthetic material has been applied to thermal-shock-resistant materials, such as insulators for spark plugs and low-expansion concrete. Cordierite is an important phase in the system $MgO–Al_2O_3–SiO_2$. Between 800 and 900°C (1470–1650°F), glasses of cordierite composition crystallize. Below 500°C (930°F) at pressures up to 500 bars (50 megapascals), cordierite in the presence of water breaks down to form chlorite + pyrophyllite. Indeed, it is often found naturally altered to these minerals. Cordierite melts incongruently at 2000 bars (200 MPa) and 1125°C (2057°F) to mullite + spinel + liquid. Natural cordierites break down at temperatures of about 800°C (1470°F) and pressures above 8 kilobars (800 kilopascals) to form enstatite, sillimanite, and quartz.



Cordierite, from Tsilaizina, Madagascar. (*Specimen from Department of Geology, Bryn Mawr College*)

Cordierite frequently occurs associated with thermally metamorphosed rocks derived from argillaceous sediments. A common reaction in regional metamorphism resulting in gneisses is garnet + muscovite → cordierite + biotite. It may occur in aluminous schists, gneisses, and granulites; though usually appearing in minor amounts, cordierite occurs at many localities throughout the world. Paul B. Moore

Cordilleran belt

A mountain belt or chain which is an assemblage of individual mountain ranges and associated plateaus and intermontane lowlands. A cordillera is usually of continental extent and linear trend; component elements may trend at angles to its length or be nonlinear.

The term cordillera is most frequently used in reference to the mountainous regions of western South and North America, which lie between the Pacific Ocean and interior lowlands to the east (see **illus.**). The term was first applied to the Andes Mountains of South America in their entirety (Cordillera de los Andes), but individual mountain ranges within the Andean belt are now called cordilleras by some authorities. Farther north, the extensive and geologically diverse mountain terrane of western North America is formally known as the Cordilleran belt or orogen. This belt includes such contrasting elements within the United States as the Sierra Nevada, Central Valley of California, Cascade Range, Basin and Range Province, Colorado Plateau, and Rocky Mountains. *See* MOUNTAIN SYSTEMS.

Cordilleras represent zones of intense deformation of the Earth's crust produced by the convergence and interaction of large, relatively stable areas known as plates. J. F. Dewey and J. M. Bird have analyzed mountain belts in terms of different modes of plate convergence. They contrast cordilleran-type mountain belts, such as the North American Cordillera, with collision-type belts, such as the Himalayas. The former develop during long-term convergence of an oceanic plate toward and beneath a continental plate, whereas the latter are produced by the convergence and collision of one continental plate with another or with an island arc. Characteristics of cordilleran-type mountain belts include their position along a continental margin, their widespread volcanic and plutonic igneous activity, and their tendency to be bordered on both sides by zones of low-angle thrust faulting directed away from the axis of the belt. The deformational, igneous, and metamorphic characteristics of cordilleran belts appear to be largely related to crustal compression, to melting of

The arrangement of the mountains and the continents of the world. (*After P. E. James, An Outline of Geography, Ginn and Co., 1935*)

rocks at depth along the inclined plate boundary, and to attendant thermal effects in the overlying continental plate. *See* OROGENY. Gregory A. Davis

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Core loss

The rate of energy conversion into heat in a magnetic material due to the presence of an alternating or pulsating magnetic field. It may be subdivided into two principal components, hysteresis loss and eddy-current loss. *See* EDDY CURRENT.

Hysteresis loss. The energy consumed in magnetizing and demagnetizing magnetic material is called the hysteresis loss. It is proportional to the frequency and to the area inside the hysteresis loop for the material used. Hysteresis loss can be approximated empirically by using Eq. (1), where K_h is a constant

$$P_h = K_{ith} f B^n_{\max} \tag{1}$$

characteristic of the material, f is the frequency, $B_{\max}$ is the maximum flux density, and n, called the Steinmetz coefficient, is often taken as 1.6 although it may vary from 1.5 to 2.5. *See* MAGNETIZATION.

Most rotating machines are stacked with silicon steel laminations, which have low hysteresis losses. The cores of large units are sometimes built up with cold-reduced, grain-oriented, silicon iron punchings having exceptionally low hysteresis loss, as well as high permeability when magnetized along the direction of rolling.

Eddy-current loss. Induced currents flow within the magnetic material because of variation in the flux. This eddy-current loss may be expressed to close approximation by using Eq. (2), where K_e is

$$P_e = K_e (B_{\max} f \tau)^2 \tag{2}$$

a constant depending on the volume and resistivity of the iron, $B_{\max}$ the maximum flux density, f the frequency, and τ the thickness of the lamination in the core. For 60-cycle rotating machines, core lamination of 0.014–0.018 in. (0.35–0.45 mm) are usually used to reduce eddy-current loss.

Measured core loss. The measured core loss in a rotating machine also includes eddy-current losses in solid structural parts, such as the frame, ventilating duct spacers, pole faces, and damper windings, as well as those due to burrs or other contacts between punchings. A number of precautions are taken to minimize these components, which become appreciable in large machines. Structural parts close to the core, including clamping plates, I-beam spacers, dovetail bars, and shields, may be made of nonmagnetic material. Some of these parts may be shielded from the variable flux by low-resistance plates or by flux traps of laminated, high-permeability, low-loss steel. The core punchings are deburred and are coated with a baked-on insulating varnish. The finished cores are often tested with an ac magnetizing coil to locate and correct hot spots caused by damage during assembly. Pole-face losses are reduced by avoiding excessive slot-width to air-gap ratios, by surface grooving of the poles, and by low-resistance amortisseur windings. *See* ELECTRIC ROTATING MACHINERY.

Leon T. Rosenberg

Coriander

A strong-scented annual herb. Coriander is cultivated in many places throughout the world for both seeds and leaves. The two forms are quite different in taste from one another, and both are used for flavor in a variety of foods. Only one species, *Coriandrum sativum*, is cultivated. Coriander is a member of the carrot family, Apiaceae (Umbelliferae), and is closely related to other spice seed plants such as cumin, caraway, anise, dill, and fennel. A number of distinct cultivars have been developed. Some, with longer maturity times and resulting higher leaf yield, are grown for cilantro, also called Chinese parsley. Other seed-producing types, having a more uniform seed set, and types that resist splitting have been developed in Russia and India. *See* ANISE; APIALES; CARAWAY; CUMIN; DILL; FENNEL.

The growing of cilantro from seed to a harvestable size takes 40–60 days, and full maturity as coriander (dry ripe fruit) is reached in approximately 120 days. Coriander occurs as an erect herbaceous plant with one to many stems that reach about 4 ft (1.2 m) in height. When the plant is young, small deeply segmented leaves are formed, but as the plant ages the leaves become more and more divided until they become feathery in appearance, similar to dill.

The term coriander comes from the Greek *koris,* meaning bedbug, because the leaves and green fruit of this plant have an odor similar to bedbugs. Although some find it objectionable, it imparts a distinctive authentic taste to Mexican and Asian foods. Coriander seeds are used in pickling, curries, and for flavoring alcoholic beverages such as gin. The "seed," which is actually the whole fruit, is a two-seeded schizocarp borne in umbels and is approximately 0.1–0.3 in. (3–7 mm) in diameter. Longitudinal ridges run from top to bottom.

Cultivation is accomplished by planting seed in the spring at a rate of 9–14 lb/acre (10–15 kg/hectare). Pollination and weed control are similar to that of dill. *See* APIALES; SPICE AND FLAVORING.

Seth Kirby

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Coriolis acceleration

An acceleration which arises as a result of motion of a particle relative to a rotating system. Only the components of motion in a plane parallel to the equatorial plane are influenced. Coriolis accelerations are important to the circulation of planetary atmospheres, and also in ballistics. They are so called after G. de Coriolis, the French engineer and mathematician whose analysis of the phenomenon was published in 1835. *See* ACCELERATION; BALLISTICS.

Newton's second law of motion is valid only when the motions and accelerations are those observed in a coordinate system that is not itself accelerating, that is, an inertial reference frame. In order to utilize familiar concepts in mathematical treatment, the Earth is commonly treated as if it were fixed, as it appears to one observing from a point on the surface, and the Coriolis force is introduced to balance the acceleration observed by virtue of the observer's motion in the rotating frame. *See* FRAME OF REFERENCE; NEWTON'S LAWS OF MOTION.

As with the influenced components of motion, the Coriolis force is directed perpendicularly to the Earth's axis, that is, in a plane parallel to the equatorial plane. Since the direction of its action is also perpendicular to the particle velocity itself, the Coriolis force affects only the direction of motion, not the speed. This is the basis for referring to it as the deflecting force of the Earth's rotation. The magnitude of the Coriolis force is equal to the product of twice the projection of particle velocity into the equatorial plane, with the angular velocity of the Earth's rotation ($7.292 \times 10^{-5}\ s^{-1}$).

The Coriolis force is directed to the right of the direction toward which the horizontal wind blows or the missile flies in the Earth's Northern Hemisphere, and to the left in the Southern. The horizontal component of the deflecting force is zero at the Equator, and a maximum at the poles. While negligible for the dynamics of small-scale phenomena such as cumulus convection and thunderstorms, Coriolis effects are critical to the dynamics of the Earth's large-scale wind currents. Indeed, the general circulations of planetary atmospheres owe their zonal nature and some other characteristics largely to the forces that arise by virtue of planetary rotation.

A simple illustration of a Coriolis effect in the Northern Hemisphere is afforded by a turntable in counterclockwise rotation, and an external observer who moves a marker steadily in a straight line from the axis to the rim of the turntable. The trace on the turntable is a right-turning curve, and obviously this is also the nature of the path apparent to an observer who rotates with the table. Now consider the contrasting case of an air parcel near the North Pole that moves directly south (away from the Earth's axis of rotation) so that its motion to an observer on the Earth is in a straight line. To a nonrotating observer in space, this same motion appears curved toward the east because of the increased linear velocity of the meridian at lower latitudes. The force necessary to produce the eastward acceleration in the inertial frame is equal to the Coriolis force and would be produced by a gradient of air pressure from west to east, and shown by north-south–oriented isobars. In the absence of the pressure gradient force, the Coriolis force would cause the trajectory of the southward-moving air to curve westward on the Earth's surface. Then an air parcel moving uniformly away from the North Pole along a line which appears straight to an observer in space would appear to earthbound observers to curve westward. *See* GEOSTROPHIC WIND; ISOBAR (METEOROLOGY). Edwin Kessler

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Corn

Zea mays occupies a larger area than any other grain crop in the United States, where 60% of the world production is grown.

Production

Production is widely distributed throughout the United States, but it reaches its greatest concentration in the states of Iowa, Illinois, Indiana, Ohio, Nebraska, Minnesota, Wisconsin, Michigan, and Missouri. This area, called the Corn Belt, is characterized by moderately high temperature, fertile, well-drained soils, and normally adequate rainfall. The Corn Belt accounts for approximately 80% of corn production in the United States. Although corn is grown in the United States primarily for livestock feed, about 10% is used for the manufacture of starch, sugar, corn meal, breakfast cereals, oil, alcohol, and several other specialized products. In many tropical countries, corn is used primarily for human consumption.

Origin and description. From its presumed origin in Mexico or Central America, corn has been introduced into all the countries of the world that have suitable climatic conditions. However, the corn of today is far different from the primitive types found in prehistoric sites excavated in Arizona, Mexico, and Peru. The origin of corn is still unsettled, but the most widely held hypothesis assumes that corn developed from its wild relative teosinte (*Z. mexicana*) through a combination of favorable mutations, recognized and selectively propagated by early humans. Corn migrated from its center of origin and was being cultivated by the Indians as far north as New England upon the arrival of the first European colonists, whose survival was due largely to the use of corn as food.

Botanically, corn is a member of the grass family. Certain seed types within the species *Z. mays* were given subspecific rank by early investigators. Among these types are the dents (*indentata*), flints (*indurata*), soft or flour (*amylaceae*), sweet (*saccharata*), pop (*everta*), and pod (*tunicata*). Each form (botanical variety) is conditioned by fairly few genetic differences, and each may exhibit the full range of differences in color, plant type, maturity, and so on, characteristic of the species. All types have the same number of chromosomes (10 pairs), and all may be intercrossed to produce fertile progeny. Dent corns are the most important in the United States. Kernel texture is less homogeneous in other areas of the world. Soft types tend to predominate at higher elevations, flint types at lower elevations. This pattern is due, in part, to differences in methods of food preparation, but it has also been influenced by the greater resistance of flint types to stored-grain insect pests, which are more prevalent at lower elevations. Sweet corn is grown more extensively in the United States than in any other country. It is eaten as fresh corn or canned or frozen. In other countries, flint, dent, or flour corns may be eaten fresh, but at a much more mature stage than the sweet corn eaten in the United States. The commercial production of popcorn is almost exclusively American. Pod corn is grown only as a genetic curiosity. *See* CYPERALES; GENETICS; REPRODUCTION (PLANT).

Varieties and types. Corn is a cross-pollinated plant; the staminate (male) and pistillate (female) inflorescences (flower clusters) are borne on separate parts of the same plant (**Fig. 1**). Plants of this type are called monoecious. The staminate inflorescence is the tassel; it produces pollen that is carried by the wind to the silks produced on the ears. Natural cross-pollination permits maintenance of a high degree of genetic variability. As corn was carried by the Indians to different environments in North, Central, and South America, a large array of varieties ultimately was developed. Many of these primitive varieties still exist today. Extensive efforts have been devoted to the collection, classification, and maintenance of this valuable reservoir of genetic variability. Settlers migrating westward took with them their corn seed (botanically fruits). In time, by both planned and natural selection, a large number of varieties and local strains became established and adapted to the new ecological conditions. These strains varied in color of grain, plant, and ear characteristics, and in length of time required to reach maturity. Because of the variability associated with cross-pollination, corn is a highly plastic species, and varieties have been developed that are well adapted to a frost-free growing season of less than 90 days or, in contrast, grow 12–15 ft (3.5–4.5 m) tall and require more than 200 days to reach maturity, as in certain areas in Guatemala. *See* FLOWER; INFLORESCENCE; POLLINATION.

Hybrids. The development of varieties and strains of corn made possible the extension of its culture under diverse soil and climatic conditions. However, modern research methods, used for its further improvement, led to the present widespread use of hybrid corn. Essentially all of the corn grown in the United States is planted to hybrid seed, and this technology is being adopted in other areas of the world as rapidly as suitable hybrids are developed. *See* BREEDING (PLANT); HETEROSIS.

Fig. 1. A corn plant in full tassel and silk. The tassel produces pollen that is blown by wind to the silks. (*Courtesy of J. W. McManigal*)

Hybrid corn is the first generation of cross involving inbred lines. Inbred lines are developed by controlled self-pollination. When continued for several generations, self-pollination leads to reduction in vigor but permits the isolation of types which are genetically pure or homozygous. Intense selection is practiced during the inbreeding phase to identify and maintain genotypes having the desired plant and ear type and maturity characteristics, and relative freedom from insect and disease attacks. After the inbred lines have become fairly pure, they are further evaluated in hybrid combinations. Crosses involving any two unrelated lines will exhibit heterosis, that is, yields above the means of the two parents. Only a very few combinations, however, exhibit sufficient heterosis to equal or surpass hybrids in current commercial use. Hence large-scale experimental testing is required to identify new useful combinations.

The first commercial hybrids were double crosses produced by crossing two single crosses, each, in turn, having been produced by the crossing of two inbred lines. Hybrid seed for commercial planting is produced in special crossing blocks (isolated fields). The field is planted with the parents (inbred lines or single crosses) in alternating groups of rows.

The plants in blocks to be used as female parents are detasseled before silk emerges. Thus all seed produced will be pollinated by the male parent. After drying, sizing, and treatment, the seed harvested from the female rows becomes the hybrid seed of commerce. Since the early 1960s the use of single-cross hybrids has been increasing, and in the Corn Belt today probably accounts for 80% or more of the seed used.

Several techniques have been used to control pollination. Initially, manual removal of the tassels was used exclusively. Then cytoplasmic male sterility was used. This type of male sterility is transmitted only through the cytoplasm of the female parent. Since no fertile pollen is produced, no detasseling is required. With this system, pollen production in the farmers' fields is provided either by blending (artificial mixing of sterile and fertile types) or by the use of genetic fertility-restoring factors introduced through the male parent. In 1970 possibly 90% of the hybrid seed used in the United States utilized a single type of cytoplasmic sterility: the Texas type. This cytoplasmic type proved to be susceptible to a new mutant race (race T) of one of the leaf-blight fungi, *Helminthosporium maydis*, and thus the use of this type of sterility was distincontinued. Investigations of other types of cytoplasmic sterility are under way. Machines which cut or pull tassels in the seed fields have been developed and are being used extensively. Other types of genetic control of pollen production have been developed, and some attention is being given to the possible use of chemical sterilants.

Companies specializing in hybrid seed production produce and market the entire seed supply. Gains from the use of hybrid seed have been spectacular. The shift from open-pollinated varieties to hybrids, beginning in the 1930s, accounted for a yield increase of 25%. In succeeding years these first hybrids have been replaced by newer, higher-yielding types which have greater disease and insect resistance. Hybrid succession is a continuing process; few hybrids have a commercial life of more than 5 years. The per-acre yield of corn has increased about threefold since the first introduction and use of hybrid seed. *See* AGRICULTURAL SCIENCE (PLANT).

Planting. Planting dates depend upon temperature and soil conditions. Germination is very slow at soil temperatures of 50°F (10°C), and seedling growth is limited at temperatures of 60°F (16°C) or below. Because of these temperature relations, planting begins in Florida and southern Texas in early February and is completed in New York and New England by late May or early June. Planting rates are influenced by water supply, soil type, and fertility and by the maturity characteristics of the hybrid grown. Planting rates for full-season hybrids may vary from 8000 to 12,000 plants per acre (20,000 to 30,000 per hectare) in eastern Texas to 20,000 to 24,000 (50,000 to 59,000) in the central Corn Belt. Check-planting, with hills and rows spaced 38–42 in. (95–105 cm) apart, has been almost completely replaced by drilling. With planting rates above 16,000 plants per acre (40,000 per hectare), drilling in rows 24–36 in. (60–90 cm) apart has become common practice. The use of nitrogen fertilizer has increased greatly; lesser amounts of phosphorus and potash are applied as needed. Soil tests and experience provide useful guides to economic rates of fertilizer use under different environmental conditions.

There has been a marked trend toward reducing the amount of tillage in seedbed preparation. The variations in the planting systems used are influenced by soil type and topography, amount of crop residues on the soil surface, and the weed-control system to be employed. The use of the minimum tillage system, in which all soil preparation as well as planting is performed in one passage across the field, is increasing. This system, and less extreme modifications of the conventional system, reduces total energy costs. *See* AGRICULTURAL SOIL AND CROP PRACTICES.

Weed control. Weed control may be effected by cultivation or herbicides or both. With minimum tillage planting methods, weed control may be more difficult than with conventional seedbed preparation because of crop residues left on or near the surface. Weeds are easiest to control mechanically when they are small, preferably before they emerge. The most efficient and economical tool for killing weeds at this stage is the rotary hoe. Unfortunately this or other mechanical cultivation systems are relatively ineffective during extended periods of rainy weather. Disk or shovel cultivators are used after the corn is 6–8 in. (15–20 cm) in height.

Increasing use has been made of selective herbicides. Most broadleaf and grassy weeds may be controlled without damage to corn. Herbicides may be applied either "preplant" or "preemergence." If applied prior to planting, herbicides may be left on the soil surface or incorporated into the soil. Preemergence applications may be made as the seed is planted, or at any time prior to crop emergence. The choice of the many herbicides available is dependent upon many factors, including the type of weeds to be controlled and the farming system used. Under unfavorable early-season weather conditions, neither mechanical nor chemical control nor their combination may be completely effective, and sizable yield reductions may result. *See* HERBICIDE.

Harvesting. Harvesting of corn has undergone a major revolution since 1930. In the 1930s most corn was husked by hand, and the ears were stored in slatted cribs. Harvesting began when the moisture content of the grain had been reduced, by natural drying, to 20–24%. The mechanical picker supplanted hand harvesting. The mechanical picker, in turn, has been replaced by the picker-sheller or corn combine, which harvests the crop as shelled grain (**Fig. 2**). Energy requirements, however, have increased materially over the years. When harvested as shelled grain, at a relatively high moisture content (20–30%), the grain must be dried artificially for safe storage. High-moisture corn to be used for livestock feed may be stored in airtight silos or may be treated with certain chemical preservatives such as propionic acid. Corn stored under either of these systems is not suitable either for industrial processing or for seed. *See* AGRICULTURAL MACHINERY.

G. F. Sprague

Fig. 2. Two-row mounted picker for harvesting corn.

Productivity. Corn is highly productive largely because it can use solar energy so efficiently. It is classed as a C-4 species, which means that its leaves use the more efficient of the two photosynthetic processes found in crop plants. This is the same photosynthetic system used by sugarcane, sorghum, other tropical grasses, and many persistent weeds. In addition to relatively efficient leaves, corn's growth habit allows planting densities thick enough to almost completely shade the soil. Thus, a well-managed cornfield receives almost all the solar energy the environment provides and uses it as efficiently as any plant known. *See* PHOTOSYNTHESIS.

The higher productivity of modern corn hybrids, as compared with earlier hybrids, when both are grown under disease-free conditions, results to a considerable degree from their ability to tolerate higher plant populations without excessive barrenness. This capability is largely due to the greater plant-to-plant uniformity introduced by single cross hybrids and to the development of varieties with more erect leaves. Such foliage minimizes mutual shading and permits more uniform illumination of all leaf surfaces.

The actual rate of dry matter production by an area of corn with ample water and fertility depends on the average amount of light and on the temperature. The highest value reported, 2 oz (52 g) of dry matter per 11 ft^2 (1.0 m^2) of land area per day, was for high-population corn under cloudless conditions at Davis, California. A more representative range of values for the Corn Belt of the United States would be 0.9–1 oz (26–32 g) of dry matter per 11 ft^2 (1.0 m^2) per day. Day-to-day variation is large because of differences in cloudiness and in temperatures. Such estimates suggest dry matter growth rates of 230–285 lb per acre per day (258 to 319 kg per hectare per day).

The corn plant grows vegetatively until about silking, after which all weight increase is in the form of grain. There is little transfer of earlier growth to grain, so almost the entire grain yield results from photosynthesis during the grain growth period, which runs from silking to maturity. Thus, grain yield results from a combination of the rate of dry matter production after silking and the duration of the grain growth period. Contrary to much popular opinion, grain yields are highest under cool conditions, when the lengthened grain growth period more than compensates for the slower growth rate. Thus, yields for single planting are much greater at higher altitudes in the tropics than at warmer, lower locations. Highest average grain yields are in favored areas of Washington and Oregon in the United States, in the North Island of New Zealand, and in cooler long-season locations in Europe. Consistently high yields in the Corn Belt of the United States result more from favorable soil moisture and excellent management than from climatic superiority.

Relationships among solar radiation, temperature, growing-season length, soil moisture, day length, soil fertility, and corn genotype in producing grain yields are complex and not well understood. Attempts to study the system as a whole, using simulation models on digital computers, may add considerably to knowledge of the subject. William G. Duncan

Diseases

More than 100 diseases of corn are known worldwide; yet damage or yield loss from disease seldom forces a grower out of production. World reduction in grain production due to disease is estimated to average 9% and in the Corn Belt to average 7–17%. The widespread practices of continuous cropping, increased fertilization, high plant populations, and relative genetic uniformity of hybrids have sometimes resulted in epidemics: Stewart's bacterial wilt, northern corn leaf blight epidemics in 1939–1943, the maize dwarf mosaic epidemics in the 1960s, and the southern corn leaf blight epidemic of 1970–1971.

Diseases are caused by bacteria, fungi, nematodes, viruses, several mycoplasma-like organisms, and one parasitic seed plant (*Striga* spp.). Pollutants, pesticides, and unfavorable climatic and soil factors are responsible for still other diseases.

Seedling diseases. Seed decay and seedling blight caused by seed- and soil-borne *Diplodia, Fusarium, Penicillium,* and *Pythium* species are troublesome when grain is planted in cool, moist soil. Planting sound, mature, and chemically treated seed reduces these problems.

Leaf diseases. Of approximately 25 leaf blights, only a few are economically important in the United States. Southern corn leaf blight, caused by *Helminthosporium maydis,* accounted for a 15% loss in yield in the 1970 epidemic in the nation. Yellow leaf blight, caused by *Phyllosticta maydis,* occurred about the same time, and both blights are found most commonly in hybrids with the Texas male-sterile cytoplasm. Northern corn leaf blight, caused by *Helminthosporium* (*=Exserohilum*) *turcicum,* has been destructive and can cause 50% loss in yield if the disease strikes before pollination. With new conservation tillage practices, other leaf diseases have become increasingly important due to fungi that overwinter on crop debris left on the ground. Resistant hybrids and, sometimes, crop rotation are generally used for control. Two of the bacterial leaf blights are of major concern. Stewart's wilt, caused by *Erwinia stewartii,* results in a severe wilt of sweet corn and a leaf blight of dent corn in eastern North America. Control is obtained by use of resistant hybrids or by insecticides that control the flea beetle vector. Goss's bacterial wilt and blight, or leaf freckles, occurs in Colorado, South Dakota, Nebraska, and Kansas, and is caused by *Corynebacterium nebraskense*. All types of corn are susceptible, and various degrees of blighting and stunting occur.

Smuts and rusts. Common or boil smut, caused by *Ustilago maydis,* is found wherever corn is grown, but losses in yield seldom exceed 2% over a wide area. Galls may appear on any part of the plant and are most prevalent in vigorously growing plants in soil high in organic matter and nitrogen, often under dry conditions, and increase with hail and other

Fig. 3. Corn smut on various parts of plant. (*University of Minnesota Agricultural Experimental Station*)

mechanical injuries (**Fig. 3**). Large galls on or above the ear are more destructive than galls below the ear. Control is to plant resistant hybrids. The small cinnamon brown to black pustules of common rust, caused by *Puccinia sorghi,* on leaves are found wherever corn is grown. Most widely used hybrids have good field resistance. Southern rust, *P. polysora,* found mainly in the southeastern United States and other countries, appears to be spreading to northern states of the Corn Belt.

Stalk and root diseases. Stalk rots are universally important and among the most destructive diseases of corn in the world (**Fig. 4**). They are caused by *Fusarium moniliforme, F. roseum* "Graminearum" (*Gibberella zeae*), *Macrophomina phaseolina,* and to a lesser extent by *Diplodia zeae* and *Colletotrichum graminicola,* and several dozen other fungi and bacteria. Losses vary by season and region, but yield losses of 10–20% can occur among susceptible hybrids in the United States and 25–33% in other countries. Conditions favoring disease may cause plants to die before maturity. This results in poorly filled ears, but the greatest loss may come from stalk lodging that interferes with harvesting, or from ears fallen to the ground. Many factors affect stalk rot: unbalanced soil fertility, high plant populations, dry weather, leaf diseases, insect damage, hail, and, sometimes, continuous cropping to corn. The best control is to grow resistant hybrids and to follow good management practices. Root rots are caused usually by the same organisms that cause stalk rot, except that nematodes (eel- or roundworms) are sometimes involved. In fact, more than 40 species of nematodes have been reported to feed on corn roots. They can stunt plants, cause yellowing, and aid root-infecting fungi. *See* NEMATA.

Ear diseases. Considerable damage to ears from ear and kernel infection occurs in humid regions where rainfall is above normal late in the season, and from insect and bird feeding, early frosts, and fallen stalks (**Fig. 5**). Infected grain reduces yield and lowers grain quality, and grain may contain mycotoxins (aflatoxins, estrogens, and vomitoxin) which makes animals ill when used as feed. Infections occur in the field from fungi such as *Diplodia, Fusarium* (*Gibberella*), *Helminthosporium,* and *Nigrospora,* or in storage from such fungi as *Aspergillus, Cladosporium,* and *Penicillium*. Storage fungi can be controlled if grain is stored at 13–15% moisture and at uniform temperatures between 39 and 50°F (4 and 10°C), with provision for adequate aeration.

Viral and mycoplasma diseases. Prior to 1963, viruses were not a factor in corn production except in localized areas outside the United States. That year, maize dwarf mosaic virus (MDMV) caused economic losses in the United States. Almost complete destruction of susceptible corn occurred in some areas. MDMV has been identified in 15–20 states in the Corn Belt, as well as in the East and South. Aphids are vectors of MDMV, but leafhoppers are vectors for maize chlorotic dwarf virus (MCDV). Wheat streak mosaic virus (WSMV), widespread on certain inbred lines and hybrid corns in the Corn Belt, is transmitted by the mite *Eriophyes tulipae*. Other naturally occurring viruses of corn are sugarcane mosaic (a complex of Potyviruses that contain the MDMV subgroup), maize mosaic virus, maize chlorotic mottle virus (MCMV), and maize rayado fino virus. Corn lethal necrosis is a synergistic interaction between MCMV and either MDMV or WSMV, and is potentially destructive in the United States, but is currently confined to Kansas and Nebraska.

Some diseases once thought to be caused by viruses are now known to be caused by a spiroplasma or a mycoplasma-like organism. Corn stunt, transmitted by a leafhopper, occurs in Texas and in the Rio

Fig. 4. Corn stalk rot, one of the most widespread corn diseases. (*a*) Corn lodged from stalk rot. (*b*) Bacterial stalk rot, with healthy corn stem on left. (*Ohio Agricultural Research and Development Center*)

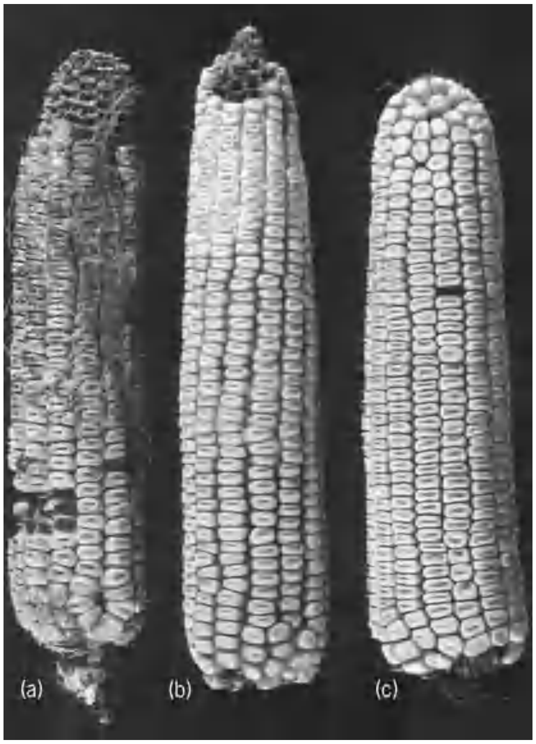

Fig. 5. Ear rots. (*a*) Storage rot. (*b*) Field rot. (*c*) Healthy ear. (*Ohio Agricultural Research and Development Center*)

Grande Valley, and is caused by a spiroplasma. The maize bushy stunt pathogen is a similar organism and has the approximate range of corn stunt in the United States and South America. The economic importance of virus diseases of corn has increasingly been recognized. *See* PLANT PATHOLOGY; PLANT VIRUSES AND VIROIDS.

Thor Kommedahl

Processing

Corn kernels (seeds) are subjected to both wet and dry milling. The goal of both processes is to separate the germ, the endosperm, and the pericarp (hull). The mean moisture content of corn kernels is 17% (range 7–23%). Kernel composition on a percent dry basis is given in **Table 1**. *See* CELLULOSE; HEMICELLULOSE; LIGNIN.

TABLE 1. Composition of corn kernels, on percent dry basis

Components	Mean value,%	Range,%
Starch	71	64–78
Protein	9.9	8–14
Fiber	9.5	8.3–11.9
Hemicelluloses	6.2	5.8–6.6
Cellulose	3.1	3.1–4.1
Lignin	0.2	
Oil	4.5	3.1–5.7
Ash	1.4	1.1–3.9
Sugars	2.6	1.0–3.0

Wet milling. Wet milling separates the chemical constituents of corn into starch, protein, oil, and fiber fractions (**Fig. 6**), the primary objective being to produce refined corn starch. The world production of corn grain in 1996–1997 was approximately 640 million tons (580 million metric tons) with more than 40% being produced in the United States. Products from milling of the United States crop are shown in **Table 2**. The amount wet-milled in 1997 was 16.5% of the crop.

There are variations in the equipment used for wet milling from plant to plant and within processing plants. The process begins with shelled No. 2 yellow dent corn being cleaned on vibrating screens to remove both coarse and fine material. The kernels are then placed in steep tanks that hold 2000–13,000 bushels (60–360 tons or 55–330 metric tons) and covered with steepwater (8–9 gal/bushel or 1.2–1.3 liter/kg) heated to 118–125°F (48–52°C). The steepwater is transferred in a countercurrent system, usually through batteries of about 12 tanks, with as many as 50 being used. The original steepwater contains 0.12–0.20% of added sulfur dioxide (SO_2). Dissolution of sulfur dioxide in water produces sulfurous acid, which assists in breaking down the starch-protein matrix. Kernels release about 6.5% of their dry substance as solubles into the steepwater. From the solubles, bacteria in the steepwater produce lactic acid, an important component for pH control. As the steepwater advances through the tanks in stages, the SO_2 content decreases to 0.01% or less and the lactic acid content increases to

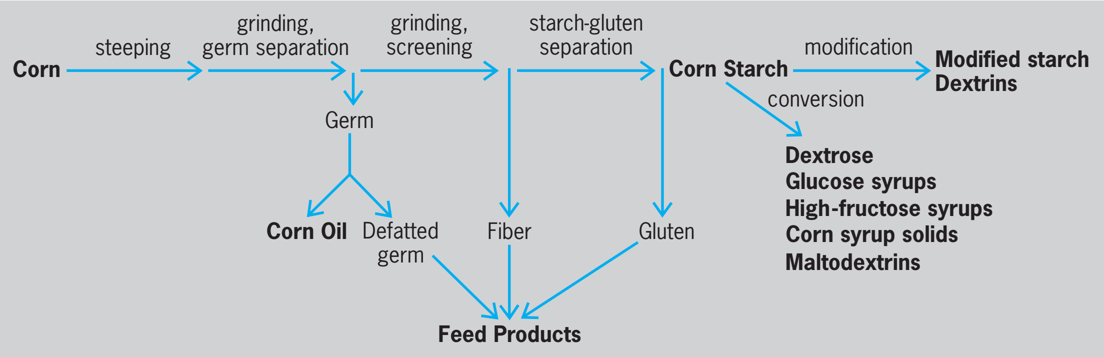

Fig. 6. Corn wet-milling process.

TABLE 2. Products obtained from corn in the United States[*]

Products	Production, 10^6 lb	Percent of nonfeed use
Wet-milled products	37,885	56.8
Starch products[†]	5,938	13.2
Conversion products[‡]	31,947	43.6
Fuel ethanol		28.4
Dry-milled products		7.5
Beverage alcohol		7.3
Coproducts of wet milling[§]		
Corn oil	1,284	
Corn gluten feed and corn oil meal	12,547	
Corn gluten meal	2,593	
Steepwater	1,118	

[*] Based on 1997 data; Corn Refiners Association, Washington, DC.
[†] Corn starches, modified corn starches, and dextrins.
[‡] Dextrose (d-glucose), glucose syrups, high-fructose syrups, D-fructose, syrup solids, maltodextrins.
[§] Does not include coproducts from fuel alcohol (ethanol) production.

1.6–1.7%. However, the pH remains a rather constant 4.0–4.1 throughout the process. The steeping process usually takes 20–40 h. At its end, the kernels are hydrated (45% moisture), swollen, and softened. The final steepwater is evaporated to 45–50% solids and mixed with corn fiber. The mixture is sold as corn gluten feed after drying. *See* PH.

The remainder of the process is continuous. The softened corn kernels are passed through coarse grinding mills that have one stationary and one rotating disk. The clearance between the disks is adjusted to minimize both the number of whole kernels and the number of broken germs. The discharge is pumped through banks of hydroclones to remove the germs, which have a lower density. The germs are washed on screens, dewatered in screw presses to about 50% solids, and dried. To recover the oil, the germs are heated to 250°F (120°C), steamed or passed through an extruder, and pressed in an oil expeller which reduces the oil content from 45% to 6%. Alternatively, after reducing the oil content to 13–20%, the germs are flaked and extracted with hexane. Crude corn oil is shipped to refiners. The remaining corn germ meal contains 23–25% protein. *See* FAT AND OIL (FOOD).

The slurry of corn kernels minus their germs is screened to separate "fiber" (mostly the pericarp) from the starch and protein. At this point, the fiber contains some attached starch. The slurry of fiber is again passed through rotating disk mills that free the starch with a minimum of fiber destruction. The milled slurry is again screened to separate the starch from the fiber. The fiber fraction remaining on the screens is dewatered to 42–48% moisture, mixed with evaporated steepwater, dried to 8–11% moisture, and sold as corn gluten feed (21% protein), often after pelletizing.

The starch slurry now contains only starch, protein, and some solubles. Because the protein has a specific gravity of 1.06 and the starch a specific gravity of 1.5, they can be separated in centrifuges. This separation produces a gluten fraction of more than 68% protein, which is dried to about 12% moisture and sold as corn gluten meal. *See* CENTRIFUGATION.

Most of the remaining protein (3–5% of the weight of starch) is removed from the starch by countercurrent washing in stages using banks of hydroclones 0.4 in. (10 mm) in diameter. The slurry of refined starch (40% solids) is centrifuged or vacuum-filtered to produce a cake that is dried in belt or flash driers and milled; or is pumped into tanks for various modifications; or is pumped through jet cookers for various conversions.

A typical composition of commercial common corn starch is starch 88%, moisture 11%, protein 0.35%, ash 0.1%, lipid 0.87%, and crude fiber 0.1%. A typical yield distribution of products obtained from the wet-milling process is starch of 11% moisture (74% yield), corn gluten feed of 21% protein (27%), corn gluten meal of 60% protein (6%), and corn oil (4%). Corn gluten feed and meal are used as animal feed. *See* ANIMAL FEEDS.

While by far the majority of the corn subjected to wet milling is common corn, waxy maize (less than 1% apparent amylose) and high-amylose corn (class V around 55% apparent amylose, and class VII around 73% apparent amylose) are grown under contract for wet millers and used for specialty starch production.

Corn starch. The United States produces almost 60% of the world's starch. Since corn is the source of more than 90% of the starch produced in the United States and starch is also produced from corn in other countries, by far the primary source of starch is corn. The world production of starch was around 40 million tons (36 million metric tons) in 1996, with 80% coming from corn. A large proportion (80–85%) of this starch is converted into other products such as sweeteners. Some is hydrolyzed to D-glucose which is used as the carbon source in fermentation to produce ethanol, a fuel additive; one-third of the starch produced by wet-milling of corn in the United States in 1997 was used to produce fuel ethanol. *See* ALCOHOL FUEL; ETHYL ALCOHOL; STARCH.

Not only does the source of starch vary from country to country, so does the ratio of products going to the various end uses. In the United States the starch of commerce is predominantly corn starch, and the primary market for corn starch, other than for the production of sweeteners and ethanol, is in the paper industry. Manufacture of paper, paper board, and corrugated board products consumes about 60% of the starch produced in the United States. About 20% of the starch is used in prepared foods. Approximately 20% of corn starch products are used as a textile size, in building materials, and in various other consumer and industrial products. The great majority of all corn starch used in any of these applications is first modified by etherification, esterification, acid-catalyzed depolymerization, oxidation, or a physical process (**Fig. 7**). It is not uncommon for a starch product to have been doubly, triply, or quadruply modified to

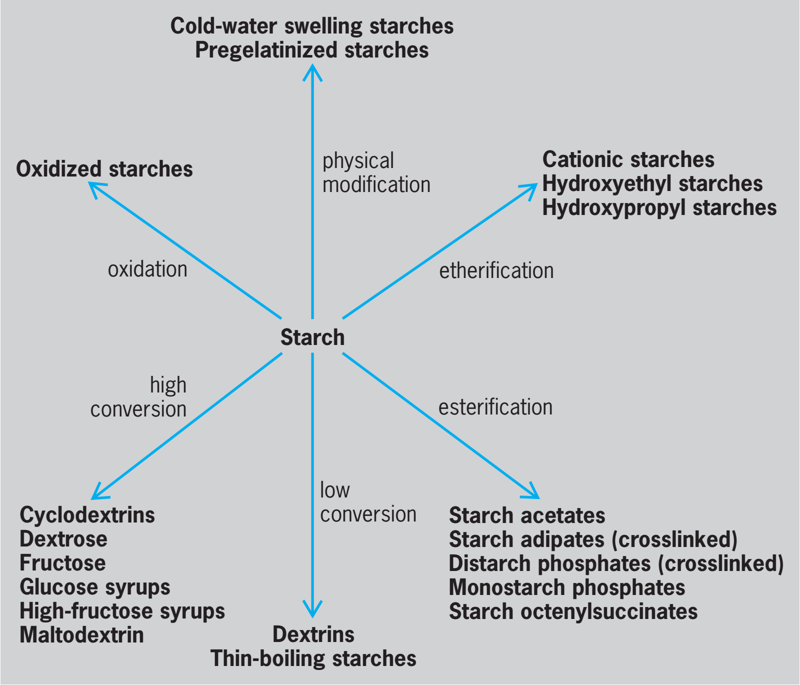

Fig. 7. Starch modification.

give it more desirable attributes for a particular application. Most modified food starch products made in the United States are based on waxy maize starch. For other corn starch products, the base starch is common corn starch.

Sweeteners. Worldwide, the production of nutritive sweeteners is the largest use for the starch obtained from corn. Residents of the United States consume more sweetener derived from corn than they do sucrose (sugar). *See* SUGAR.

Sweeteners can be made from any starch and are essentially identical regardless of which starch is used as the raw material, but in the United States all such products are made from corn starch and are often referred to as refinery products. The manufacture of corn sweeteners begins with the wet milling process. The starch, obtained as a slurry of granules in water, is first cooked, or pasted (**Fig. 8**). Then, the starch polymers are hydrolyzed (depolymerized) to the desired extent using an acid, an enzyme, a combination of enzymes, or an acid-enzyme combination. In all-enzyme conversion processes (the most commonly used), the starch paste is first rapidly thinned with an alpha-amylase (liquefying enzyme), then treated with one or more so-called saccharifying enzymes to convert partially degraded polymers into lower-molecular-weight carbohydrates—for example, to make high-glucose or high-maltose products, that is, solutions containing primarily D-glucose or maltose, respectively. The resulting solutions are refined and concentrated to 70–80% solids. These syrups, of whatever composition, are known worldwide as glucose syrups, but in the United States are often called corn syrups.

The syrups and all other breakdown products of starch are characterized by a value known as dextrose equivalency (DE). The DE value of a hydrolysis product is its reducing power expressed as a percentage of the reducing power of pure dextrose (D-glucose) and is inversely proportional to its

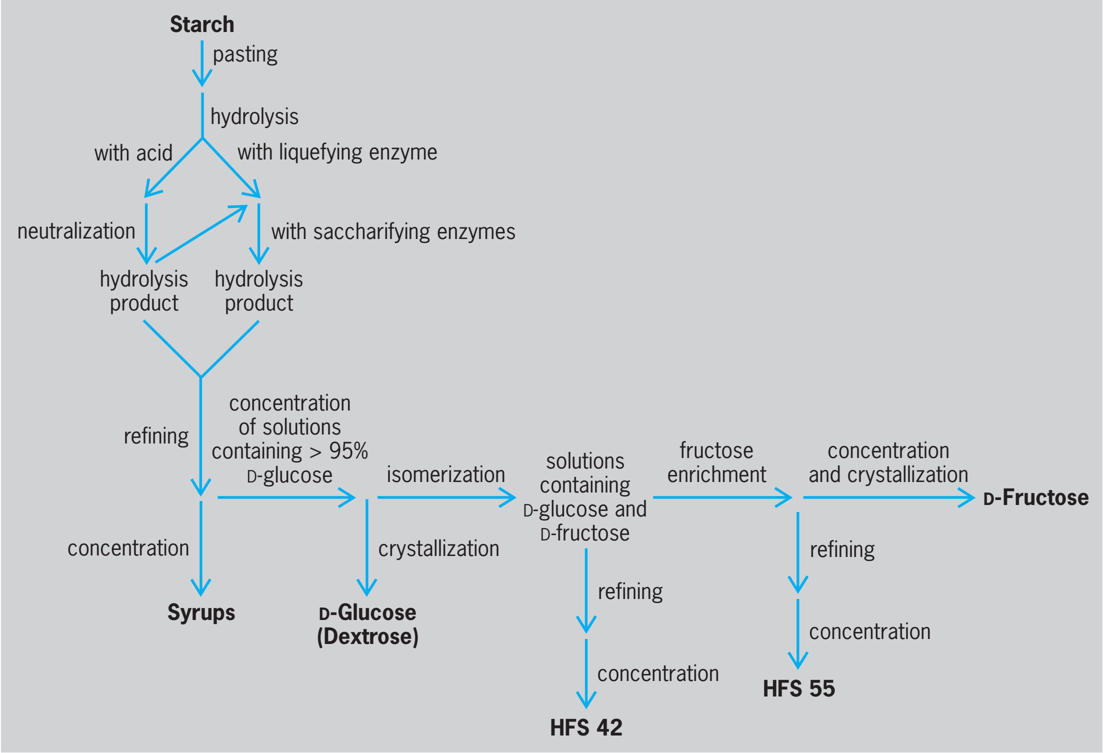

Fig. 8. Sweetener manufacture from starch.

average molecular size. Starch has a DE value of 0, while a solution of D-glucose has a DE value of 100. (Glucose and dextrose are interchangeable terms for the same substance, with D-glucose being the formal chemical name and dextrose being a term of commerce. Commercial products which contain less than 98% of the substance are usually referred to as glucose syrups, and the pure crystalline material is usually called dextrose.) Liquid solutions of nutritive saccharides obtained from starch (glucose syrups) have DE values of 20 or more. Their degree of sweetness is a function of the types and amounts of saccharides they contain. The degree of hydrolysis, that is, the composition of the hydrolyzate, also determines viscosity, fermentability, flavor enhancement, and freezing-point depression.

Glucose syrups are used in a wide variety of products. Besides having different sweetness levels, the functionalities they impart vary with saccharide composition. They may provide body (viscosity) or desirable mouthfeel to certain liquid products such as pancake and waffle syrups and certain beverages. They bind and hold water, providing desirable texture and mouthfeel to other products; for example, a 65 DE syrup is often used in soft cookies to help retain chewiness. Glucose syrups may also be used in bakery products to generate crust color and flavor or to provide texture to reduced-fat products without making them too sweet. They are often used in icings and glazes. A major use can be in candy manufacture, but relative amounts used in various applications vary from country to country. In addition to food uses, glucose syrups are a feedstock for fermentation processes that produce ethanol and other alcohols, vitamins, amino acid feed supplements, citric acids, and antibiotics. High-glucose syrups are hydrogenated to produce the polyol sorbitol; high-maltose syrups are hydrogenated to produce the polyol maltitol; and other syrups are used to produce hydrogenated starch hydrolyzates.

When starch is completely hydrolyzed, that is, converted into its monomer units, the only product is D-glucose (dextrose), which can be crystallized from concentrated solutions. Crystalline dextrose is produced in several different forms. It is about 60% as sweet as sucrose and has limited food applications. Dextrose monohydrate absorbs heat as it dissolves, so it imparts a cooling sensation when used in a sugar coating, and is used in donut glazes and sandwich cookie and sugar wafer fillings. It is used to make polydextrose, a food bulking agent and dietary fiber with reduced caloric value. Dextrose is used in preparing solutions for intravenous injection and for renal dialysis, in tableting, and in oral medications.

Isomerization of some of the D-glucose in a high-glucose hydrolyzate to D-fructose produces high-fructose corn syrups (HFCS), which are known simply as high-fructose syrups (HFS) outside the United States. Fructose is approximately 20% sweeter than sucrose on an equal weight basis. Converting some of the D-glucose to D-fructose makes a product similar to invert sugar, which is the 50:50 mixture of glucose and fructose made by hydrolysis of sucrose and is sweeter than sucrose. Two major products are HFCS 42 and HFCS 55, which contain, respectively, 42% and 55% fructose. HFCS is the sweetener for almost all soft drinks made in the United States that do not use a high-intensity sweetener. Most of the HFCS in colas is HFCS 55, which is made by enriching HFCS 42 with fructose. Many fruit-flavored drinks use HFCS 42. HFCS 42 is also used in most commercially produced yeast-raised breads, rolls, and cakes. The sugars in HFCS are fermentable. When HFCS is used in breadmaking, for example, yeast preferentially ferments glucose, leaving a higher percentage of fructose and the desired slight sweetness. HFCS is used in ice creams, frozen desserts, yogurt, chocolate milk, and other dairy products. It is blended with sucrose and a glucose syrup for use in fruit canning. The world production of high-fructose syrups was 12.5 million tons (11.3 million metric tons) in 1998–1999, with three-fourths of that amount (9.5 million tons or 8.6 million metric tons) being produced in the United States.

Crystalline (pure) fructose provides a rapid but short sweet taste, allowing other flavors to be sensed. For this reason, it is used in some fruit and fruit-flavored products such as jams, jellies, drinks, and sorbets.

Other starch conversion products. Corn starch is less extensively depolymerized to make products other than sweeteners. Very slight hydrolysis makes products known as acid-modified or thin-boiling starches. These products are still granular but cook more easily than the native starch. Their primary use is as film formers and adhesives; they also form gels with increased clarity and strength. A little more modification with an acid produces dextrins. Dextrins have some degree of cold-water solubility and generally have the same applications as thin-boiling starches. One application is as remoistenable adhesives on envelopes.

Hydrolysis catalyzed by acid or enzymes to DE values less than 20 produces starch oligomers, which are known as maltooligosaccharides or maltodextrins. Maltodextrins are easily dispersible and rapidly soluble, form films, have low hygroscopicity, and are generally bland, although some have slight sweetness. They are used extensively in foods for their bulking and binding properties and the protection they give to frozen foods. Special maltodextrins have properties that make them useful as fat replacers or sparers. Hydrolysis to DE 20–60 gives mixtures of breakdown products that, when dried, are known as corn syrup solids. Corn syrup solids dissolve rapidly, are mildly sweet, and are used as bulking materials in food.

Any one and often mixtures of the sweetener and other starch conversion products—that is, mixtures of dextrose, fructose, glucose or corn syrups, corn syrup solids, maltodextrins, hydrogenated sugars or syrups, and polydextrose—may be used to prepare functional, isotonic and oral rehydration beverages, enteral and parenteral fluids, infant formulas, and adult diet supplements.

TABLE 3. Typical compositions of products of corn dry milling in percent

Product	Mesh size	Moisture	Protein	Lipid	Crude fiber	Ash	Starch	Other polysaccharides
Coarse grits	−10 to +15	11.5	7.5	0.7	0.2	0.3	78	1.8
Regular grits	−15 to +30	11.5	7.5	0.7	0.2	0.3	78	1.8
Flaking grits	−3.5 to +6	11.7	7.0	0.6	0.2	0.2	78	2.0
Corn flour	−60 to +325	13.0	5.2	2.0	0.5	0.4	76	2.5

Dry milling. The amount of corn dry-milled in the United States in 1997 was 1.45% of the produced crop. Most of the processing is done by tempering-degerming systems. Corn, usually No. 2 yellow dent, but also white and other corns, is cleaned to remove metal, fines, pieces of cob, and broken corn. The whole kernels are then washed. Cleaned kernels are transferred to a tempering bin, where they are held for various times at various temperatures depending on the miller and the desired product. Tempered kernels at 20% moisture are passed through a degerminator, which removes the bran (pericarp) and germ while leaving the endosperm intact. But some bran and germ remain and must be removed by subsequent milling and aspiration; some endosperm remaining associated with the germ + bran fractions is also subsequently obtained.

Large pieces of endosperm, known as tail hominy, are dried, cooled, and sifted. Part of this fraction is isolated as large flaking grits which are used to make corn flakes breakfast cereal. The remainder is sent through roller mills for reduction to smaller fractions (coarse, medium, and fine grits; meals; flours).

The bran + germ fraction is dried, cooled, and aspirated to remove the bran. Corn oil is obtained from the germ by expelling or hexane extraction. The residue is the germ cake. Fines from the bran + germ fraction, the germ cake, the bran, and broken corn are combined, dried, and milled to produce hominy feed, the main by-product.

The endosperm may be converted into as many as 16 different fractions. The main products are regular grits, coarse grits, flaking grits, and corn flour (**Table 3**). Other products are corn cones and corn meal, −40 to +80 and −30 to +60 Standard U.S. mesh, respectively.

Nixtamalization. Nixtamalization is the process of cooking and soaking corn kernels in water containing calcium hydroxide (lime) to soften the pericarp and hydrate the protein matrix and starch of the endosperm. Subsequent washing removes leached solubles and excess lime. The cooked, steeped product, called nixtamal, is then ground, using stone attrition mills. The product, masa, is sheeted, cut into pieces, and baked, producing tortillas, tortilla chips, taco shells, and corn chips. The temperature, and particularly the time of each step, is varied depending on the desired product. The general process is as follows. Yellow, white, or blue corn (700 lb or 320 kg; alone or in mixtures) is cooked (200–212°F or 95–100°C) for around 4 to more than 30 min under alkaline conditions produced by adding 7 lb (3.2 kg) of powdered lime (calcium hydroxide; 1% based on the weight of corn) to 110 gal (415 liters) of water. Cooking is stopped by adding unheated water to drop the temperature to 150°F (65°C) or below. The corn kernels are then usually steeped for 8–16 h in this solution at about 105–115°F (40–45°C). Rotating drums equipped with pressurized water sprayers are used to wash the swollen kernels and remove the pericarp, lime, and solubles. The washed nixtamal is then ground in attrition mills with one stationary and one rotating stone to form masa. Subsequent processes vary, depending on the product desired. Masa may be dried for later tortilla making. *See* FOOD ENGINEERING; FOOD MANUFACTURING.

James N. BeMiller

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Cornales

An order of flowering plants, division Magnoliophyta (Angiospermae), in the superordinal Asteridae group of Eudicotyledon. The order consists of 5 families (Cornaceae, Grubbiaceae, Hydrangeaceae, Hydrostachyaceae, and Loasaceae), approximately 50 genera, and about 600 species. The members of the order show dramatic differences in habitat, ranging from temperate and tropical trees, to herbaceous perennials (Loasaceae), to submerged aquatics (Hydrostachyaceae). The order is mostly characterized by opposite leaves and flowers with four or five perianth parts that usually grow from the top of the ovary (epigynous) (see **illus.**). The fruit is either a fleshy berry or dehiscent capsule. The various species of dogwoods (*Cornus*) and sour gum (*Nyssa sylvatica*, family Cornaceae) are well known. Various species of Hydrangeaceae (deutzia, hydrangea, mock-orange)

Bunchberry or dwarf colonel (*Cornus canadensis*), a common dwarf, woody plant of the boreal forest of North America. (*a*) Four, large, white bracts surround the cluster of small flowers. (*b*) Each flower produces a red berry at maturity. (*Ken Sytsma, University of Wisconsin*)

are important cultivated shrubs. *See* ASTERIDAE; DOGWOOD; PLANT KINGDOM; TUPELO. K. J. Sytsma

Corner reflector antenna

A directional antenna consisting of the combination of a reflector comprising two conducting planes forming a dihedral angle and a driven radiator or dipole which usually is in the bisecting plane. It is widely used both singly and in arrays, gives good gain in comparison with cost, and covers a relatively wide band of frequency. Corner reflector antennas are used in very high-frequency (VHF) and ultrahigh-frequency (UHF) communications systems, telemetry systems, and electronic intelligence gathering systems.

The **illustration** shows the general configuration for a 90° corner reflector. The distance S from the driven radiator D to edge E need not be critically chosen with respect to wavelength; for a 90° reflector D may lie between 0.25 and 0.7 wavelength. The overall dimensions of the reflector need not exceed 2 wavelengths in order to approximate the performance obtained with very large reflectors. Gain, as compared with an isotropic radiator, is about 12 dB.

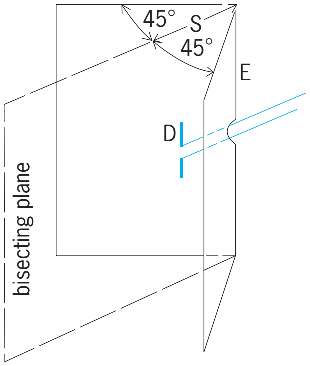

Diagram of corner reflector antenna.

The reflecting planes may be metal sheets or parallel wires separated by a small fraction of a wavelength and extending in the direction of current flow. *See* ANTENNA (ELECTROMAGNETISM). J. C. Schelleng

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Corona discharge

A type of electrical conduction that generally occurs at or near atmospheric pressure in gases. A relatively strong electric field is needed. External manifestations are the emission of light and a hissing sound. The particular characteristics of the discharge are determined by the shape of the electrodes, the polarity, the size of the gap, and the gas or gas mixture.

In some cases corona discharge may be desirable and useful, whereas in others it is harmful and attempts are made to minimize it. The effect is used for voltage division and control in direct-current nuclear particle accelerators. On the other hand, the corona discharge that surrounds a high-potential power transmission line represents a power loss and limits the maximum potential which can be used. Because the power loss due to i^2r heating decreases as the potential difference is increased, it is desirable to use maximum possible voltage.

The shape of the electrodes has a very profound effect on the potential current characteristic. If the radius of curvature of the positive electrode is small compared to the gap between electrodes, the transition from the dark current region to the field-sustained discharge will be quite smooth. The effect here is to enable the free electrons to ionize by collision in the high field surrounding this electrode. One electron can produce an avalanche in such a field, because each ionization event releases an additional

Breakdown streamers in positive-point corona crossing from positive point to cathode below. (*From L. B. Loeb, Fundamental Processes of Electrical Discharge in Gases, Wiley, 1939*)

electron, which can then make further ionization. To sustain the discharge, it is necessary to collect the positive ions and to produce the primary electrons far enough from the positive electrode to permit the avalanche to develop. The positive ions are collected at the negative electrode, and it is their low mobility that limits the current in the discharge. The primary electrons are thought to be produced by photoionization (see **illus.**). For a discussion of ionic mobility *see* ELECTRICAL CONDUCTION IN GASES; DARK CURRENT.

The situation at the negative electrode is quite important. The efficiency for ionization by positive ions is much less than for electrons of the same energy. Most of the ionization occurs as the result of secondary electrons released at the negative electrode by positive-ion bombardment. These electrons produce ionization as they move from the strong field at the electrode out into the weak field. This, however, leaves a positive-ion space charge, which slows down the incoming ions. This has the effect of diminishing the secondary electron yield. Because the positive ion mobility is low, there is a time lag before the high field conditions can be restored. For that reason the discharge is somewhat unstable.

From the preceding it may be seen that the electrode shape is important. The dependence on the gas mixture is difficult to evaluate. Electronegative components will tend to reduce the current at a given voltage, because heavy negative ions have a low mobility and are inefficient ionization agents. The excess electron will not be tightly bound, however, and may be released in a collision. The overall effect is to reduce the number of electrons that can start avalanches near the positive electrode. Further, if a gas with low-lying energy states is present, the free electrons can lose energy in inelastic collisions. Thus it is more difficult for the electrons to acquire enough energy to ionize. In electrostatic high-voltage generators in pressurized tanks, it is quite common to use Freon and nitrogen to take advantage of this effect to reduce corona. In a pure monatomic gas such as argon, corona occurs at relatively low values of voltage.

In the potential current characteristic, the corona region is found above the dark current region and is field-sustained. Near the upper end it goes into either a glow discharge or a brush discharge, depending on the pressure. Higher pressure favors the brush discharge. *See* GLOW DISCHARGE.

For still higher potential difference, breakdown takes place and a continuously ionized path is formed. *See* ELECTRIC SPARK. **Glenn H. Miller**

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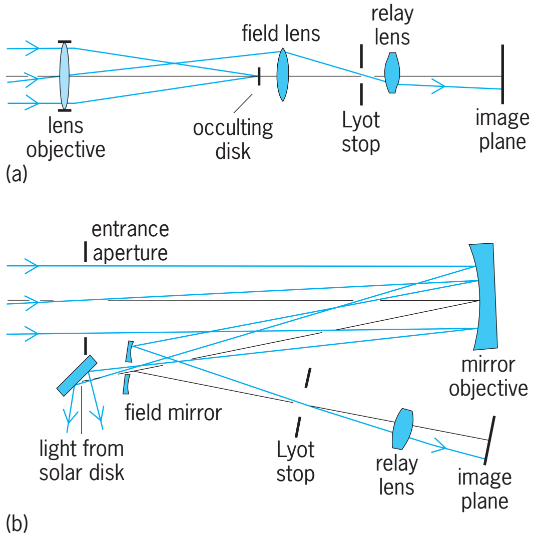
Coronagraph

A specialized astronomical telescope substantially free from instrumentally scattered light, used to observe the solar corona, the faint atmosphere surrounding the Sun. Coronagraphs can record the emission component of the corona (spectral lines emitted by high-temperature ions surrounding the Sun) and the white-light component (solar photospheric light



Basic designs of coronagraphs. (*a*) Lyot coronagraph with lens objective. (*b*) Reflecting coronagraph.

scattered by free electrons surrounding the Sun) routinely from high mountain sites under clear sky conditions. The emission and white-light components are typically only a few millionths the brightness of the Sun itself. Hence, the corona is difficult to observe unless the direct solar light is completely rejected, and unless instrumentally diffracted and scattered light that reaches the final image plane of the coronagraph is small relative to the coronal light. *See* SOLAR CORONA; SUN.

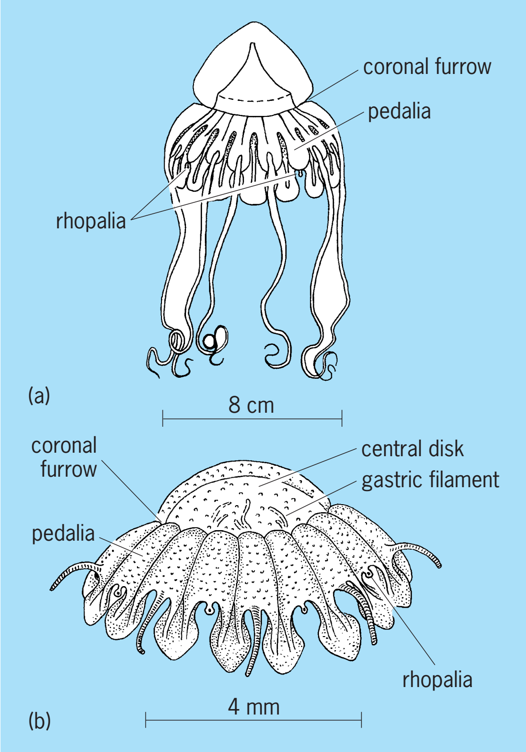
The basic design (**illus.** *a*), as invented by B. Lyot, has an occulting disk in the primary image plane of the telescope to block the image of the Sun itself. In addition, the primary objective (a lens or superpolished mirror) is specially fabricated to minimize scattered light. Also, light diffracted by the objective rim must be suppressed. For this, an aperture (Lyot stop) is placed at an image of the objective as produced by a field lens, with the aperture diameter slightly smaller than that of the objective image. A relay lens behind the Lyot stop forms the coronal image at the final image plane.

To observe the emission corona, optical filters or spectrographs are used to isolate the wavelengths corresponding to the various coronal emission lines and thus minimize the contribution due to the sky. To observe the white-light corona with ground-based coronagraphs, polarization subtraction techniques are required to discriminate the coronal electron-scattered light (polarized with the electric vector tangential to the limb) from the variably polarized sky background. Coronagraphs designed for operation on satellites usually have a circular mask out in front of the objective to completely shade it. This external occulting is more efficient in terms of instrumentally scattered light, when no sky background is present, than if only an internal occulting disk is used, but the inner corona is then vignetted, reducing the angular resolution in this region.

The development of superpolished mirror technology allowed the construction of coronagraphs based on mirror objectives, with significant advantages compared with the singlet-lens objectives used in traditional Lyot coronagraphs. For example, achromaticity allows high imaging quality independent of wavelength, simultaneous multiwavelength observations of the inner solar corona can be achieved, and large apertures are possible. In an off-axis design (illus. *b*), an annular field mirror is located at the image plane formed by the primary objective. The image of the solar disk passes through the hole in the annular mirror and is reflected out to the sky, while the field mirror reflects the coronal field to the lens system that forms the final image. A Lyot stop is located at the image of the entrance aperture, as formed by the field mirror. Raymond N. Smartt

Coronatae

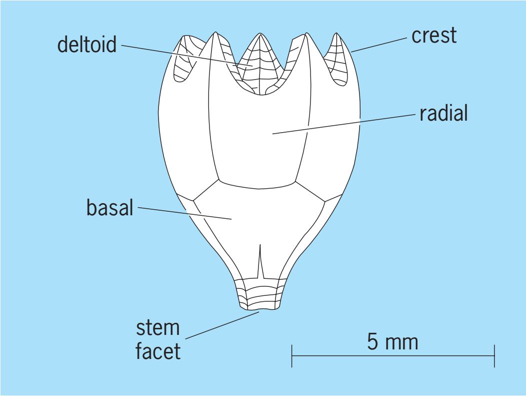
An order of the cnidarian class Scyphozoa which includes mainly abyssal species. The exumbrella is divided by a circular or coronal furrow into two parts, an upper central disk and a lower coronal part (see **illus.**). The central disk is usually domelike, but in *Periphylla* it often narrows toward the top. The coronal part has gelatinous thickenings, or pedalia, situated on the radii running from the center of the umbrella to the tentacles and the sensory organs. The pedalia are separated from one another by clefts, running down the radii, that are halfway between each tentacle and rhopalium (a sensory organ). The mouth has four lips. There are four groups of gastral filaments within the central stomach. Abyssal forms of this group are dark brown or reddish purple. The littoral species of *Nausithoë* is reported to show alternation of generations, but the life history of abyssal forms remains unknown. *See* SCYPHOZOA. Tohru Uchida



Coronatae. (*a*) *Periphylla*. (*b*) *Nausithoë*. (*After L. H. Hyman, The Invertebrates, vol. 1, McGraw-Hill, 1940*)

Coronoidea

A small class of “arm”- and brachiole-bearing, stemmed echinoderms in the subphylum Crinozoa, based on five genera known from the Middle Ordovician to Late Silurian of Europe and North America. Coronoids have a crested theca or body with well-developed pentameral symmetry and plate arrangement very similar to that found in blastoids (see **illus.**). Skeletal plates include three basals (two large and one smaller), five radials extending up to form the crests and bearing central notches for the ambulacra, five small plates supporting the arms, and four regular deltoids plus two anal deltoids in the fifth position around the mouth. The mouth is central on top of the theca and has five ambulacral



***Stephanocrinus gemmiformis*, Middle Silurian, Tennessee; side view of the theca.**

grooves radiating from it. A coiled arm is attached to a mounting plate at the end of each ambulacral groove; each arm has biserial plating with smaller biserial branches (=brachioles) on both sides. The projecting crests have internal canals that connected with the body cavity and apparently served as respiratory structures. A thin stem supported the theca above the sea floor, allowing coronoids to live as attached, low- to medium-level suspension feeders. Coronoids had previously been assigned to the blastoids, eocrinoids, or crinoids by different researchers, but they have been elevated in rank to a separate class. Coronoids appear to be most closely related to the Blastoidea and may have been the ancestors of this class. *See* BLASTOIDEA; ECHINODERMATA; EOCRINOIDEA.

James Sprinkle

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Correspondence principle

A fundamental hypothesis according to which classical mechanics can be understood as a limiting case of quantum mechanics; or conversely, many characteristic features in quantum mechanics can be approximated on the basis of classical mechanics, provided classical mechanics is properly reinterpreted. This idea was first proposed by N. Bohr in the early 1920s as a set of rules for understanding the spectra of simple atoms and molecules.

Bohr's formulations. In 1913 Bohr used classical mechanics to calculate the energy levels of the electron in the hydrogen atom, but this result could not be understood in the conventional manner. Although the electron presumably orbits the proton like a planet around the Sun, Bohr had to assume that its electric charge radiates (or absorbs) light only when it makes a transition from one energy level to another. The frequency ν of the light is always the difference between the two energy levels divided by Planck's constant h.

Bohr's original quantization rules are readily applied to the simplest spectra, in particular to the electrons of hydrogenlike atoms and ions, as well as the vibrations and rotations of small molecules. The classical motions in these simple dynamical systems can be understood as composed of independent partial motions, each with its own degree of freedom, like the motion of the electron toward and away from the nucleus, and its motion around the nucleus. Each degree of freedom accumulates its own classical action-integral. This is the integral defined by Eq. (1), calculated along a closed orbit in terms of

$$I = \int p\,dq \tag{1}$$

the position q and momentum p. The classical energy is a function of these action integrals. Every action I is then related to the quantum number n by the Bohr-Sommerfeld rule, given by Eq. (2). A complete

$$I = nh \tag{2}$$

classification of the spectrum in quantum mechanics is obtained in terms of the quantum numbers. *See* ACTION; ATOMIC STRUCTURE AND SPECTRA; DEGREE OF FREEDOM (MECHANICS); MOLECULAR STRUCTURE AND SPECTRA.

The frequency ν of the classical motion for any particular degree of freedom is given by the partial derivative of the energy function with respect to the corresponding action. Bohr noticed that this classical result yields the correct quantum-theoretical result for the light frequency in a transition from one energy level to another, say from $n + 1$ down to n, provided the derivative is replaced by the difference in the energies. Moreover, precise information about the possibility of such transitions and their intensities is obtained by analyzing the related classical motion. This information becomes better as the quantum numbers involved become larger. The apparent inconsistencies in Bohr's quantum theory are thereby overcome by a set of rules that came to be called the correspondence principle.

This approach to the interpretation of spectra turned out to be very useful to the experimenters. Moreover, in 1925 W. Heisenberg's program of replacing all classical derivatives systematically by the corresponding differences led to the new quantum mechanics, as opposed to the old quantum theory. The complete and overwhelming success of the new quantum mechanics, particularly the equivalent approach of E. Schrödinger (wave mechanics), reduced the correspondence principle to a somewhat vague article of faith among physicists.

Use in statistical mechanics. The appeal to classical mechanics is still convenient for some rather crude estimates such as the total number $N(E)$ of levels below a given energy E. As in statistical mechanics, $N(E)$ depends on the volume of phase space, wherein every point gives the complete information on the state of the dynamical system. The phase space of a system with f degrees of freedom has $2f$ dimensions: f for the position in ordinary space, and f for the momentum. If E is sufficiently large, $N(E)$ approaches the volume of phase space with energy less than E divided by h^f. This estimate helps in finding the approximate shape of large atoms and large nuclei in the Thomas-Fermi model; each particle experiences the average effect of all the others, and only the exclusion principle, not the wavelike nature of the particles, is invoked. *See* EXCLUSION PRINCIPLE; STATISTICAL MECHANICS.

Application to quantum chaos. The correspondence principle, however, has assumed a more profound significance. Experimental techniques in atomic, molecular, mesoscopic, and nuclear physics have improved dramatically. High-precision data for many thousands of energy levels are available where the traditional methods of quantum mechanics are not very useful or informative. However, the basic idea behind the correspondence principle must still be valid: Quantum mechanics must be understandable in terms of classical mechanics for the highly excited states, even in difficult cases like the three-body problem, where the classical motion cannot be resolved into independent partial motions. In these cases, two trajectories that started out at almost the same initial position and with almost the same initial momentum do not stay together in the long run, and their overall behavior seems unpredictable and chaotic.

The challenge of extracting quantum information from classical data is called the problem of quantum chaos. The structure of the trajectories in phase space is fractal; that is, the same patterns occur repeatedly as the scale is reduced. Quantum mechanics does not allow this kind of self-similarity because it describes atoms, objects that cannot be subdivided into ever smaller pieces, and electrons and nuclei are, therefore, represented by waves. Nevertheless, these waves follow the classical rays or trajectories very closely, and their amplitudes act like a bunch of classical particles. These "semiclassical" waves can be superimposed on one another, and thereby manifest all the interference phenomena that are typical of wave optics, and are the essence of quantum mechanics. They yield surprisingly good approximate numerical results as well as intuitive insight, where the standard methods yield only numerical results, often massive calculations. *See* FRACTALS; INTERFERENCE OF WAVES.

The wider application of Bohr's correspondence principle allows many basic but difficult problems to be seen in a new light. The spectra of the hydrogen atom in a strong magnetic field, of the helium atom when both electrons are excited, and of the donor impurity in a semiconductor, and the fluctuations in the electric conductivity for a mesoscopic device are all closely related to the structure of closed orbits in the corresponding classical problem. The statistical properties and the correlations among the energy levels, as well as the fluctuations in the scattering cross sections, for the more complicated nuclei are now understood in terms of the underlying chaos in their classical analogs. *See* CHAOS; MESOSCOPIC PHYSICS; NONRELATIVISTIC QUANTUM THEORY; QUANTUM MECHANICS.

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Corrosion

In broad terms, the interaction between a material and its environment that results in a degradation of the physical, mechanical, or even esthetic properties of that material. More specifically, corrosion is usually associated with the oxidation and/or dissolution of a metal, oxide, or semiconductor. For example, immersing a piece of iron in a moderately acidic solution is a typical example of corrosion; the vigorous reaction is the electrochemical oxidation of iron from the zero valence state to divalent ferrous ions (Fe^{+2}) dissolved in the water. Corrosion encompasses principles from diverse fields such as electrochemistry, metallurgy, physics, chemistry, and biology.

Economic impact. The cost of corrosion in the United States and other industrial countries has been estimated to be about 4% of the gross national product. This cost represents both the replacement of structures or components and the protection against corrosion. Such direct losses are relatively easy to assess in comparison to indirect losses, which include the cost of shutdown, loss of product or efficiency, contamination, and even loss of life. Another economic consideration is the source of corrosion-resistant metals. For example, chromium is considered to be of critical importance since it is responsible for the high-temperature oxidation resistance and aqueous corrosion resistance of a wide range of iron- and nickel-based alloys. Much of the chromium being used is considered irreplaceable. Since chromium ores occur primarily in South Africa and Russia, the Western industrialized nations often express concern regarding a perceived vulnerability in supply. *See* CHROMIUM.

Engineering systems for service environments require materials that are chemically stable or that can be made chemically stable. Moreover, modern technology continues to demand materials that can perform in increasingly hostile environments such as high-temperature coal gasification plants, deep sour-gas [natural gas containing hydrogen sulfide (H_2S)] wells, magnetohydrodynamic channels, and fusion reactors. Additionally, as engineering systems continue to evolve, they will use new or advanced materials. Thin-film electronic, magnetic, and optical devices will require special attention to corrosion issues. Likewise, it is necessary to deal with problems associated with traditional systems, such as the aging transportation infrastructure, underground tanks and pipelines, structures exposed to salt water, and conventional coal-burning power stations.

Thermodynamic stability of metals. Metals that are thermodynamically stable in their environment exhibit the best corrosion resistance, but only rarely are such metals of practical use. The stability of a metal in aqueous solutions can be assessed from data on the equilibrium potential that is established by an electrochemical reaction. The relationship between the equilibrium potential of a reaction and the activities of each species is determined by the Nernst equation. By convention, all electrochemical reactions are written in terms of reduction, reaction (1).

$$\mathrm{Fe}^{+2} + 2e^- \rightarrow \mathrm{Fe} \qquad (1)$$

The Nernst equation for these reactions is given in general terms by Eq. (2), where E is the equilibrium

$$E = E^\circ + \frac{2.303RT}{nF} \log \frac{\prod [a_O]^q}{\prod [a_R]^p} \qquad (2)$$

potential, E° is the equilibrium potential under standard conditions, $\Pi[a_R]^p$ and $\Pi[a_O]^q$ are the products of the activities of the reduced and oxidized species, respectively, where p and q are the coefficients for each term in the reaction; n is the number of moles of electrons transferred; F is Faraday's constant; R is the gas constant; and T is temperature. The activities are related to concentration, and in Eq. (2) a_R is the activity of the metal ions (for example, Fe^{2+}). The standard condition is unit activity, which means pure metals or 1 mole/liter for dissolved ions.

The standard reduction potentials for various reactions are given in the **table**. Also included are the standard potentials for the hydrogen evolution and oxygen reduction reactions. The equilibrium potential for the hydrogen evolution reaction at pH 0 is arbitrarily designated as zero volts, and all other potentials are referenced to this value.

This table can be used to predict the thermodynamic tendency of a metal to corrode by comparing the equilibrium potential of the metal dissolution reaction to that of a cathodic reaction. For example, comparing gold dissolution and oxygen reduction would lead to the conclusion that gold is thermodynamically stable under standard conditions. Alternatively, the equilibrium potential for iron (Fe^{2+}/Fe) is more negative than the equilibrium potentials for both cathodic reactions (oxygen evolution and hydrogen ion reduction); iron will, therefore, dissolve to form ferrous ions in solution. Copper has an equilibrium potential more positive than that of the hydrogen reaction and will dissolve only with oxygen reduction under standard conditions.

Standard reduction potentials* for various reactions

Metal	Electrode reaction	E°, V
Gold	$\mathrm{Au}^{3+} + 3e^- \rightarrow \mathrm{Au}$	1.50
Oxygen reduction	$\mathrm{O_2} + 2\mathrm{H_2O} + 4e^- \rightarrow 4\mathrm{OH}^-$	1.23
Copper	$\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu}$	0.34
Hydrogen evolution	$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H_2}$	0.00
Tin	$\mathrm{Sn}^{2+} + 2e^- \rightarrow \mathrm{Sn}$	−0.14
Nickel	$\mathrm{Ni}^{2+} + 2e^- \rightarrow \mathrm{Ni}$	−0.25
Iron	$\mathrm{Fe}^{2+} + 2e^- \rightarrow \mathrm{Fe}$	−0.44
Chromium	$\mathrm{Cr}^{3+} + 3e^- \rightarrow \mathrm{Cr}$	−0.74
Zinc	$\mathrm{Zn}^{2+} + 2e^- \rightarrow \mathrm{Zn}$	−0.76
Aluminum	$\mathrm{Al}^{3+} + 3e^- \rightarrow \mathrm{Al}$	−1.66

* $T = 25^\circ\mathrm{C}$ (77°F), $a = 1$ mol/liter.

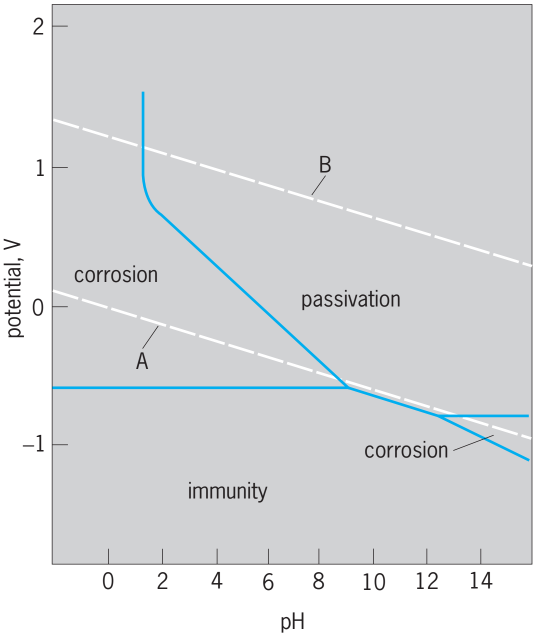

Fig. 1. Potential–pH diagram for the iron–water system: A = hydrogen equilibrium [see reaction (4)]; B = oxygen equilibrium [see reactions (5) and (6)]. (*After M. Pourbaix, ed., Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston, 1974*)

The pH–potential diagram is an alternative way of representing thermodynamic data that also accounts for the important variable pH. For example, **Fig. 1** shows a potential–pH diagram for the iron–water system at 25°C (77°F). Such diagrams are also known as Pourbaix diagrams. The lines on the diagram are derived from the application of the Nernst equation to reactions involving coexisting phases, both solids and dissolved species. Therefore, areas bounded by these lines represent regions of potential and pH values where the various species predominate. For application to corrosion, the activity of dissolved ions is taken (arbitrarily) as 10^{-6} mole/liter, a value small enough to represent very small, or trivial, corrosion. Also superimposed on the diagram are lines, A and B, representing the limit of stability of water. Therefore, from a consideration of the dominant reactions expected for given values of potential and pH, one can infer whether corrosion, thermodynamic stability (immunity), or passivation is likely. For example, in Fig. 1 in the region of stability of ferric [iron (III)] oxide ($\mathrm{Fe_2O_3}$), iron is protected from corrosion by a thin film of this oxide, a phenomenon known as passivation. In regions where the ferrous ions (Fe^{2+}) or other soluble species are stable, iron will corrode.

Similar diagrams have been compiled for a wide variety of metal-solution systems. However, it is noted that these diagrams allow only thermodynamic predictions and cannot predict the kinetics (rate) of a particular reaction. *See* ACTIVITY (THERMODYNAMICS); CHEMICAL THERMODYNAMICS.

Reactions. Electrolytic corrosion consists of two partial electrochemical reactions: anodic (oxidation) and cathodic (reduction) [**Fig. 2**]. For thermodynamic considerations (as in the table), the cathodic

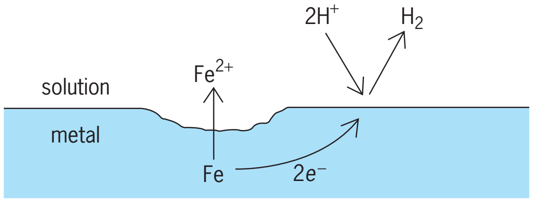

Fig. 2. Diagram of a corrosion cell showing the anodic and cathodic partial processes for a piece of iron in an acidic solution.

reaction is the reverse of the anodic reaction. However, in most aqueous corrosion situations, the anodic reaction is the dissolution of metal and the cathodic reaction is the reduction of a different species—for example, the reduction of dissolved oxygen or hydrogen ions. The loss of metal that is the usual manifestation of the corrosion process is a result of the anodic reaction (3), and the cathodic reaction could be reaction (4). Reaction (4) is often

$$\mathrm{Fe(S)} \rightarrow \mathrm{Fe}^{+2} + 2e^- \qquad (3)$$

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H_2(g)} \qquad (4)$$

the dominant cathodic reaction in systems at low pH. The hydrogen-evolution reaction can itself cause corrosion-related problems, since atomic hydrogen (H) can enter the metal, causing embrittlement, a phenomenon that results in the degradation of the mechanical properties and can cause catastrophic failure. *See* EMBRITTLEMENT.

At steady state, the rates of each reaction will be such that the electrons (e^-) produced by the oxidation reaction will be consumed by the reduction reaction. The anodic reaction can occur uniformly over a metal surface or can be localized to a specific area. If the dissolved metal ion can react with the solution to form an insoluble compound, a buildup of corrosion products can accumulate at the anodic site. *See* OXIDATION-REDUCTION.

The second important cathodic reaction is the oxygen reduction, given by reactions (5) and (6). These

$$\mathrm{O_{2(dissolved)}} + 4\mathrm{H}^+ + 4e^- \rightarrow 2\mathrm{H_2O} \qquad (5)$$

$$\mathrm{O_{2(dissolved)}} + 2\mathrm{H_2O} + 4e^- \rightarrow 4\mathrm{OH}^- \qquad (6)$$

represent typical reactions in acidic and alkaline solutions, respectively. Equation (6) is usually dominant in solutions of neutral and alkaline pH. In order for this reaction to proceed, a supply of dissolved oxygen is necessary; hence, the rate of this reaction is sometimes limited by the transport of oxygen to the metal surface.

Equations (4), (5), and (6), in practice, can occur by a sequence of reaction steps. In addition, the reaction sequence can be dependent upon the metal surface, resulting in significantly different rates of the overall reaction on different metals. The cathodic reactions are important to corrosion processes since many methods of corrosion control depend on altering the cathodic process. Although the cathodic reactions can be related to corrosion processes, which are usually unwanted, they are essential for many applications such as energy storage and generation.

Rate of corrosion. Corrosion rates can be expressed in several different ways, reflecting the method of measurement. Loss of thickness per unit time [for example, mils (1/1000 in.) per year (MPY)], is commonly used in published data tables, but equivalent corrosion rates can be expressed as weight change per unit area–time (mg/cm^2-day) or as a current density (amperes per unit area). For many applications, 1–5 MPY is considered excellent corrosion resistance. General (uniform) corrosion rates can vary from centimeters per year [for example, iron in sulfuric acid (H_2SO_4)] to micrometers per year. Relatively large corrosion rates can be tolerated for some large structures, whereas for other structures small amounts of corrosion can result in catastrophic failure. For example, with the advent of technology for making extremely small devices, future generations of integrated circuits will contain components that are nanometers (10^{-9} m) in size, and even small amounts of corrosion could cause device failure. For medical devices implanted in the body, one meaningful measure of corrosion reflects the release rate of certain corrosion products into the body, such as milligrams of Ni^{2+} (from stainless steel) per unit area of device per day. The limitation on corrosion due to toxicity might be much more stringent than limitations based on structural damage.

Passivation. Many metals and alloys that exhibit a thermodynamic tendency to corrode actually have remarkable corrosion resistance in many environments due to the formation of a passive film. Passivation is the formation of a thin protective oxide on the surface of a metal. Passive films are usually less than 10 nm thick, but are highly stable and can prevent severe corrosion of the underlying metal. Stainless steels, such as Fe, 18% Cr, 8% Ni, form a highly stable, thin chromium oxide layer. This is the main reason for the widespread application of stainless steels in industry as corrosion-resistant alloys. Likewise, Al_2O_3 passive films protect aluminum alloys in solutions that are not extremely acidic or basic.

The electrochemical characteristics of a metal or alloy usually are measured by a combination of experimental techniques of which the current density–potential behavior is the most common. **Figure 3** shows a current density–potential diagram for AISI (American Iron and Steel Institute) 304 stainless steel (18–20% Cr, 8.0–10.5% Ni, <0.08% C) in 1 N H_2SO_4 solution at 25°C (77°F). The current density is often plotted on a logarithmic scale, as in this figure, due to the exponential relationship between current density and potential for many electrochemical reactions. In Fig. 3, it can be seen that the open-circuit potential, or corrosion potential, is about −0.38 V; and as the potential is increased, the current density increases rapidly to a maximum. At this point, a stable passive film is formed on the surface, and increasing the potential further results in a decrease in current density to a low value. At more positive

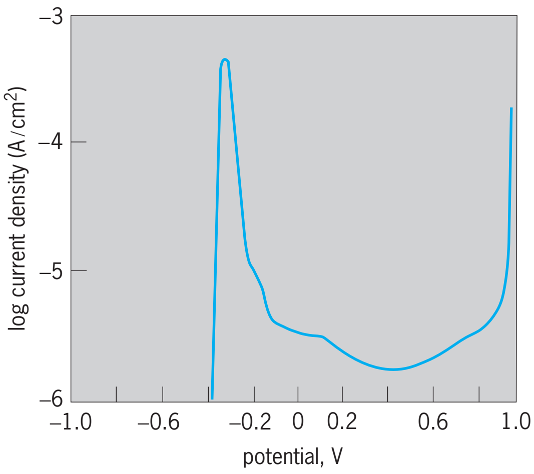

Fig. 3. Current–potential diagram for AISI 304 stainless steel in sulfuric acid (1 *N* H_2SO_4), $T = 25°C$ (77°F), scan rate = 0.3 mV/s.

potentials, the current density increases again at about 1 V because of oxygen evolution from the surface. This plot is typical for alloys that exhibit passivation over a range of potential in a given solution.

The continuous stability of the passive film is critical for most corrosion-resistance applications. A passive film can become unstable in an environment in which it can dissolve chemically or in the presence of certain aggressive anions. Halide ions, and in particular chloride ions, are the most common species that can cause passive film breakdown, and consequently many types of corrosion problems are related to exposure to seawater or other chloride-containing environments. This type of corrosion attack usually is characterized by localized breakdown of the film. For many common engineering alloys, the sites of localized attack usually are related to inhomogeneities such as precipitates or secondary phases.

Types. In some situations, corrosion can occur only at localized regions on a metal surface. This type of corrosion is characterized by regions of locally severe corrosion, although the general loss of thickness can be relatively small. Common types of localized corrosion are pitting corrosion and crevice corrosion. Other types of localized corrosion include galvanic corrosion, stress corrosion cracking, and hydrogen embrittlement.

Pitting. This type of corrosion is usually associated with passive alloys, although this is not always the case. Pit initiation is usually related to the local breakdown of a passive film, and pitting is often related to the presence of halide ions in solution (**Fig. 4**). The local environment within a pit can become extremely acidic, resulting in a high rate of corrosion within this small region. For the common situation of a metal in salt water, the dissolution of metal within the pit results in the formation of metal chlorides. When sufficiently concentrated, these salts react with water (hydrolyze) to form hydrochloric acid (HCl) within the pit, as shown in reaction (7).

$$Fe^{+2} + 2Cl^- + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2Cl^- \qquad (7)$$

The decrease in pH within the pit caused by acid formation further increases the rate of metal dissolution, and such self-accelerating reactions are often called autocatalytic.

Crevice corrosion. This type of corrosion occurs in restricted or occluded regions, such as at a bolted joint, and are often associated with solutions that contain halide ions (**Fig. 5**). Crevice corrosion is initiated by a depletion of the dissolved oxygen in the restricted region. For this situation to occur, the dimension of the restricted region is typically less than 1 mm. As the supply of oxygen within the crevice is depleted, cathodic oxygen reduction from the region adjacent to the crevice takes over, allowing the anodic current on the interior metal surface to continue. The ensuing reactions within the crevice are the same as those described for pitting corrosion; that is, halide ions migrate to the crevice, where they are then hydrolyzed to form metal hydroxides and hydrochloric acid. In neutral salt solutions, the pH within a crevice can fall to a value as low as 2.

Galvanic coupling. Corrosion can also be accelerated in situations where two dissimilar alloys are in electrical contact with each other and with the same solution. This form of corrosion is known as galvanic corrosion. Because the two alloys have different corrosion potentials, a voltage difference arises which drives the anodic reaction on one alloy and the cathodic reaction on the other. The possibility of galvanic corrosion and the identification of the alloy that will become the anode (and hence will experience accelerated corrosion rates) can best be determined from a galvanic series, which is a table of corrosion potentials in a particular solution. The alloy with the more negative potential becomes the anode, while the alloy with the more positive potential sustains the cathodic reaction. For example, a copper water pipe connected to a steel water pipe constitutes a galvanic couple, with the water

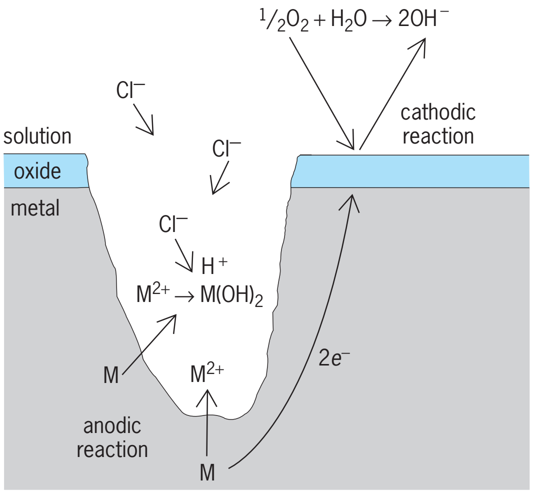

Fig. 4. Diagram of pitting corrosion. The diffusion of chloride ions into the pit to maintain electroneutrality is followed by hydrolysis of metal chlorides, resulting in the formation of hydrochloric acid (HCl).

inside acting as the corroding solution. The steel pipe (anode) will corrode rapidly at locations close to the copper/steel joint. A useful example of galvanic corrosion is the application of a zinc coating to steel (galvanized steel). Zinc has the more negative corrosion potential, so it selectively corrodes, protecting the steel (**Fig. 6**). Another example is the use of magnesium alloy anodes to protect steel ships and steel underground pipelines from corrosion.

Stress corrosion cracking. Stress corrosion cracking (SCC) and hydrogen embrittlement are corrosion-related phenomena associated with the presence of a tensile stress. Stress corrosion cracking results from a combination of stress and specific environmental conditions so that localized corrosion initiates cracks that propagate in the presence of the tensile (stretching) stress. Stress corrosion cracking is particularly dangerous because alloys that normally are quite ductile, and that are used at normally safe design stresses, can fail suddenly without warning by brittle fracture. There are many examples of the specificity of the combination of alloy/environment leading to stress corrosion cracking. For example, mild steels are susceptible to stress corrosion cracking in strongly basic environments (often called caustic cracking). Austenitic stainless steels are susceptible in the presence of chloride ions (Cl^-) and hydroxyl ions (OH^-). For example, in the medical device field stainless-steel implants used to mechanically support broken or diseased bones have been known to fail by stress corrosion cracking, because the environment is a warm, low-oxygen, high-chloride solution. Other alloys that are susceptible under specific conditions include certain brass, aluminum, and titanium alloys.

Hydrogen embrittlement is caused by the entry of hydrogen atoms into a metal or alloy, resulting in a loss of ductility and cracking promotion if the stress is sufficiently high. The source of the hydrogen is usually from corrosion (that is, cathodic hydrogen evolution) or from cathodic protection. Metals and alloys that are susceptible to hydrogen embrittlement include certain carbon steels, high-strength steels, nickel-based alloys, titanium alloys, and some aluminum alloys. *See* ALLOY; STAINLESS STEEL; STEEL.

Other types. Corrosion can be stimulated by biological organisms (such as microbially induced corrosion in soil and pitting induced corrosion beneath barnacles in seawater), where the local chemistry at the metal surface is altered by secretions from the organisms. Contaminants in the air also can accelerate corrosion rates. For example, sulfate particles or acidic droplets (acid rain) accelerate the corrosion of outdoor structures. Dust particles indoors have been shown to corrode unprotected microelectronic circuit boards. *See* ACID RAIN.

Control. In general, the resolution of a corrosion problem starts with the identification of the predominant type of corrosion and a determination of an acceptable design lifetime. Many corrosion problems can be solved simply by modifying the solution composition (pH control) or by selecting a more resistant alloy composition (stainless steel versus mild steel) to achieve a lower rate of corrosion. If large reductions in the rate of corrosion are needed, a useful approach is to separate the aqueous solution from the metal surface with a barrier, for example, using a passivated alloy (stainless steel), applying an overlayer (chrome plating), or adding an inhibitor to the solution. Inhibitors operate by controlling the metal/solution interface. Inorganic salts, such as chromates (CrO_4^{2-}), nitrites (NO_2^-), and phosphates (PO_4^{3-}), either form a barrierlike layer by reacting with the metal surface or stimulate film formation. Organic inhibitors are generally long-chain polar molecules with nitrogen, sulfur, oxygen, or

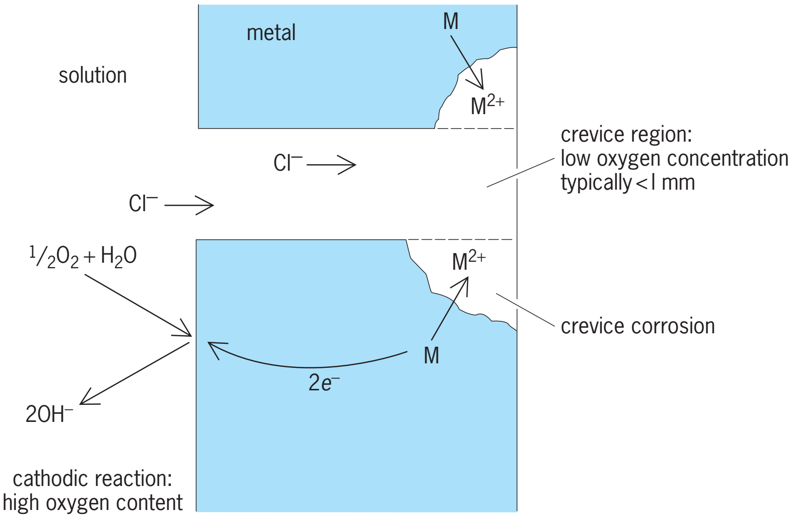

Fig. 5. Diagram of crevice corrosion, showing the mechanisms involved.

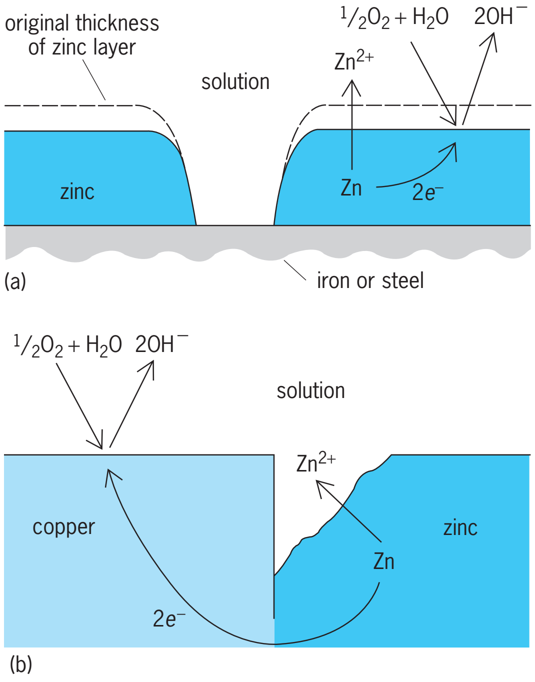

Fig. 6. Reactions of dissimilar metals in contact in the same solution. (*a*) Iron or steel protected from corrosion by a galvanic zinc coating. (*b*) Galvanic corrosion.

hydroxyl groups that strongly chemisorb to the metal surface and thereby separate metal and solution. For some specialized applications, such as protecting parts while they are being stored or shipped, adding a vapor-phase inhibitor to the package can be effective. *See* INHIBITOR (CHEMISTRY); METAL COATINGS.

A different approach is needed for pitting and crevice corrosion problems. Modifying the alloy's surface by cleaning or polishing or by adding a coating may help reduce or avoid the initiation of pits. Crevice corrosion usually can be avoided by redesigning to avoid crevices (for example, joining by welding instead of bolts) or by applying a watertight gasket to the joints. Galvanic corrosion problems can be avoided by choosing alloys with similar corrosion potentials or, if the design allows, by electrically isolating the parts. Designing to avoid stress concentrations (fair out corners) and removing residual stresses that arise from welding can reduce the risk of stress corrosion cracking.

In practice, the application of the above principles often is complicated by additional constraints. Materials selected might need to meet mechanical property specifications and cost restrictions. Clearly, it is impractical to gold-plate automobiles for corrosion resistance, but gold is routinely used for dental crowns, in part because of its corrosion resistance. In some applications, such as the chemical and food-processing industries, the composition of the corroding solution can be quite inflexible, or the solution cannot realistically be altered (for example, seawater). In the biomedical field, the cost of the material chosen for an implant is secondary to achieving the intended function with an appropriate service lifetime; however, the rate of release of potentially toxic corrosion products can be a stringent corrosion limitation. This is one of the newer, challenging areas of corrosion engineering.

Electrochemical techniques also can be used for corrosion control in some applications. For example, cathodic protection is the application of a cathodic current to a structure that prevents it from sustaining an anodic reaction. This can be achieved either by coupling the metal to be protected with a metal having a more negative open-circuit potential (sacrificial anode, such as magnesium) or by applying a cathodic current through an auxiliary electrode (impressed current).

For large structures, such as an underground pipeline, cathodic protection is usually applied in conjunction with a coating, since the current required to protect a large, uncoated structure would be uneconomical. Large marine structures, such as oil drilling platforms, are frequently cathodically protected.

Future. Traditional corrosion engineering problems have included systems such as steam generators, heat exchangers, reaction vessels, bridges, oil platforms, and motor vehicles. These areas will continue to be important in terms of materials selection and corrosion control. Corrosion and its control also will continue to be important in energy systems. The continuing development of alternative energy sources, such as geothermal energy and sour oil and gas wells, require processing in highly corrosive environments. In addition, there is a continuing search for more efficient and less costly materials for fuel cells, batteries, photoelectrolysis, and other emerging technologies.

The current generation of thin-film devices for integrated circuits and magnetic storage, using submicrometer scale ($<10^{-6}$ m) features, pose significant challenges because a small amount of corrosion will cause a device failure. Microprocessors are being used in increasingly aggressive environments, such as process plants and automobiles, where the importance of corrosion control in terms of device packaging will become critical. The current and continuing emphasis on cost reduction is being applied to many different kinds of devices. Corrosion control is increasingly difficult in these circumstances and will require new and ingenious solutions from corrosion scientists and engineers.

All engineering materials are susceptible to some form of environmental degradation. Users of such materials must be aware of the limits of chemical stability of these materials in service environments. *See* ELECTROCHEMISTRY.

David A. Shores; R. M. Latanision; Peter C. Searson

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Cortex (plant)

The mass of primary tissue in roots and stems extending inward from the epidermis to the phloem. The cortex may consist of one or a combination of three major tissues: parenchyma, collenchyma, and sclerenchyma. In roots the cortex almost always consists of parenchyma, and is bounded, more or less distinctly, by the hypodermis (exodermis) on the periphery and by the endodermis on the inside.

Cortical parenchyma is composed of loosely arranged thin-walled living cells. Prominent intercellular spaces usually occur in this tissue. In stems the cells of the outer parenchyma may appear green due to the presence of chloroplasts in the cells (**Fig. 1**). This green tissue is sometimes called chlorenchyma, and it is probable that photosynthesis takes place in it.

In some species the cells of the outer cortex are modified in aerial stems by deposition of hemicellulose as an additional wall substance, especially in the corners or angles of the cells. This tissue is called collenchyma, and the thickening of the cell walls gives mechanical support to the shoot.

The cortex makes up a considerable proportion of the volume of the root, particularly in young roots, where it functions in the transport of water and ions from the epidermis to the vascular (xylem and phloem) tissues (**Fig. 2**). In older roots it functions primarily as a storage tissue. The cells of the root cortex generally are similar in appearance and may occur in radial files, but histochemical tests reveal a variety of cell types in root cortex.

In addition to being supportive and protective, the cortex functions in the synthesis and localization of many chemical substances; it is one of the most fundamental storage tissues in the plant. The kinds of cortical cells specialized with regard to storage and synthesis are numerous.

Because the living protoplasts of the cortex are so highly specialized, patterns and gradients of many substances occur within the cortex, including starch, tannins, glucosides, organic acids, crystals of many kinds, and alkaloids. Oil cavities, resin ducts, and laticifers (latex ducts) are also common in the midcortex of many plants. *See* SECRETORY STRUCTURES (PLANT).

The young cortex in roots is functional in the selection and passage of solutes and ions into the plant. Experiments with radioactive ions indicate a pileup of solutes in the innermost cells of the cortex next to the endodermis. Radioactive isotopes used in experimental work accumulate just outside the endodermis by a screening action of the endodermis and the innermost cells of the cortex. Cortical cells next to the endodermis apparently act as a selective barrier with the endodermis to the kinds of ions taken into the stele and vascular tissue.

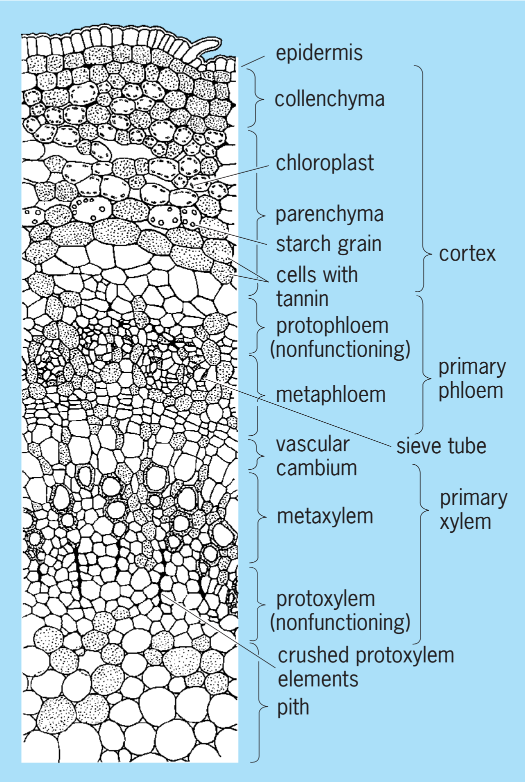

Fig. 1. Transverse section of the *Prunus* stem showing the cortex which is composed of collenchyma and parenchyma. The parenchyma has cells containing chloroplasts, starch grains, and tannin. (*After K. Esau, Plant Anatomy, 2d ed., John Wiley and Sons, 1967*)

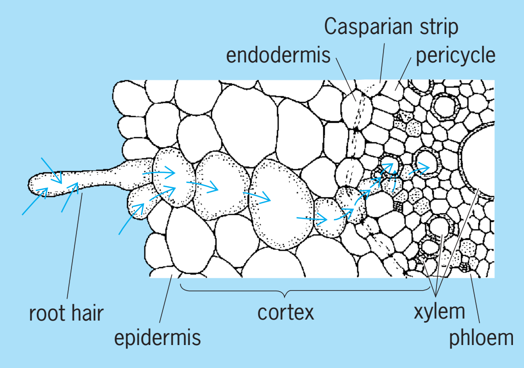

Fig. 2. Transverse section of wheat root, illustrating the kinds of cell that may be crossed by water and salts absorbed from the soil before they reach the tracheary elements of the xylem. The arrows indicate the direction of the movement through a selected series of cells. Among these, the living cells are partly stippled. The Casparian strip in the endodermis is shown as though exposed in surface views of the end walls. (*After K. Esau, Plant Anatomy, 2d ed., John Wiley and Sons, 1967*)

There appears to be complete freedom of movement of water, solutes, and ions through the cortex from the epidermis, but the Casparian strips limit freedom of movement through the endodermis into the stele. The piling up of solutes in the inner cortex limits freedom of movement and may function in the selection of the kinds of ions that pass from the cortex through the endodermis into the stele. Numerous substance gradients, as well as gradients of oxidizing potential across the cortex, may be significant in the uptake of solutes in the active growing portion of young roots. The passage and transport of solutes and ions from the cortex into the vascular system is most pronounced in the cortex just back of the growing tip of the root. In this zone of nutrient absorption, it is believed that passage of solutes into the vascular tissue is effected by an active metabolic transport system in the inner cells of the cortex, with an active system of selection in the endodermis.

The gradient of decreasing oxygen and increasing carbon dioxide across the cortex and into the vascular tissue is associated with a low level of metabolic activity in the cells around the vascular xylem vessels. Cells around the xylem with low metabolic activity would be expected to lose salts, since energy is required to hold salts, into the open vessels of the xylem. Diffusion of solutes back into the cortex is prevented by the impervious Casparian band between all endodermal cells. A unidirectional movement of solutes into the xylem vessels of the plant is a result of the action of the cortex and endodermis. *See* CELL WALLS (PLANT); COLLENCHYMA; ENDODERMIS; HYPODERMIS; PARENCHYMA; ROOT (BOTANY); SCLERENCHYMA; STEM.

D. S. Van Fleet

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Cosmic background radiation

The blackbody radiation left over from the origin of the universe, also known as the cosmic microwave background (CMB). This radiation was emitted before any astronomical objects such as stars, galaxies, or quasars existed, and is now observed to be like the thermal emission from a black object with a temperature of 2.725 K (degrees above absolute zero, or −454.8°F). Blackbody radiation is emitted by an isothermal object that absorbs all incident radiation. Its spectrum, or amount of power at different frequencies, depends only on its temperature and is given by the Planck function. The energy density of this radiation, which peaks at wavelengths near 1 mm, is larger than that of any other cosmic radiation field. Its existence was predicted in 1947 and 1948 by George Gamow, Ralph Alpher, and Robert Herman as part of their model for the formation of the elements during a hot dense phase in the early history of the universe. *See* HEAT RADIATION.

The properties of the cosmic microwave background rule out almost all cosmological models except for these hot big bang models. Observations of the spectrum of the cosmic microwave background show that less than 60 parts per million of the energy in the cosmic microwave background was generated later than 2 months after the creation of the universe and thus indicate that the universe started in a very hot and dense state. The anisotropy of the cosmic microwave background—the difference in the temperature of the blackbody radiation from point to point on the sky—reveals the structure of the universe at the time of recombination, 380,000 years after the big bang, when the free electrons and protons of the cosmic plasma combined into transparent hydrogen and helium gas. After recombination, the photons could freely travel very long distances, so that the small inhomogeneities that existed 380,000 years after the big bang became the small anisotropies that are now observed. *See* BIG BANG THEORY.

History of observations. The model for elememt formation developed by Gamow, Alpher, and Herman encountered difficulties accounting for the creation of elements heavier than lithium. These difficulties led to a general neglect of the model's prediction of the cosmic microwave background, even though the development of radar during World War II and the invention of a sensitive radiometer by Robert Dicke provided the tools necessary for the direct detection of the cosmic microwave background, and Dicke had placed a limit of less than 20 K on the temperature of the sky. The first indirect evidence for the cosmic microwave background was the rotational excitation of the interstellar cyanogen (CN) radical seen in 1939 by Andrew McKellar, but this observation was not connected to Gamow's prediction, except in a review by Fred Hoyle of a book by Gamow. Hoyle, who was co-inventor of the steady-state model of the universe, which was then a rival of the big bang model, felt that the 2.3 K measured by McKellar was too low for the big bang model, but Alpher and Herman had published detailed calculations allowing a current temperature of 1 to 5 K. Unfortunately, neither the big bang proponents nor the steady-state proponents followed up this discrepancy. Thus, the effective discovery of the cosmic microwave background was made by Arno Penzias and Robert Wilson in 1965, as they systematically tried to identify all the sources of noise in a very sensitive antenna used by Bell Labs for early communication satellite experiments. In every direction of sky they saw a nearly constant level of excess noise (**Fig 1*a***), and neither instrumental noise nor atmospheric emission could account for this emission. Dicke, James Peebles, Peter Roll, and David Wilkinson were building a radiometer to look for the cosmic microwave background when they heard of the Penzias and Wilson discovery.

Searches were carried out for the anisotropy of the cosmic microwave background, that is, for temperature differences in the cosmic microwave background in different directions on the sky. These searches led to a tentative detection of a dipole pattern by E. K. Conklin in 1969 which was confirmed

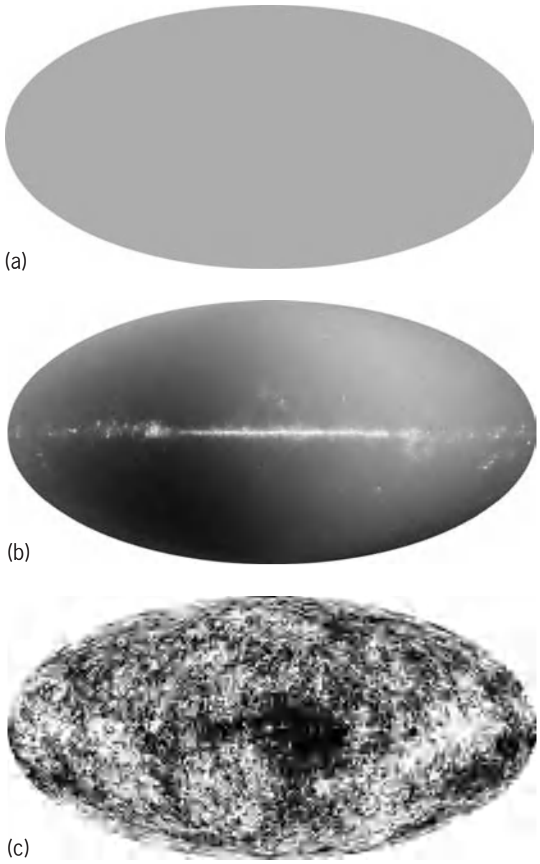

Fig. 1. Plots of the cosmic microwave background (CMB) temperature in a Molleweide projection in galactic coordinates. (*a*) CMB temperature from the *Cosmic Background Explorer* (*COBE*) Differential Microwave Radiometer (DMR), plotted without contrast enhancement. (*b*) Contrast enhanced by a factor of 400 to show the dipole anisotropy and emission from the Milky Way. (*c*) Dipole-subtracted linear combination of different frequency maps chosen to cancel the Milky Way emission, showing the CMB temperature fluctuations with contrast enhanced by a factor of 20,000.

by Paul Henry (a graduate student working with Wilkinson) in 1971, Brian Corey and Wilkinson in 1976, and George Smoot and his colleagues in 1977. A dipole pattern has two poles, with one side of the sky hotter than average, peaking at a hot pole, and the other side cooler than average, giving a cold pole. This dipole pattern is a measure of the motion of the solar system at 368 km/s (823,000 mi/h) relative to the observable universe (Fig 1*b*). After the dipole pattern was subtracted out of the observed temperature map, the anisotropy was less than the sensitivity of these early experiments, which was a few hundred parts per million.

The *Cosmic Background Explorer* (*COBE*) project, proposed in 1974 but not launched by the National Aeronautics and Space Administration (NASA) until 1989, carried an instrument to search for deviations of the cosmic microwave background spectrum from a blackbody, the Far-InfraRed Absolute Spectrophotometer (FIRAS), and an instrument to search for anisotropy, the Differential Microwave Radiometers (DMR). The FIRAS instrument limited distortions of the cosmic microwave background spectrum to less than 50 parts per million root-mean-square. The detection of nondipole anisotropy by the *COBE* DMR at a level of 11 parts per million was described as the "discovery of the century, if not of all time" by Stephen Hawking in 1992.

A second satellite to study the cosmic microwave background was launched by NASA in 2001. This satellite project was led Charles Bennett and Wilkinson, and after Wilkinson's death in 2002, the satellite was renamed the *Wilkinson Microwave Anisotropy Probe* in 2003. *Planck*, a third satellite to study the cosmic microwave background, is scheduled to be launched by the European Space Agency after 2007. *See* WILKINSON MICROWAVE ANISOTROPY PROBE.

Spectrum of CMB. The best measurement of the spectrum of the cosmic microwave background was made by the FIRAS instrument on *COBE*. This spectrometer compared the sky with a very good blackbody on the spacecraft and thus made a very sensitive measurement of deviations from a Planck function. The measured cosmic microwave background spectrum agrees with the spectrum of a blackbody to within 50 parts per million, and the temperature of the blackbody that best matches the sky is measured to be 2.725±0.002 K. **Figure 2** shows the spectrum of the cosmic microwave background plotted such that a blackbody is a horizontal line. The cosmic microwave background is remarkably close to a blackbody.

The expansion of the universe produces a redshift that preserves the blackbody character of the radiation. When the universe was 0.1% of its current size, the photons of the blackbody radiation field had 1000 times more energy than they do now. Since this time the wavelengths of the photons have increased by a factor of 1000, while the size of the universe has also increased by a factor of 1000. This ratio of the final wavelength λ_{obs} to the initial wavelength λ_{em} is used to define z, the redshift, via the formula $1 + z = \lambda_{obs}/\lambda_{em}$. Thus, when the universe was 0.1% of its current size, the color temperature deduced from the photon energy was 1000 times higher than T_0=2.725 K. However, the number density of the photons was 10^9 times higher than the current number density, and the energy density was 10^{12} times higher than the current energy density. This is exactly the energy density proportional to T^4 law seen for blackbodies. Thus, once a blackbody radiation field is produced, the expansion of the universe acts in a way that preserves the blackbody character of the radiation, with only the temperature changing. *See* REDSHIFT.

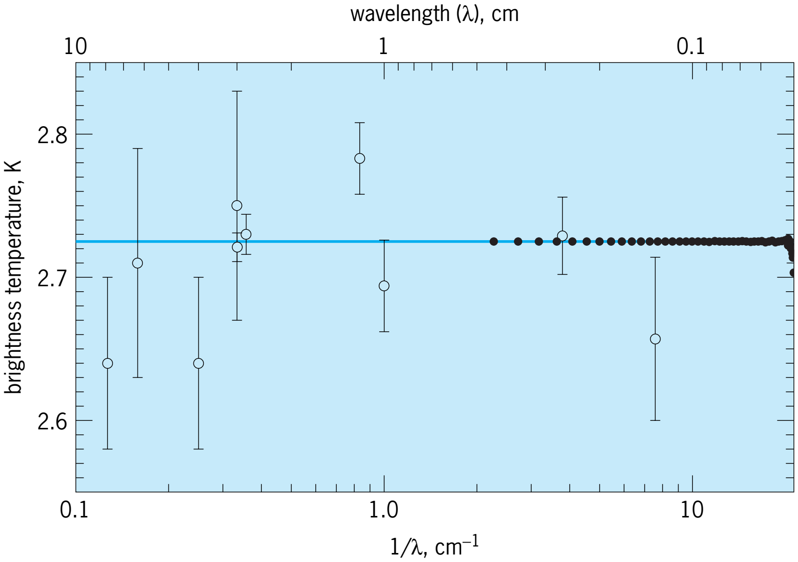

Fig. 2. Brightness temperature of the cosmic microwave background as a function of wavelength λ. For a perfect blackbody, the brightness temperature is independent of wavelength. The horizontal line is a blackbody at a temperature of 2.725 K. The closed points are the very precise Far-InfraRed Absolute Spectrophotometer (FIRAS) data.

Isotropy of CMB. The cosmic microwave background is completely isotropic to about 1 part per thousand and, except for the velocity of the solar system, would be isotropic to better than 40 parts per million. Figure 1*a* shows the temperature of the sky without any contrast enhancement, and no structure can be seen. This is quite a remarkable property that is best explained by the inflationary scenario which postulates an immense expansion of the universe during the first picosecond after the big bang. *See* INFLATIONARY UNIVERSE COSMOLOGY.

Anisotropy of CMB. When the contrast of the temperature map is increased by a factor of 400, as shown in Fig. 1*b*, a systematic variation across the sky can be seen. This figure uses an equal-area Molleweide projection to show the entire sky in an ellipse with a 2:1 aspect ratio, and the equator of the map is the galactic plane, with the center of the Milky Way Galaxy occupying the center of the map. The "dipole" pattern with a hot pole in the upper right and a cold pole in the lower left can be explained by a Doppler shift between the frame of reference of the solar system and a frame of reference at rest relative to the observable universe. *See* DOPPLER EFFECT; MAP PROJECTIONS.

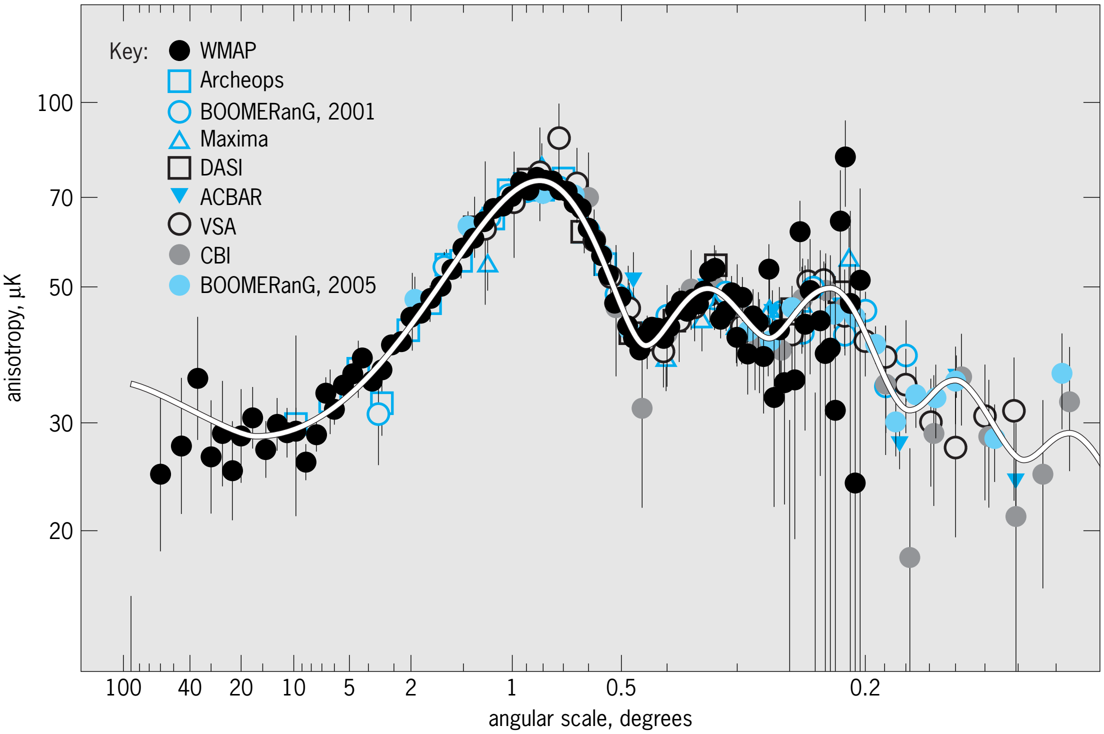

Fig. 3. Angular power spectrum of the cosmic microwave background as measured by the *Wilkinson Microwave Anisotropy Probe* (*WMAP*) and other experiments, including the balloon-borne Archeops, BOOMERanG (data published in 2001 and 2005), and Maxima experiments, the ground-based Very Small Array (VSA) and Cosmic Background Imager (CBI), and DASI and ACBAR at the South Pole. The curve shows the predicted angular power spectrum for a model of the universe with Euclidean (flat) geometry, dominated by vacuum energy (dark energy).

Since the pattern produced on the sky by a Doppler shift can be predicted, the dipole anisotropy can be removed from the map, giving a no-dipole map. After this, the largest signal that remains is due to the radio and millimeter wave emission from the Milky Way. This emission is much stronger at centimeter wavelengths than at millimeter wavelengths, so if a fraction of a long-wavelength map is subtracted from a short-wavelength map, almost all of the emission from the Milky Way can be canceled while still leaving a strong cosmic microwave background anisotropy signal. Figure 1*c* shows such a no-dipole, no-Galaxy map based on data from the *Wilkinson Microwave Anisotropy Probe*.

The dominant cause of the temperature fluctuations for large angular scales is the gravitational redshift. Dense regions have negative gravitational potential wells, and the photons of the cosmic microwave background lose energy as they leave the potential wells. This effect is larger than the normal density effect wherein gases become hotter when compressed. However, at small angular scales the situation changes, in part because the density fluctuations have time to change between the big bang and recombination. The photons and the baryons plus electrons (ordinary matter) are tightly coupled before recombination, so the density fluctuations travel as acoustic waves at the sound speed in the plasma. Because there are billions of photons for every baryon, the radiation pressure from the photons is large compared with the energy density from the baryon rest mass, so the speed of sound c_s is very high, and is comparable to the speed of light c, being given approximately by the formula $c_s{\sim}c/\sqrt{3}=170{,}000$ km/s (380,000,000 mi/h). If the wavelength of a fluctuation is set so that it goes through one-half cycle of oscillation before recombination, the effects of the photon density and the gravitational redshift are in phase at recombination instead of partially canceling. This wave has a frequency of 42 femtohertz (4.2×10^{-14} Hz, more than 52 octaves below middle C) and a wavelength of 400,000 light-years. It shows up on the sky as a 1.6° angle with peaks separated by 0.8° from adjacent valleys. Thus, there will be more anisotropy in bumps about 0.8° in size compared to other angular scales. This phenomenon is evident in **Fig. 3**, a plot of the amount of anisotropy versus angular scale, or the angular power spectrum, which has a peak at an angular scale of 0.8°.

Conclusions. Observations of the cosmic microwave background provide a wealth of information about the universe. The cosmic microwave background spectrum gives a picture of the universe from 2 months after the big bang. (Prior to 2 months any spectral distortions were eliminated, while after 2 months the distortions were modified by electron scattering but still survived.) The anisotropy of the cosmic microwave background shows the state of the universe 380,000 years after the big bang, but that state was established during the inflation epoch less than 1 picosecond (10^{-12} s) after the big bang.

From the heights of the peaks and the depths of the troughs in the angular power spectrum (Fig. 3), the density of baryons (protons and neutrons in atomic nuclei) and the density of cold dark matter in the universe have been found: 0.42 ± 0.02 yoctogram (1 yg $= 10^{-24}$ g) per cubic meter for baryons and 2.1 ± 0.2 yg/m^3 for dark matter. In combination with other data, the cosmic microwave background results also show that the universe has Euclidean (Flat) geometry, that 75% of the energy in the universe is vacuum energy (dark energy), and that the universe is 13.7×10^9 years old. *See* COSMOLOGY; DARK ENERGY; DARK MATTER; UNIVERSE. Edward Wright

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Cosmic rays

Electrons and the nuclei of atoms—largely hydrogen—that impinge upon Earth from all directions of space with nearly the speed of light. Before they enter the atmosphere they are typically referred to as primary cosmic rays, to distinguish them from the particles generated by their interaction with the terrestrial atmosphere. Secondary cosmic rays, comprising a large variety of species of charged and neutral particles, cascade down through the atmosphere all the way to the ground and below. Study of cosmic rays at high energy now is often referred to as particle astrophysics.

Cosmic rays are studied for a variety of reasons, not the least of which is a general curiosity over the process by which nature can produce such energetic nuclei. Apart from this, primary cosmic rays provide the only direct sample of matter from far outside the solar system. Measurement of their composition can aid in understanding which properties of the matter making up the solar system are typical of the Milky Way Galaxy as a whole and which may be so atypical as to yield specific clues to the origin of the solar system. Cosmic rays are electrically charged; hence they are deflected by the magnetic fields which are thought to exist throughout the Milky Way Galaxy, and may be used as probes to determine the nature of these fields far from Earth. Outside the solar system the energy contained in the cosmic rays is comparable to that of the magnetic field, so the cosmic rays probably play a major role in determining the structure of the field. Collisions between cosmic rays and the nuclei of the atoms in the tenuous gas which permeates the Milky Way Galaxy change the cosmic-ray composition in a measurable way and produce gamma rays which can be detected at Earth, giving information on the distribution of this gas. *See* GAMMA-RAY ASTRONOMY.

This modern understanding of cosmic rays evolved through a process of discovery which at many times produced seemingly contradictory results, the ultimate resolution of which led to fundamental discoveries in other fields of physics, most notably high-energy particle physics. At the turn of the century several different types of radiation were being studied, and the different properties of each were being determined with precision. One result of many precise experiments was that an unknown source of radiation existed with properties that were difficult to characterize. In 1912 Viktor Hess made a definitive series of balloon flights which showed that this background radiation increased with altitude in a dramatic fashion. Far more penetrating then any other known at that time, this radiation had many other unusual properties and became known as cosmic radiation, because it clearly did not originate in the Earth or from any known properties of the atmosphere.

Unlike the properties of alpha-, beta-, gamma-, and x-radiation, the properties of cosmic radiation are not of any one type of particle, but are due to the interactions of a whole series of unstable particles, none of which was known at that time. The initial identification of the positron, the muon, the π meson or pion, and certain of the K mesons and hyperons were made from studies of cosmic rays.

Thus the term cosmic ray does not refer to a particular type of energetic particle, but to energetic particles being considered in their astrophysical context. The effects of cosmic rays on living cells are discussed in a number of other articles: for example, *See* ELEMENTARY PARTICLE; RADIATION INJURY (BIOLOGY).

Cosmic-ray detection. Cosmic rays are usually detected by instruments which classify each incident particle as to type, energy, and in some cases time and direction of arrival. A convenient unit for measuring cosmic-ray energy is the electronvolt, which is the energy gained by a unit charge (such as an electron) accelerating freely across a potential of 1 V. One electronvolt equals about 1.6×10^{-19} joule. For nuclei it is usual to express the energy in terms of electronvolts per nucleon, since the relative abundances of the different elements are nearly constant as a function of this variable. Two nuclei with the same energy per nucleon have the same velocity.

Flux. The intensity of cosmic radiation is generally expressed as a flux by dividing the average number seen per second by the effective size or "geometry factor" of the measuring instrument. Calculation of the geometry factor requires knowledge of both the sensitive area (in square centimeters) and the angular acceptance (in steradians) of the detector, as the arrival directions of the cosmic rays are randomly distributed to within 1% in most cases. A flat detector of any shape but with area of 1 cm^2 has a geometry factor of π cm$^2 \cdot$ sr if it is sensitive to cosmic rays entering from one side only. The total flux of cosmic rays in the vicinity of the Earth but outside the atmosphere is about 0.3 nucleus/(cm$^2 \cdot$ s $\cdot$ sr) [2 nuclei/(in.$^2 \cdot$ s $\cdot$ sr)]. Thus a quarter dollar, with a surface area of 4.5 cm^2 (0.7 in.^{2}), lying flat on the surface of the Moon will be struck by $0.3 \times 4.5 \times 3.14 = 4.2$ cosmic rays per second.

Energy spectrum. The flux of cosmic rays varies as a function of energy. This function, called an energy spectrum, may refer to all cosmic rays or to only a selected element or group of elements. Since cosmic rays are continuously distributed in energy, it is meaningless to attempt to specify the flux at any exact energy. Normally an integral spectrum is used, in which the function gives the total flux of particles with energy greater than the specified energy [in particles/($cm^2 \cdot s \cdot sr$)], or a differential spectrum, in which the function provides the flux of particles in some energy interval (typically 1 MeV/nucleon wide) centered on the specified energy, in particles/[$cm^2 \cdot s \cdot sr \cdot$ (MeV/nucleon)]. The basic approach of cosmic-ray research is to measure the spectra of the different components of cosmic radiation and to deduce from them and other observations the nature of the cosmic-ray sources and the details of where the particles travel on their way to Earth and what they encounter on their journey.

Types of detectors. All cosmic-ray detectors are sensitive to moving electrical charges. Neutral particles (neutrons, gamma rays, and neutrinos) are studied by observing charged particles produced in the collision of the neutral primary with some type of target. At low energies the ionization of the matter through which they pass is the principal means of detection. Such detectors include cloud chambers, ion chambers, spark chambers, Geiger counters, proportional counters, scintillation counters, solid-state detectors, photographic emulsions, and chemical etching of certain mineral crystals or plastics in which ionization damage is revealed. The amount of ionization produced by a particle is given by the square of its charge multiplied by a universal function of its velocity, the Bethe-Bloch relation. A single measurement of the ionization produced by a particle is therefore usually not sufficient both to identify the particle and to determine its energy. However, since the ionization itself represents a significant energy loss to a low-energy particle, it is possible to design systems of detectors which trace the rate at which the particle slows down and thus to obtain unique identification and energy measurement. *See* GAMMA-RAY DETECTORS; GEIGER-MÜLLER COUNTER; IONIZATION CHAMBER; JUNCTION DETECTOR; PARTICLE TRACK ETCHING; PHOTOGRAPHIC MATERIALS; SCINTILLATION COUNTER.

At energies above about 500 MeV/nucleon, almost all cosmic rays will suffer a catastrophic nuclear interaction before they slow appreciably. Some measurements are made using massive calorimeters which are designed to trap all of the energy from the cascade of particles which results from such an interaction. More commonly an ionization measurement is combined with measurement of a physical effect that varies in a different way with mass, charge, and energy. Cerenkov detectors and the deflection of the particles in the field of large superconducting magnets (or the magnetic field of the Earth itself) provide the best means of studying energies up to a few hundred gigaelectronvolts per nucleon. Detectors of x-ray transition radiation are useful for measuring composition at energies up to a few thousand GeV per nucleon. Transition radiation detectors are also used to study electrons having energies of 10–200 GeV which, because of their lower rest mass, are already much more relativistic than protons of the same energies. *See* CERENKOV RADIATION; SUPERCONDUCTING DEVICES; TRANSITION RADIATION DETECTORS.

Above about 10^{14} eV, direct detection of individual particles is no longer practical, simply because they are so rare. Such particles are studied by observing the large showers of secondaries they produce in Earth's atmosphere. These showers are detected either by counting the particles which survive to strike ground-level detectors or by looking at the flashes of light the showers produce in the atmosphere with special telescopes and photomultiplier tubes. It is not possible to directly determine what kind of particle produces any given shower. Because of the extreme energies involved, which can be measured with fair accuracy and have been seen as high as 10^{20} eV (16 J), most of the collision products travel in the same direction as the primary and at essentially the speed of light. This center of intense activity has typical dimensions of only a few tens of meters, allowing it to be tracked (with sensitive instruments) like a miniature meteor across the sky before it hits the Earth at a well-defined location. In addition to allowing determination of the direction from which each particle came, the development of many such showers through the atmosphere may be studied statistically to gain an idea of whether the primaries are protons or heavier nuclei. The main idea behind these studies is that a heavy nucleus, in which the energy is initially shared among several neutrons and protons, will cause a shower that starts higher in the atmosphere and develops more regularly than a shower which has the same total energy but is caused by a single proton. *See* PARTICLE DETECTOR; PHOTOMULTIPLIER.

Atmospheric cosmic rays. The primary cosmic-ray particles coming into the top of the terrestrial atmosphere make inelastic collisions with nuclei in the atmosphere. The collision cross section is essentially the geometrical cross section of the nucleus, of the order of 10^{-26} cm^2 (10^{-27} in.^{2}). The mean free path for primary penetration into the atmosphere is given in **Table 1**. (Division by the atmospheric density in g/cm^3 gives the value of the mean free path in centimeters.)

TABLE 1. Mean free paths for primary cosmic rays in the atmosphere

Charge of primary nucleus	Mean free path in air, g/cm^2*
$Z = 1$	60
$Z = 2$	44
$3 \leq Z \leq 5$	32
$6 \leq Z \leq 9$	27
$10 \leq Z \leq 29$	21

*1 g/cm^2 = 1.42 × 10^{-2} lb/in.^{2}

When a high-energy nucleus collides with the nucleus of an air atom, a number of things usually occur. Rapid deceleration of the incoming nucleus leads to production of pions with positive, negative, or neutral charge; this meson production is closely analogous to the generation of x-rays, or bremsstrahlung, produced when a fast electron is deflected by impact with the atoms in a metal target. The mesons, like the bremsstrahlung, come off from the impact in a narrow cone in the forward direction. Anywhere from 0 to 30 or more pions may be produced, depending upon the energy of the incident nucleus. The ratio of neutral to charged pions is about 0.75. A few protons and neutrons (in about equal proportions) may be ejected with energies up to a few GeV. They are called knock-on protons and neutrons. *See* BREMSSTRAHLUNG; MESON; NUCLEAR REACTION.

A nucleus struck by a proton or neutron with energy greater than approximately 300 MeV may have its internal forces momentarily disrupted so that some of its nucleons are free to leave with their original nuclear kinetic energies of about 10 MeV. The nucleons freed in this fashion appear as protons, deuterons, tritons, alpha particles, and even somewhat heavier clumps, radiating outward from the struck nucleus. In photographic emulsions the result is a number of short prongs radiating from the point of collision, and for this reason it is called a nuclear star.

All these protons, neutrons, and pions generated by collision of the primary cosmic-ray nuclei with the nuclei of air atoms are the first stage in the development of the secondary cosmic-ray particles observed inside the atmosphere. Since several secondary particles are produced by each collision, the total number of energetic particles of cosmic-ray origin will at first increase with depth, even while the primary density is decreasing. Since electric charge must be conserved and the primaries are positively charged, positive particles outnumber negative particles in the secondary radiation by a factor of about 1.2. This factor is called the positive excess.

Electromagnetic cascade. Uncharged π^0 mesons decay into two gamma rays with a lifetime of about 9×10^{-17} s. The decay is so rapid that π^0 mesons are not directly observed among the secondary particles in the atmosphere. The two gamma rays, which together have the rest energy of the π^0, about 140 MeV, plus the π^0 kinetic energy, each produce a positron-electron pair. Upon passing sufficiently close to the nucleus of an air atom deeper in the atmosphere, the electrons and positrons convert their energy into bremsstrahlung. The bremsstrahlung in turn creates new positron-electron pairs, and so on. This cascade process continues until the energy of the initial π^0 has been dispersed into a shower of positrons, electrons, and photons with insufficient individual energies ($\leq$1 MeV) to continue the pair production. The shower, then being unable to reproduce its numbers, is dissipated by ionization of the air atoms. The electrons and photons of such showers are referred to as the soft component of the atmospheric (secondary) cosmic rays, reaching a maximum intensity at an atmospheric depth of 150–200 g/cm^2 and then declining by a factor of about 10^2 down to sea level. *See* ELECTRON-POSITRON PAIR PRODUCTION.

Muons. The $\pi^\pm$ mesons produced by the primary collisions have a lifetime about 2.6×10^{-8} s before they decay into muons: $\pi^\pm \rightarrow \mu^\pm +$ neutrino. With a lifetime of this order a $\pi^\pm$ possessing enough energy (greater than 10 GeV) to experience significant relativistic time dilatation may exist long enough to interact with the nuclei of the air atoms. The cross section for $\pi^\pm$ nuclear interactions is approximately the geometrical cross section of the nucleus, and the result of such an interaction is essentially the same as for the primary cosmic-ray protons. Most low-energy $\pi^\pm$ decay into muons before they have time to undergo nuclear interactions.

Except at very high energy (above 500 GeV), muons interact relatively weakly with nuclei, and are too massive (207 electron masses) to produce bremsstrahlung. They lose energy mainly by the comparatively feeble process of ionizing air atoms as they progress downward through the atmosphere. Because of this ability to penetrate matter, they are called the hard component. At rest their lifetime is 2×10^{-6} s before they decay into an electron or positron and two neutrinos, but with the relativistic time dilatation of their high energy, 5% of the muons reach the ground. Their interaction with matter is so weak that they penetrate deep into the ground, where they are the only charged particles of cosmic-ray origin to be found. At a depth equivalent of 300 m (990 ft) of water the muon intensity has decreased from that at ground level only by a factor of 20; at 1400 m (4620 ft) it has decreased by a factor of 10^3.

Atmospheric neutrinos. In the late 1990s, detectors became available with sufficient sensitivity to exploit atmospheric neutrinos. Neutrinos of different types are produced in association with muons and electrons, and it is possible to calculate the expected flux of each type with some accuracy. Production of other types of neutrinos is predicted to be quite small. The detected flux of muon neutrinos is significantly lower than the calculation, in analogy with a similar deficit in the neutrino flux from the Sun. Data from the large detector Super Kamiokande in Japan gave the first indication that the atmospheric deficit is due to transformation (known as oscillation) of muon neutrinos into other types of neutrinos. The Sudbury Neutrino Observatory in Canada has confirmed this transformation, demonstrating that the rest mass of the neutrino, while very small, is not zero. Astrophysical consequences of a nonzero rest mass are profound, as a particle with a rest mass interacts gravitationally in a way totally different from that of a particle (such as a photon) with no rest mass. Huge numbers of neutrinos permeate the universe, and details of their gravitational interaction are crucial to the understanding of galaxy formation. *See* NEUTRINO.

Nucleonic component. The high-energy nucleons—the knock-on protons and neutrons—produced by the primary-particle collisions and a few pion collisions proceed down into the atmosphere. They produce nuclear interactions of the same kind as the primary nuclei, though of course with diminished energies. This cascade process forms the nucleonic component of the secondary cosmic rays.

When nucleon energy falls below about 100 MeV, stars and further knock-ons can no longer be produced. At the same time the protons are rapidly disappearing from the cascade because their ionization losses in the air slow them down before they can make a nuclear interaction. Most of the hadrons in the lower atmosphere are thus neutrons, which are already dominant at 3500 m (11,550 ft), about 300 g/cm^2 (4.3 lb/in.^{2}) above sea level, where they outnumber the protons four to one. Thus the final stages of the cascade involve mainly neutrons in a sequence of low-energy interactions which convert them to thermal neutrons (neutrons of kinetic energy of about 0.025 eV) in a path of about 90 g/cm^2 (1.3 lb/in.^{2}). These thermal neutrons are readily detected in boron trifluoride (BF_3) and helium-3 (^{3}He) counters. The nucleonic component increases in intensity down to a depth of about 120 g/cm^2 (1.7 g/cm^3), and thereafter declines in intensity, with a mean absorption length of about 200 g/cm^2 (2.8 lb/in.^{2}).

The various cascades of secondary particles in the atmosphere are shown schematically in **Fig. 1**. About 48% of the initial primary cosmic-ray energy goes into charged pions, 25% into neutral pions, 7% into the nucleonic component, and 20% into stars. The nucleonic component is produced principally by the lower-energy (about 5 GeV) primaries. Higher-energy primaries put their energy more into meson production. Hence in the lower atmosphere, a Geiger counter responds mainly to the higher-energy primaries (about 5 GeV) because it counts the muons and electrons, whereas a BF_3 counter detecting thermal neutrons responds more to the low-energy primaries.

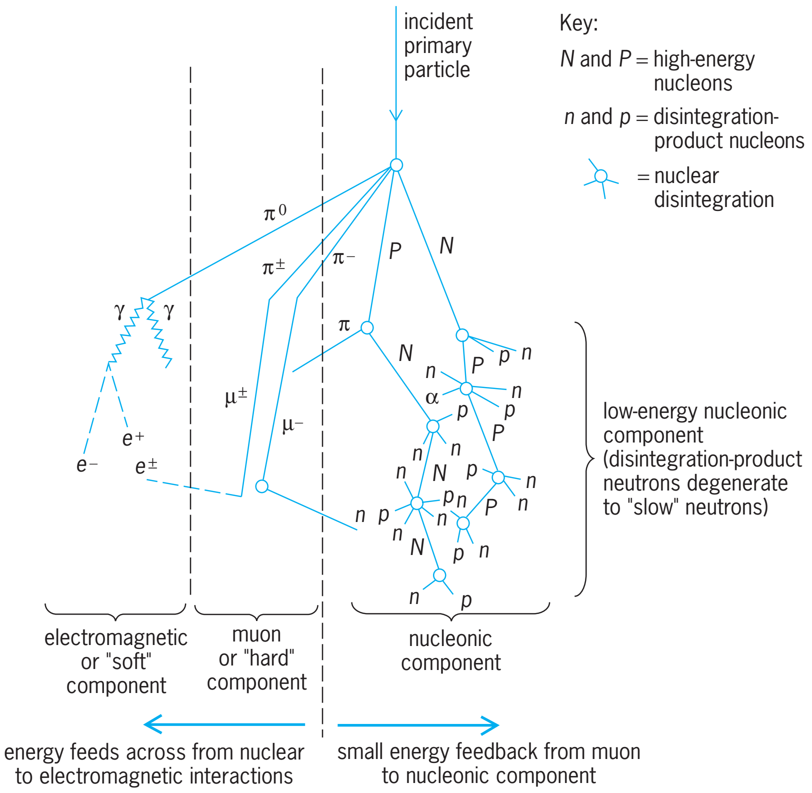

Fig. 1. Cascade of secondary cosmic-ray particles in the terrestrial atmosphere.

Neutrinos. Cosmic neutrinos, detected for the first time from the explosion of the supernova 1987A, provide confirmation of theoretical calculations regarding the collapse of the cores of massive stars. Although neutrinos are produced in huge numbers (over 10^{15} passed through a typical human body from this supernova), they interact with matter only very weakly, necessitating a very large detector. Detectors consisting of huge tanks containing hundreds of tons of pure water located deep underground to reduce the background produced by other cosmic rays recorded less than two dozen neutrino events. Still larger detectors, which are under construction in the Antarctic ice and underwater at several locations, will permit observation of more distant supernovae and allow sensitive searches for point sources of high-energy neutrinos. Additionally, by measuring the fraction of non-neutrino-induced events containing multiple muons, these new detectors can investigate the composition of cosmic rays at energies above 10^{15} eV. Some preliminary measurements indicate that these high-energy cosmic rays may consist primarily of iron nuclei rather than the protons that dominate at lower energies. Much of the interest in the new neutrino observatories derives from the success of the now maturing field of measurement of the flux of solar neutrinos, which is really quite a different problem. With the realization that neutrinos have mass, increasingly precise measurements of the solar neutrino flux, coupled with such techniques as helioseismology, continue to make fundamental contributions to the study of the internal structure of the Sun. *See* NEUTRINO ASTRONOMY; SOLAR NEUTRINOS; SUPERNOVA.

Relation to particle physics. Investigations of cosmic rays continue to make fundamental contributions to particle physics. Neutrino detectors, besides detecting oscillations of atmospheric neutrinos, have set the best limit yet (about 10^{32} years) on the lifetime of the proton. Cosmic rays remain the only source of particles with energies above 1000 GeV. With the continued increase in the size and sensitivity of detectors, study of cosmic rays should continue to provide the first indications of new physics at ultrahigh energies. *See* FUNDAMENTAL INTERACTIONS; PROTON.

Geomagnetic effects. The magnetic field of Earth is described approximately as that of a magnetic dipole of strength 8.1×10^{15} weber-meters (8.1×10^{25} gauss · cm^3) located near the geometric center of Earth. Near the Equator the field intensity is 3×10^{-5} tesla (0.3 gauss), falling off in space as the inverse cube of the distance to the Earth's center. In a magnetic field which does not vary in time, the path of a particle is determined entirely by its rigidity, or momentum per unit charge; the velocity simply determines how fast the particle will move along

TABLE 2. Properties of particles when all have a rigidity of 1 gigavolt

Particle	Charge	Nucleons	Kinetic energy		Momentum, MeV/*c*
			MeV	MeV/nucleon	
Electron	1	—	1000	—	1000
Proton	1	1	430	430	1000
^{3}He	2	3	640	213	2000
^{4}He	2	4	500	125	2000
^{16}O	8	16	2000	125	8000

this path. Momentum is usually expressed in units of eV/*c*, where *c* is the velocity of light, because at high energies, energy and momentum are then numerically almost equal. By definition, momentum and rigidity are numerically equal for singly charged particles. The unit so defined is dimensionally a volt, but the relationship to electric potential is neither obvious nor particularly useful in practice. **Table 2** gives examples of these units as applied to different particles with rigidity of 1 gigavolt. This corresponds to an orbital radius in a typical interplanetary (10^{-9} tesla or 10^{-5} gauss) magnetic field of approximately 10 times the distance from the Earth to the Moon. *See* RELATIVISTIC ELECTRODYNAMICS.

The minimum rigidity of a particle able to reach the top of the atmosphere at a particular geomagnetic latitude is called the geomagnetic cutoff rigidity at that latitude, and its calculation is a complex numerical problem. Fortunately, for an observer near the ground, obliquely arriving secondary particles, produced by the oblique primaries, are so heavily attenuated by their longer path to the ground that it is usually sufficient to consider only the geomagnetic cutoff for vertically incident primaries, which is given in **Table 3**. Around the Equator, where a particle must come in perpendicular to the geomagnetic lines of force to reach Earth, particles with rigidity less than 10 GV are entirely excluded, though at higher latitudes where entry can be made more nearly along the lines of force, lower energies can reach Earth. Thus, the cosmic-ray intensity is a minimum at the Equator, and increases to its full value at either pole—this is the cosmic-ray latitude effect. Even deep in the atmosphere the variation with latitude is easily detected with BF_3 counters (**Fig. 2**). North of 45° the effect is slight because the additional primaries admitted are so low in energy that they produce few secondaries.

TABLE 3. Geomagnetic cutoff

Geomagnetic latitude	Vertical cutoff, gigavolts
0°	15
±20°	11.5
±40°	5
±60°	1
±70°	0.2
±90°	0

Accurate calculations of the geomagnetic cutoff must consider the deviations of the true field from that of a perfect dipole and the change with time of these deviations. Additionally the distortion of the field by the pressure of the solar wind must often be accounted for, particularly at high latitude. Such corrections vary rapidly with time because of sudden bursts of solar activity and because of the rotation of the Earth. Areas with cutoffs of 400 MV during the day may have no cutoff at all during the night. This day-night effect is confined to particles with energies so low that neither they nor their secondaries reach the ground, and is thus observed only on high-altitude balloons or satellites.

Since the geomagnetic field is directed from south to north above the surface of Earth, the incoming cosmic-ray nuclei are deflected toward the east. Hence an observer finds some 20% more particles incident from the west. This is known as the east-west effect. *See* GEOMAGNETISM.

Solar modulation. **Figure 3** presents portions of the proton and alpha-particle spectra observed near the Earth but outside of the magnetosphere in 1973. Below 20 GeV/nucleon the cosmic-ray intensity varies markedly with time. S. Forbush was the first to show that the cosmic-ray intensity was low during the years of high solar activity and sunspot number, which follow an 11-year cycle. This effect is clearly seen in the data of Fig. 2 and has been extensively studied with ground-based and spacecraft instruments. While this so-called solar modulation is now understood in general terms, it has not been

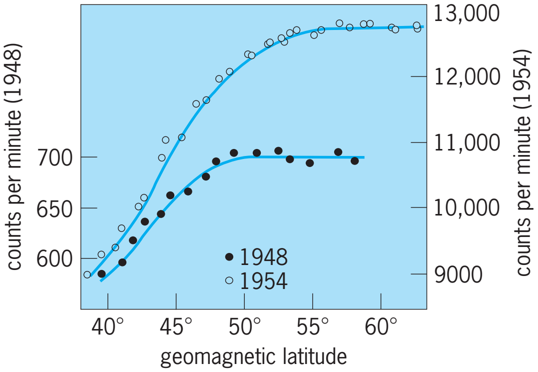

Fig. 2. Latitude variation of the neutron component of cosmic rays in 80°W longitude and at a height corresponding to an atmospheric pressure of 30 kPa (22.5 cm of mercury) in 1948, when the Sun was active, and 1954, when the Sun was deep in a sunspot minimum.

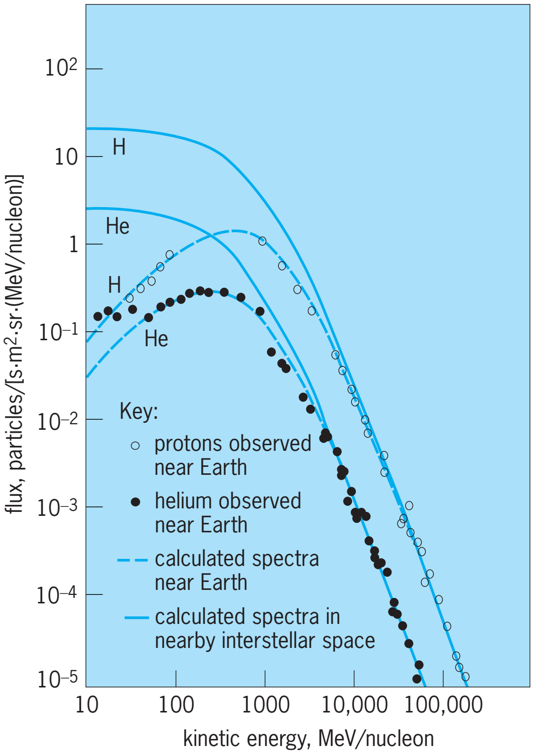

Fig. 3. Spectra of cosmic-ray protons and helium at Earth and in nearby interstellar space, showing the effect of solar modulation. Observations were made in 1973, when the Sun was quiet.

calculated in detail, in large part because there are few direct measurements out of the ecliptic plane and in the outer heliosphere.

The primary cause of solar modulation is the solar wind, a highly ionized gas (plasma) which originates from the solar corona and propagates radially from the Sun at a velocity of about 400 km/s (250 mi/s). The wind is mostly hydrogen, with typical density of 5 protons/cm^3 (80 protons/in.^{3}). This density is too low for collisions with cosmic rays to be important. Rather, the high conductivity of the medium traps part of the solar magnetic field and carries it outward. The rotation of the Sun and the radial motion of the plasma combine to create the observed archimedean spiral pattern of the average interplanetary magnetic field. Turbulence in the solar wind creates fluctuations in the field which often locally obscure the average direction and intensity. This complex system of magnetic irregularities propagating outward from the Sun deflects and sweeps the low-rigidity cosmic rays out of the solar system. *See* SOLAR MAGNETIC FIELD.

In addition to the bulk sweeping action, another effect of great importance occurs in the solar wind, adiabatic deceleration. Because the wind is blowing out, only those particles which chance to move upstream fast enough are able to reach Earth. However, because of the expansion of the wind, particles interacting with it lose energy. Thus, particles observed at Earth at 10 MeV/nucleon actually started out at several hundred megaelectronvolts per nucleon in nearby interstellar space, while those with only 100–200 MeV/nucleon initial energy probably never reach Earth at all. This is particularly unfortunate because at these lower energies the variation with energy of nuclear reaction probabilities would allow much more detailed investigation of cosmic-ray history. Changes in the modulation with solar activity are caused by the changes in the pattern of magnetic irregularities rather than by changes in the wind velocity, which are quite small. *See* MAGNETOHYDRODYNAMICS; PLASMA (PHYSICS).

Heliosphere. Solar modulation is important in a region around the Sun termed the heliosphere, a large bubble formed in the interstellar medium by the solar wind. The density, and therefore the energy and momentum, of the solar wind drop as the material expands with increasing distance from the Sun, eventually becoming too small to push back the interstellar material. The typical distance to the interface is thought to be approximately 100 AU, but the actual distance in any direction is determined by local variations in both the solar wind and the interstellar medium. (1 AU, or astronomical unit, is the average Earth-Sun separation, 1.49×10^8 km or 9.26×10^7 mi.).

The spacecraft *Voyager 1* crossed the termination shock of the solar wind on December 16, 2004, at some 94 astronomical units (AU) or more than 8.7×10^9 miles from the Sun, as evidenced by an abrupt increase in the magnetic field. The termination shock is the innermost, and probably the best-defined, structure in this boundary region. Outside the termination shock several centuries worth of decelerated solar wind are probably piled up, producing a region that is still capable of modulating cosmic-ray intensity. The Sun, carrying the heliosphere with it, is moving through the interstellar medium at approximately 20 km/s (12 mi/s). Eventually all of the solar material blends into the interstellar medium by turbulent interactions. The termination shock had been universally thought to be a prodigious accelerator of particles and *Voyager 1* largely confirmed this. At the shock there is a remarkable increase in particle intensity with a distinctive energy spectrum.

Forbush decreases. Apart from the 11-year modulation cycle, there are many different types of cosmic-ray variation associated with irregularities in the solar wind. The most dramatic is the Forbush decrease, wherein worldwide cosmic-ray intensity may drop as much as 20% in one day, followed by a slow recovery lasting many days or even weeks. Most Forbush decreases are associated with severe magnetic disturbances in the solar wind that result from massive ejections of material from the solar corona into interplanetary space. Often these ejections accompany solar flares. When magnetic disturbances encounter the Earth, they can cause geomagnetic storms and other phenomena that are disruptive to human activity. This complex set of interactions has come to be called space weather. Observing changes in cosmic-ray fluxes from several places on Earth simultaneously is one important tool for investigating the interaction of a magnetic disturbance with Earth. *See* SOLAR WIND; SUN.

Composition of cosmic rays. Nuclei ranging from protons to lead have been identified in the cosmic radiation. The relative abundances of the elements ranging up to nickel are shown in **Fig. 4**, together with the best estimate of the "universal abundances" obtained by combining measurements of solar spectra, lunar and terrestrial rocks, meteorites, and so forth. Most obvious is the similarity between these two distributions. However, a systematic deviation is quickly apparent: the elements lithium-boron and scandium-manganese as well as most of the odd-charged nuclei are vastly overabundant in the cosmic radiation. This effect has a simple explanation: the cosmic rays travel great distances in the Milky Way Galaxy and occasionally collide with atoms of interstellar gas—mostly hydrogen and helium—and fragment. This fragmentation, or spallation as it is called, produces lighter nuclei from heavier ones but does not change the energy/nucleon very much. Thus the energy spectra of the secondary elements are similar to those of the primaries. *See* SPALLATION REACTION.

Calculations involving reaction probabilities determined by nuclear physicists show that the overabundances of the secondary elements can be explained by assuming that cosmic rays pass through an average of about 5 g/cm^2 (0.07 lb/in.^{2}) of material on their way to Earth. Although an average path length can be obtained, it is not possible to fit the data by saying that all particles of a given energy have exactly the same path length; furthermore, results indicate that higher-energy particles traverse less matter in reaching the solar system, although their original composition seems energy independent. *See* ELEMENTS, COSMIC ABUNDANCE OF.

When spallation has been corrected for, differences between cosmic-ray abundances and solar-system or universal abundances still remain. The most important question is whether these differences are due to the cosmic rays having come from a special kind of material (such as would be produced in a supernova explosion), or simply to the fact that some atoms might be more easily accelerated than others. It is possible to rank almost all of the overabundances by considering the first ionization potential of the atom and the rigidity of the resulting ion, although this approach gives no prediction of the magnitude of the enhancement. Relative abundances of particles accelerated in solar flares are also far from constant from one flare to the next. Accounting for these abundance variations is one of the most important constraints on models of solar particle acceleration, the exact mechanism of which remains an unsolved problem. *See* IONIZATION POTENTIAL.

Isotopes. Much current cosmic-ray research is concentrated on determining isotopic composition of the elements, partly because this is less likely to be changed by acceleration than the elemental composition and thus is more accurately representative of the composition of the source material. As an example, the low-energy helium data in Fig. 3 are not well represented by the calculation. The excess flux, which is referred to as the anomalous component, is nearly all ^{4}He, whereas higher-energy cosmic rays are nearly 10% ^{3}He. A similar enhancement of low-energy nitrogen is pure ^{14}N, while at higher energies nitrogen is half ^{15}N. Measuring isotopes allows conclusive identification of the anomalous component as a sample of originally neutral interstellar material that has been ionized and energized by processes in the solar wind.

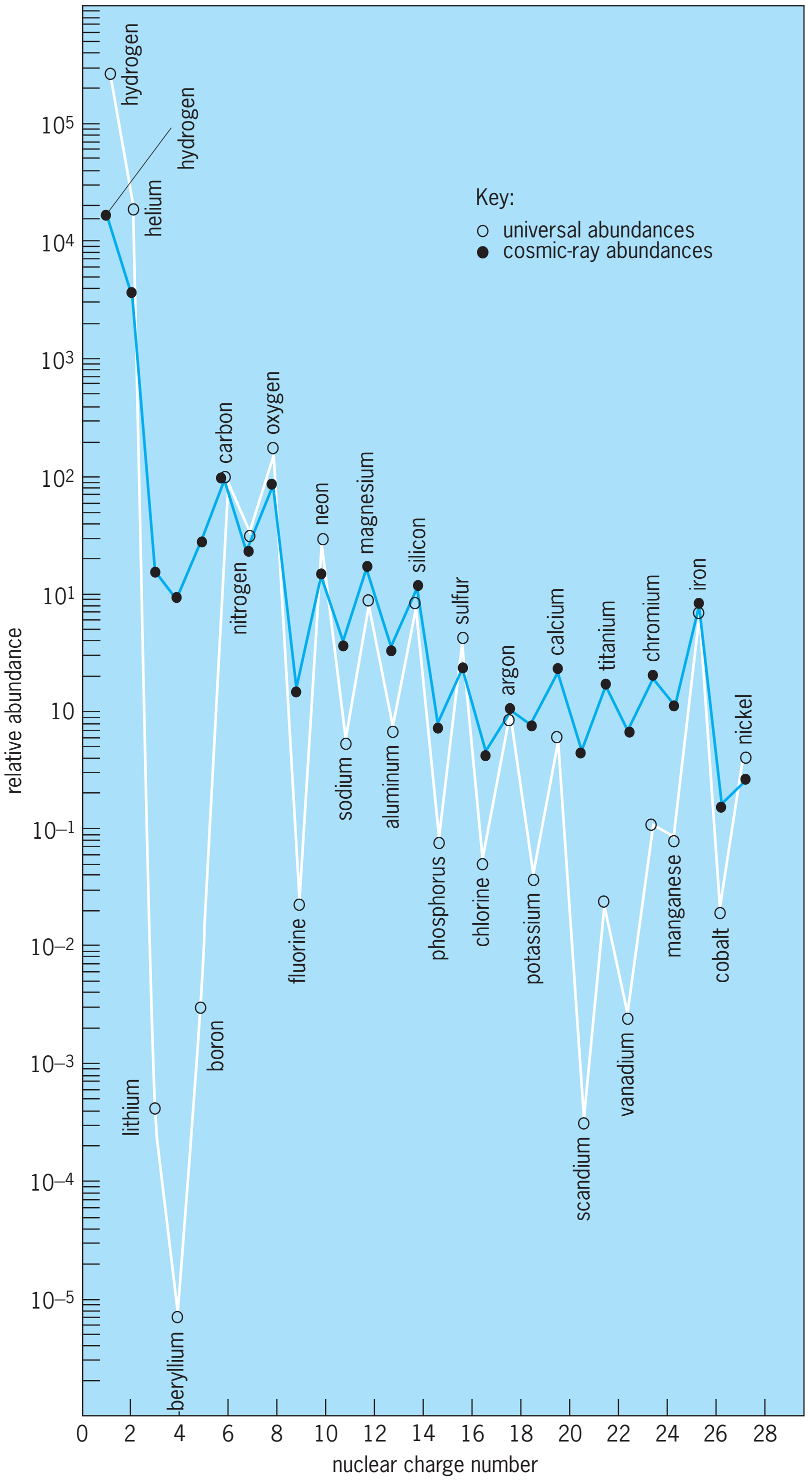

Fig. 4. Cosmic-ray abundances compared to the universal abundances of the elements. Carbon is set arbitrarily to an abundance of 100 in both cases.

Other variations in the isotopic composition are not currently understood. For example, the ratio of

^{22}Ne to ^{20}Ne in the cosmic-ray sources is estimated to be 0.37, while the accepted solar system value for this number is 0.12, which agrees well with the abundances measured in solar-flare particles. However, another direct sample of solar material—the solar wind—has a ratio of 0.08, indicating clearly that the isotopic composition of energetic particles need not reflect that of their source. Conclusions drawn from the observed difference in the solar and cosmic-ray values must be viewed as somewhat tentative until the cause of the variation in the solar material is well understood. *See* ISOTOPE.

Electron abundance. Cosmic-ray electron measurements pose other problems of interpretation, partly because electrons are nearly 2000 times lighter than protons, the next lightest cosmic-ray component. Protons with kinetic energy above 1 GeV are about 100 times as numerous as electrons above the same energy, with the relative number of electrons decreasing slowly at higher energies. But it takes about 2000 GeV to give a proton the same velocity as a 1-GeV electron. Viewed in this way electrons are several thousand times more abundant than protons. (Electrical neutrality of the Milky Way Galaxy is maintained by lower-energy ions which are more numerous than cosmic rays although they do not carry much energy.) It is thus quite possible that cosmic electrons have a different source entirely from the nuclei. It is generally accepted that there must be direct acceleration of electrons, because calculations show that more positrons than negatrons should be produced in collisions of cosmic-ray nuclei with interstellar gas. Measurements show, however, that only 10% of the electrons are positrons. As the number of positrons seen agrees with the calculated secondary production, added confidence is gained in the result that there is indeed an excess of negatrons. *See* ELECTRON.

Electrons are light enough to emit a significant amount of synchrotron radiation as they are deflected by the 10^{-10}-tesla (10^{-6}-gauss) galactic magnetic field. Measurement of this radiation by radio telescopes provides sufficient data for an approximate calculation of the average energy spectrum of electrons in interstellar space and other galaxies. Comparison of spectra of electrons and positrons measured at Earth with those calculated to exist in interstellar space provides the most direct measurement of the absolute amount of solar modulation. *See* RADIO ASTRONOMY; SYNCHROTRON RADIATION.

Properties of the energy spectrum. At energies above 10^{10} eV, the energy spectra of almost all cosmic rays are approximated over many decades by functions in which the flux decreases as the energy raised to some negative, nonintegral power referred to as the spectral index. Such a power-law relationship is of course a straight line when plotted using logarithmic axes. A steep or "soft" (that is, more rapidly falling with increasing energy) spectrum thus has a higher spectral index than a flat or "hard" spectrum. The straight-line regions of the spectra in Fig. 3 correspond to a variation of flux with a spectral index of -2.7. A spectral index of -2.7 provides a good fit with the data up to 10^{15} eV total energy. Between 10^{15} and 10^{19} eV a steeper spectrum, with an index around -3.0, seems to be well established. Above 10^{19} eV the spectrum hardens once more, returning to an index of about -2.7. The spectral index above 10^{20} eV has not been determined, because particles are so rare that they are almost never seen, even in detectors which cover several square kilometers and operate for many years. At such high energies, the individual particles are not identified, and changes in the measured-energy spectrum could be the result of composition changes. However, the evidence available indicates that the composition is essentially unchanged.

The Pierre Auger Observatory, which began operation in 2005, has a detection area the size of Rhode Island (over 3000 km^2 or 1200 mi^2) located in western Argentina's Mendoza Province. The Auger Observatory is a hybrid detector, employing two independent methods to detect and study high-energy cosmic rays. One technique is ground-based and detects high-energy particles through their interaction with water. Each of the 1600 detectors contains 11,000 L (3000 gals) of ultrapure, deionized water. The other technique tracks the development of air showers by observing ultraviolet light emitted high in the Earth's atmosphere.

Age. Another important result which can be derived from detailed knowledge of cosmic-ray isotopic composition is the "age" of cosmic radiation. Certain isotopes are radioactive, such as beryllium-10 (^{10}Be) with a half-life of 1.6×10^6 years. Since beryllium is produced entirely by spallation, study of the relative abundance of ^{10}Be to the other beryllium isotopes, particularly as a function of energy to utilize the relativistic increase in this lifetime, will yield a number related to the average time since the last nuclear collision. Measurements show that ^{10}Be is nearly absent at low energies, yielding an estimate of the age of the cosmic rays of approximately 10^7 years. An implication of this result is that the cosmic rays propagate in a region in space which has an average density of 0.1–0.2 atom/cm^3 (1.5–3 atoms/in.^{3}). This is consistent with some astronomical observations of the immediate solar neighborhood.

Very high energy particles cannot travel long distances in the 2.7 K blackbody-radiation field which permeates the universe. Electrons of 15 GeV energy lose a good portion of their energy in 10^8 years by colliding with photons via the (inverse) Compton process, yet electrons are observed to energies of 100 GeV and over. A similar loss mechanism becomes effective at approximately 10^{20} eV for protons. These observations are of course not conclusive, but a safe statement is that a cosmic-ray age of 10^7 years is consistent with all currently available data. *See* COMPTON EFFECT; COSMIC BACKGROUND RADIATION.

Several attempts have been made to measure the constancy of the cosmic-ray flux in time. Variations in ^{14}C production, deduced from apparent deviations of the archeological carbon-dating scale from that derived from studies of tree rings, cover a period of about 10^3 years. Radioactive ^{10}Be in deep-sea sediments allows studies over 10^6 years, whereas etching of tracks left by cosmic rays in lunar minerals covers a period of 10^9 years. None of these methods has ever indicated a variation of more than a factor of 2 in average intensity. There are big differences in these time scales, and the apparent constancy of the flux could be due to averaging over variations which fall in the gaps as far as the time scales are concerned. Nevertheless, the simplest picture seems to be that the cosmic rays are constant in time at an intensity level which is due to a long-term balance between continuous production and escape from the Galaxy, with an average residence time of 10^7 years. *See* COSMOGENIC NUCLIDE; RADIOCARBON DATING.

Although small, variations in cosmic-ray intensity show systematic patterns over historical and geologic time scales. Some of this variation is undoubtedly due to variability in the magnetic field of the Earth that results in changes in the geomagnetic cutoff. However, over the past several thousand years, when the magnetic field has been reasonably constant, cosmic-ray intensity has shown a distinct anticorrelation with measures of overall global temperature. Low cosmic-ray fluxes, indicative of enhanced solar activity, typically go together with warm periods. The relationship is far from understood, but this is one of many observations that must be considered in the complex, nonlinear problem of global warming.

Origin. Although study of cosmic rays has yielded valuable insight into the structure, operation, and history of the universe, their origin has not been determined. The problem is not so much to devise processes which might produce cosmic rays, but to decide which of many possible processes do in fact produce them.

In general, analysis of the problem of cosmic-ray origin is broken into two major parts: origin in the sense of where the sources are located, whatever they are, and origin in the sense of how the particles are accelerated to such high energies. Of course, these questions can never be separated completely.

Location of sources. It is thought that cosmic rays are produced by mechanisms operating within galaxies and are confined almost entirely to the galaxy of their production, trapped by the galactic magnetic field. The intensity in intergalactic space would only be a few percent of the typical galactic intensity, and would be the result of a slow leakage of the galactic particles out of the magnetic trap. It has not been possible to say much about where the cosmic rays come from by observing their arrival directions at Earth. At lower energies (up to 10^{15} eV) the anisotropies which have been observed can all be traced to the effects of the solar wind and interplanetary magnetic field. The magnetic field of the Milky Way Galaxy seems to be completely effective in scrambling the arrival directions of these particles.

For several decades in energy above 10^{15} a smoothly rising anisotropy is measured, ranging from 0.1 to 10%, but the direction of the maximum intensity varies in a nonsystematic way with energy. At these energies, particles have a radius of curvature which is not negligible compared to galactic structures, and thus their arrival direction could be related to where they came from but in a complex way. Above 10^{19} eV the radius of curvature in the galactic magnetic field becomes comparable to or larger than galactic dimensions, making containment of such particles in the disk of the Milky Way Galaxy impossible. Only a few hundred events greater than 10^{19} eV have been detected, with no systematic anisotropy. Clustering of events (of marginal statistical significance) in the data of individual observatories has been reported, but so far never confirmed by other detectors. The Pierre Auger Observatory should, over several years, increase the number of events observed by orders of magnitude and may possibly permit statistically definitive determinations of features in the arrival direction distribution. Actual identification of sources, however, will probably come only from detection of neutral radiation (photons and neutrinos) produced in cosmic-ray interactions.

Cerenkov telescopes, such as HESS in Namibia and MAGIC at the Roque de los Muchachos Observatory in the Canary Islands, have produced remarkable images of objects in the light of 10^{12}-eV gamma rays. Supernova remnants have been clearly resolved to show structures within them, and emission from x-ray binary systems has been definitively observed. Several sources unassociated with known objects are also being studied. It is generally believed that gamma rays of energy greater than 10^{12} eV can be produced only through interactions of high-energy protons or other hadrons. These gamma rays provide important information on the structure and operation of these exotic objects but the key question of whether these particles escape to become galactic cosmic rays remains unanswered. *See* ASTROPHYSICS, HIGH-ENERGY; BINARY STAR; CERENKOV RADIATION; X-RAY ASTRONOMY.

Direct detection of cosmic rays propagating in distant regions of the Milky Way Galaxy is possible by observing the electromagnetic radiation produced as they interact with other constituents of the Milky Way Galaxy. Measurement of the average electron spectrum using radio telescopes has already been mentioned. Proton intensities are mapped by studying the arrival directions of gamma rays produced as they collide with interstellar gas. Unfortunately, the amount of radiation in these processes depends upon both the cosmic-ray flux and the magnetic-field intensity or density of interstellar gas. Areas where cosmic rays are known to exist can be pointed out because the radiation is observed. But where no radiation is seen, it is not known whether its absence results from lack of cosmic rays or lack of anything for them to interact with. In particular, very little radiation is seen from outside the Milky Way Galaxy, but there is also very little gas or magnetic field there. There is therefore no direct evidence either for or against galactic containment.

A major difficulty with the concept of cosmic radiation filling the universe is the large amount of energy needed to maintain the observed intensity in the face of an expanding universe—probably more energy than is observed to be emitted in all other forms put together. *See* COSMOLOGY.

Confinement mechanisms. Three possible models of cosmic-ray confinement are under investigation. All assume that cosmic rays are produced in sources, discrete or extended, scattered randomly through the galactic disk. Most popular is the "leaky box" model, which proposes that the particles diffuse about in the magnetic field for a few million years until they chance to get close to the edge of the Milky Way Galaxy and escape. This is a phenomenological model in that no mechanism is given by which either the confinement time or the escape probability as a function of energy can be calculated from independent observations of the galactic structure. Its virtue is that good fits to the observed abundances of spallation products are obtained by using only a few adjustable parameters. Variations of the model which mainly postulate boxes within boxes—ranging from little boxes surrounding sources to a giant box or static halo surrounding the whole Milky Way Galaxy—can be used to explain variations from the simple predictions. However, all attempts to calculate the details of the process have failed by many orders of magnitude, predicting ages which are either far older or far younger than the observed age.

A second model is that of the dynamical halo. Like the earlier static-halo model, it is assumed that cosmic rays propagate not only in the galactic disk but also throughout a larger region of space, possibly corresponding to the halo or roughly spherical but sparse distribution of material which typically surrounds a galaxy. This model is based on the observation that the energy density of the material which is supposed to be contained by the galactic magnetic field is comparable to that of the field itself. This can result in an unstable situation in which large quantities of galactic material stream out in a galactic wind similar in some respects to the solar wind. In this case the outward flow is a natural part of the theory, and calculations have predicted reasonable flow rates. In distinction to the solar wind, in which the cosmic rays contribute almost nothing to the total energy density, they may provide the dominant energy source in driving the galactic wind.

A third model assumes that there is almost no escape; that is, cosmic rays disappear by breaking up into protons which then lose energy by repeated collision with other protons. To accept this picture, one must consider the apparent 5-g/cm^2 (0.07-lb/in.^{2}) mean path length to be caused by a fortuitous combination of old distant sources and one or two close young ones. Basically, the objections to this model stem from the tendency of scientists to accept a simple theory over a more complex (in the sense of having many free parameters) or specific theory when both explain the data. *See* MILKY WAY GALAXY.

Acceleration mechanisms. Although the energies attained by cosmic-ray particles are extremely high by laboratory standards, their generation can probably be understood in terms of known astronomical objects and laws of physics. Even on Earth, ordinary thunderstorms generate potentials of millions of volts, which would accelerate particles to respectable cosmic-ray energies (a few megaelectronvolts) if the atmosphere were less dense. Gamma rays and neutrons have, in fact, been detected from lightning strikes. Consequently, there are many theories of how the acceleration could take place, and it is quite possible that more than one type of source exists. Two major classes of theories may be identified—extended-acceleration regions and compact-acceleration regions.

Extended-acceleration regions. Acceleration in extended regions (in fact the Milky Way Galaxy as a whole) was first proposed by E. Fermi, who showed that charged particles could gain energy from repeated deflection by magnetic fields carried by the large clouds of gas which are known to be moving randomly about the Milky Way Galaxy. Many other models based on such statistical acceleration have since been proposed, the most recent of which postulates that particles bounce off shock waves traveling in the interstellar medium. Such shocks, supposed to be generated by supernova explosions, undoubtedly exist to some degree but have an unknown distribution in space and strength, leaving several free parameters which may be adjusted to fit the data.

Compact-acceleration regions. The basic theory in the compact-acceleration class is that particles are accelerated directly in the supernova explosions themselves. One reason for the popularity of this theory is that the energy generated by supernovas is of the same order of magnitude as that required to maintain the cosmic-ray intensity in the leaky box model.

However, present observations indicate that the acceleration could not take place in the initial explosion. Cosmic rays have a composition which is similar to that of ordinary matter and is different from the presumed composition of the matter which is involved in a supernova explosion. At least some mixing with the interstellar medium must take place. Another problem with an explosive origin is an effect which occurs when many fast particles try to move through the interstellar gas in the same direction: the particles interact with the gas through a magnetic field which they generate themselves, dragging the gas along and rapidly losing most of their energy. In more plausible theories of supernova acceleration, the particles are accelerated gradually by energy stored up in the remnant by the explosion or provided by the intense magnetic field of the rapidly rotating neutron star or pulsar which is formed in the explosion.

Acceleration of high-energy particles was first observed in the Crab Nebula, the remnant of a supernova observed by Chinese astronomers in 1054. This nebula is populated by high-energy electrons which radiate a measurable amount of their energy as they spiral about in the magnetic field of the nebula. So much energy is released that the electrons would lose most of their energy in a century if it were not being continuously replenished. Pulses of gamma rays also show that bursts of high-energy particles are being produced by the neutron star—the gamma rays coming out when the particles interact with the atmosphere of the neutron star. Particles of cosmic-ray energy are certainly produced in this object, but it is unlikely that they escape from the trapping magnetic fields in the nebula and join the freely propagating cosmic ray population. As noted above, observation of 10^{12}-eV gamma rays now allows mapping of energetic hadrons in these objects, but the issue of an escape mechanism remains. *See* CRAB NEBULA; NEUTRON STAR; PULSAR.

Acceleration in the solar system. The study of energetic particle acceleration in the solar system is valuable in itself, and can give insight into the processes which produce galactic cosmic rays. Large solar flares, about one a year, produce particles with energies in the gigaelectronvolt range, which can be detected through their secondaries even at the surface of the Earth. It is not known if such high-energy particles are produced at the flare site itself or are accelerated by bouncing off the shock fronts which propagate from the flare site outward through the solar wind. Nuclei and electrons up to 100 MeV are regularly generated in smaller flares. In many events it is possible to measure gamma rays and neutrons produced as these particles interact with the solar atmosphere. X-ray, optical and radio mappings of these flares are also used to study the details of the acceleration process. By relating the arrival times and energies of these particles at detectors throughout the solar system to the observations of their production, the structure of the solar and interplanetary magnetic fields may be studied in detail.

In addition to the Sun, acceleration of charged particles has been observed in the vicinity of the Earth, Mercury, Jupiter, and Saturn—those planets which have significant magnetic fields. Details of the acceleration mechanism are not understood, but certainly involve both the rotation of the magnetic fields and their interactions with the solar wind. Jupiter is such an intense source of electrons below 30 MeV that it dominates other sources at the Earth when the two planets lie along the same interplanetary magnetic field line of force. The anomalous component is known to be local interstellar material, accelerated by a mechanism that is not fully understood but probably is situated near the interface between the solar wind and the interstellar medium. However, there was no evidence in the *Voyager 1* crossing of the termination shock that this production occurs immediately at this particular structure. *See* JUPITER; MERCURY (PLANET); PLANET; SATURN.

Direct observation of conditions throughout most of the solar system will be possible in the next few decades, and with it should come a basic understanding of the production and propagation of energetic particles locally. This understanding will perhaps form the basis of a solution to the problem of galactic cosmic rays, which will remain for a very long time the main direct sample of material from the objects of the universe outside the solar system.

Paul Evenson

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Cosmic spherules

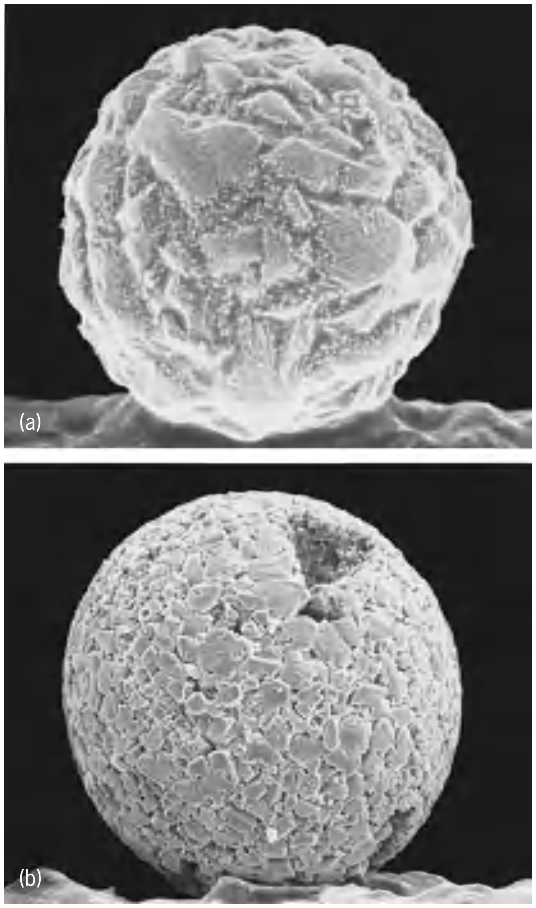
Solidified droplets of extraterrestrial materials that melted either during high-velocity entry into the atmosphere or during hypervelocity impact of large meteoroids onto the Earth's surface. Cosmic spherules are rounded particles that are millimeter to microscopic in size and that can be identified by unique physical properties. Although great quantities of the spheres exist on the Earth, they are ordinarily found only in special environments where they have concentrated and are least diluted by terrestrial particulates. *See* METEOR.

The most common spherules are ablation spheres produced by aerodynamic melting of meteoroids as they enter the atmosphere. Typical ablation spheres are produced by melting of submillimeter asteroidal and cometary fragments that enter the atmosphere at velocities ranging from 6.5 to 43 mi (11 to 72 km) per second. Approximately 10,000 tons of such particles collide with the Earth each year, and cosmic spheres in the size range of 0.004 to 0.04 in. (0.1 to 1.0 mm) are the most abundant form of this material that survives to reach the Earth's surface. The spheres are formed near 48 mi (80 km) altitude, where deceleration, intense frictional heating, melting, partial vaporization, and solidification all occur in only a few seconds time. During formation, the larger particles can be seen as luminous meteors or shooting stars. Impact spheres constitute a second and rarer class of particles that are produced when giant meteoroids impact the Earth's surface with sufficient velocity to produce explosion craters that eject molten droplets of both meteoroid and target materials.

Impact spheres. These are very abundant on the Moon, but they are rare on the Earth, and they have been found in only a few locations. Impacts large enough to produce explosion craters occur on the Earth every few tens of thousands of years, but the spheres and the craters themselves are rapidly degraded by weathering and geological processes. Meteoritic spherules have been found around a number of craters, including Meteor Crater in Arizona, Wabar in Saudi Arabia, Box Hole and Henbury in Australia, Lonar in India, and Morasko in Poland. They have also been found at the Sikhote-Alin meteorite shower site and at the location of the Tunguska explosion in Russia. Spheres from these craters include ablation spheres as well as true impact spheres produced either by shock melting of target and meteoroid or by condensation from impact-generated vapor. Impact spheres are also produced by the larger cratering events, some of which may have played roles in biological extinctions. Silica-rich glass spheroids (microtektites) are found in thin layers that are contemporaneous with the conventional tektites. Microtektites are believed to be shock-melted sedimentary materials that were ejected from large impact craters. They were ejected as plumes that covered substantial fractions of the surface of the Earth. The cumulative mass of microtektites in the 35-million-year-old North American tektite field is estimated to be equivalent in mass to 36 mi^3 (100 km^3) of solid rock. Microspherules of a different composition have been found in the thin iridium-rich layer associated with the global mass extinctions at the Cretaceous–Tertiary boundary. *See* TEKTITE.

Ablation spheres. These fall to Earth at a rate of one 0.1-mm-diameter sphere per square meter per year, and every rooftop contains these particles. Unfortunately they are usually mixed in with vast quantities of terrestrial particulates, and they are very difficult to locate. They can, however, be easily found in special environments that do not contain high concentrations of terrestrial particles that could be confused with cosmic spheres larger than 0.004 in. (0.1 mm) in diameter. Such environments include the mid-Pacific ocean floor and certain ice deposits in Greenland and Antarctica. In mid-Pacific sediments the accumulation of terrestrial sediments is only a few meters per million years, and the spherules larger than 0.004 in. (0.1 mm) than are found in concentrations of roughly 10–100 per kilogram of sediment. Cosmic spheres are easily extracted from the sediment because most spherules are ferromagnetic and much larger than typical sediment particles. The highest ablation spherule concentrations on Earth (over one per gram of sediment) are found in the melt zones of the Greenland ice cap, where melting ice leaves dust particles concentrated directly on the ice surface. *See* MARINE SEDIMENTS.

Cosmic ablation spherules can be grouped into two major types: type S (stony) and type I (iron). In polished sections it can be seen that the S spheres are composed of olivine, magnetite, and glass, with textures consistent with rapid crystallization from melt. Both of the type S spherules shown in the **illustration** have elemental compositions similar to those of stony meteorites. In general, types S spheres have compositions that are a close match with chondritic meteorites except for depletion of volatile elements such as sulfur and sodium that are lost during atmospheric entry. Many spheres are also depleted in nickel by a process that may also lead to the formation of the iron spheres. Typical type I spheres consist of iron oxide (magnetite and wustite) surrounding a core of either nickel-iron metal or a small nugget of platinum group elements. Nickel and the platinum group elements are concentrated during brief oxidation when the sphere is molten. Some of the iron spheres may be droplets of iron meteorites, but the most common ones appear to be droplets that separated from the stony spheres during atmospheric melting.



Scanning electron photomicrographs of stony cosmic spherules about 300 μm in diameter collected from the mid-Pacific ocean floor. (*a*) Sphere with so-called turtleback texture, indicative of rapid cooling from a very hot molten droplet. (*b*) Sphere with porphyritic texture, indicative of formation of a particle that was not so strongly heated during hypervelocity entry into the atmosphere as the sphere in *a*.

Identification. Cosmic spherules are of particular scientific interest because they provide information about the composition of comets and asteroids and also because they can be used as tracers to identify debris resulting from the impact of large extraterrestrial objects. The ablation spherules can be positively identified because of several unique properties, including distinctive oxygen isotope compositions and the presence of isotopes that are produced by cosmic rays such as aluminum-26 and manganese-53. Some spheres did not melt entirely, and they also retain high concentrations of noble gases implanted by the solar wind. In general, cosmic spherules can be confidently identified on the basis of their elemental and mineralogical compositions, which are radically different from nearly all spherical particles of terrestrial origin. Don E. Brownlee, II

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Cosmic strings

Hypothetical thin tubes that carry very large amounts of vacuum energy. They belong to the class of objects known as topological defects. As the universe expands, its temperature decreases and its microscopic properties, such as the strength with which fundamental particles interact, sometime change abruptly in what are called phase transitions. A well-known example of such a transition is when water freezes into ice when the temperature drops below 0°C (32°F). Strings are predicted to form at these transitions. In this context, the lowest energy state of the universe, which is called the "vacuum" although it is not necessarily empty, can have a nontrivial structure in space, and strings appear as defects in this structure. *See* DARK ENERGY; ENERGY LEVEL (QUANTUM MECHANICS); PHASE TRANSITIONS.

Two possible kinds of strings are predicted, namely, local and global strings. The energy of local strings is concentrated within a very short distance of the defect tube, called the core. As a result, local strings have only contact interactions. They are predicted in almost all cosmologically realistic grand unified theories describing all interactions as a single one at high energies. The energy density of global strings, on the other hand, is not well localized along the core, so these strings have long-range interactions. Global strings are a consequence of many models based on superstring theories; they are often called axionic strings because they contain hypothetical particles, called axions, which appear naturally in the low-energy limit of these theories. In practice, both kinds of strings could exist. *See* DARK MATTER; GRAND UNIFICATION THEORIES; SUPERSTRING THEORY.

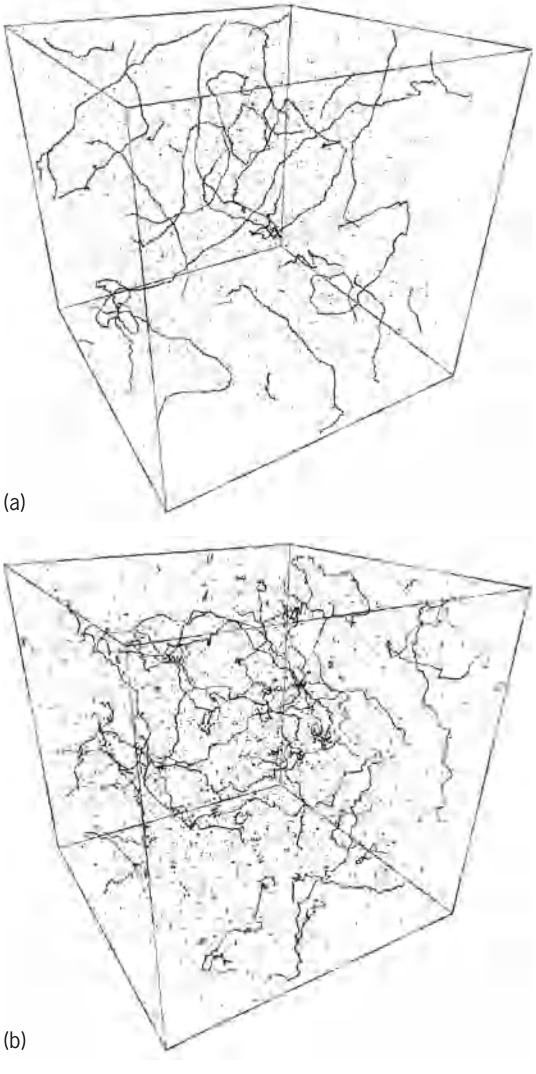
Formation. Phase transitions are believed to have taken place in the early universe, namely, immediately after the big bang, when the temperature was much higher than it is now. As such a phase transition proceeded in the early universe, regions having different microscopic properties grew independently. When their boundaries met, there could be mismatches in these properties, resulting in defects such as cosmic strings. The process was very similar to a phase transition that is observed in liquid crystals: At high temperature, molecules in such a material move rapidly and their relative orientations are random. When the temperature is lowered below a critical value, the forces between the molecules, which tend to cause them to be aligned, can overcome the thermal motion, and in any given region of space all the molecules end up pointing in the same direction. In uncorrelated locations of the crystal sample, those directions will be different, so that at various interfaces between such regions the molecules cannot have a preferred direction. The original, randomly distributed state persists in a region near such an interface; such a region is called a defect. The geometry of the defects is fixed by the original properties of the system. In the universe, although other defects, such as monopoles, domain walls, and textures, could in principle be formed, they are in practice ruled out as they would induce cosmological consequences that are not observed. *See* CRYSTAL DEFECTS; LIQUID CRYSTALS; SYMMETRY BREAKING.

Strings exist for topological reasons. Therefore, they are stable and cannot have ends, at least in simple models. In more sophisticated theories, strings can be terminated by monopoles or by connecting domain walls, but these theories are usually incompatible with cosmological observations. Therefore, strings can be seen in the form of either closed loops or infinite strings. The latter are often assumed to be, in fact, loops whose dimension is larger than the size of the observable universe, called the Hubble radius. *See* BIG BANG THEORY.

Evolution of string networks. Once a network of local strings has been formed at a phase transition, its cosmological consequences depend on its subsequent evolution. Initially, in what is called the friction-dominated phase, the network interacts very strongly with its environment, namely the very dense primeval plasma. The expansion of the universe makes the plasma density decrease, until the interactions between the strings and the particles become negligible. At this point, another effect comes into play: Whenever two pieces of strings cross each other, they have a large probability (set to unity in actual numerical simulations) to exchange extremities. This contact interaction is called intercommutation or reconnection. Long strings and loops then tend to fragment and produce large numbers of small loops. In turns, these loops lose their energy in gravitational radiation. This energy loss mechanism is compensated by the effect of the expansion, which pulls more and more strings within a Hubble volume as the Hubble radius, namely the size of the observable universe, increases. *See* GRAVITATIONAL RADIATION.

After some relaxation time, the string network eventually reaches a special configuration, known as a scaling solution: Snapshots of the string distribution (see **illustration**) taken at two different times would have similar statistical properties, with characteristic lengths increased because of expansion. The observable universe thus contains at any time an almost fixed number of long strings, somewhere between 10 and 100, separated by a typical distance of the order of the Hubble radius divided by the number of strings. Nowadays, that would be between 10^8 and 10^9 light-years. Thanks to the scaling, the density contained in the string network relative to the overall density of the universe is constant in time; it is evaluated to be of the order of 10^{-5}.

Observational consequences. The weak, strong, and electromagnetic forces appear to be very different at the low energies at which particle physics experiments can be performed. However, it is believed that they are in fact different faces of a single interaction, much in the same way as electric and magnetic effects are merged, at accelerator energies, into the



Snapshots of the simulated string distribution, that is, the string network, at two different times. (*a*) Radiation-dominated epoch. (*b*) Matter-dominated era. The size of the simulation box is that of the visible universe. (*C. Ringeval, after D. Bennett and F. Bouchet, High-resolution simulations of cosmic-string evolution: i. Network evolution, Phys. Rev. D, 41:2408–2433, 1990*)

electromagnetic interaction. Above a given energy scale, known as the grand unified scale, the differences among these three interactions disappear. If strings are formed at this grand unified scale, then their energy per unit length is of the order of the equivalent of 10^{15} tons per centimeter, concentrated in a radius of 10^{-29} cm. *See* FUNDAMENTAL INTERACTIONS.

Strings have a tension that is equal to the mass density times the velocity of light squared. As for any kind of string, transverse disturbances travel along strings at a velocity that is given by the square root of the tension divided by the mass per unit length. For a cosmic string, this velocity is therefore the speed of light, and strings are therefore very relativistic objects. Strings also move with respect to the cosmological frame (the frame in which the cosmic microwave background is at rest) with velocities comparable to that of light. As a consequence, the gravitational effects they induce are special to them, leading to specific signatures. In particular, although strings are extremely massive, the gravitational field around a string vanishes. This vanishing means that an observer at rest with respect to a string will experience no gravity. Test particles can, however, feel a gravitational disturbance provided that they move with respect to the string. Because of this disturbance, two particles are instantly projected toward one another at relativistic velocities whenever a string passes between them. This phenomenon was proposed in 1980 as a mechanism capable of seeding large-scale structure formation, namely galaxies, clusters of galaxies, and so on. Nowadays, it is believed that this mechanism is not the chief reason that the primordial featureless soup ended up with all the structures that are now observed, the basic seeds having resulted from another mechanism such as inflation. *See* INFLATIONARY UNIVERSE COSMOLOGY.

Light can be deflected by strings. This deflection is due to the fact that, if one circles around a string, the angle measured falls short of 2π by a very small but nonzero value called the missing angle. The first consequence of this deflection is that moving strings induce a Doppler-like shift in the frequency of a beam of light passing by; this phenomenon is called the Kaiser-Stebbins effect. Such shifts, being independent of the photon wavelength, are seen as temperature fluctuations in the cosmic microwave background radiation, superimposed over the primordial ones. Present studies indicate that these secondary fluctuations cannot contribute at a level higher than 10% of the total fluctuations. The remaining 90% were most probably produced during an inflationary epoch in the early universe and therefore did not result from cosmic strings. *See* COSMIC BACKGROUND RADIATION.

A light ray passing near a string would travel along a trajectory that takes into account the missing angle, and would be bent by half this amount. As a result, if a string is present between an observer and a point source, the source will be lensed and thus seen as two absolutely identical objects by the observer. Unambiguously observing such a double image would be a proof of the existence of cosmic strings. Obtaining such an observation is, however, a difficult task as even the most massive strings produce a missing angle of only a few seconds of arc. Moreover, actual pairs of almost identical objects are very common in the sky, so that, as yet, it has never been possible to distinguish between a coincidence and a lensing effect. Good candidates are currently being examined and the existence of cosmic strings might thus shortly be proven. *See* GRAVITATIONAL LENS.

Superconducting strings. The strings can be coupled to many particles, and in some cases the trapping of those particles in the string cores is energetically favored. In such cases, the trapped particles behave as current carriers, and the strings become superconducting, with currents up to 10^{20} ampères. It has been proposed that such high currents could be the sources for ultrahigh-energy cosmic rays. Current-carrying loops of strings can form equilibrium states (named vortons), which would not decay into gravitational radiation as do their non-current-carrying counterparts. The energy density they contain would then not be transferred into the radiation fluid, a condition necessary to reach scaling. Vortons would then come to dominate the universe and lead it to a premature collapse, a big crunch. Such scenarios lead to very strong constraints on the theories that predict them. *See* COSMIC RAYS; SUPERCONDUCTIVITY.

Cosmic superstrings. At energies higher than the grand unified scale, particle properties are expected to be described by superstring theory. This theory is based on the idea that the fundamental building blocks of nature are not pointlike particles. Rather, they are extended, one-dimensional objects, also called strings, which are so small that they appear to be pointlike in all conceivable experiments. However, under some conditions, some strings (not to be confused with the axionic strings, also produced by the same theories) could be of cosmological dimensions. In this case, their properties are expected to be similar to those of the local strings described above. The main difference is that the reconnection probability could be much lower, resulting in a network that could have difficulties reaching scaling, and in potentially observable cosmological consequences, currently under investigation. It is hoped that such consequences will perhaps provide the first testable prediction of superstring theory.

Patrick Peter

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Cosmochemistry

The science of the chemistry of the universe, particularly that beyond the Earth. As currently practiced, cosmochemistry is concerned primarily with inferences on pre-solar-system events, solar nebular processes, and early planetary processes as deduced from minerals in meteorites and from chemical and isotopic compositions of meteorites and their parts. *See* ISOTOPE; METEORITE.

Minerals in Meteorites

Meteorites provide a great deal of otherwise unobtainable information about the formation and early history of the solar system. The solar system formed from the solar nebula, a large cloud of gas and dust. The chemical composition of the solar system, which can be assumed to be the same as that of the solar nebula, is known in detail from spectroscopic analysis of the Sun, which contains 99.9% of its mass. From a combination of this knowledge, an estimate of temperature and pressure from hydrodynamic models, and thermodynamic data for all possible gas, liquid, and solid species, it can be determined which minerals would have become stable as the gas cloud underwent gravitational collapse, spun down into a disk, and cooled. Pressure in the solar nebula was probably so low that condensation occurred at temperatures below the melting points of the minerals, and they condensed as solids. Different minerals became stable at different temperatures, giving rise to a condensation sequence, which can be calculated (**Table 1**). *See* ASTRONOMICAL SPECTROSCOPY; ELEMENTS, COSMIC ABUNDANCE OF; HYDRODYNAMICS; PROTOSTAR; SOLAR SYSTEM; SUN; THERMODYNAMIC PRINCIPLES.

Detailed chemical information, however, requires samples, and the Earth is too geologically active to provide samples dating to its formation. Meteorites are therefore studied because, in general, they have undergone much less modification than terrestrial rocks.

Carbonaceous chondrite inclusions. A certain type of meteorite, the carbonaceous chondrite, contains millimeter-sized rocklets, or refractory inclusions, that are composed of the very minerals (especially hibonite, perovskite, melilite, spinel, and fassaite; Table 1) believed to have been among the first to condense from the solar nebula. This finding indicates that assumptions used to calculate the condensation sequence are reasonably accurate. Corundum, the first major condensate, is very rare, however. Most of it probably reacted with the nebular gas to form hibonite, or it may have entered clumps of minerals that melted and crystallized other phases upon cooling. The absence of forsterite (FeO-free olivine; Table 1) and other lower-temperature phases from

TABLE 1. Stability ranges of major high-temperature equilibrium solar nebula condensates*

Phase	Formula	Temperature limits, K† Upper‡	Temperature limits, K† Lower§
Corundum	Al_2O_3	1770	1726
Hibonite	$CaAl_{12}O_{19}$	1728	1686
Grossite	$CaAl_4O_7$	1698	1594
Perovskite	$CaTiO_3$	1688	1458
Melilite	$Ca_2Al_2SiO_7$-$Ca_2MgSi_2O_7$	1580	1434
Spinel	$MgAl_2O_4$	1488	1400
Metallic nickel-iron	(Fe, Ni)	1462	
Fassaite	$Ca(Mg, Ti, Al)(Al, Si)_2O_6$	1458	
Forsterite	Mg_2SiO_4	1444	
Anorthite	$CaAl_2Si_2O_8$	1406	
Enstatite	$MgSiO_3$	1366	

*Total pressure = 10^{-3} atm = 100 Pa.

†°F = (K × 1.8) − 459.67.

‡For condensation with decreasing temperature or disappearance with rising temperature.

§For conversion from or to forms stable at lower temperatures.

SOURCE: D. Ebel and L. Grossman, Condensation in dust-enriched systems, *Geochimica et Cosmochimica Acta*, 64:339-366, 2000.

most of these refractory inclusions indicates that they were somehow isolated from the nebular gas at very high temperatures. *See* CORUNDUM; MELILITE; PEROVSKITE; SPINEL.

The most abundant refractory inclusions that are thought to be condensates, found in the C3 group of carbonaceous chondrites, are the so-called fluffy type-A inclusions. These inclusions are mainly composed of melilite, with lesser amounts of spinel, perovskite, and hibonite. Most have very irregular shapes and appear to be aggregates of individually formed nodules. Many contain melilite crystals in which aluminum oxide (Al_2O_3), rather than magnesium oxide (MgO), increases from core to rim. This trend is opposite to that expected for crystallization from a liquid, but it could be produced by condensation from the nebular gas at about 1460 K (2170°F) during a period of falling pressure.

In contrast, type-B inclusions, also found in C3s, are round and contain spinel, melilite, fassaite, and anorthite. Results of experiments in which artificial refractory inclusions were crystallized from liquids at known temperatures and cooling rates suggest that these type B inclusions crystallized from liquids that formed by incomplete melting of preexisting solids, and cooled at rates ranging from a few tenths of a degree to tens of degrees per hour from temperatures of about 1400°C (2550°F). *See* CRYSTALLIZATION.

Unlike terrestrial rocks, most meteorites contain metallic iron-nickel alloys, indicative of formation in a reducing (oxygen-poor) environment. Other minerals within refractory inclusions can be used to estimate the oxygen abundance. On Earth, titanium is most commonly found as Ti^{4+}, but in refractory inclusions there are some minerals (for example, hibonite, fassaite) which also contain titanium in its more reduced form, Ti^{3+}. The Ti^{3+}/Ti^{4+} ratios in these minerals in many cases are quantitatively consistent with their formation in the highly reducing environment of a gas of solar nebular composition.

Formation of chondrites. Condensation probably continued at lower temperatures, after isolation of the refractory inclusions from the nebular gas. The C2 carbonaceous chondrites contain single crystals of forsterite and enstatite (Table 1) that are believed to be condensates, and the C3 chondrites contain ameboid olivine aggregates, which are irregularly shaped clumps of grains that also appear to be condensates. Based on the olivine compositions (FeO-bearing) and the presence of nepheline and sodalite, which contain sodium oxide (Na_2O) or potassium oxide (K_2O), these objects continued to react with the solar nebular vapor to temperatures as low as about 500 K (440°F). There is much olivine in the chondritic meteorites, but most of it is present in objects termed chondrules, which are millimeter-sized spheres of crystals and glass that once were molten droplets. Chondrules are found in carbonaceous and ordinary chondrite meteorites, the latter being aptly named since they are the most abundant type of meteorite. Chondrule formation was thus a major, widespread process in the early solar system. As is the case for many refractory inclusions, chondrules are thought to have crystallized from liquids formed by melting of preexisting solids, but the nature of the heat source that caused the melting is not well understood. *See* ENSTATITE; NEPHELINE; OLIVINE; PYROXENE.

In the C3 carbonaceous chondrites, the refractory inclusions and the chondrules are enclosed in a later-formed, fine-grained matrix dominated by FeO-rich olivine, plus Fe-sulfides and iron-bearing compounds. The matrix must have formed at a much lower temperature than the chondrules and refractory inclusions, because FeO is not sufficiently stable to enter silicates significantly above about 900 K (1160°F) and the carbonaceous materials require low temperatures in order to be stable as well. Thus, diverse components—condensate inclusions, melted inclusions, and chondrules—with different histories were all assembled without much reheating into objects that became carbonaceous chondrites.

In addition, components were efficiently sorted, giving rise to different chondrite groups. The C1 carbonaceous chondrites contain no chondrules or inclusions, just single olivine and pyroxene crystals in a fine-grained matrix of sheet silicates (a water-bearing mineral, similar to the clay minerals). These are the most primitive meteorites, containing solar proportions of all but the most volatile elements. The C2 carbonaceous chondrites contain small refractory inclusions that consist mostly of nonsilicate, oxide minerals (hibonite, perovskite, and spinel), and olivine-rich chondrules in a matrix dominated by sheet silicates. Many of the chondrules and inclusions were altered by some sort of FeO-water-rich fluid. This process may have occurred on the parent body. The C3 carbonaceous chondrites have more abundant chondrules and larger, more silicate-rich refractory inclusions than the C2 chondrites, in an anhydrous, olivine-rich matrix.

Ordinary chondrites consist mainly of chondrules, chondrule fragments, and very rare refractory inclusions in a very small amount of matrix. Many have been heated and have very uniform olivine and pyroxene compositions, especially with respect to their Mg/Fe ratios; these are the equilibrated ordinary chondrites. Others have not been heated and are known as unequilibrated ordinary chondrites. All chondrites contain FeO-bearing olivine, and determining how olivine with such compositions, especially that in ordinary chondrites and carbonaceous chondrite matrices, could have formed in the solar nebula is one of the major unsolved problems in the study of meteorites. Calculations show that, at the (low) temperature at which FeO becomes stable enough to enter olivine in a gas of solar composition, its rate of diffusion into grains would be so slow that negligible amounts, much lower than are observed, would enter olivine before diffusion stops altogether. The stability temperature of FeO would be higher, however, allowing more extensive diffusion, in a more oxygen-rich gas. One way this could have occurred would be if oxygen-bearing dust were added to the nebula, increasing the dust/gas ratio over the solar ratio. But only by using the maximum dust/gas ratio permitted by nebular models, with oxygen-rich, water ice-bearing dust, and olivine grains with radii of approximately 1 micrometer, do condensation models predict the formation of olivine with FeO contents within the range observed in ordinary chondrites. This set of requirements is not a satisfactory solution to the problem of accounting for the observed FeO contents of olivine in chondrites.

Some meteorites also contain trace amounts of grains of carbon-rich minerals (silicon carbide, diamond, and graphite) whose condensation requires a gas with a carbon/oxygen ratio greater than 1, whereas that of the Sun is 0.5. This finding, along with very large isotopic anomalies for many elements, provides strong evidence that these grains are interstellar in origin, predating the Sun by as much as about 2.4×10^9 years. These grains should have disappeared by reacting with the solar nebular gas, however; why they did not and how they survived long enough to be incorporated into meteorites are not yet understood. *See* DIAMOND; GRAPHITE; INTERSTELLAR MATTER; SILICON.

Meteorites from planets. The presence of a wide variety of objects in chondrites—interstellar grains, refractory inclusions, chondrules, and matrix— which date back to the formation of the solar system and have survived virtually unchanged, shows that these meteorites were generally not subjected to destructive geologic processes on their parent bodies. This fact indicates that those bodies were small and inactive. Some objects, presumably with chondritic bulk compositions, did grow large enough to become geologically active. In such bodies, heat from gravitational compression and radioactive decay caused interior melting. The first liquid produced by melting of chondritic rock consists mostly of metallic nickel-iron and sulfur. Since this liquid is twice as dense as silicates, it will sink, forming an iron-rich metallic core.

Iron meteorites are completely composed of metallic nickel-iron that was once molten. In some cases, as they cooled, the nickel preferentially entered one phase and the iron entered another, forming alternating bands in a process called exsolution. From the bulk composition of a meteorite and the iron-nickel phase diagram, the starting temperature for exsolution can be determined, and from the thicknesses and compositions of the bands, how far it progressed. Then, application of experimentally determined diffusion rates yields the cooling rate. Results for various iron meteorites fall between 1 and 100°C (2 and 180°F) per million years, evidence for origins deep within planets with radii between 100 and 300 km (60 and 180 mi). At least a dozen parent bodies appear to be represented. The pallasite meteorites, with coarse olivine crystals enclosed in a matrix of metallic nickel-iron, probably come from core-mantle boundaries of former planets.

Stony (silicate) meteorites called achondrites, which do not contain chondrules and do not have chondritic (near-solar) compositions, are from the silicate portions of planets that underwent internal melting. Just above the core-mantle boundary of such planets should be metal-poor zones of coarse-grained rocks that formed by settling of large crystals. Ureilites (olivine-rich meteorites) and diogenites (pyroxene-rich meteorites) probably formed in such zones.

The eucrites, another group of achondrites, are essentially basaltic rocks, and microscopic study shows that many of them consist of rock fragments that were broken up by meteorite impacts on their parent body. This finding indicates that they formed at or near the surface, as do terrestrial basalts. Other meteorites, termed howardites, appear to be lithified soils, and consist of rock, mineral, and glass fragments in a fine-grained matrix, as do lunar soils. In howardites the rock fragments are mainly diogenites and eucrites, showing that these meteorite types originated on the same parent body.

The irons and achondrites provide evidence of internal melting in small planets. Radiometric dating indicates that these meteorites are about as old as the solar system itself. Therefore, planet formation took place on a fairly short time scale, with bodies becoming large enough to undergo internal melting soon after the formation of the solar system. *See* MINERAL; PLANETARY PHYSICS.

A group of relatively young meteorites is also very important—the SNC (shergottite-nakhlite-chassignite) group. These are crystalline rocks with ages of less than 1.3 billion years, much younger than other igneous meteorites (4.5 billion years) or lunar samples (the youngest returned samples are about 3.1 billion years old; some unsampled units may be younger). The relatively young ages of the SNCs indicate that they had a fairly large parent body, because larger planets lose their internal heat more slowly and remain geologically active longer than small planets. Because all of the known asteroids are too small to have produced 1.3-billion-year-old internal melts, Mars was proposed as the source of the SNCs. This idea has become widely accepted. Strong evidence that Mars is the source of the SNCs, in addition to their young ages, comes from the rovers *Spirit* and *Opportunity*, which have analyzed rocks with compositions like those of basaltic shergottites. Additional evidence includes similarities between the compositions of shergottites and that of the soil at the *Viking*, *Spirit*, and *Opportunity* landing sites, and a close match between the composition of trapped gas in the SNCs and that of the Martian atmosphere as measured by *Viking* spacecraft. For some years an argument against Mars as the source of the SNCs was the absence of lunar meteorites from collections. But in 1983 the discovery of the first lunar meteorite was confirmed, on the basis of detailed comparison with analyses of lunar samples returned by the *Apollo* astronauts. *See* MARS; SPACE PROBE. Steven B. Simon

Chemical Compositions of Meteorites

The chemical composition of meteorites and independently formed objects within them have taught much about pre-solar-system events, solar nebular processes, and early planetary processes.

Cosmochemical properties of elements. Before discussing examples of the results of meteorite studies, it is necessary to understand a few basic properties of the elements.

Cosmochemical affinity. The elements can be divided into four groups based on their cosmochemical affinity: siderophile or metal-seeking elements; chalcophile or sulfide-seeking elements; lithophile or oxide and silicate-seeking elements; and atmophile elements, which do not condense and are found in atmospheres (**Fig. 1**). This classification of elements applies to the highly reducing conditions of the solar nebula, which is dominated by hydrogen. Conditions on the surface of the Earth and other planets are more oxidizing, so that some elements classified here as siderophile or chalcophile, such as lead, have lithophile characteristics in the Earth's crust and mantle. *See* ELEMENTS, GEOCHEMICAL DISTRIBUTION OF.

Volatility. The elements show a wide range of volatility in a gas of solar composition (**Fig. 2**). The refractory elements are generally considered to be those that are totally condensed in about the first 5% of the total condensable matter of the solar system, corresponding to about 1475 K (2195°F) in a gas of solar composition at a total pressure of 10^{-3} atmosphere (10^2 pascals). A subset of the refractory trace elements are sometimes referred to as the ultrarefractory elements, because they are already completely condensed before the first major mineral, hibonite, condenses at 1743 K (2677°F). The moderately volatile elements show variable degrees of depletion in chondrites and planets compared to cosmic abundances; they have condensation temperatures between 1475 and 700 K (2195 and 800°F). The highly volatile elements are strongly depleted in chondrites and planets and have condensation temperatures below 500 K (440°F). The solar nebula is highly reducing, because of the high abundance of hydrogen compared to other elements. The relative volatilities of some elements change under more oxidizing conditions. For example, under oxidizing conditions cerium becomes a moderately volatile element, whereas all remaining rare-earth elements remain refractory.

Compatibility. Some lithophile elements have large ionic radii and do not fit readily into the crystal structures of the major minerals that make up most rocks: olivine, pyroxene, and plagioclase. These elements are often referred to as incompatible elements. They tend to be enriched in the melt when a rock is partially melted. Examples of incompatible elements are potassium, rubidium, light rare-earth elements, and uranium.

Presolar events. As mentioned above, a number of types of interstellar grains have been separated from primitive meteorites. Presolar grains identified include silicon carbide, graphite, diamond, titanium carbide, zirconium carbide, molybdenum carbide, ruthenium carbide, metallic iron, aluminum oxide, titanium oxide, hibonite, and spinel. While chemistry alone has not unambiguously identified any of these grains as presolar, chemistry does help to understand the formation conditions of objects whose isotopic composition proves a presolar origin. A good example is silicon carbide, most of which is believed, on the basis of isotopic arguments, to come from the circumstellar envelopes of asymptotic

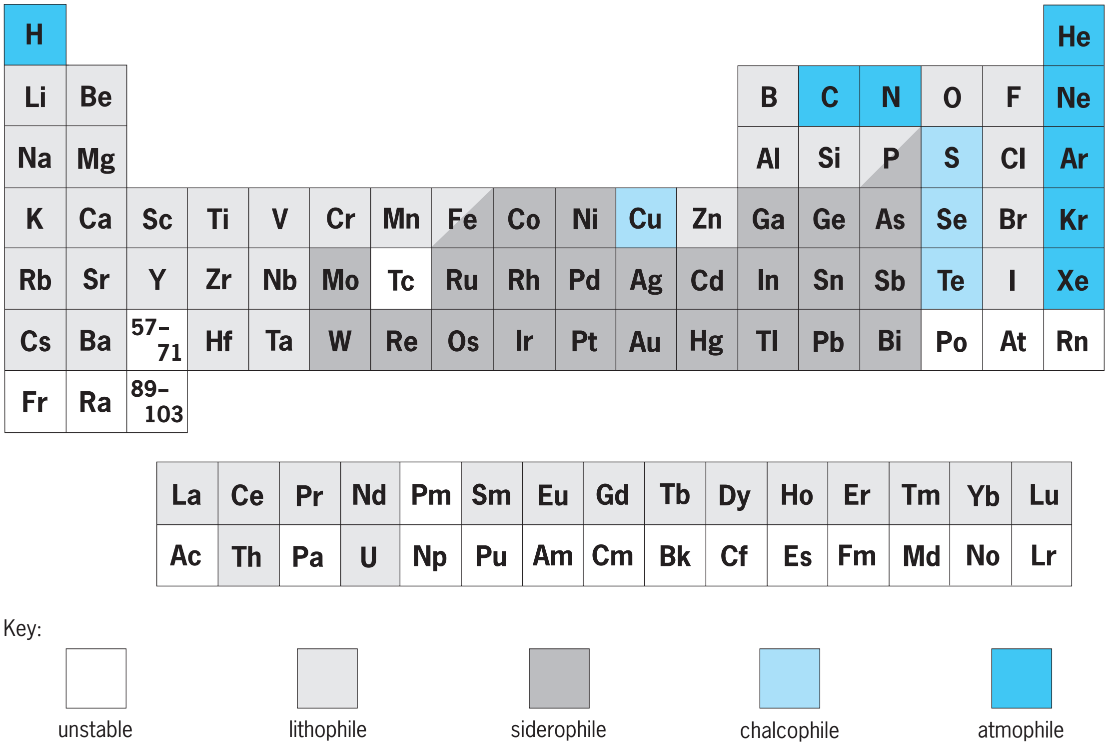
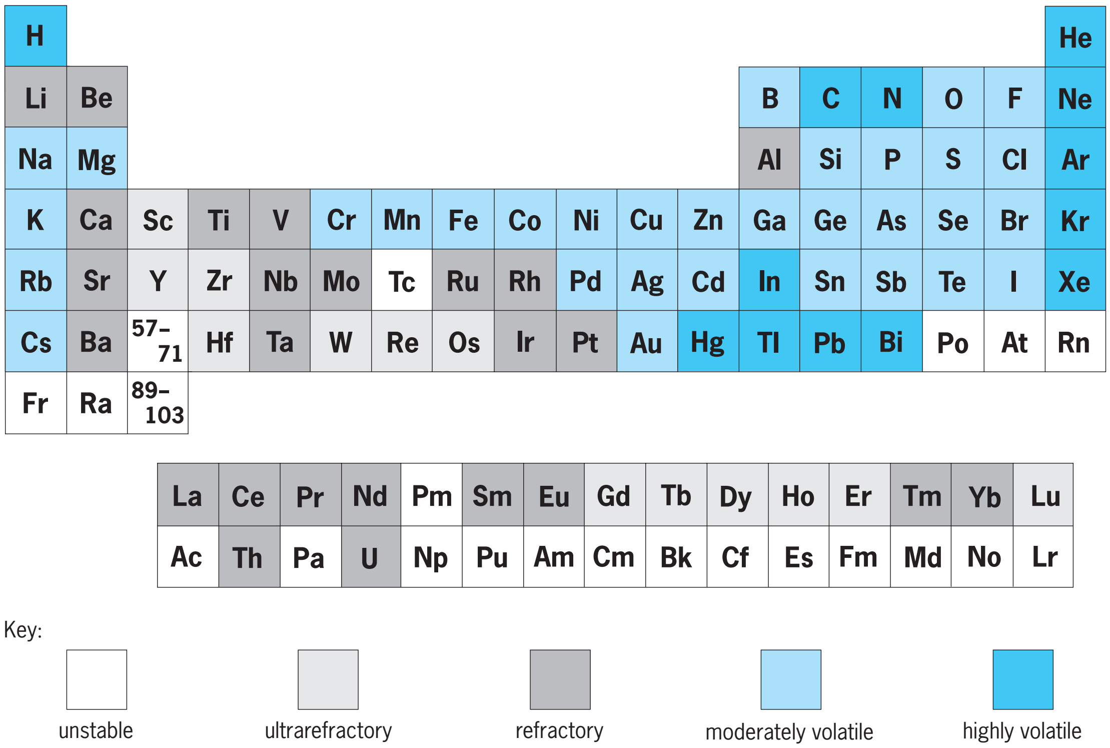


Fig. 1. Periodic table of the elements, showing their cosmochemical affinity under the highly reducing conditions found in the solar nebula.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	57–71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89–103															

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig. 2. Periodic table of the elements, with the elements classified according to their volatility in a gas of solar composition.

giant branch stars. The silicon carbide with isotope anomalies that is separated from meteorites is enriched in a number of trace elements that are predicted to condense at high temperatures as carbides in reducing environments, such as zirconium, titanium, molybdenum, strontium, barium, and the rare-earth elements. These enrichments are entirely consistent with the proposed origin of silicon carbide by high-temperature condensation in the circumstellar envelopes of carbon-rich stars. *See* CARBON STAR; GIANT STAR.

Solar nebular processes. Chemistry has been used to infer a number of important processes in the solar nebula. These include high-temperature condensation and vaporization, melting and crystallization of millimeter- to centimeter-sized objects in the solar nebula, separation of metal from silicate grains, and reaction of condensed grains with solar nebular gas. Investigation of these processes helps determine important properties of the solar nebula, such as its temperature, how long it lasted, and what the planets, which formed from the nebula, are made of.

Condensation and evaporation. As mentioned above, most carbonaceous chondrites contain refractory inclusions, which are enriched in refractory elements relative to cosmic abundances. The most common type is enriched by about 20 times relative to cosmic abundances in all refractory elements, regardless of whether they are lithophile or siderophile. Some other refractory inclusions show evidence for volatility fractionation of refractory elements from one another. This fractionation requires higher temperatures and is likely to have occurred within a few degrees of condensation of hibonite, above 1700 K (2600°F). Thermodynamic calculations done to model this fractionation assume equilibrium, so they cannot distinguish between volatilization and condensation.

Kinetically controlled processes can lead to isotopic and chemical fractionation effects that would not have occurred under equilibrium. One example comes from the refractory inclusions. The bulk chemical compositions of refractory inclusions are depleted in magnesium and silicon compared with the calculated bulk composition of material condensing from a gas of solar composition. These inclusions also display isotopic mass fractionation effects, in which they are enriched in heavy isotopes of magnesium and silicon relative to normal solar system material. Both effects have been reproduced in the laboratory by melting and evaporating synthetic refractory inclusions in vacuum or in low-pressure hydrogen. It now seems likely that most refractory inclusions have experienced heating and evaporation in the solar nebula under kinetically controlled conditions. In contrast, chondrules in chondritic meteorites generally do not display isotopic fractionation effects and are likely to have been heated under conditions that were closer to equilibrium.

Depletion of volatile elements. Relative to cosmic abundances, the terrestrial planets and many types of meteorites are depleted in the moderately volatile elements, with the depletions growing larger with increasing volatility. A useful element pair for seeing this fractionation comprises potassium, a moderately volatile element, and uranium, a refractory element. Both are incompatible elements. Within a single planet or meteorite parent body, the potassium/uranium ratio is relatively constant, because igneous fractionation processes tend to exclude both elements from major minerals. Both have long-lived radioactive isotopes that are gamma-ray emitters, so measurements are available from Mars and Venus. Chondritic meteorites have potassium/uranium ratios near the cosmic value of about 65,000, whereas the Earth, Moon, Venus, Mars, and the parent body of the basaltic achondrites [probably the 500-km-diameter (300-mi) asteroid Vesta] have lower potassium/uranium ratios. The potassium depletion in the terrestrial planets is strong evidence for a nebula-wide event that swept away the volatile elements before they could condense.

Planetary processes. A number of important planetary processes, such as separation and differentiation of a metallic core and differentiation of the silicate portion of a planet into mantle and crust, can be studied through the chemical compositions of meteorites.

Core formation. The siderophile elements are powerful recorders of metal-silicate fractionation processes in parent bodies, that is, core formation. Some elements, such as tungsten, are strongly but not completely partitioned into metal during core formation. In igneous differentiation processes, the tungsten that remains behind in the silicate is highly incompatible, such that its ratio to other incompatible but strongly lithophile elements, such as lanthanum, remains constant. In each major planetary body, such as the Earth, Moon, the parent body of the igneous SNC (shergottite-nakhlite-chassignite) meteorites (probably Mars, as discussed before), and the basaltic achondrite parent body, the ratio of tungsten to lanthanum remains constant, although the absolute concentrations can be quite variable among different samples. There are differences from one parent body to the next in the tungsten/lanthanum ratio, which are due to differences in how metallic cores separated from the silicate mantle of each parent body.

Core differentiation. When the core of a planet forms, it is initially molten (otherwise the mechanical properties of metal and silicate would not have allowed it to separate). The process of crystallization of cores of now-disrupted small parent bodies can be followed through the chemical compositions of some classes of iron meteorites. About 800 iron meteorites are known. About 80% of them can be classified into 12 groups, based primarily on the concentrations of four diagnostic elements: nickel, gallium, germanium, and iridium. During crystallization of an initially molten core, some elements, such as gold, tend to partition into solid metal while others, such as iridium, tend to remain in the liquid. Several of the 12 groups of iron meteorites show correlations between siderophile trace elements that are consistent with slow crystallization of planetary cores.

Asteroid melting. The chondritic meteorites, which have textures indicating that they never melted, show variable depletions of moderately volatile elements, but these depletions are independent of whether a trace element is incompatible or not. In contrast, the basaltic achondrites are composed of basalt, which is a rock that can form by partial melting of a chondritic source composition. The eucrites, which are igneous basaltic achondrites, show a range of trace-element concentrations that indicate that they crystallized from a melt enriched in incompatible elements compared to cosmic abundances. This range of trace-element concentrations is due to fractional crystallization, where, compared to the melt, the first eucrites to crystallize are depleted in incompatible elements and the last eucrites are enriched in incompatible elements. *See* ASTEROID.

Sampling the solar system. Much of what is known about the chemistry of the solar system comes from meteorites, which are believed to have sampled asteroids, Mars, and the Moon. Now, more that 30 years after the Apollo missions to return lunar samples, new missions are sampling the Sun, a comet, and an asteroid, and further sample-return missions are in the planning stages.

Genesis. The first of the new generation of sample-return missions, *Genesis*, exposed high-purity materials such as silicon, aluminum oxide, and diamond film to the solar wind for over 2 years. The spacecraft crashed in Utah when its parachute failed to open, but the solar wind collectors survived. Analyses will measure the chemical and isotopic compositions of many elements in the samples, allowing tests of how well spectroscopic methods measure solar composition and whether the Sun has the same isotopic composition as the Earth and meteorites.

Stardust. The *Stardust* mission flew close to the nucleus of comet Wild 2 in January 2004 and collected dust particles in silica aerogel. The spacecraft returned to Earth in January 2006. Dust grains as small as 1 μm across were extracted from the aerogel and analyzed for their crystal structure and chemical and isotopic composition. The mission should dramatically increase our knowledge of comets. It is currently unknown whether the dust in comets is formed mostly within the solar system or is an aggregation of presolar material that was never significantly modified during formation of the solar system.

Hayabusa. In early February 2006, the *Hayabusa* spacecraft was orbiting the asteroid Itokawa after having landed twice on the surface of the asteroid, with the purpose of collecting a sample to return to Earth. The spacecraft had a number of problems: it may not have collected a sample; it will not return to the Earth until at least 2010, three years later than previously planned; and scientists were attempting to resume communication, which was interrupted in December 2005. It will be of great interest to see how closely asteroids resemble the meteorites in the world's collections, and, regardless of the fate of *Hayabusa*, other robotic sample return missions to asteroids are being proposed and planned. *See* SPACE PROBE.

Andrew M. Davis

Isotopic Compositions of Meteorites

Studies of the relative abundances of isotopes in meteorites provide a unique source of information about the age of the solar system, the time scales for formation of the first solid bodies in the solar system and the growth and evolution of small planets, the prehistory (nucleosynthesis) of the material out of which the solar system formed, and the interaction of solar and galactic cosmic rays with matter.

Chronology: age of solar system and formation of planets. Meteorites are the oldest objects available for scientists to study in the laboratory and provide the best indication of the age of the solar system. Nineteen radioactive decay schemes with half-lives ranging from a remarkably short 53 days to more than 100 billion years (**Table 2**) have been utilized to determine the ages of samples varying in size from individual mineral grains less than 1 μm across to whole meteorites. The radionuclide systems in Table 2 are generally divided into two classes according to the half-life of the radioactive parent isotope: short-lived radionuclides have half-lives of less than about 100 million years, while long-lived radionuclides have half-lives of greater than 500 million years. This distinction is based on the practical issue of observability. Radioactive species with half-lives shorter than about 100 million years are now extinct in the sense that whatever amount may have existed at the birth of the solar system has completely decayed away. For this reason conventional dating of terrestrial rocks is based solely on the long-lived radionuclides listed at the bottom of Table 2. Most meteorites, in contrast, formed sufficiently early to preserve evidence of the short-lived radionuclide parents, and chronologies based on these short-lived radionuclides provide a powerful tool for examining time scales during the first 50 million years of solar system history.

The oldest meteoritic samples are the refractory, calcium-aluminum-rich inclusions found in carbonaceous chondrites. The 4.567-billion-year age of these objects provides the best estimate for the condensation of the first solid material in the solar system. Chondrules, millimeter-size spherules of glass and crystals, began to form 1 to 3 million years after refractory inclusions as the solar nebula cooled. The oldest basaltic meteorites crystallized from molten lavas on small asteroids within roughly 3 million years following the formation of the carbon-aluminum-rich inclusions (that is, ages of 4.564–4.552 billion years). Most chondritic meteorites have less precisely determined ages encompassing the range covered by chondrules and basaltic achondrites. The tight clustering of ages of the oldest meteorites reflects a period of very rapid growth during the first 5 million years of solar system history, as millimeter-to-centimeter-size objects collided and coalesced to form meter-to-kilometer-size planetesimals. The younger ages of some meteorites indicate that disturbances due to shock and thermal metamorphism began as early as 4.55 billion years ago and continued for several hundred million years. Collisions between planetesimals led to coagulation and differentiation, the growth of larger bodies, and the eventual formation of the terrestrial planets, including the Earth-Moon system, within about 50 million years following the solar system's birth. *See* EARTH, AGE OF; ROCK AGE DETERMINATION.

TABLE 2. Radionuclides and solar system chronology

Nuclide[*]	Half-life, 10^{9} years	Daughter	Abundance[†]
^{7}Be	1.5×10^{-10}	^{7}Li	^{7}Be/^{9}Be $\sim 6 \times 10^{-3}$
^{41}Ca	0.00010	^{41}K	^{41}Ca/^{40}Ca $\sim 1.4 \times 10^{-8}$
^{36}Cl	0.00030	^{36}S	^{36}Cl/^{35}Cl $\sim 2 \times 10^{-4}$
^{26}Al	0.00072	^{26}Mg	^{26}Al/^{27}Al $\sim 5 \times 10^{-5}$
^{10}Be	0.0015	^{10}B	^{10}Be/^{11}Be $\sim 1 \times 10^{-3}$
^{60}Fe	0.0015	^{60}Ni	^{60}Fe/^{56}Fe $\sim 1 \times 10^{-6}$
^{53}Mn	0.0037	^{53}Cr	^{53}Mn/^{55}Mn $\sim (0.9\text{-}4) \times 10^{-5}$
^{107}Pd	0.0065	^{107}Ag	^{107}Pd/^{108}Pd $\sim 2 \times 10^{-5}$
^{182}Hf	0.009	^{182}W	^{182}Hf/^{180}Hf $\sim 1 \times 10^{-4}$
^{129}I	0.016	^{129}Xe	^{129}I/^{127}I $\sim 1 \times 10^{-4}$
^{244}Pu	0.081	Xe fission	^{244}Pu/^{238}U ~ 0.007
^{146}Sm	0.103	^{142}Nd	^{146}Sm/^{142}Sm ~ 0.008
^{235}U	0.704	^{207}Pb	^{207}Pb/^{204}Pb $= 10.29$
^{40}K	1.25	^{40}Ar	^{40}Ar/^{36}Ar $= 295.5$
^{238}U	4.47	^{206}Pb	^{206}Pb/^{204}Pb $= 9.307$
^{232}Th	13.9	^{208}Pb	^{208}Pb/^{204}Pb $= 29.48$
^{187}Re	41.6	^{187}Os	^{187}Os/^{188}Os $= 0.0956$
^{87}Rb	48.8	^{87}Sr	^{87}Sr/^{86}Sr $= 0.6988$
^{147}Sm	106	^{143}Nd	^{143}Nd/^{146}Nd $= 0.5068$

[*] Short-lived radionuclides, listed above in the top of the table, have half-lives shorter than 100 million years; long-lived radionuclides appear in the bottom half.

[†] Short-lived radionuclides: inferred initial abundance of the parent nuclide 4.566 billion years ago. If the initial abundance is not well established, the range of values is shown. Long-lived radionuclides: initial abundance of daughter isotope.

One unusual group, the SNC meteorites, whose appearance and composition is similar to that of terrestrial basalts, is the exception to the rule with much younger crystallization ages of approximately 1.3 billion years. The young ages of the SNCs require an origin on a planetary body larger than the Moon, on which radioactive heating could sustain igneous activity for at least 3 billion years. It is now generally accepted that this group of meteorites originated on Mars, an argument strengthened by recent evidence that the isotopic compositions of hydrogen, nitrogen, and noble gases in the SNC meteorites and the Martian atmosphere are strikingly similar and distinct from those in the Earth and other meteorites.

The first short-lived radionuclide, ^{129}I, was discovered in the early 1960s by way of the observation that some meteorites have a greater abundance of daughter ^{129}Xe than do others. Twelve short-lived species with half-lives ranging from 53 days to 103 million years (Table 2) are now confirmed to have existed at the birth of the solar system. Suggestive evidence of three additional radionuclides has been reported but awaits confirmation. The evidence of short-lived radionuclides is distributed across all classes of meteorites and provides a compelling argument not only that meteorites are the oldest objects in the solar system but also that they formed rather quickly over a very short interval. Although these nuclides can no longer be observed directly, evidence that they were present during the earliest epoch of solar system history is preserved as variations in the relative abundances of the daughter isotopes of the extinct radionuclides. For example, large excesses of ^{26}Mg, produced by the decay of ^{26}Al (half-life of 0.72 million

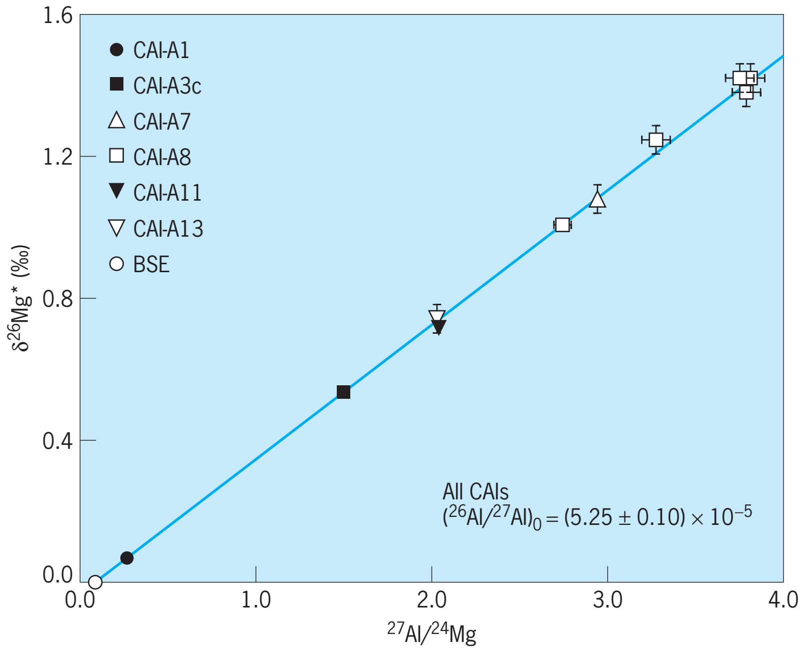


Fig. 3. Correlation of the $^{26}Mg/^{24}Mg$ ratio, expressed as $\delta^{26}Mg$ (the deviation in parts per thousand from normal Mg), with the $^{27}Al/^{24}Mg$ ratio for a group of calcium-aluminum-rich inclusions (CAIs) from the Allende meteorite. The correlation line is generated by the ingrowth of radiogenic ^{26}Mg, produced by the decay of ^{26}Al within the inclusions. The slope of the correlation line, corresponding to $^{26}Al/^{27}Al = 5.25 \times 10^{-5}$, indicates the abundance of the short-lived radionuclide ^{26}Al at the beginning of the solar system, 4.567 billion years ago. The point labeled BSE represents the Mg isotope composition of the silicate portion of the Earth. The fact that all six inclusions lie along a single line indicates that most CAIs formed at the same time, within ~50,000 years. (*After M. Bizzarro, J. A. Baker, and H. Haack, Nature, 431:275–278, 2004*)

years), are found in aluminum-rich, magnesium-poor minerals in refractory inclusions in carbonaceous chondrites (**Fig. 3**). The correlation between the relative abundance of ^{26}Mg and the Al/Mg ratio shown in Fig. 3 indicates that the inclusion crystallized before the ^{26}Al had decayed, while the slope of the line provides the relative ^{26}Al abundance at the time of formation, $^{26}Al/^{27}Al \sim 5 \times 10^{-5}$. The nearly uniform abundance of ^{26}Al among refractory inclusions suggests that the majority of these objects formed over an interval no longer than 100,000 years. No material formed in the solar system is known to have higher $^{26}Al/^{27}Al$, that is, to have formed prior to refractory inclusions.

The short-lived nuclides are not restricted to primitive chondritic meteorites but are also prominent in meteorites produced by planetary-scale melting. Asteroids similar to Vesta must have grown and differentiated within a few million years after the formation of refractory inclusions. A similar time scale is found for parent-body metamorphism of undifferentiated chondritic meteorites. These observations require an efficient and fast-acting heat source to drive planetary melting and differentiation. The long-lived radionuclides ^{40}K, ^{232}Th, ^{235}U, and ^{238}U decay much too slowly to produce melting on small planets within a few million years, and the short-lived nuclides ^{26}Al and ^{60}Fe are the most plausible sources. The abundances of ^{26}Al and ^{60}Fe found, respectively, in refractory inclusions ($^{26}Al/^{27}Al \sim 5 \times 10^{-5}$) and chondrules ($^{60}Fe/^{56}Fe \sim 1 \times 10^{-6}$) are sufficient to melt the interiors of parent bodies larger than a few kilometers. A new wealth of new data from the Hf-W, Fe-Ni, Mn-Cr, and Al-Mg parent-daughter systems in differentiated meteorites provides conclusive evidence for the dominant role of short-lived radionuclides for melting and core formation on small planetesimals.

The discovery of short-lived radionuclides also has important implications for what may be called presolar chronology, or the time-scale of events immediately preceding the birth of the solar system. The widespread presence of short-lived nuclides indicates that the time interval between nucleosynthesis and the formation of the solar system was extremely short. The upper limit to this interval is set by the lifetime of ^{41}Ca (Table 2). The refractory inclusions containing ^{41}Ca must have formed within a few mean lives, that is, a few hundred thousand years of the time of ^{41}Ca production. This time scale is so short that it suggests the formation of the solar system may have been triggered by a shock wave from a nearby exploding star containing freshly synthesized nuclear material. The one radionuclide with an even shorter half-life of 53 days, ^{7}Be, must have been produced by energetic particle interactions between gas and dust within the nascent solar nebula and cannot be used to limit the time since nucleosynthesis.

Isotope anomalies and presolar grains. Except for the variations in isotopic abundances related to decay of radionuclides discussed above, for the most part there is a close similarity between the isotopic compositions of meteorites, the Moon, and the Earth. For many years this apparent homogeneity was taken as evidence that the solar nebula was chemically and physically well mixed before the formation of the first solid bodies. The development of new analytical techniques permitting the determination of isotopic compositions in small (<1 μm) constituents of meteorites has, however, led to the discovery of large differences in isotopic abundances for many elements which cannot be explained in terms of radioactive decay or cosmic-ray interactions. These isotope anomalies provide unequivocal evidence that dust grains that condensed around a variety of different stars were incorporated into primitive meteorites and offer a window through which nucleosynthesis and stellar evolution are revealed with unprecedented clarity.

Two distinct types of meteoritic material with isotope anomalies can be distinguished: (1) samples closely related to chondritic meteorites but containing unusual isotope abundances for selected elements, and (2) authentic interstellar grains. Refractory inclusions are the primary example of the first type of material. These inclusions unquestionably formed within the solar system but exhibit unusual isotope abundances for a number of elements, including oxygen, magnesium, silicon, calcium, titanium, chromium, iron, zinc, strontium, barium, neodymium, and samarium. The variations in O-isotope abundances are particularly significant, because they hold an important clue to understanding nebular and planetary processes in the early solar system. Oxygen in refractory inclusions is enriched in ^{16}O by up to 4% relative to the average solar composition; no other element exhibits such a large variation in terms of the total number of atoms.

Aside from oxygen, the most prominent nucleosynthetic isotope effects in refractory inclusions are excesses and deficits of the neutron-rich isotopes in elements of the iron abundance peak. Correlated effects for these isotopes provide definitive evidence for the preservation of an exotic component, produced in a supernova during neutron-rich nucleosynthesis. These same inclusions also contain large (percent-level) oxygen, magnesium, and silicon anomalies due to mass-dependent shifts in relative isotope abundance. The connection between isotope anomalies reflecting stellar nucleosynthesis and those due to fractionation processes is poorly understood and remains a subject of current investigation.

Oxygen isotope anomalies are found on all scales studied, from less than a micrometer to many kilometers. The characteristic patterns of oxygen isotopes are similar to those found in refractory inclusions—large variations in the ^{16}O abundance with very small changes in the ^{17}O/^{18}O ratio. Different meteorite classes [the H (heavy), L (light), and LL chondrites] have distinct oxygen isotope compositions, requiring at least two different oxygen reservoirs in the solar nebula. The ^{16}O-rich reservoir most plausibly consisted of dust grains, while the ^{16}O-poor reservoir, containing the greater part of the solar system's oxygen, was gaseous. Mixing and exchange between these reservoirs as the solar nebula evolved gave rise to the heterogeneous array of oxygen-isotope compositions seen today. The only group of meteorites to have bulk oxygen isotope abundances similar to those of the Earth and Moon are the enstatite chondrites.

The isotope anomalies found in refractory inclusions represent a mixture of exotic stardust from other stars diluted with normal solar system material; the inclusions themselves clearly are not presolar material. A major new discovery in meteorite research is the identification in primitive chondrites of whole interstellar grains, formed outside the solar system in stellar atmospheres and incorporated into primitive meteorites essentially intact. These grains survived transit through the interstellar medium and injection into the forming solar system and preserve the isotopic and chemical compositions of the stellar nuclear sources for both major and trace elements. Presolar grains show isotope anomalies for all elements, and the size of the anomalies is at least a factor of 100 times larger than that of anomalies found in refractory inclusions.

At least 11 distinct types of presolar grains have been identified in meteorites: diamond, silicon carbide (SiC), titanium carbide (TiC), rutile (TiO_2), graphite, hibonite ($CaAl_{12}O_{19}$), corundum (Al_2O_3), spinel ($MgAl_2O_4$), silicon nitride (Si_3N_4), and, most recently, the common magnesium-rich silicate minerals, olivine and forsterite. These presolar grains have high formation temperatures and, with the exception of diamond, are generally about 1 micrometer in size. The abundance of the different types of grains varies widely among different meteorites, but diamond is always most abundant, while titanium carbide, rutile, and silicon nitride are least abundant. Presolar grains were originally incorporated into all classes of chondritic meteorites. Today, primitive meteorites of low petrologic type (for example, CI or CM chondrites) that never experienced high metamorphic temperatures contain the highest abundance of presolar grains. The pattern of decreasing abundance with increasing petrologic grade of the host meteorite reflects the selective destruction of presolar grain populations during parent body metamorphism. The abundance of presolar grains (diamond and silicon carbide, primarily) now provides a useful measure of the extent of meteorite parent body metamorphism.

With an abundance of approximately 0.05% by mass in carbonaceous chondrites, diamond is by far the most prevalent interstellar material. Interstellar diamonds are exquisitely small (mean size of only about 3 nanometers) and can be analyzed only as aggregates containing hundreds of thousands of grains. The carbon isotope composition of nanodiamonds is very similar to that of average solar system material, and the presolar origin of nanodiamonds is indicated by large enrichments in ^{14}N and Xe-HL (an exotic xenon component characterized by excesses of both the light and heavy Xe isotopes). Despite their small size, diamonds contain 50–90% of the Xe-HL in bulk chondrites. A supernova environment provides the best explanation for the observed properties of presolar diamonds.

Presolar SiC is much less abundant, about 10–15 parts per million (ppm), and much larger (about 0.1–20 μm) than the nanodiamonds. Carbon and nitrogen in SiC exhibit an extraordinary range in isotopic composition; ^{12}C/^{13}C ratios extend from 2 to 7000, compared to the range in terrestrial materials of 88 to 90, while ^{14}N/^{15}N ratios vary from 5 to more than 20,000, compared to the range in terrestrial materials of 260 to 284. Presolar SiC exhibits isotope anomalies for all elements measured, including helium, neon, magnesium, aluminum, silicon, potassium, calcium, titanium, zirconium, barium, and molybdenum. These isotope abundance patterns cannot be found anywhere in the solar system and indicate that most SiC grains formed as condensates in the atmospheres of carbon-rich, red-giant stars. Approximately 1% of SiC exhibits particularly unusual isotopic properties indicative of supernova origin; the few silicon nitride grains are also related to supernovae.

Interstellar graphite is slightly less abundant, about 10 ppm, than SiC and occurs as micrometer-size spherules which, in turn, often contain even smaller grains of Ti-, Zr-, and Mo-carbide. Presolar graphite exhibits a wide range in carbon and nitrogen isotope compositions, similar to SiC, and also contains essentially pure ^{22}Ne, extreme enrichments in ^{18}O, and large excesses of ^{26}Mg from the decay of extinct ^{26}Al. The inferred initial ^{26}Al/^{27}Al ratios range up to about 0.2, compared to a maximum of 5×10^{-5} in refractory inclusions. The diverse array of isotopic compositions cannot be explained by a single type of stellar source, and requires several different sources, including Wolf-Rayet stars, novae, and carbon-rich giant stars. *See* NOVA; WOLF-RAYET STAR.

Interstellar oxide grains are nearly 1000 times less abundant than presolar SiC, range from 0.5 to 5 μm in size, and are identified as presolar by their extremely anomalous oxygen isotope ratios. The $^{16}O/^{18}O$ ratio extends from 100 to greater than 5000, compared to the solar value of 499. Most presolar oxide grains contain excess ^{26}Mg from the decay of ^{26}Al and have isotope compositions, indicating a red giant branch star (RGB) progenitor.

Of particular interest is the discovery of presolar silicate grains whose chemical composition (rich in magnesium, silicon, and oxygen) is nearly indistinguishable from that of normal meteoritic and terrestrial minerals. Although astronomical observations indicated the presence of silicate grains in dust shells surrounding young stars, previous searches for presolar silicates proved unsuccessful. The presolar silicates were identified using a new type of imaging mass spectrometer to locate small grains displaying extreme oxygen isotope ratios, up to 100-fold enrichments in ^{17}O and ^{18}O relative to solar system matter. These presolar silicates are also found in interplanetary dust particles (IDPs) and have a surprisingly high abundance, ~70 ppm of the whole meteorite, making silicates the second most abundant type of presolar material. Like SiC and graphite, presolar silicates appear to have originated from intermediate-mass asymptotic giant branch stars.

Nucleosynthesis. Studies of isotope anomalies and presolar grains in primitive meteorites have yielded important new clues to nucleosynthesis and the types of stars contributing material to the nascent solar nebula. The very large range of isotope abundances measured in presolar grains cannot be generated by a single stellar source, and is ample proof that the solar system is the product of contributions from disparate stars. Hydrogen and the bulk of the helium in the solar system are relicts of big bang nucleosynthesis, while the elements carbon through iron were produced dominantly in charged particle reactions in massive stars. The radionuclides ^{129}I, ^{232}Th, ^{235}U, ^{238}U, and ^{244}Pu are all produced by neutron-rich nucleosynthesis, the *r*-process, in supernovae. The abundance of short-lived radionuclides requires the late addition of fresh nucleosynthetic material, most plausibly from massive, red-giant stars, to the solar nebula less than a few hundred thousand years prior to the formation of the first meteorites. The short-lived beryllium nuclei, ^{7}Be and ^{10}Be, cannot be produced in stellar nucleosynthesis and must the product of energetic particle interactions in the protosolar nebula. *See* BIG BANG THEORY; NUCLEOSYNTHESIS; STELLAR EVOLUTION; SUPERNOVA.

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Cosmogenic nuclide

A rare nuclide produced by nuclear reactions between high-energy cosmic radiation and terrestrial or extraterrestrial material. Cosmogenic nuclides may be used to examine the history of exposure to cosmic rays, and have numerous applications in earth science and archeology.

Origin of terrestrial nuclides. Primary cosmic radiation is present in space and consists of nuclear particles (mostly protons and alpha particles) with energies that are greater than typical nuclear binding energies. Collisions between cosmic-ray particles and atomic nuclei produce fragments, including cosmogenic nuclides, and also alter the characteristics of the cosmic radiation. As cosmic radiation enters the atmosphere, its flux decreases and its composition becomes dominated by neutrons rather than protons and alpha particles (which react with atmospheric gases). This reduction in flux continues through the atmosphere; at ground level, small but measurable quantities of cosmogenic nuclides are produced in solid material within about 1 m (3.3 ft) of the Earth's surface. The cosmogenic nuclides produced in these two reservoirs (atmosphere and lithosphere) may be employed for examination of different geological processes. Because of their wide range of half-lives and chemical properties, cosmogenic nuclides have a wide range of applications in geological, geomorphological, and biogeochemical studies. *See* ALPHA PARTICLES; COSMIC RAYS; COSMOCHEMISTRY; PROTON.

Production. Production of cosmogenic nuclides varies over both space and time. The flux of cosmic rays, and hence cosmogenic nuclide production rates, decreases exponentially (by a factor of 2 for every ~100 g/cm^2 increase in pressure) with depth into the atmosphere (**Fig. 1**). In addition, the Earth's magnetic field—weakest at the magnetic poles and strongest at the Equator—diverts charged particles before they enter the upper atmosphere. As a result, production rates are greater at high geomagnetic latitude than at low geomagnetic latitude (Fig. 1).

Production of cosmogenic nuclides also varies with time. The three major potential variables are solar activity, the primary flux of galactic cosmic rays, and the Earth's magnetic field. Solar activity has an ~11-year cycle, varying around a mean that is fairly constant over longer periods. The galactic cosmic-ray flux is believed to have been relatively constant for at least the past 10^7 years. Therefore, geomagnetic field variability is probably the most important source of production rate changes over the past 10^3–10^6 years.

The earliest measurements of cosmogenic nuclides utilized radioactive decay counting and established the bases of many present-day studies. The development of exceptionally sensitive techniques (accelerator mass spectrometry and static mass spectrometry) during the 1980s improved detection limits by factors of up to 10^6 and greatly broadened the range of applications of these nuclides. *See* ACCELERATOR MASS SPECTROMETRY.

Atmospheric nuclides. Numerous nuclides are produced in measurable quantities in the atmosphere (**Table 1**). Their half-lives and their chemical reactivities determine their applications in earth science. *See* RADIOISOTOPE (GEOCHEMISTRY).

Short-lived nuclides. Short-lived nuclides, including beryllium-7 (^{7}Be), sodium-22 (^{22}Na), phosphorus-32 (^{32}P), and phosphorus-33 (^{33}P), have been employed in studies of atmospheric circulation, particularly stratospheric-tropospheric exchange. Because production rates are far higher in the stratosphere than in the troposphere, concentrations of these nuclides in atmospheric aerosol particles are related to the extent of exchange processes. *See* STRATOSPHERE; TROPOSPHERE.

These nuclides also have applications in oceanography. Phosphorus is an essential nutrient element in the surface ocean; its isotopes ^{32}P and ^{33}P have half-lives appropriate for studies of surface-layer oceanic biological productivity. The tendency for beryllium in aquatic systems to adsorb onto particle surfaces makes ^{7}Be useful in tracing sediment transport and accumulation, on time scales up to several months, in estuarine and coastal regions.

Longer-lived nuclides. Because of its highly successful applications in dating, carbon-14 (^{14}C; radiocarbon) is the best-known cosmogenic nuclide. Essentially all atmospheric ^{14}C is in the form of gaseous carbon dioxide ($^{14}CO_2$); it thus has an atmospheric residence time long enough for the ratio of ^{14}C to ^{12}C (the stable isotope) to become homogeneous throughout the atmosphere. Living organisms and inorganic carbonates incorporate carbon with an isotope ratio reflecting that of the atmosphere. Upon removal from contact with the atmosphere, the ratio ^{14}C/^{12}C decreases through radioactive decay of ^{14}C. With knowledge of the initial ratio and the half-life of ^{14}C, measurement of ^{14}C/^{12}C allows calculation of the age of a sample. This technique has been extensively used in archeology and geology for samples as old as 4 × 10^4 years. High-precision ^{14}C dates of inorganic carbon dissolved in seawater are also used to deduce global oceanic circulation rates and patterns by determining the time since a particular water mass had contact with the atmosphere. *See* OCEAN CIRCULATION; RADIOCARBON DATING; SEAWATER.

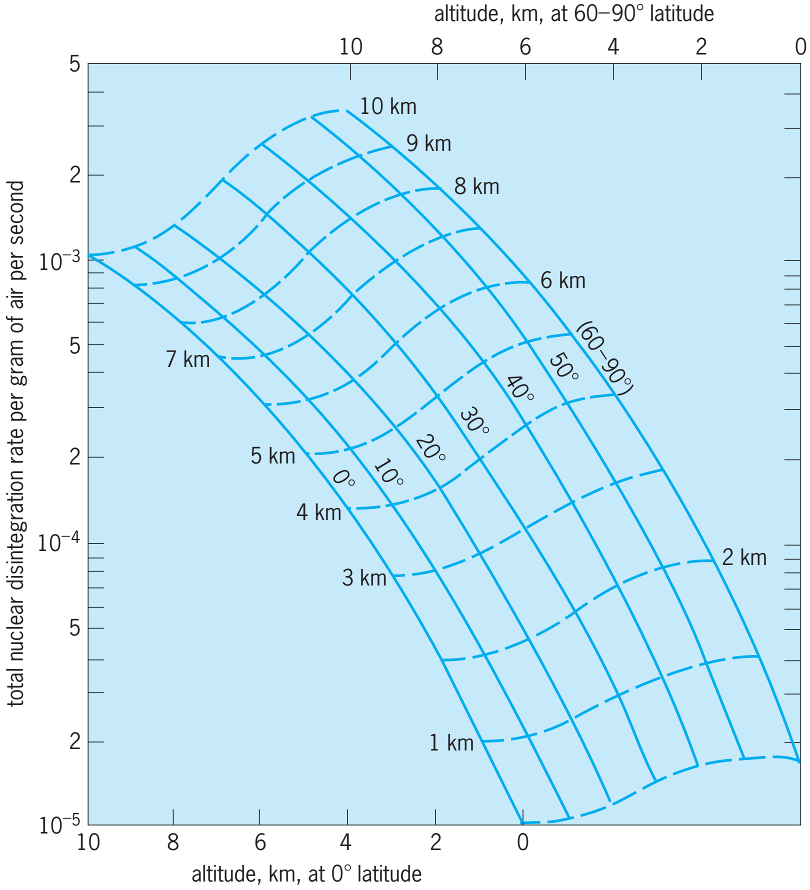

Fig. 1. Total rate of nuclear disintegrations in the atmosphere (with energy release greater than 40 MeV) is plotted as a function of altitude for various geomagnetic latitudes. Curves for each latitude (0–90°, in steps of 10°) are successively displaced by 1 km (0.6 mi) along the abscissa. It can be seen that disintegration rates increase exponentially with altitude and are lower at low geomagnetic latitude. The relationship between the total nuclear disintegration rate and the production rate differs slightly for each nuclide. (*After D. Lal and B. Peters, Cosmic ray produced radioactivity on the earth, in S. Flugge, ed., Handbuch der Physik, vol. 46/2, pp. 551–612, Springer-Verlag, 1967*)

Production rates of cosmogenic nuclides play a key role in setting the initial value of isotope ratios used in calculating ages. The record of the ^{14}C/^{12}C ratio in annual tree rings allowed reconstruction of production rate variations over the past 10^4 years. This range has been extended to about 3 × 10^4 years by measurements of the ^{14}C/^{12}C ratio in independently dated corals. These results indicate that the ^{14}C/^{12}C ratio in the atmosphere was ~1.4 times the present value during the period between 2–3 × 10^4 years ago. *See* DENDROCHRONOLOGY.

Unlike ^{14}C, most other cosmogenic nuclides have atmospheric residence times on the order of months, and thus they may provide information on cosmogenic nuclide production rate variations on time

TABLE 1. Principal cosmogenic nuclides produced in the atmosphere and their applications

Nuclide	Major target elements	Half-life	Main applications
Beryllium-7 (^{7}Be)	Nitrogen, oxygen	53 days	Tracing of atmospheric mixing Sediment transport and deposition
Beryllium-10 (^{10}Be)	Nitrogen, oxygen	1.5×10^6 years	Dating and tracing of marine sediments Examination of soil formation Ice core studies
Carbon-14 (^{14}C)	Nitrogen	5730 years	Dating of organic carbon, shells, and so forth Determination of rates of oceanic circulation
Sodium-22 (^{22}Na)	Argon	2.6 years	Tracing of atmospheric mixing
Silicon-32 (^{32}Si)	Argon	130 years	Upper-ocean biological processes and mixing
Phosphorus-32 (^{32}P)	Argon	14.3 days	Tracing of atmospheric mixing Upper-ocean biological processes
Phosphorus-33 (^{33}P)	Argon	25 days	Tracing of atmospheric mixing Upper-ocean biological processes
Chlorine-36 (^{36}Cl)	Argon (chlorine in aerosols)	3.0×10^5 years	Dating and tracing of ground waters

scales of years to decades. Records of ^{10}Be concentrations in ice cores drilled in Antarctica and Greenland extend as far back as $\sim 1.5 \times 10^5$ years. These results are useful for determining precipitation rates and establishing chronologies. However, with careful normalizations they also may be used to examine past variability in production rates. Similarly, a record of beryllium-10 (^{10}Be) fluxes combined from several marine sediment cores provides a 200,000-year history of cosmogenic nuclide production.

Beryllium-10 has also been used for dating marine sediment cores and manganese encrustations up to 1.5×10^7 years old. If ^{10}Be is homogenized with the stable isotope (^{9}Be) in the oceanic water column, the beryllium incorporated into sediments will have a known isotope ratio. Any changes in the ^{10}Be/^{9}Be ratio down the sediment core can then be assumed to be due to radioactive decay of ^{10}Be. The tendency of beryllium to adsorb onto particles in aqueous systems gives it a relatively short oceanic residence time, making it necessary to consider the possibility of past variation in the oceanic ^{10}Be/^{9}Be ratio. Details of the incorporation of beryllium into marine sediments have been obtained by comparison of ^{10}Be with thorium-230 (^{230}Th) and protactinium-231 (^{231}Pa), other so-called particle-reactive radionuclides. *See* MANGANESE NODULES; MARINE SEDIMENTS.

Atmospheric cosmogenic nuclides can be used to trace mixing between geological reservoirs. For example, the ratio of cosmogenic chlorine-36 (^{36}Cl) to stable chlorine differs greatly in atmospheric, continental, and marine material; chlorine isotopes are thus used to examine the relative contributions of these possible sources to salts in saline lakes and ground waters. Similarly, because ^{10}Be has very high concentrations in marine sediments, its presence within mineral matrices of arc volcanic rocks provides evidence for the role of subducted young sediment in the associated magma. In addition, ^{10}Be concentrations in fluids emitted by ocean-ridge hydrothermal systems can quantify the extent of interaction between those fluids and marine sediments.

Cosmogenic nuclides also have applications in examining soils and ground waters. Chlorine-36 produced in the atmosphere and brought to the Earth's surface in precipitation remains in solution; it is used for tracing and dating ground waters. In contrast, beryllium has very low mobility in neutral-to-alkaline ground waters. The inventory of ^{10}Be in a soil profile is related either to the age of the profile or to the residence time (relative to removal in ground water or by erosion) of beryllium in the profile.

Ground-level nuclides. A small but significant flux of cosmic rays is present at ground level (Fig. 1). This radiation produces cosmogenic nuclides within mineral lattices of exposed rock. In-situ-produced cosmogenic nuclides are used to examine geological problems (**Table 2**). In contrast to the case of cosmogenic nuclides produced in the atmosphere, in which applications are linked to the geochemical behavior of each element as well as the half-life of the nuclide, the uses of in-situ-produced cosmogenic nuclides in exposed rock surfaces depend primarily on the half-lives of the nuclides.

In-situ-produced cosmogenic nuclides are useful for dating periods of surface exposure. Their production rates decrease by a factor of 2 for every ~40 cm (16 in.) depth below an exposed rock surface, so accumulation of cosmogenic nuclides can date geological events that bring material to the Earth's surface. For example, the theoretical evolution of the concentration of ^{10}Be as a function of time for various erosion rates can be calculated (**Fig. 2**). The method has been used to date exposure of rocks brought to the surface by processes including glaciation, volcanic activity, and meteor impact. It has also been used to date the formation of geomorphological features (such as alluvial fans or glacial moraines) deposited over active faults and subsequently offset by fault movement. This provides a quantitative

TABLE 2. Principal cosmogenic nuclides produced in situ within surface rock

Nuclide	Half-life, years	Major target elements	Advantages	Disadvantages
Helium-3 (^{3}He)	Stable	Oxygen, magnesium, silicon, iron	High production rate; low analytical detection limits	Loss by diffusion; corrections for primordial and nucleogenic ^{3}He
Beryllium-10 (^{10}Be)	1.5×10^{6}	Oxygen, magnesium, silicon, iron	Production fairly independent of rock composition	Potential contamination by atmospheric ^{10}Be
Carbon-14 (^{14}C)	5730	Oxygen, magnesium, silicon, iron	Less influence of exposure before current episode	Only for exposure ages under 15,000 years
Neon-21 (^{21}Ne)	Stable	Magnesium, aluminum, silicon, iron	Stable isotope with low diffusive loss rate	Corrections for atmospheric, primordial and nucleogenic ^{21}Ne
Aluminum-26 (^{26}Al)	7.2×10^{5}	Silicon, aluminum, iron	Minimal atmospheric production	Significant noncosmogenic production
Chlorine-36 (^{36}Cl)	3.0×10^{5}	Iron, calcium, potassium, chlorine	Ease of chemical purification	Production rates highly dependent on rock composition

approach to determine slip rates on faults and earthquake recurrence intervals. Such results could not have been obtained by conventional methods. *See* GEOMORPHOLOGY.

Erosional losses of in-situ-produced nuclides limit their use in certain cases. In fact, outside of Antarctica (where erosion rates are exceedingly slow), cosmic-ray-exposure dating is generally applicable only to exposures of less than a few hundred thousand years. However, in cases where independent evidence indicates that exposure has been sufficiently long for nuclides to reach their steady-state concentrations, cosmogenic nuclide concentrations may be used to calculate mean physical erosion rates (Fig. 2). In some cases, this approach may be extended to the scale of a watershed by assuming that the cosmogenic nuclide content of sediment discharged by a river represents the average concentration—weighted for area and denudation rate of the various erosional environments present—for the basin as a whole. In addition, spatial distributions of in-situ-produced nuclides and ratios of nuclides with differing half-lives can provide criteria for understanding whether rocks have undergone previous episodes of exposure and burial. *See* ROCK AGE DETERMINATION.

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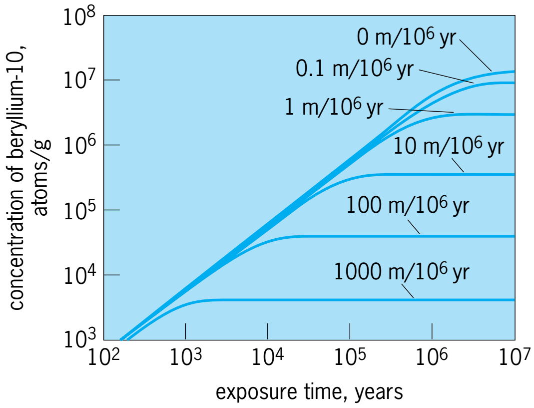

Fig. 2. Theoretical accumulation of in-situ-produced ^{10}Be as a function of time for various erosion rates. These curves are based on calculations using present-day production rates for sea level and high latitude. Concentrations increase with time to reach steady-state values with respect to radioactive decay and erosional loss. Nuclides with other half-lives have similar behavior, but with different time scales. (*After E. T. Brown et al., Examination of surface exposure ages of moraines in Arena Valley, Antarctica using in-situ-produced beryllium-10 and aluminum-26, Geochim. Cosmochim. Acta, 55:2269–2283, 1991*)

Meteorites. Collisions among the solid bodies of the solar system produce many small fragments. A fragment from a collision that finds its way to the top of the Earth's atmosphere is known as a meteoroid. A meteoroid becomes a meteorite when it lands on the Earth. While a meteoroid is in space, cosmic rays bombard its surface and penetrate to depths of a few meters. The exposure age of an extraterrestrial object is the time during which cosmic rays bombarded it in space.

Because cosmic rays penetrate just a few meters of solid matter, cosmogenic nuclides cannot form deep in the interiors of large bodies such as asteroids. The accumulation of cosmogenic nuclides begins when a collision lifts deep-seated material to the surface or ejects it into space as part of a small body. When a meteorite hits the Earth, the accumulation of cosmogenic nuclides effectively stops. The reason is that the Earth's atmosphere and magnetic field screen out most cosmic rays.

Identification. The total amounts of the cosmogenic nuclides in a meteorite are related to its exposure age. They also indicate the size of the meteoroid. To get this information, it is necessary to be able to identify cosmogenic nuclides as such and measure their concentrations. Many of the nuclides found in terrestrial materials are radioactive. All of them have lifetimes of a few million years or less. Most bodies in the solar system solidified about 4.5×10^{9} years ago. Thus, even if an asteroid contained some noncosmogenic ^{10}Be when it formed, that ^{10}Be would long since have vanished. Accordingly, when ^{10}Be is found in a meteorite today, it is likely that cosmic rays produced it recently. The same conclusion applies to other radioactive nuclides found in terrestrial materials.

The stable nuclides pose a different kind of problem in identification. For example, the total concentration of purely cosmogenic neon-21 (^{21}Ne) seldom reaches 1 part per billion, an extremely low value. If a meteorite parent body contained much noncosmogenic ^{21}Ne when it formed, then that ^{21}Ne would drown any later contribution due to cosmic rays. As it happens, the parent bodies of meteorites crystallized with very few atoms of neon. Indeed, the low "primordial" abundance of neon is one reason why ^{21}Ne is such an important stable cosmogenic nuclide. Some meteorites do contain measurable concentrations of primordial neon. For them, a general knowledge of isotope abundance patterns can help in sorting out the cosmogenic and noncosmogenic components (**Table 3**). *See* ISOTOPE.

Measurement of exposure ages. The concentrations of cosmogenic nuclides in meteorites are so low that very sensitive techniques are needed to measure them. Formerly, the only practical method for measuring the radioactive nuclides was to observe their rates of decay, a slow process requiring large samples. With the development of accelerator mass spectrometry, it became possible to measure directly the number of atoms of cosmogenic nuclides. Accelerator mass spectrometry has largely replaced decay counting for cosmogenic radionuclides with half-lives greater than a few thousand years. Conventional methods of mass spectrometry give reliable results for the stable cosmogenic nuclides. *See* MASS SPECTROMETRY.

If the concentration of a stable cosmogenic nuclide N grows at a constant rate P in a meteoroid, then after an exposure lasting t years the meteorite will contain a concentration N equal to $P \times t$. The value t for a meteorite can be calculated by measuring the concentration N, provided that the value of the production rate P is known. One way to obtain a value for production rate is to calculate it from basic physical principles. Another is to use the information given by the radioactive cosmogenic nuclides.

TABLE 3. Some important cosmogenic nuclides in extraterrestrial materials

Isotope	Half-life
Hydrogen-3 (^{3}H)	12.3 years
Helium-3 (^{3}He)	Stable
Beryllium-7 (^{7}Be)	53 days
Carbon-14 (^{14}C)	5730 years
Neon-21 (^{21}Ne)	Stable
Sodium-22 (^{22}Na)	2.6 years
Aluminium-26 (^{26}Al)	7.1×10^5 years
Magnesium-26 (^{26}Mg)	Stable
Chlorine-36 (^{36}Cl)	3.0×10^5 years
Argon-36 (^{36}Ar)	Stable
Argon-38 (^{38}Ar)	Stable
Argon-37 (^{37}Ar)	35 days
Argon-39 (^{39}Ar)	269 years
Potassium-40 (^{40}K)	1.3×10^9 years
Potassium-39 (^{39}K)	Stable
Potassium-41 (^{41}K)	Stable
Calcium-41 (^{41}Ca)	1×10^5 years
Manganese-53 (^{53}Mn)	3.5×10^6 years
Manganese-54 (^{54}Mn)	312 days
Nickel-59 (^{59}Ni)	7.6×10^4 years
Iron-60 (^{60}Fe)	1.5×10^6 years
Cobalt-60 (^{60}Co)	5.27 years
Krypton-81 (^{81}Kr)	2.1×10^5 years
Krypton-78 (^{78}Kr)	Stable
Krypton-80 (^{80}Kr)	Stable
Krypton-82 (^{82}Kr)	Stable
Krypton-83 (^{83}Kr)	Stable
Iodine-129 (^{129}I)	1.6×10^7 years
Xenon-124 (^{124}Xe)	Stable
Xenon-132 (^{132}Xe)	Stable

The values for meteorite exposure ages range from times too short to measure to 2.5×10^9 years. Stony meteorites generally have exposure ages of $2–20 \times 10^6$ years. Iron meteorites have much longer exposure ages, about 5×10^8 years on average, than do stony meteorites, perhaps because iron meteorites resist destruction better. Many groups of meteorites have several members with the same exposure age. The stony meteorites known as H-chondrites provide a striking example of exposure age clustering at about 7×10^6 years. The existence of such clusters suggests that the meteorites involved originated in the same body in a single collision. Interestingly, many of the meteorites known as diogenites, eucrites, and howardites seem to have a common exposure age of about 2×10^7 years. This observation supports the idea that all three groups come from the same object, even though they differ in chemical and mineral composition.

Lunar meteorites have some of the shortest exposure ages measured, no doubt because they had only a short distance to travel. Research related to the problem of meteorite exposure ages is focused on improving the values of production rates, determining the exposure ages of rare but important new meteorites, refining existing values, deciphering exposure histories of objects that underwent more than one episode of irradiation, and understanding the behavior of cosmic rays from the Sun and from the stars over time. *See* METEORITE. G. F. Herzog

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Cosmological constant

The constant gravitational source added to the general theory of relativity by Einstein to balance the gravitational field equations necessary for a static universe. In formulas it is denoted Λ (lambda) and has units of curvature, or $(\text{length})^{-2}$. The existence of the cosmological constant would mean that empty space gravitates as if it were filled by a static, uniform energy density $\rho = \Lambda c^4/8\pi G$, where G is the newtonian constant of gravitation, and pressure $p = -\rho$. It is speculated to be responsible for dark energy, since a sufficiently large cosmological constant would cause the accelerated expansion of spacetime. However, the physical origin of the cosmological constant is not understood. Quantum theory predicts the existence of the cosmological constant, but with an energy density that is approximately 10^{120} times too large to be compatible with observations. This gross mismatch between theory and observation, known as the cosmological-constant problem, is a deep enigma of astrophysics and physics. It is thought that a resolution requires a quantum theory of gravity. Testing for the existence of the cosmological constant is a major goal of current physics and astronomy research. *See* ACCELERATING UNIVERSE; DARK ENERGY; QUANTUM GRAVITATION; RELATIVITY.

Introduction by Einstein. The cosmological constant was introduced by Albert Einstein in 1917, in the first application of general relativity to cosmology. In order to balance theoretical and practical considerations in constructing a mathematical model of the universe, Einstein found it necessary to invoke a new cosmological term, Λ. He regarded this term as a universal constant whose value would be determined empirically. The effect of adding the Λ was to cut off the gravitational influence of distant matter and balance the field equations for a static universe. This cosmological model was consistent with contemporary observations of the slow kinetic motions of stars and nebulae. Though the 1929 discovery of the cosmic redshift-distance by Edwin Hubble, soon interpreted as expansion, invalidated Einstein's construction, the cosmological constant survived. Later, when discussing the discovery of the expanding universe with George Gamow, Einstein is reputed to have called the introduction of the cosmological constant "the greatest blunder" of his life.

De Sitter model. Shortly after Einstein's introduction of the cosmological constant, Willem de Sitter proposed a theoretical model universe containing the cosmological constant but no other forms of matter. This solution of the gravitational field equations is an idealization of the present-day universe, wherein the stars and galaxies are regarded as test particles that sit atop a perfect sea of static, uniform energy. Since general relativity dictates that pressure gravitates in addition to mass-energy, the negative pressure or tension of the cosmological constant causes spacetime to expand at an accelerating rate. Hence, test particles recede from each other as if under the influence of a repulsive gravitational potential. The theoretical prediction of a cosmological redshift can be traced back to this work, also. In the big bang cosmology, the inflationary universe is well described by de Sitter's solution, as is the distant future of the universe filled with dark energy in the form of the cosmological constant. *See* BIG BANG THEORY; INFLATIONARY UNIVERSE COSMOLOGY.

Quantum vacuum as a source. The quantum vacuum was proposed as the source of the cosmological constant by Yakov Zeldovich in 1967. He showed that the irreducible, quantum zero-point energy of elementary particles—a foaming sea of virtual particles—contributes a static, spatially uniform source of gravitation. Consequently, the cosmological constant is interpreted to represent the cosmological vacuum, the lowest energy state of the universe. The magnitude of this energy density depends sensitively on the maximum particle energy allowed in the quantum theory. Zeldovich found that any reasonable estimate for this energy scale, based on the known properties of particles, results in a cosmological energy density that is too large by many orders of magnitude.

There has been debate whether the cosmological constant is a consequence of the geometry of spacetime or of the gravitating sources, traditionally corresponding to the left- and right-hand sides of the gravitational equations, respectively. Einstein placed Λ on the left-hand side, identifying it as a property of the spacetime. Zeldovich placed Λ on the right-hand side, advocating the view that the cosmological constant, as well as gravitation itself, traced their origins to the quantum properties of particles and fields. The difference is largely semantic, since general relativity dictates that the gravitating sources are balanced by the curvature of spacetime.

Arguments for zero value. Prior to the discovery of the cosmic acceleration, most efforts to solve the cosmological constant problem sought to explain that Λ must be identically zero. One such proposal suggested that under a quantum theory of gravity Λ is a quantum-mechanical variable with a vanishing expectation value. Alternatively, it was argued that boundary conditions at the big bang set Λ to zero. In neither case are there additional, testable consequences of the proposed solution. Supersymmetry, a theory of fundamental interactions beyond the standard model of particle physics, offers a solution which can be tested by laboratory experiments. If this new symmetry of nature is valid, it implies that the cosmological vacuum, and hence Λ, is zero. *See* QUANTUM MECHANICS; SUPERSYMMETRY.

Relation to cosmic acceleration. The discovery of cosmic acceleration puts these arguments in limbo. Current observations are consistent with a nonvanishing cosmological constant, although they are not precise enough to eliminate other possibilities. If observations prove that dark energy can be explained only by the cosmological constant, the challenge will be to explain why the magnitude of Λ is so much smaller than the naive estimate.

Energy scales. The cosmological constant based on Zeldovich's calculation can be expressed as $\Lambda = E^4/2\pi(E_P\hbar c)^2$, where E is the maximum allowed zero-point energy, $\hbar$ is Planck's constant divided by 2π, and c is the speed of light. The natural choice for this energy is the Planck energy, $E_P \equiv \sqrt{\hbar e^5/G} \approx 10^{19}$ GeV, the energy scale at which quantum and gravitational effects are thought to unify. However, the resulting value of Λ is approximately 120 orders of magnitude too large. Consistency with the observed accelerating expansion requires that $\Lambda = 3\Omega_\Lambda H_0^2/c^2$, where $\Omega_\Lambda \approx 0.7$ gives the fraction of the total energy density of the universe contributed by the cosmological constant, and $H_0 \approx 70$ km/s/Mpc is the Hubble constant. These figures give $\Lambda \approx (3000\ \text{Mpc})^{-2}$ and an energy $E \approx 0.008$ eV $\approx 10^{-21}$ J. The significance of this energy is unclear, since virtual particles exist at energies well above this scale. The proximity of this energy to an energy scale associated with neutrino masses has prompted speculation of new physics. Other proposals have linked this energy scale with novel theories of gravity beyond Einstein's general relativity. *See* HUBBLE CONSTANT; NEUTRINO.

Consequences of nonzero value. The existence of the cosmological constant would imply the existence of a cosmological event horizon, a spherical boundary centered on any observer marking a distance beyond which no causal contact is possible. A light signal sent from the center could never reach the boundary because the expansion of spacetime is so rapid. This horizon is similar to the event horizon surrounding a black hole, viewed from within. If the dark energy is a cosmological constant, the horizon is located at a radius $r = \sqrt{3/\Lambda} \sim 5000$ Mpc. Correspondingly, no rocket or light signal that we may send can reach objects currently beyond a redshift $z \approx 1.7$ within the lifetime of the universe. *See* BLACK HOLE; REDSHIFT.

Prospects. Precision measurements of cosmic distances and the evolution of the universe will help refine the evidence for the cosmological constant. Current evidence is ambiguous as to whether Λ is dark energy. If not, it will likely be accepted in practice that Λ is zero. Confirmation of the existence of a nonzero cosmological constant would have a tremendous impact on physics and our view of the universe. *See* COSMOLOGY; UNIVERSE.

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Cosmology

The study of the structure and the origin of the universe, including the origin of galaxies, the elements, and matter itself.

Big bang model. When Albert Einstein proposed his theory of general relativity, the universe was believed to be static. Einstein had to modify his equations so that general relativity would allow a static universe by adding a cosmological constant term. Today, this term is incorporated into the current cosmological model. *See* COSMOLOGICAL CONSTANT; RELATIVITY.

At the time of Einstein's work, astronomers were uncertain about the nature of the faint spiral nebulae and the size of the visible universe. Some contended that they were regions of star formation that were part of the Milky Way Galaxy, while others argued that they were distant galaxies much like the Milky Way. This debate was settled in 1923 by E. Hubble's discovery of 12 Cepheid variable stars in M31, the Andromeda Nebula. There is a simple empirical relationship between the period of the Cepheids and their luminosity. Thus, Hubble's observations allowed him to determine that the Andromeda Nebula was at a very large distance and was a galaxy much like the Milky Way. *See* ANDROMEDA GALAXY; CEPHEIDS; GALAXY, EXTERNAL; MILKY WAY GALAXY.

Hubble continued his study of galaxies and found that most were receding from the Earth. Hubble proposed a simple linear relationship between the distance to a galaxy and its recessional velocity Eq. (1),

$$v = Hr \tag{1}$$

where v is the recessional velocity of the galaxy, usually measured in kilometers per second, and r is the distance to the galaxy, usually measured in megaparsecs (1 Mpc = 3.26×10^6 light-years = 3.1×10^{19} km = 1.9×10^{19} mi). Various techniques now yield consistent measurements of the Hubble constant, $H \sim 70$ (km/s)/Mpc. *See* HUBBLE CONSTANT.

Hubble's observations of the expanding universe then implied that the addition of a cosmological constant to the equations of general relativity was unnecessary. In the 1920s, G. Lemaître and A. Friedmann independently proposed a general relativistic model of the expanding universe. One of the simplest solutions to Einstein's relativity equation, this model assumes that the universe is homogeneous and expanding. When Lemaître and Friedmann made their proposal, there was no real evidence for their simplifying assumptions. Only since the late 1980s have observations become sensitive enough to confirm them.

The Friedmann-Lemaître model, often called the big bang model, implies that the universe began in an extremely dense state and expanded and cooled. In this model, the Hubble law is predicted as an approximate description of the expansion valid for galaxies within a few hundred megaparsecs of the Milky Way Galaxy. The model implies that radiation is redshifted as the universe expands. Thus, radiation from distant objects should appear at lower frequencies than those at which it was emitted. Observations of atomic lines from distant quasars confirm that radiation is redshifted just as predicted. *See* QUASAR; REDSHIFT.

The Friedmann-Lemaître model, while fully relativistic, can be described in the language of newtonian physics. The Hubble law implies that a shell of galaxies of radius R and mass m expands with velocity HR. Thus, the kinetic energy of the shell is $m(HR)^2/2$. If M is the mass interior to the shell, then the gravitational binding energy of the shell is GMm/R, where G is the newtonian constant of gravitation. The total energy E of the shell is therefore given by Eq. (2). Since it has been assumed that the

$$E = \frac{m(HR)^2}{2} - \frac{GMm}{R} \tag{2}$$

universe is uniform, the mass M within the shell can be replaced with the quantity $4\pi R^3/3$, where ρ is the density of the universe and $4\pi R^3/3$ is the volume of a shell of radius R. Then Eq. (2) can be rewritten as Eq. (3), where Ω is the ratio of the density of

$$\frac{E}{mR^2} = \frac{H^2}{2}\left(1 - \frac{8\pi G\rho}{3H^2}\right) = \frac{H^2}{2}(1 - \Omega) \qquad (3)$$

the universe to the critical density of the universe, $3H^2/(8\pi G)$. If $\Omega < 1$, the total energy of the shell is positive, and the universe will continue to expand forever. If $\Omega > 1$, the total energy of the shell is negative, gravity will eventually stop the expansion, and the universe will eventually collapse. Some physicists speculate that this so-called big crunch will be followed by a future big bang. If $\Omega = 1$, the total energy is zero, and the universe stands on the balance between open and closed and corresponds to a special solution called the Einstein-de Sitter model. *See* GRAVITATION.

This simple newtonian model, while accurately describing the dynamics of the expanding universe, can lead to a conceptual error. The newtonian shell has a center, since newtonian theory cannot deal with a uniform mass density. General relativity, however, allows the universe to be isotropic and to be expanding uniformly without having a special center point. In the Friedmann-Lemaître model, the Milky Way Galaxy is not a special place in the universe.

Geometry of the universe. The density of the universe determines not only the final fate of the universe but also its geometry. If $\Omega > 1$, the universe is closed and its geometry is that of a three-dimensional sphere. (A circle is a one-sphere and the surface of the Earth is a two-sphere.) If two pilots leave New York in opposite directions, one heading east and the other heading west, they will meet somewhere over the Pacific. If the Earth were flat, the two pilots would continue to head directly away from each other. Similarly, if the universe is closed, two light rays sent off in opposite directions will eventually bend toward each other. If $\Omega = 1$, the universe is flat and the two light rays will continue to move away from each other. If $\Omega < 1$, the geometry of the universe is hyperbolic, much like that of a saddle. A common misconception is that if the universe is open it must be spatially infinite. This relationship need not be true, as general relativity does not constrain the topology of the universe. If $\Omega < 1$, the universe could be either infinite or finite and periodic.

Microwave background radiation. One of the most dramatic discoveries of modern physics was the detection of the microwave background radiation by A. Penzias and R. Wilson. Most cosmologists believe that this radiation is the leftover heat from the big bang.

In the hot big bang model, the universe started in an extremely hot dense state. In this state, the universe was composed of electrons, positrons, quarks, neutrinos, and photons. As the universe expanded, most of the matter annihilated with antimatter into photons. These photons then cooled as the universe expanded. Thermal physics predicts that the spectrum of radiation from the big bang would be similar to that emitted by a blackbody, a so-called Planck spectrum. The Friedmann-Lemaître model predicts that this radiation should be uniform since the big bang started in a uniform state. *See* HEAT RADIATION.

The observations of the *Cosmic Background Explorer* (*COBE*) satellite, launched in 1989, provided strong confirmation of the hot big bang model. The observed spectrum of the microwave background radiation agrees closely with the predicted Planck spectrum. The *COBE* experiment also confirmed that the microwave background radiation is uniform to nearly 1 part in 50,000, consistent with the homogeneity assumption of the hot big bang model.

Observations of small fluctuations in the temperature of the microwave background have become a powerful tool for studying the basic properties of the universe. Since most of the microwave background photons last interacted with matter when the universe was only 500,000 years old, these tiny fluctuations in temperature are directly probing variations in the density of the universe soon after the big bang. *See* COSMIC BACKGROUND RADIATION.

Nucleosynthesis. Within the context of the hot big bang model, the conditions in the universe now can be extrapolated back to the first moments after the big bang. The temperature of the cosmic background radiation now is 2.73 kelvins above absolute zero. When the universe was half its present size, the background temperature was twice as high. One second after the big bang, the universe was only 3×10^{-11} of its present size and the temperature of the microwave background was roughly 10^{10} K (1.8×10^{10} °F). At this high temperature, the universe consisted of a thermal sea of photons, electrons, positrons, and neutrinos. In addition, there were a handful of protons and neutrons. There was approximately 1 baryon (proton or neutron) for every 10^{10} photons. *See* BARYON; ELECTRON; NEUTRINO; NEUTRON; POSITRON; PROTON.

As the universe cooled, the protons and neutrons combined to make deuterium. Most of this deuterium then interacted to make helium, while trace amounts combined to make lithium. One of the successes of the big bang model is its ability to account for the observed abundances of light elements. The universe today consists of roughly 28% helium, 70% hydrogen, and 2% other elements, calculated by their masses. Nucleosynthesis in stars produces roughly equal amounts of helium and heavier elements from hydrogen. Thus, it is difficult to understand the helium abundance without big bang nucleosynthesis. *See* DEUTERIUM; HELIUM; HYDROGEN; LITHIUM.

The amounts of deuterium, helium, and lithium produced in the big bang depend sensitively on the number of baryons per photon in the early universe and on the number of neutrino flavors. Based on the observed abundances of this isotope and these elements in old stars, it was predicted that there should be only three flavors of neutrino. Experiments at particle accelerators have confirmed this prediction based on the first moments of the early universe. *See* FLAVOR.

The observed light-element abundances also lead to a prediction for the density of protons and neutrons. The current best estimates suggest that the density in atoms is 5×10^{-31} gram/cm^3. Measurements of the amplitude of microwave background fluctuations also measure the density in atoms as the pattern of fluctuations depends on the atomic density. The best fit value for the density of atoms based on microwave background fluctuations agrees with the estimate based on light-element abundances to better than 10% (and well within the current statistical errors). *See* BIG BANG THEORY; NUCLEOSYNTHESIS.

Lambda cold dark-matter model. Over the past few decades, a simple cosmological model called the lambda cold dark-matter (lambda CDM) model has emerged as the best fit to the current observational data. The lambda CDM model is a version of the standard hot big bang model. The big bang model assumes that general relativity is valid on cosmological scales and that the distribution of matter on large scales is homogeneous. This set of assumptions implies that the universe is expanding: the distances between galaxies are constantly growing. Since the universe is expanding, it is constantly getting cooler and less dense. In the standard big bang model, the shape and evolution of the universe depend on its composition.

The lambda CDM model assumes that the universe is composed of atoms, dark matter, and vacuum energy. The total energy density of the universe is very close to the critical density so that the geometry of the universe is flat. *See* DARK ENERGY; DARK MATTER.

This model has five basic parameters: the expansion rate of the universe (the Hubble constant), the density of matter in the universe, the density of atoms in the universe, the amplitude of the primordial density fluctuations, and how the amplitude of fluctuations varies with scale. With these five parameters, the model can fit a host of astronomical data, including measurements of positions of millions of galaxies, observations of microwave background fluctuations, measurements of distances to both nearby galaxies and distant supernovae, as well as a host of other astronomical observations. While simple, the lambda CDM model posits the existence of two novel forms of matter: cold dark matter and vacuum or dark energy.

Evolution of structure. The inflationary universe model is an attractive scenario for simultaneously explaining the homogeneity of the universe on large scales and the fluctuations in density observed on the smaller scales. In this scenario, the universe in its first few moments underwent a period of exponential expansion. This rapid expansion, which took place before nucleosynthesis, stretched out any initial density variations and eliminated any monopoles or other unwanted objects that formed before the inflationary epoch. During this inflationary epoch, quantum fluctuations generated new density fluctuations that are predicted to be the initial source of structure. The inflationary scenarios predict that the density parameter Ω should be extremely close to 1. *See* INFLATIONARY UNIVERSE COSMOLOGY.

Since different regions of space underwent different amounts of inflationary expansion, this process generated large-scale variations in the density of the universe. The inflationary universe model predicts that the variations in density should be gaussian random-field fluctuations. This implies that the statistical properties of both fluctuations in the microwave background and the fluctuations in the galaxy density distribution are characterized by its overall amplitude and its dependence on scale.

Observations of the microwave background radiation probe these conditions in the early universe. In most cosmology models, the microwave photons that are detected on Earth last interacted with electrons when the universe was one-thousandth its present size. Thus, fluctuations in the microwave background temperature reflect the density fluctuations in the early universe.

During its first 500,000 years, the early universe was a hot plasma of electrons, protons, electromagnetic and radiation (photons). The density fluctuations generated by inflation set up sound waves that propagated as long as the universe was ionized. When the universe cooled and atoms formed, radiation was able to travel freely to our telescopes and satellites. These density variations and the sound waves that they generated produced a characteristic pattern of fluctuations. Since the early universe was nearly uniform, simple linear physics describes the generation and evolution of these fluctuations. The characteristic size of these fluctuations equals the distance that sound waves can travel in 500,000 years. The amplitude of the fluctuations depends on the amount of matter and the density of atoms in the early universe.

The cosmic microwave background temperature fluctuations are very small: variations of only a few millionths of a degree. Over 25 years of searches for these fluctuations were rewarded in 1992, when the *COBE* satellite detected fluctuations in the microwave background temperature of about 2 parts in 100,000. NASA's *Wilkinson Microwave Anisotropy Probe* (*WMAP*) satellite and several ground and balloon-based measurements have been making ever more accurate measurements of these fluctuations (**Fig. 1**). With the launch of the European Space Agency's *Planck* satellite and a new generation of more sensitive ground-based experiments in development, the accuracy of these measurements will continue to rapidly improve. *See* WILKINSON MICROWAVE ANISOTROPY PROBE.

These inflationary density fluctuations grew to form the observed pattern of galaxies. Regions that were slightly overdense expanded more slowly; thus, these overdense regions collapsed and formed galaxies and clusters. On the other hand, underdense regions expanded more rapidly than the surrounding universe. These underdense regions eventually developed into voids. Astronomers using wide-field surveys such as the Sloan Digital Sky Survey and the 2dF

Galaxy Redshift Survey have now measured the positions of several hundred thousand galaxies. They have found that the clustering pattern matches the predictions of the lambda CDM model. *See* SLOAN DIGITAL SKY SURVEY.

Cosmologists now use massive computer simulations to model the clustering of matter and the formation of galaxies. These simulations are compared with observations of the large-scale distribution of galaxies and with observations of galaxy and cluster properties. Simulations based on the lambda CDM model match a wide range of astronomical observations. Remarkably, the inflationary model successfully describes the statistical properties of both galaxies and the microwave background and fits astronomical observations over a range of 10^4 in scale and 10^{12} in mass (**Fig. 2**).

Measuring the size of the universe. Measuring the distance to astronomical objects remains a great scientific challenge. Astronomers are able to measure the distances to the nearest stars by using parallax. They then must rely on empirical properties of stars to extrapolate to more distant objects. Observations of globular clusters and open clusters in the Milky Way Galaxy are needed to calibrate the luminosity–period relation for Cepheid variable stars. *See* PARALLAX (ASTRONOMY); STAR.

Primary extragalactic distance indicators are used to measure the distance to nearby galaxies such as the Magellanic Clouds and the Andromeda Galaxy. Variable stars, such as Cepheids and RR Lyrae stars, are still important tools in determining the distances to these objects. Observations of the expansion of the dust shell around Supernova 1987A in the Large Magellanic Cloud have provided an alternative method for measuring distances. All these techniques imply that the Large Magellanic Cloud is at a distance of roughly 50,000 parsecs. *See* MAGELLANIC CLOUDS; SUPERNOVA; VARIABLE STAR.

Secondary distance indicators are then used to determine the relative distance to the Virgo Cluster. For example, the brightest red and blue stars in a distant galaxy in the Virgo Cluster are assumed to have the same luminosity as the brightest stars in Andromeda. Other secondary distance indicators include the brightness of typical globular clusters or planetary nebulae. *See* VIRGO CLUSTER.

Tertiary distance indicators are then used to extrapolate from the Virgo Cluster to more distant clusters. Galaxies in the Virgo Cluster are observed to have a simple relationship, noted by B. Tully and R. Fisher, between their gas velocities and their luminosity. This relation is used to measure the relative distance to distant galaxies. Together with Doppler-shift measurements of recessional velocity, this technique yields estimates of the Hubble constant. *See* DOPPLER EFFECT.

Observations using the *Hubble Space Telescope* have significantly improved our measurements of the Hubble constant. These observations suggest that the Hubble constant is 65–80 (km/s)/Mpc. If the lambda CDM model is assumed, the *Wilkinson Microwave Anisotropy Probe's* measurements of primordial fluctuations imply a Hubble constant of 68–76 (km/s)/Mpc. Estimates of the Hubble constant using other techniques (for example, time delays from multiple imaged quasars) yield consistent results.

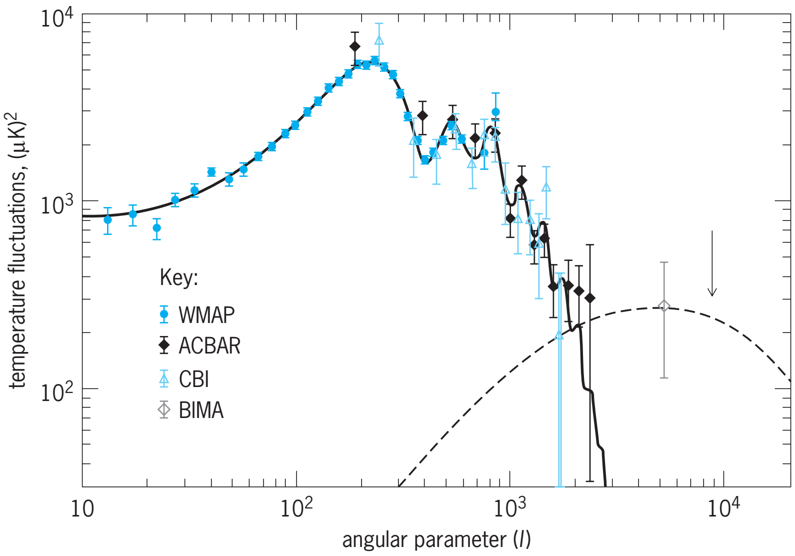

Fig. 1. Measurements of the amplitude of temperature fluctuations as a function of angular scale. The solid line is the predictions of the lambda CDM model. The data points are from the *Wilkinson Microwave Anisotropy Probe* (*WMAP*) and three ground-based experiments. The broken line shows an estimate of the expected level of contamination from hot gas in clusters. The horizontal axis is an angular parameter, *l*, and the angular scale measured is 180°/*l*. The vertical axis shows the amplitude of the temperature fluctuations in millionths of a degree (μK). (*A. Readhead; CBI team*)

Observations of supernovae have become a powerful tool for measuring distances to distant galaxies. Type Ia supernovae, supernovae produced by the explosive burning of a white dwarf star, have nearly the same luminosity. By measuring the time evolution of these supernovae, astronomers can correct for variations in their absolute luminosities and use these standard candles to determine the distances to galaxies. By measuring the distances to supernovae as a function of their redshifts, astronomers have been able to determine the geometry and expansion history of the universe. Current data suggest that the universe is accelerating and is well fit by the basic parameters of the lambda CDM model. *See* ACCELERATING UNIVERSE.

Ground-based supernova observations have found that supernovae at redshifts of 0.3–0.8 are systematically dimmer than predicted in cosmological models without dark energy (**Fig. 3**). The observations imply that the universe is now accelerating. Hubble telescope observations of supernovae at redshifts greater than 1 (not shown in Fig. 3) find that these more distant supernovae are actually brighter than expected in a universe without dark energy. The observations of these more distant supernovae imply that, earlier in its history, the expansion of the universe was slowing and that dark energy has been dominating the expansion only during the past 5×10^9 years. The current supernova data fit the lambda CDM model well and are one of the key pieces of evidence for the existence of dark energy.

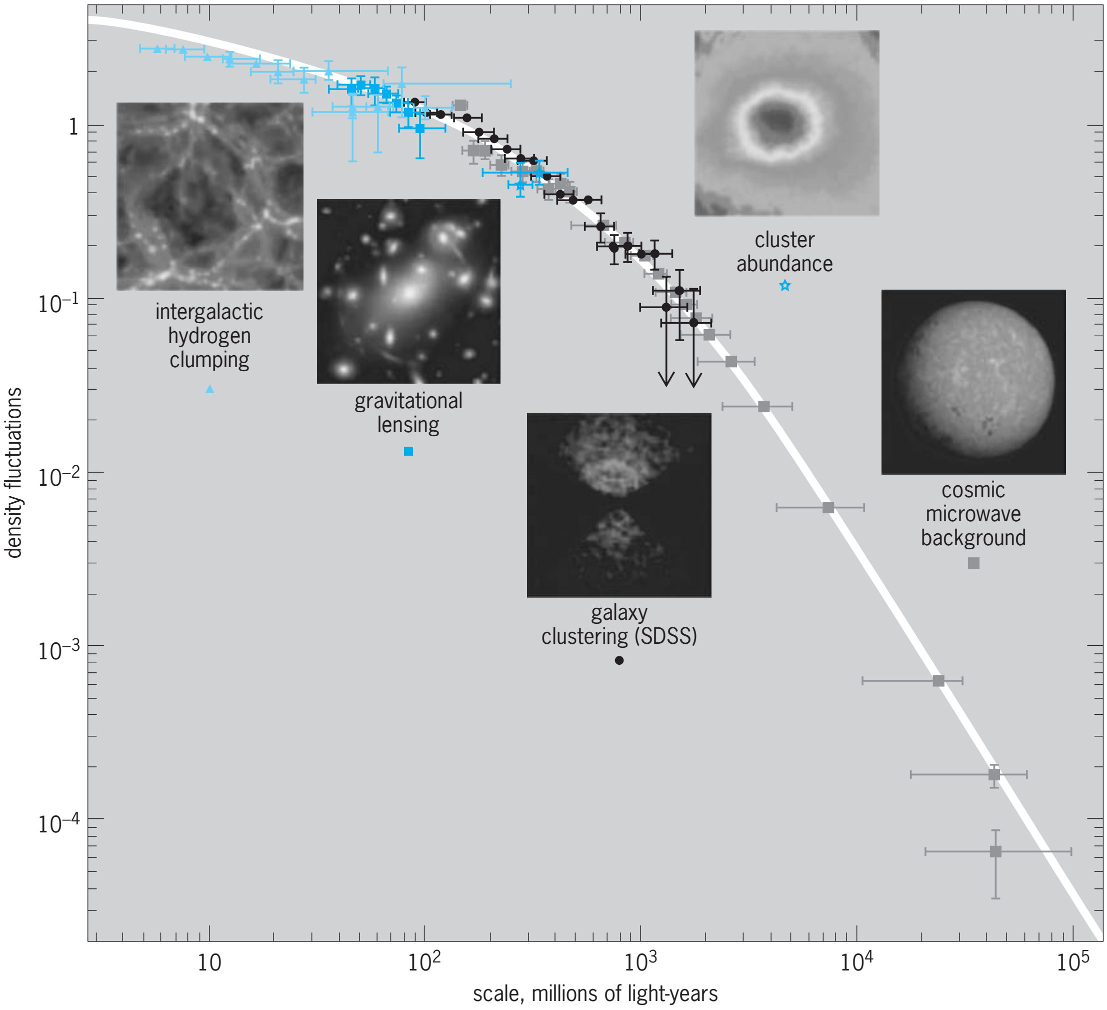

Fig. 2. Amplitude of density fluctuations as a function of scale. The insets indicate the various types of observations that measure the fluctuations and the data points that represent them in this figure. The microwave background observations measure the amplitude of fluctuations 500,000 years after the big bang; the clumping of gas measures the amplitude of fluctuations 2 × 10^9 years after big bang; and the galaxy and clustering measurements and gravitational lensing observations measure the amplitude of clustering in the nearby universe. The galaxy clustering measurements are based on the Sloan Digital Sky Survey (SDSS). The intergalactic hydrogen abundance is based on measurement of the absorption by its Lyman alpha line of light from distant quasars and galaxies. Cluster abundance is illustrated by an image of x-ray emission from a cluster. The amplitudes have been extrapolated to today using the lambda CDM model. The curve shows the prediction of the model. (*Max Tegmark*)

Age of the universe. The universe ought to be older than any visible star; thus, the inferred ages of the stars in the Milky Way Galaxy place a lower limit on the age of the universe. The oldest known stars are in globular clusters, dense concentrations of roughly 100,000 stars, believed to be 12–20 × 10^9 years old. These age estimates are based on models of stellar evolution that predict when a star of a given mass becomes a red giant. *See* STAR CLUSTERS; STELLAR EVOLUTION.

Distant elliptical galaxies are composed almost entirely of old stars. Measurements of their spectra constrain the age of the universe as a function of redshift. Measurements of the age of the universe provided the first strong hints of the existence of dark energy. The current measurements of the Hubble constant imply that a flat universe without dark energy would be only 9 × 10^9 years old, much younger than some of the stars in our galaxy. In a flat universe without dark energy, light from objects with a redshift of 2 was emitted when the universe was only 1.7 × 10^9 years old, which is difficult to reconcile with observations showing the existence of 2.5 × 10^9-year-old stars in galaxies with this redshift. On the other hand, models with dark energy provide a good fit to measurements of stellar and galactic ages (**Fig. 4**).

Just as radioactivity lifetimes can be used to date archeological artifacts, nuclear dating provides an alternative independent measure of the age of the Milky Way Galaxy. By using these techniques, the minimum age of the Galaxy has been estimated to be 10 × 10^9 years. The oldest white dwarf stars detected are 9 × 10^9 years old, and the Sun is believed to be 4.5 × 10^9 years old. These age measurements place a firm lower limit on the age of the universe. *See* SOLAR SYSTEM; WHITE DWARF STAR.

Observations of the microwave background fluctuations yield a direct geometric measurement of the age of the universe. The fluctuations have a characteristic size set by the distance that sound waves can travel in 500,000 years. By measuring the angular size of the typical fluctuation, cosmologists have determined an age of the universe as 13–14 × 10^9 years.

Dark-matter problem. Astronomers have been in an embarrassing situation for several decades: the amount of mass measured dynamically in galaxies by observing stellar and gas motions is roughly 10 times the mass observed in dust, gas, and known stars. This discrepancy suggests that either there is a basic flaw in newtonian physics or 90% of the mass in galaxies is in some yet unknown form, usually referred to as dark matter.

Evidence for dark matter. Some of the strongest evidence for existence of dark matter comes from radio observations of hydrogen gas and optical observations of star motions in spiral galaxies like the Milky Way Galaxy. The neutral gas and stars in the disks of galaxies are moving in nearly circular orbits. The centrifugal acceleration of the gas (and stars), v^2/r outward (where v is the velocity of motion and r is the orbit radius), must balance the gravitational acceleration of the galaxy, yielding Eq. (4), where $M(r)$

$$v^2 = \frac{GM(r)}{r} \qquad (4)$$

is the mass of the galaxy within radius of the gas or stellar orbit. Thus, observations of the gas or stellar velocity are a direct measure of the mass interior to its orbit. Most of the light in a galaxy like the Milky Way Galaxy is located in the inner 15,000 parsecs. (The Sun is roughly 8000 parsecs from the galactic center.) If mass were distributed as light, the gas rotation velocity should begin to fall off outside the optical edge of the galaxy. In all optical and radio observations of spiral galaxies, the gas rotation velocity is not falling but is either flat or slowly rising. This situation implies that there is mass where there is no light.

Observations of hot x-ray-emitting gas in elliptical galaxies provide a method for measuring their mass distribution. Since the gas pressure gradients must balance the force of gravity, gas density and temperature profiles can be directly related to the elliptical galaxy mass profiles. Data from x-ray satellites suggest that the galactic dark-matter problem is ubiquitous: all galaxies, whether spiral or elliptical, dwarf or normal, seem to have halos of dark matter. *See* X-RAY ASTRONOMY.

Observations of groups and clusters of galaxies provide an alternative method of weighing galaxies. The velocities of galaxies in clusters can be used to determine the mass of the entire cluster. This technique for measuring galactic mass, first applied in the 1930s, also implies a dynamical galactic mass that vastly exceeds the mass in luminous material.

General relativity implies that mass curves space. Thus, the path of light rays moving through a cluster of galaxies is bent by the mass within the cluster (**Fig. 5**). Hence, dense clusters of galaxies can act as gravitational lenses that distort the images of galaxies behind the cluster into arcs. Measurements of these distorted arcs confirm the evidence for enormous amounts of dark matter in clusters. *See* GRAVITATIONAL LENS.

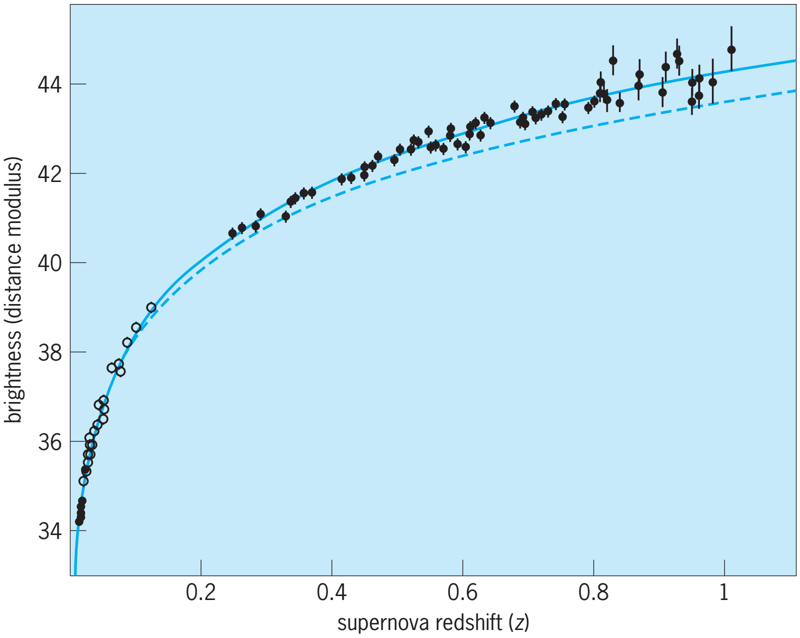

Fig. 3. Brightness of supernovae as a function of their redshift. The supernova brightnesses are measured in terms of the distance modulus, which is related to the magnitude (it is the difference between the apparent and absolute magnitudes), and are corrected for variations in supernova properties. The broken line shows the predictions for a flat universe with no dark energy. The solid line shows the predictions of the lambda CDM model. (*P. Astier; Supernova Legacy Survey*)

Candidates for dark matter. Candidates for the dark matter range in mass from microelectronvolt axions to 10^6-solar-mass black holes. Many groups of physicists and astronomers are actively searching for various candidates for the dark matter.

Baryons (such as ordinary protons and neutrons) make up most of the mass of the Earth and the Sun. Baryons are the most obvious dark-matter candidate. These baryons cannot be bound into luminous stars, nor can they be in either hot or cold gas. Cold gas can be detected through hyperfine and molecular lines. Hot gas is detectable by ultraviolet and x-ray satellites. Current observations constrain the gas mass to be much less than the mass needed to account for the dark matter. Within our galaxy, baryons could have escaped direct detection if they were bound together into clumps, either as comets, bound by atomic forces, or as planets or very low mass stars, bound by gravitational forces. However, microwave background observations provide a more direct total accounting of the composition of the universe. These observations imply that the total density in atoms is only one-sixth of the density in matter, so ordinary matter is no longer considered a likely candidate for the dark matter.

Black holes have been proposed as another possible candidate for the dark matter. If the first generation of star formation consisted of very massive stars, these objects would rapidly burn hydrogen to

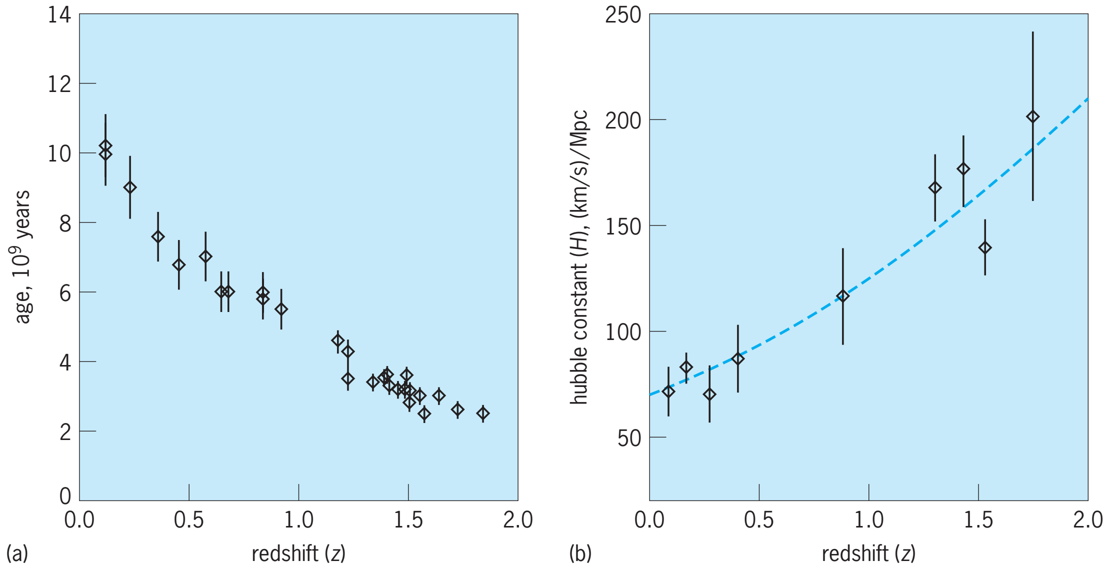

Fig. 4. Comparison of galactic ages with predictions of the lambda CDM model. (*a*) Ages of the oldest galaxies as a function of redshift. (*b*) Data points and bars show the Hubble constant inferred from the galactic ages. The curve shows the predictions of the lambda CDM model. (*J. Simon, L. Verde, R. Jimenez*)

heavier elements and then collapse to black holes. Observational constraints on element abundance require that these massive stars not lose much of the carbon, oxygen, or iron produced during their stellar evolution to the interstellar medium. Models of very massive star evolution suggest that these stars could swallow most of their mass and form a halo of black holes. This scenario is rather tentative, since very little is understood about pregalactic star formation. These black holes could also be detected in the current gravitational lensing searches. *See* BLACK HOLE.

The currently favored hypothesis is that the dark matter consists of some as yet undetected particle. Particle physicists have suggested several possible candidates for the dark matter. The most popular of these particles is predicted in an extension of standard physics called supersymmetry. This particle, named a WIMP (weakly interacting massive particle), could potentially be detected in deep underground experiments or created in particle accelerators. The upcoming generation of dark-matter experiments at CERN may be able to produce these particles in the laboratory. *See* ELEMENTARY PARTICLE; SUPERSYMMETRY; WEAKLY INTERACTING MASSIVE PARTICLE (WIMP).

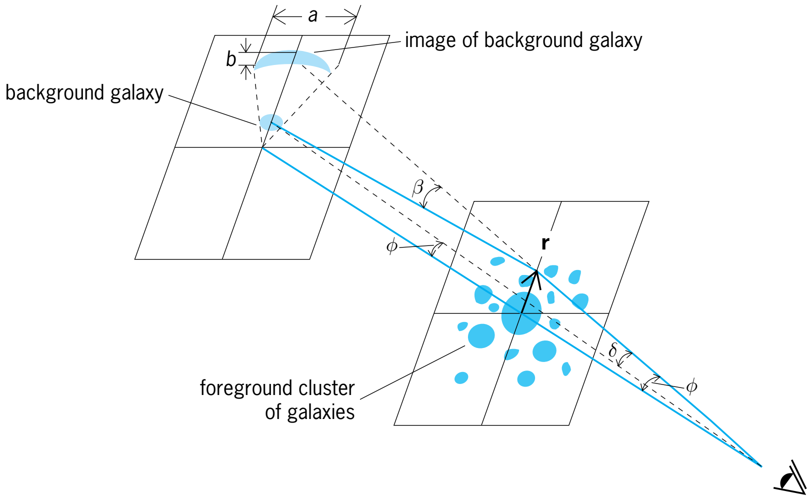

Fig. 5. Gravitational displacement and distortion (lensing) of a distant background galaxy by a compact foreground cluster of galaxies. A light ray passing the cluster plane at an impact parameter vector r is gravitationally bent through an angle β. Thus, it is seen displaced (through an angle δ) from ϕ, its true angular distance from the cluster centroid, to the larger angle ϕ. Because of its finite width, the image also is distorted into a circular arc (of length *a* and width *b*) concentric with the cluster. (*After A. Tyson, Mapping dark matter with gravitational lenses, Phys. Today, 45(6):24–32, June 1992*)

Dark energy. Measurements of distances to supernovae, galaxies, and the microwave background imply that most of the energy in the universe is not in the form of matter but dark energy. Measurements of the evolution of the clustering of galaxies confirm the existence of this dark energy and imply that it does not cluster gravitationally.

The most popular current idea for the dark energy is that it is energy associated with the vacuum. Einstein first posited the existence of this vacuum energy (or cosmological constant); however, the current model of fundamental physics cannot explain its measured value.

Other possible explanations for the dark energy include extremely weakly interacting ultralight fields or modifications of general relativity. Understanding the dark energy and measuring its properties is one of the most active areas of research not only in cosmology but also in all of physics.

Alternatives to the hot big bang. There have been a variety of models proposed as alternatives to the hot big bang. Historically, the most important alternative model was the steady-state model, which assumes a homogeneous expanding universe that is not evolving because matter is continuously being created out of the vacuum. This model has great difficulty accounting for the observed shape of the microwave background radiation and cannot account for the observed abundance of helium.

Another alternative is the cold big bang model in which the universe began in a big bang that started at absolute zero. It has been suggested that in this model the microwave background radiation could be due to reemitted light from iron needles. This model requires special dust grains and also cannot explain the abundances of light elements.

In H. Alfvén's plasma universe, the Milky Way Galaxy is part of a finite cloud of material expanding into empty flat space. It is very difficult for this model to explain the observed uniformity of the microwave background spectrum or the light-element abundances.

E. Segal has proposed an alternative to cosmology based on general relativity. In this chronometric theory, there is a quadratic rather than a linear relationship between redshift and distance. Modern measurements of the distances to rich clusters find that these objects obey Hubble's linear relationship rather than Segal's quadratic law. Observations of the correlation between jet expansion velocity and redshift are a direct test of the chronometric hypothesis, which it fails.

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