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11 ENVIRONMENTAL CHEMISTRY OF WATER

11.1 INTRODUCTION

This is the first of the remaining chapters in this book that deal with environmental chemistry. In the discussion of this topic, the environment will be viewed as consisting of five spheres—the hydrosphere, atmosphere, geosphere, biosphere, and anthrosphere. Although often not acknowledged as one of the environmental spheres, the anthrosphere, consisting of the things humans construct, use, and do in the environment, is very important to consider as one of these five spheres. By so doing, we can begin the essential process of using our human activities to preserve and enhance the Earth environment upon which we and all living organisms depend.

Water composes one of the five "spheres" in which environmental chemistry is discussed. This chapter introduces the environmental chemistry of water. Chapter 12 covers water pollution, and Chapter 13 discusses water treatment.

11.2 THE PROPERTIES OF WATER, A UNIQUE SUBSTANCE

Water has a number of unique properties that are essential to life and that determine its environmental chemical behavior. Many of these properties are due to water's polar molecular structure and its ability to form hydrogen bonds (discussed in Chapter 3, Sections 7.3 and 7.4). The more important special characteristics of water are summarized in Table 11.1.

11.3 SOURCES AND USES OF WATER: THE HYDROLOGIC CYCLE

The world's water supply is found in the five parts of the **hydrologic cycle** (Figure 11.1). About 97% of Earth's water is found in the oceans. Another fraction is present as water vapor in the atmosphere (clouds). Some water is contained in the solid state as ice and snow in snowpacks, glaciers, and the polar ice caps. Surface

Table 11.1 Important Properties of Water

Property	Effects and Significance
Excellent solvent	Transport of nutrients and waste products, making biological processes possible in an aqueous medium
Highest dielectric constant of any common liquid	High solubility of ionic substances and their ionization in solution
Higher surface tension than any other liquid	Controlling factor in physiology; governs drop and surface phenomena
Transparent to visible and longer-wavelength fraction of ultraviolet light	Colorless, allowing light required for photosynthesis to reach considerable depths in bodies of water
Maximum density as a liquid at 4°C	Ice floats; vertical circulation restricted in stratified bodies of water
Higher heat of evaporation than any other material	Determines transfer of heat and water molecules between the atmosphere and bodies of water
Higher latent heat of fusion than any other liquid except ammonia	Temperature stabilized at the freezing point of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

water is found in lakes, streams, and reservoirs. Groundwater is located in aquifers underground.

There is a strong connection between the *hydrosphere,* where water is found, and the *lithosphere*, or land; human activities affect both. For example, disturbance of land by conversion of grasslands or forests to agricultural land or intensification of agricultural production may reduce vegetation cover, decreasing **transpiration** (loss of water vapor by plants) and affecting the microclimate. The result is increased rain runoff, erosion, and accumulation of silt in bodies of water. The nutrient cycles may be accelerated, leading to nutrient enrichment of surface waters. This, in turn, can profoundly affect the chemical and biological characteristics of bodies of water.

The water that humans use is primarily fresh surface water and groundwater, the sources of which may differ from each other significantly. In arid regions, a small fraction of the water supply comes from the ocean, a source that is likely to become more important as the world's supply of fresh water dwindles relative to demand. Saline or brackish groundwaters may also be utilized in some areas.

In the continental United States, an average of approximately 1.48×10^{13} liters of water fall as precipitation each day, which translates to 76 cm per year. Of that
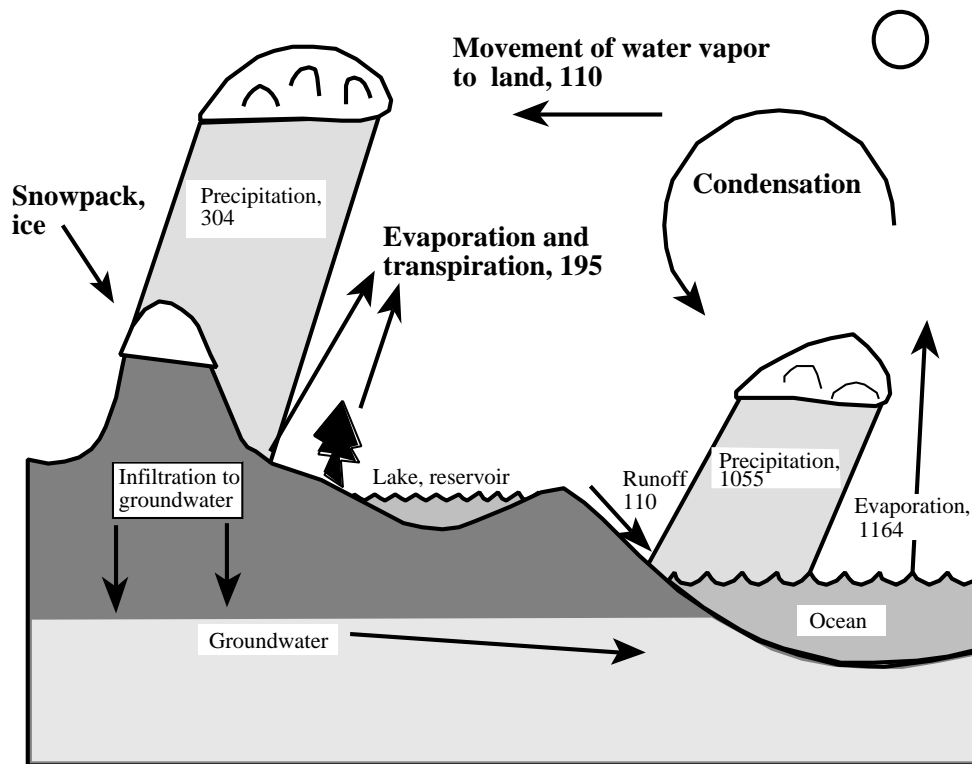
Movement of water vapor
to land, 110

Condensation

Snowpack,
ice

Precipitation,
304

Evaporation and
transpiration, 195

Infiltration to
groundwater

Lake, reservoir

Runoff
110

Precipitation,
1055

Evaporation,
1164

Groundwater

Ocean

Figure 11.1 The hydrologic cycle, quantities of water in trillions of liters per day.

amount, approximately 1.02×10^{13} liters per day, or 53 cm per year, are lost by evaporation and transpiration. Thus, the water theoretically available for use is approximately 4.6×10^{12} liters per day, or only 23 centimeters per year. At present, the U.S. uses 1.6×10^{12} liters per day, or 8 centimeters of the average annual precipitation, an almost tenfold increase from a usage of 1.66×10^{11} liters per day at the turn of the century. Even more striking is the per capita increase from about 40 liters per day in 1900 to around 600 liters per day now. Much of this increase is accounted for by high agricultural and industrial use, which each account for approximately 46% of total consumption. Municipal use consumes the remaining 8%.

Since about 1980, however, water use in the U.S. has shown an encouraging trend with total consumption down by about 9% during a time in which population grew 16%, according to figures compiled by the U.S. Geological Survey.[1] This trend, which is illustrated in Figure 11.2, has been attributed to the success of efforts to conserve water, especially in the industrial (including power generation) and agricultural sectors. Conservation and recycling have accounted for much of the decreased use in the industrial sector. Irrigation water has been used much more efficiently by replacing spray irrigators, which lose large quantities of water to the action of wind and to evaporation, with irrigation systems that apply water directly to soil. Trickle irrigation systems that apply just the amount of water needed directly to plant roots are especially efficient.
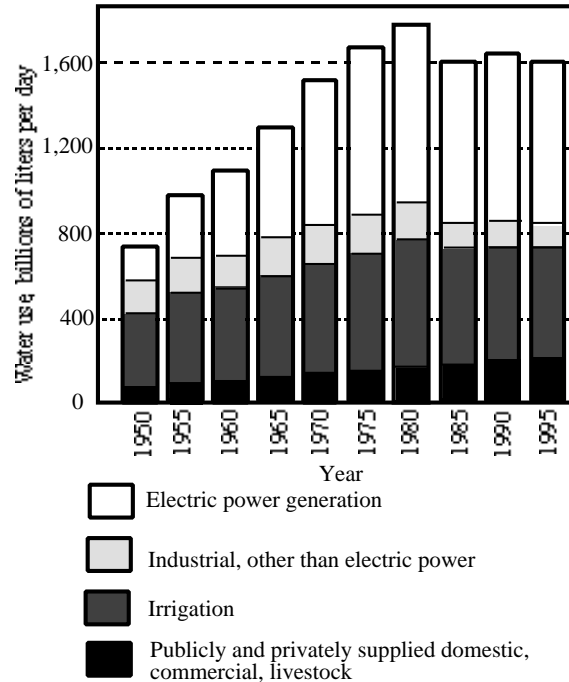
Figure 11.2 Trends in water use in the United States (data from U.S. Geological Survey).

A major problem with water supply is its nonuniform distribution with location and time. As shown in Figure 11.3, precipitation falls unevenly in the continental U.S. This causes difficulties because people in areas with low precipitation often consume more water than people in regions with more rainfall. Rapid population growth in the more arid southwestern states of the U.S. during the last four decades has further aggravated the problem. Water shortages are becoming more acute in this region which contains six of the nation's 11 largest cities (Los Angeles, Houston, Dallas, San Diego, Phoenix, and San Antonio). Other problem areas include the Northeast, plagued by deteriorating water systems; Florida, where overdevelopment of coastal areas threatens Lake Okeechobee; and the High Plains, ranging from the Texas panhandle to Nebraska, where irrigation demands on the Ogalalla aquifer are dropping the water table steadily with no hope of recharge. These problems are minor, however, in comparison with those in some parts of Africa, where water shortages are contributing to real famine conditions.

11.4   THE CHARACTERISTICS OF BODIES OF WATER

The physical condition of a body of water strongly influences the chemical and biological processes that occur in water. **Surface water** is found primarily in streams, lakes, and reservoirs. **Wetlands** are productive flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants. **Estuaries** constitute another type of body of water, consisting of arms of the ocean into which streams flow. The mixing of fresh and salt water gives estuaries unique chemical and

biological properties. Estuaries are the breeding grounds of much marine life, which makes their preservation very important.
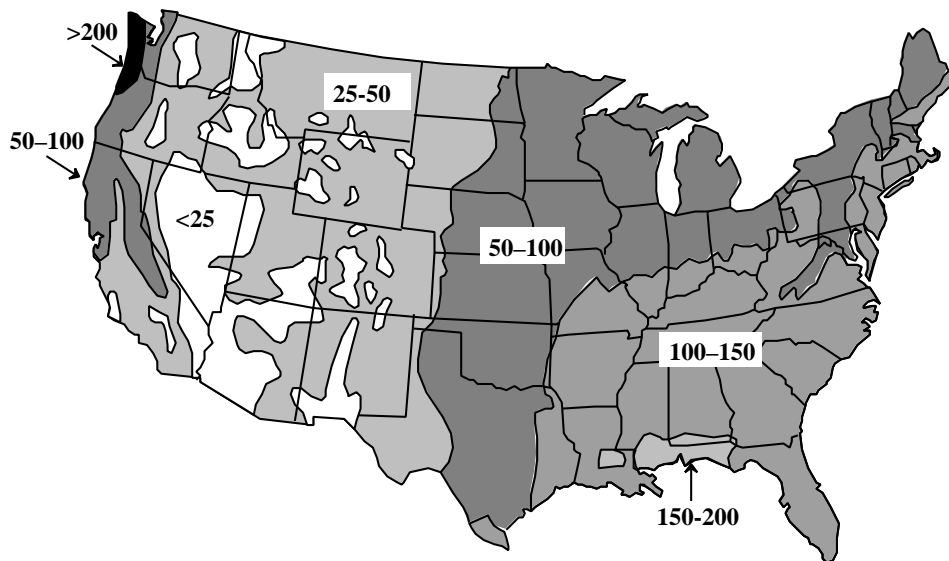

Figure 11.3 Distribution of precipitation in the continental U.S., showing average annual rainfall in centimeters.

Water's unique temperature-density relationship results in the formation of distinct layers within nonflowing bodies of water, as shown in Figure 11.4. During the summer a surface layer (**epilimnion**) is heated by solar radiation and, because of its lower density, floats upon the bottom layer, or **hypolimnion**. This phenomenon is called **thermal stratification.** When an appreciable temperature difference exists between the two layers, they do not mix, but behave independently and have very dif-
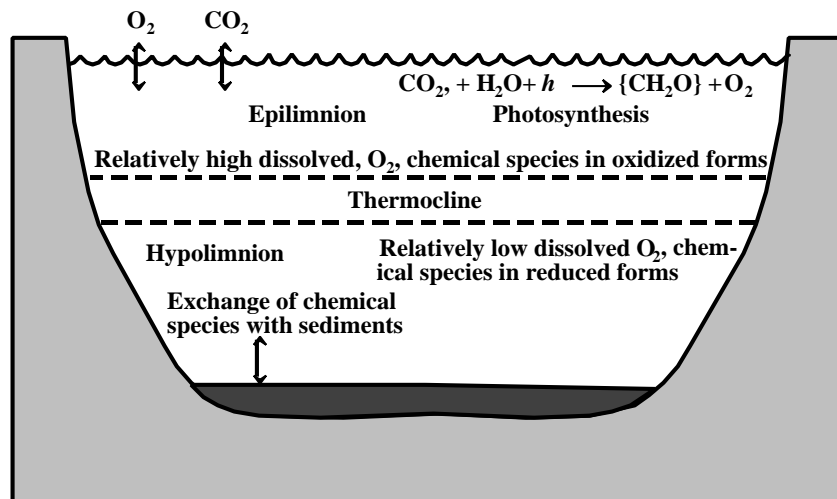

Figure 11.4 Stratification of a lake.

ferent chemical and biological properties. The epilimnion, which is exposed to light, may have a heavy growth of algae. As a result of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic. Because of the presence of O_2, oxidized species predominate in the epilimnion. In the hypolimnion, consumption of O_2 by bacterial action on biodegradable organic material may cause the water to become anaerobic. As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion.

The chemistry and biology of the Earth's vast oceans are unique because of the ocean's high salt content, great depth, and other factors. Oceanographic chemistry is a discipline in its own right. The environmental problems of the oceans have increased greatly in recent years because of ocean dumping of pollutants, oil spills, and increased utilization of natural resources from the oceans.

11.5 AQUATIC CHEMISTRY

Figure 11.5 summarizes important aspects of **aquatic chemistry** applied to environmental chemistry. As shown in this figure, a number of chemical phenomena occur in water. Many aquatic chemical processes are influenced by the action of algae and bacteria in water. For example, Figure 11.5 shows that algal photosynthesis fixes inorganic carbon from HCO_3^- ion in the form of biomass (represented as $\{CH_2O\}$), in a process that also produces carbonate ion, CO_3^{2-}. Carbonate undergoes an acid-base reaction to produce OH^- ion and raise the pH, or it reacts with Ca^{2+} ion to precipitate solid $CaCO_3$. Most of the many oxidation-reduction reactions that occur in water are mediated (catalyzed) by bacteria. For example, bacteria convert inorganic nitrogen largely to ammonium ion, NH_4^+, in the oxygen-deficient (anaer-
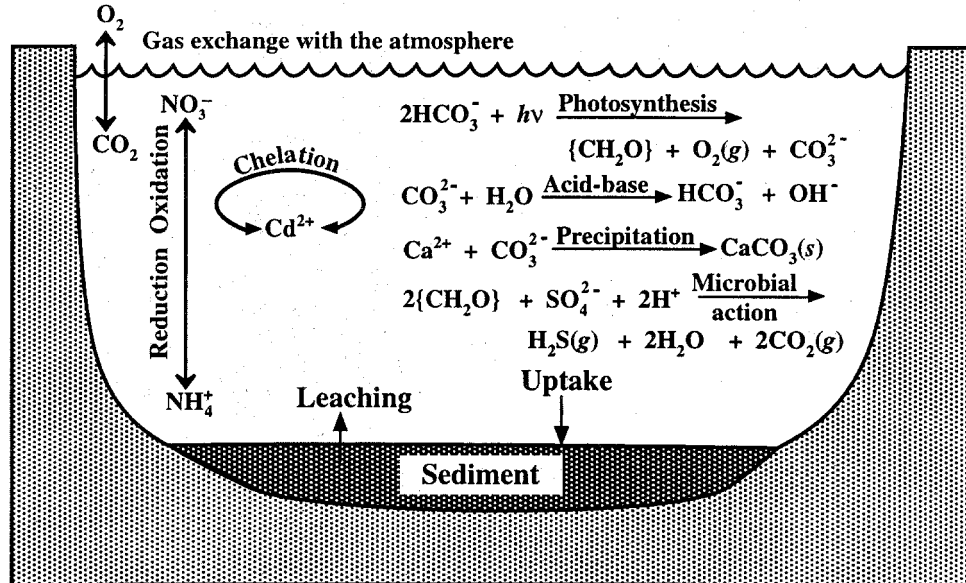

Figure 11.5 Major aquatic chemical processes.

obic) lower layers of a body of water. Near the surface, where O_2 is available, bacteria convert inorganic nitrogen to nitrate ion, NO_3^-. Metals in water may be bound to organic chelating agents, such as pollutant nitrilotriacetic acid (NTA) or naturally occurring fulvic acids. Gases are exchanged with the atmosphere, and various solutes are exchanged between water and sediments in bodies of water.

Several important characteristics of unpolluted water should be noted. One of these is **gas solubility**. Since it is required to support aquatic life and maintain water quality, oxygen is the most important dissolved gas in water. Water in equilibrium with air at 25°C contains 8.3 milligrams per liter (mg/L) of dissolved O_2. Water **alkalinity** (see Section 11.6) is defined as the ability of solutes in water to neutralize added strong acid. Water **hardness** is due to the presence of calcium ion, Ca^{2+}, and, to a lesser extent, magnesium ion, Mg^{2+}.

11.6 ALKALINITY AND ACIDITY

Alkalinity

The capacity of water to accept H^+ ions (protons) is called **alkalinity**. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Frequently, the alkalinity of water must be known to calculate the quantities of chemicals to be added in treating the water. Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids. These characteristics may be detrimental for water to be used in boilers, food processing, and municipal water systems. Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of water to support algal growth and other aquatic life. It is used by biologists as a measure of water fertility. Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:

$$HCO_3^- + H^+ \quad CO_2 + H_2O \tag{11.6.1}$$

$$CO_3^{2-} + H^+ \quad HCO_3^- \tag{11.6.2}$$

$$OH^- + H^+ \quad H_2O \tag{11.6.3}$$

Other, usually minor, contributors to alkalinity are ammonia and the conjugate bases of phosphoric, silicic, boric, and organic acids.

It is important to distinguish between high *basicity*, manifested by an elevated pH, and high *alkalinity*, the capacity to accept H^+. Whereas pH is an *intensity* factor, alkalinity is a *capacity* factor. This can be illustrated by comparing a solution of 1.00×10^{-3} M NaOH with a solution of 0.100 M $NaHCO_3$. The sodium hydroxide solution is quite basic, with a pH of 11, but a liter of this solution will neutralize only 1.00×10^{-3} mole of acid. The pH of the sodium bicarbonate solution is 8.34, much lower than that of the NaOH. However, a liter of the sodium bicarbonate solution will neutralize 0.100 mole of acid; therefore, its alkalinity is 100 times that of the more basic NaOH solution.

As an example of a water-treatment process in which water alkalinity is important, consider the use of *filter alum*, $Al_2(SO_4)_3 \cdot 18H_2O$ as a coagulant. The hydrated aluminum ion is acidic, and, when it is added to water, it reacts with base to form gelatinous aluminum hydroxide,

$$Al(H_2O)_6^{3+} + 3OH^- \quad Al(OH)_3(s) + 6H_2O \tag{11.6.4}$$

which settles and carries suspended matter with it. This reaction removes alkalinity from the water. Sometimes, the addition of more alkalinity is required to prevent the water from becoming too acidic.

In engineering terms, alkalinity frequently is expressed in units of mg/L of $CaCO_3$, based upon the following acid-neutralizing reaction:

$$CaCO_3 + 2H^+ \quad Ca^{2+} + CO_2 + H_2O \tag{11.6.5}$$
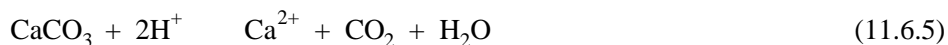
The equivalent weight of calcium carbonate is one-half its formula weight because only one-half of a $CaCO_3$ molecule is required to neutralize one OH^-. Expressing alkalinity in terms of mg/L of $CaCO_3$ can, however, lead to confusion, and equivalents/L is preferable notation for the chemist.
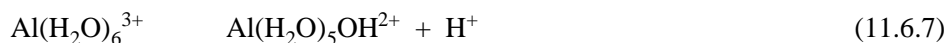
Acidity

Acidity as applied to natural water systems is the capacity of the water to neutralize OH^-. Acidic water is not frequently encountered, except in cases of severe pollution. Acidity generally results from the presence of weak acids such as $H_2PO_4^-$, CO_2, H_2S, proteins, fatty acids, and acidic metal ions, particularly Fe^{3+}. Acidity is more difficult to determine than is alkalinity. One reason for the difficulty in determining acidity is that two of the major contributors are CO_2 and H_2S, both volatile solutes that are readily lost from the sample. The acquisition and preservation of representative samples of water to be analyzed for these gases is difficult.

The term *free mineral acid* is applied to strong acids such as H_2SO_4 and HCl in water. Pollutant acid mine water contains an appreciable concentration of free mineral acid. Whereas total acidity is determined by titration with base to the phenolphthalein endpoint (pH 8.2, where both strong and weak acids are neutralized), free mineral acid is determined by titration with base to the methyl orange endpoint (pH 4.3, where only strong acids are neutralized).

The acidic character of some hydrated metal ions may contribute to acidity as shown by the following example:
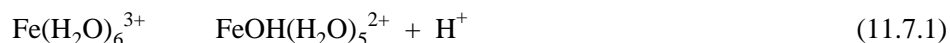
$$Al(H_2O)_6^{3+} + H_2O \quad Al(H_2O)_5OH^{2+} + H_3O^+ \tag{11.6.6}$$
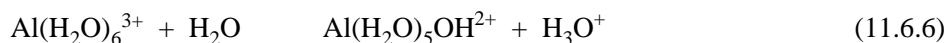
For brevity in this book, the hydronium ion, H_3O^+, is abbreviated simply as H^+ and H^+-accepting water is omitted so that the above equation becomes

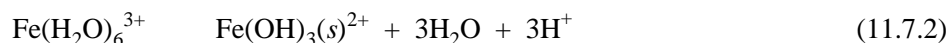$$Al(H_2O)_6^{3+} \quad Al(H_2O)_5OH^{2+} + H^+ \tag{11.6.7}$$

Some industrial wastes, for example pickling liquor used to remove corrosion from steel, contain acidic metal ions and often some excess strong acid. For such wastes, the determination of acidity is important in calculating the amount of lime, or other chemicals, that must be added to neutralize the acid.
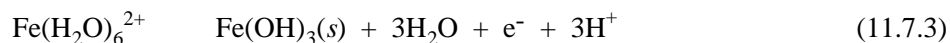
11.7 METAL IONS AND CALCIUM IN WATER

Metal ions in water, commonly denoted M^{n+}, exist in numerous forms. Despite what the formula implies, a bare metal ion, Mg^{2+} for example, cannot exist as a separate entity in water. To secure the highest stability of their outer electron shells, metal ions in water are bonded, or *coordinated*, to water molecules in forms such as the hydrated metal cation $M(H_2O)_x^{n+}$, or other stronger bases (electron-donor partners) that might be present. Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including acid-base,

$$Fe(H_2O)_6^{3+} \qquad FeOH(H_2O)_5^{2+} \ + \ H^+ \qquad\qquad (11.7.1)$$

precipitation,

$$Fe(H_2O)_6^{3+} \qquad Fe(OH)_3(s)^{2+} \ + \ 3H_2O \ + \ 3H^+ \qquad\qquad (11.7.2)$$

and oxidation-reduction reactions:

$$Fe(H_2O)_6^{2+} \qquad Fe(OH)_3(s) \ + \ 3H_2O \ + \ e^- \ + \ 3H^+ \qquad\qquad (11.7.3)$$

These all provide means through which metal ions in water are transformed to more stable forms. Because of reactions such as these and the formation of dimeric species, such as $Fe_2(OH)_2^{4+}$, the concentration of simple hydrated $Fe(H_2O)_6^{3+}$ ion in water is vanishingly small; the same holds true for many other ionic species dissolved in water.

The properties of metals dissolved in water depend largely upon the nature of metal species dissolved in the water. Therefore, **speciation** of metals plays a crucial role in their environmental chemistry in natural waters and wastewaters. In addition to the hydrated metal ions, for example, $Fe(H_2O)_6^{3+}$ and hydroxo species such as $FeOH(H_2O)_5^{2+}$ discussed above, metals may exist in water reversibly bound to inorganic anions or to organic compounds as **metal complexes**, or they may be present as **organometallic** compounds containing carbon-to-metal bonds. The solubilities, transport properties, and biological effects of such species are often vastly different from those of the metal ions themselves. Subsequent sections of this chapter consider metal species with an emphasis upon metal complexes. Special attention is given to *chelation,* in which particularly strong metal complexes are formed.

Hydrated Metal Ions as Acids

Hydrated metal ions, particularly those with a charge of +3 or more, are Brönsted acids because they tend to lose H^+ in aqueous solution. The acidity of a metal ion increases with charge and decreases with increasing radius. Hydrated iron(III) ion is a relatively strong acid, ionizing as follows:

$$\text{Fe(H}_2\text{O)}_6^{3+} \qquad \text{Fe(H}_2\text{O)}_5\text{OH}^{2+} \ + \ \text{H}^+ \tag{11.7.1}$$
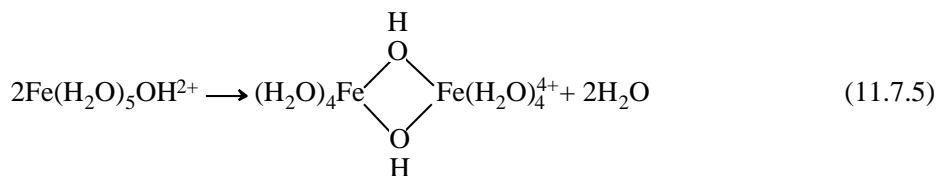
Hydrated trivalent metal ions, such as iron(III), generally are minus at least one hydrogen ion at neutral pH values or above. Generally, divalent metal ions do not lose a hydrogen ion at pH values below 6, whereas monovalent metal ions such as Na^+ do not act as acids and exist in water solution as simple hydrated ions.

The tendency of hydrated metal ions to behave as acids may have a profound effect upon the aquatic environment. A good example is *acid mine water* (see Chapter 12, Section 12.8), which derives part of its acidic character from the tendency of hydrated iron(III) to lose H^+:

$$\text{Fe(H}_2\text{O)}_6^{3+} \qquad \text{Fe(OH)}_3(s) \ + \ 3\text{H}^+ \ + \ 3\text{H}_2\text{O} \tag{11.7.4}$$
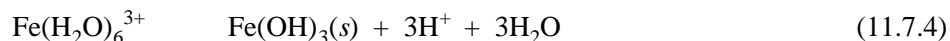
Hydroxide, OH^-, bonded to a metal ion, may function as a bridging group to join two or more metals together as shown below for iron(III) that has lost H^+:

$$2\text{Fe(H}_2\text{O)}_5\text{OH}^{2+} \longrightarrow (\text{H}_2\text{O})_4\text{Fe}\underset{\underset{\text{H}}{\text{O}}}{\overset{\overset{\text{H}}{\text{O}}}{\diamondsuit}}\text{Fe(H}_2\text{O})_4^{4+} + 2\text{H}_2\text{O} \tag{11.7.5}$$

The process may continue with formation of higher hydroxy polymers terminating with precipitation of solid metal hydroxide.

Calcium and Hardness

Of the cations found in most freshwater systems, calcium generally has the highest concentration and often has the most influence on aquatic chemistry and water uses and treatment. The chemistry of calcium, although complicated enough, is simpler than that of the transition metal ions found in water. Calcium is a key element in many geochemical processes, and minerals constitute the primary sources of calcium ion in water. Among the primary contributing minerals are gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; anhydrite, CaSO_4; dolomite, $\text{CaMg(CO}_3)_2$; and calcite and aragonite, which are different mineral forms of CaCO_3.

Calcium is present in water as a consequence of equilibria between calcium and magnesium carbonate minerals and CO_2 dissolved in water, which it enters from the atmosphere and from decay of organic matter in sediments. These relationships are depicted in Figure 11.6. Water containing a high level of carbon dioxide readily dissolves calcium from its carbonate minerals:

$$\text{CaCO}_3(s) \ + \ \text{CO}_2(aq) \ + \ \text{H}_2\text{O} \qquad \text{Ca}^{2+} \ + \ 2\text{HCO}_3^- \tag{11.7.6}$$
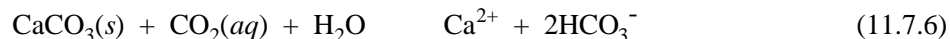
When the above reaction is reversed and CO_2 is lost from the water, calcium carbonate deposits are formed. The concentration of CO_2 in water determines the extent of dissolution of calcium carbonate. The carbon dioxide that water may gain by

equilibration with the atmosphere is not sufficient to account for the levels of calcium dissolved in natural waters, especially groundwaters. Rather, the respiration of microorganisms degrading organic matter in water, sediments, and soil accounts for the high levels of CO_2 required to dissolve $CaCO_3$ in water. This is an extremely important factor in aquatic chemical processes and geochemical transformations.
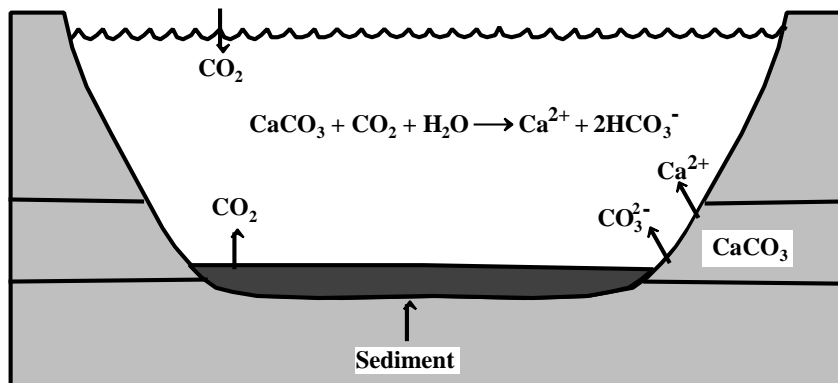

Figure 11.6 Carbon dioxide-calcium carbonate equilibria.

Calcium ion, along with magnesium and sometimes iron(II) ion, accounts for **water hardness**. The most common manifestation of water hardness is the curdy precipitate formed by the reaction of soap, a soluble sodium salt of a long-chain fatty acid, with calcium ion in hard water:

$$2C_{17}H_{33}COO^-Na^+ + Ca^{2+} \qquad Ca(C_{17}H_{33}CO_2)_2(s) + 2Na^+ \qquad (11.7.7)$$
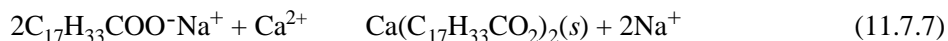
Temporary hardness is due to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water, thus causing the reversal of Equation 11.7.6:

$$Ca^{2+} + 2HCO_3^- \qquad CaCO_3(s) + CO_2(g) + H_2O \qquad (11.7.8)$$
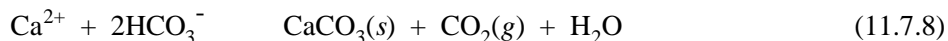
Increased temperature may force this reaction to the right by evolving CO_2 gas, and a white precipitate of calcium carbonate may form in boiling water having temporary hardness.

11.8 OXIDATION-REDUCTION

Oxidation-reduction (redox) reactions in water involve the transfer of electrons between chemical species. In natural water, wastewater, and soil, most significant oxidation-reduction reactions are carried out by bacteria, so they are considered in this section as well.

The relative oxidation-reduction tendencies of a chemical system depend upon the activity of the electron, e^-. When the electron activity is relatively high, chemical species (even including water) tend to accept electrons

$$2H_2O + 2e^- \qquad H_2(g) + 2OH^- \qquad (11.8.1)$$

and are reduced. When the electron activity is relatively low, the medium is **oxidizing**, and chemical species such as H_2O may be **oxidized**, losing electrons:

$$2H_2O \qquad O_2(g) + 4H^+ + 4e^- \qquad\qquad (11.8.2)$$

The relative tendency toward oxidation or reduction is based upon the electrode potential, E, which is relatively more positive in an oxidizing medium and negative in a reducing medium (see Section 8.10). It is defined in terms of the half reaction,

$$2H^+ + 2e^- \qquad H_2 \qquad\qquad (11.8.3)$$

for which E is defined as exactly zero when the activity of H^+ is exactly 1 (concentration approximately 1 mole per liter) and the pressure of H_2 gas is exactly 1 atmosphere. Because electron activity in water varies over many orders of magnitude, environmental chemists find it convenient to discuss oxidizing and reducing tendencies in terms of pE, a parameter analogous to pH (pH = -log a_{H^+}) and defined conceptually as the negative log of the electron activity:

$$pE = -\log a_{e^-} \qquad\qquad (11.8.4)$$

The value of pE is calculated from E by the relationship,

$$pE = \dfrac{E}{\dfrac{2.303RT}{F}} \qquad\qquad (11.8.5)$$

where R is the gas constant, T is the absolute temperature, and F is the Faraday. At 25°C for E in volts, $pE = \dfrac{E}{0.0591}$.

pE-pH Diagram

The nature of chemical species in water is usually a function of both pE and pH. A good example of this is shown by a simplified pE-pH diagram for iron in water, assuming that iron is in one of the four forms of Fe^{2+} ion, Fe^{3+} ion, solid $Fe(OH)_3$, or solid $Fe(OH)_2$ as shown in Figure 11.7. Water in which the pE is higher than that shown by the upper dashed line is thermodynamically unstable toward oxidation (Reaction 11.8.2), and below the lower dashed line water is thermodynamically unstable toward reduction (Reaction 11.8.3). It is seen that Fe^{3+} ion is stable only in a very oxidizing, acidic medium such as that encountered in acid mine water, whereas Fe^{2+} ion is stable over a relatively large region, as reflected by the common occurrence of soluble iron(II) in oxygen-deficient groundwaters. Highly insoluble $Fe(OH)_3$ is the predominant iron species over a very wide pE-pH range.

11.9 COMPLEXATION AND CHELATION

As noted in Section 11.7, metal ions in water are always bonded to water molecules in the form of hydrated ions represented by the general formula, $M(H_2O)_x^{n+}$, from which the H_2O is often omitted for simplicity. Other species may be present
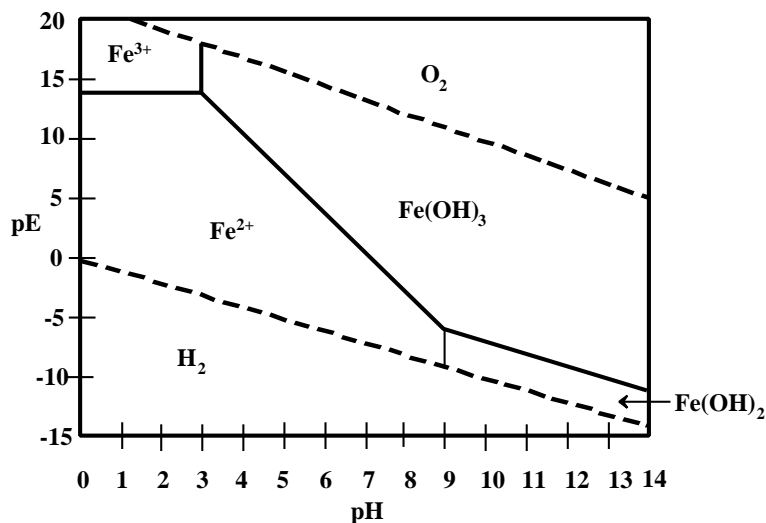
Figure 11.7   A simplified pE-pH diagram for iron in water (maximum total soluble iron concentration 1.0×10^{-5} M).

that bond to the metal ion more strongly than does water. Specifically, a metal ion in water may combine with an ion or compound that contributes electron pairs to the metal ion. Such a substance is an electron donor, or Lewis base. Called a **ligand**, it bonds to a metal ion to form a **complex** or **coordination compound** (or ion). Thus, cadmium ion in water combines with a cyanide ion ligand to form a complex ion, as shown below:

$$Cd^{2+} \ + \ CN^- \qquad CdCN^+ \qquad\qquad\qquad\qquad\qquad (11.9.1)$$

Additional cyanide ligands can be added to form the progressively weaker (more easily dissociated) complexes with the chemical formulas $Cd(CN)_2$, $Cd(CN)_3^-$, and $Cd(CN)_4^{2-}$.

In this example, the cyanide ion is a **unidentate ligand**, which means that it possesses only one site that bonds to the cadmium metal ion. Complexes of unidentate ligands are of relatively little importance in solution in natural waters. Of considerably more importance are complexes with **chelating agents.** A chelating agent has more than one atom that can be bonded to a central metal ion at one time to form a ring structure. One such chelating agent is the nitrilotriacetate (NTA) ligand, which has the following formula:
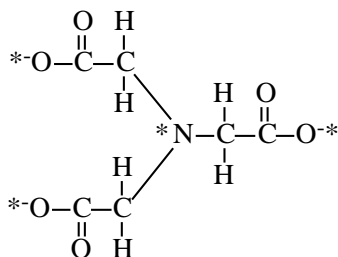
This ion has four binding sites, each marked with an asterisk in the preceding illustration, which can simultaneously bond to a metal ion, forming a structure with three rings. Such a species is known as a **chelate**, and NTA is a **chelating** agent. In general, since a chelating agent may bond to a metal ion in more than one place simultaneously, chelates are more stable than complexes involving unidentate ligands. Stability tends to increase with the number of chelating sites available on the ligand.

Structures of metal chelates take a number of different forms, all characterized by rings in various configurations. The structure of a tetrahedrally coordinated chelate of nitrilotriacetate ion is shown in Figure 11.8.

The ligands found in natural waters and wastewaters contain a variety of functional groups which can donate the electrons required to bond the ligand to a metal ion. Among the most common of these groups are:

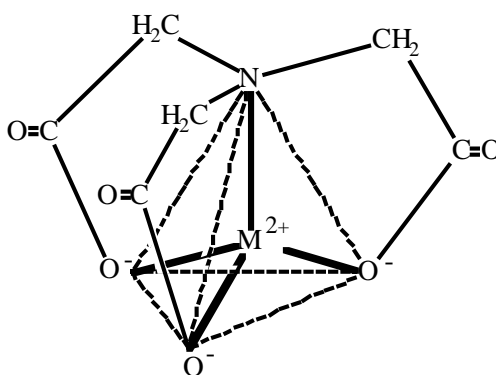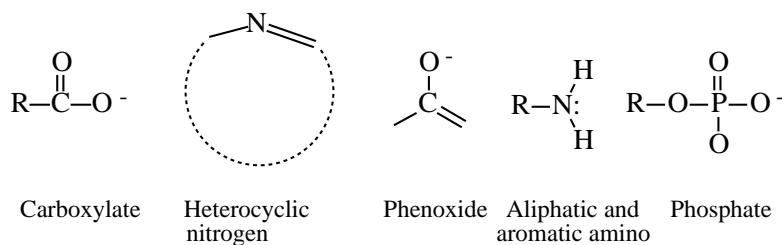| Carboxylate | Heterocyclic nitrogen | Phenoxide | Aliphatic and aromatic amino | Phosphate |

Figure 11.8 Nitrilotriacetate chelate of a divalent metal ion in a tetrahedral configuration.

These ligands complex most metal ions found in unpolluted waters and biological systems (Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, VO^{2+}). They also bind to contaminant metal ions such as Co^{2+}, Ni^{2+}, Sr^{2+}, Cd^{2+}, and Ba^{2+}.

Complexation may have a number of effects, including reactions of both ligands and metals. Among the ligand reactions are oxidation-reduction, decarboxylation, and hydrolysis. Complexation may cause changes in oxidation state of the metal and may result in a metal becoming solubilized from an insoluble compound. The formation of insoluble complex compounds removes metal ions from solution. For example, complexation with negatively charged ligands can convert a soluble metal

species from a cation to an anion, such as $Ni(CN)_4^{2-}$. Whereas cationic species are readily bound and immobilized by ion exchange processes in soil, anionic species are not strongly held by soil. Thus, codisposal of metal salts and chelating agents in wastes can result in increased hazards from heavy metals. On the other hand, some chelating agents are used for the treatment of heavy metal poisoning and insoluble chelating agents, such as chelating resins, can be used to remove metals from waste streams. Metal ions chelated by hazardous waste chelating agents, such as NTA from metal plating bath solutions, may be especially mobile in water.

Complex compounds and chelates of metals such as iron (in hemoglobin) and magnesium (in chlorophyll) are vital to life processes. Naturally occurring chelating agents, such as humic substances and amino acids, are found in water and soil. The high concentration of chloride ion in seawater results in the formation of some chloro complexes. Synthetic chelating agents such as sodium tripolyphosphate, sodium ethylenediaminetetraacetate (EDTA), sodium nitrilotriacetate (NTA), and sodium citrate are produced in large quantities for use in metal-plating baths, industrial water treatment, detergent formulations, and food preparation. Small quantities of these compounds enter aquatic systems through waste discharges.

Occurrence and Importance of Chelating Agents in Water

Chelating agents are common potential water pollutants. These substances can occur in sewage effluent and industrial wastewater such as metal plating wastewater. Chelates formed by the strong chelating agent ethylenediaminetetraacetate (EDTA) have been shown to greatly increase the migration rates of radioactive ^{60}Co from pits and trenches used for disposal of intermediate-level radioactive waste. EDTA was used as a cleaning and solubilizing agent for the decontamination of hot cells, equipment, and reactor components. Such chelates with negative charges are much less strongly sorbed by mineral matter and are vastly more mobile than the unchelated metal ions.

Complexing agents in wastewater are of concern primarily because of their ability to solubilize heavy metals from plumbing and from deposits containing heavy metals. Complexation may increase the leaching of heavy metals from waste disposal sites and reduce the efficiency with which heavy metals are removed with sludge in conventional biological waste treatment. Removal of chelated iron is difficult with conventional municipal water treatment processes. Iron(III) and perhaps several other essential micronutrient metal ions are kept in solution by chelation in algal cultures. The yellow-brown color of some natural waters is due to naturally occurring chelates of iron.
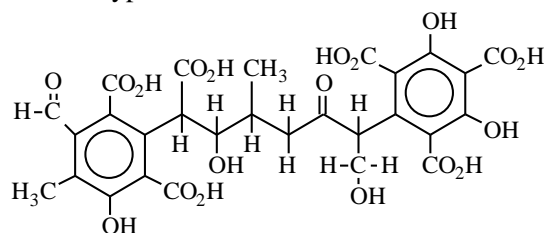
Complexation by Humic Substances

The most important class of complexing agents that occur naturally are the **humic substances.** These are degradation-resistant materials, formed during the decomposition of vegetation, that occur as deposits in soil, marsh sediments, peat, coal, lignite, or in almost any location where large quantities of vegetation have decayed. They are commonly classified on the basis of solubility. If a material containing humic substances is extracted with strong base, and the resulting solution

is acidified, the products are (a) a nonextractable plant residue called **humin**; (b) a material that precipitates from the acidified extract, called **humic acid**; and (c) an organic material that remains in the acidified solution, called **fulvic acid**. Because of their acid-base, sorptive, and complexing properties, both the soluble and insoluble humic substances have a strong effect upon the properties of water. In general, fulvic acid dissolves in water and exerts its effects as the soluble species. Humin and humic acid remain insoluble and affect water quality through exchange of species, such as cations or organic materials, with water.

Humic substances are high-molecular-mass, polyelectrolytic macromolecules. Molecular masses range from a few hundred for fulvic acid to tens of thousands for the humic acid and humin fractions.

Some feeling for the nature of humic substances can be obtained by considering the following structure of a hypothetical molecule of fulvic acid:

The binding of metal ions by humic substances is one of the most important environmental qualities of humic substances. This binding can occur as chelation between a carboxyl group and a phenolic hydroxyl group, as chelation between two carboxyl groups, or as complexation with a carboxyl group (see below):
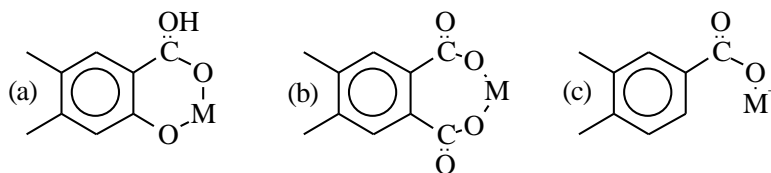

Figure 11.9 Binding of a metal ion, M^{2+}, by humic substances (a) by chelation between carboxyl and phenolic hydroxyl, (b) by chelation between two carboxyl groups, and (c) by complexation with a carboxyl group.

Soluble fulvic acid complexes of metals may be important in natural waters. They probably keep some of the biologically important transition-metal ions in solution and are particularly involved in iron solubilization and transport. Fulvic acid-type compounds are associated with color in water. These yellow materials, called **Gelbstoffe**, frequently are encountered along with soluble iron.

Insoluble humic substances, the humins and humic acids, effectively exchange cations with water and may accumulate large quantities of metals. Lignite coal, which is largely a humic-acid material, tends to remove some metal ions from water.

Special attention has been given to humic substances since about 1970, following the discovery of **trihalomethanes** (THMs, such as chloroform and dibromochloromethane) in water supplies. It is now generally believed that these suspected carcinogens can be formed in the presence of humic substances during the disinfection of raw municipal drinking water by chlorination (see Chapter 13). The

humic substances produce THMs by reaction with chlorine. The formation of THMs can be reduced by removing as much of the humic material as possible prior to chlorination.

Metals Bound as Organometallic Compounds

Another major type of metal species important in hazardous wastes consists of **organometallic compounds**, which differ from complexes and chelates in that they are bonded to the metal by a carbon-metal bond and the organic ligand is frequently not capable of existing as a stable separate species. Typical examples of organometallic compound species are monomethylmercury ion and dimethylmercury:

$$Hg^{2+} \qquad\qquad Hg(CH_2)^+ \qquad\qquad Hg(CH_2)$$

Mercury(II) ion   **Monomethylmercury ion**   **Dimethylmercury**
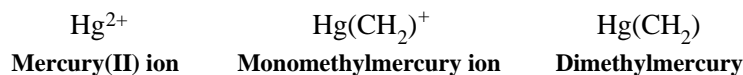
Organometallic compounds may enter the environment directly as pollutant industrial chemicals and some, including organometallic mercury, tin, selenium, and arsenic compounds, are synthesized biologically by bacteria. Some of these compounds are particularly toxic because of their mobilities in living systems and abilities to cross cell membranes.

11.10   WATER INTERACTIONS WITH OTHER PHASES

Most of the important chemical phenomena associated with water do not occur in solution, but rather through interaction of solutes in water with other phases. For example, the oxidation-reduction reactions catalyzed by bacteria occur in bacterial cells. Many organic hazardous wastes are carried through water as emulsions of very small particles suspended in water. Some hazardous wastes are deposited in sediments in bodies of water, from which they may later enter the water through chemical or physical processes and cause severe pollution effects.

Figure 11.10 summarizes some of the most significant types of interactions between water and other phases, including solids, immisicible liquids, and gases. Films of organic compounds, such as hydrocarbon liquids, may be present on the surface of water. Exposed to sunlight, these compounds are subject to photochemical reactions (see Section 16.4). Gases such as O_2 , CO_2, CH_4, and H_2S are exchanged with the atmosphere. Photosynthesis occurs in suspended cells of algae, and other biological processes, such as biodegradation of organic wastes, occur in bacterial cells. Particles contributing to the turbidity of water may be introduced by physical processes, including the erosion of streams or sloughing of water impoundment banks. Chemical processes, such as the formation of solid $CaCO_3$ illustrated in Figure 11.10, may also form particles in water.

Sediments

Sediments bind a wide variety of chemical species and are sites of many chemical and biochemical processes. Anaerobic fermentation of organic matter by bacteria produces methane gas evolved from sediments, along with CO_2 and, fre-

quently, H_2S. Similar bacteria produce mobile $HgCH_3^+$ and $Hg(CH_3)_2$ from insoluble, relatively harmless inorganic mercury compounds. Sediments are sinks for many hazardous organic compounds and heavy metal salts that have gotten into water.
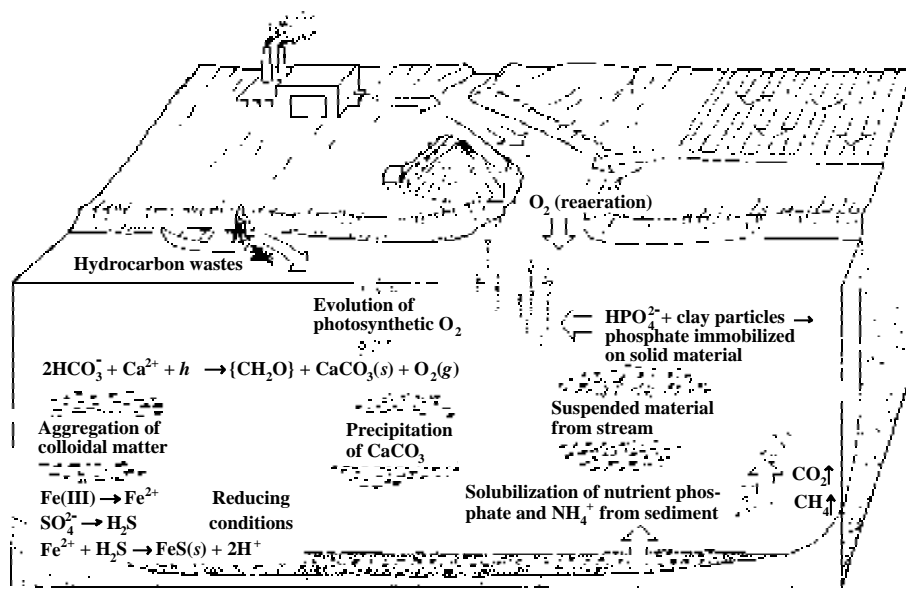

O$_2$ (reaeration)

Hydrocarbon wastes

Evolution of photosynthetic O$_2$

$2HCO_3^- + Ca^{2+} + h \rightarrow \{CH_2O\} + CaCO_3(s) + O_2(g)$

Aggregation of colloidal matter

$Fe(III) \rightarrow Fe^{2+}$ **Reducing**
$SO_4^{2-} \rightarrow H_2S$ **conditions**
$Fe^{2+} + H_2S \rightarrow FeS(s) + 2H^+$

Precipitation of CaCO$_3$

HPO$_4^{2-}$+ clay particles $\rightarrow$ phosphate immobilized on solid material

Suspended material from stream

Solubilization of nutrient phosphate and NH$_4^+$ from sediment

CO$_2\uparrow$
CH$_4\uparrow$

Figure 11.10 Aquatic chemical processes at interfaces between water and gases, solids, or other liquids.

Colloids

The most important interactions between species dissolved in aqueous solution and species in other phases occur with **colloidal particles** ranging from 0.001 micrometer (μm) to 1 μm in diameter and suspended in water, enabling maximum exposure to the water and solutes dissolved in it. Colloids have a strong influence on aquatic chemistry. Because of their extremely small size, these particles have a very high surface-to-volume ratio. Toxic substances in colloidal form are much more available to organisms in water than they are in bulk form. Special measures are required to remove colloidal particles from water. Usually, chemical treatment measures are applied to cause colloidal particles to aggregate together (processes called **coagulation** or **flocculation**), and the solids are removed by filtration.

11.11 AQUATIC LIFE

The living organisms (**biota**) in an aquatic ecosystem can be classified as either autotrophic or heterotrophic. **Autotrophic** biota utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. Autotrophic organisms that utilize solar energy to synthesize organic matter from inorganic materials are called **producers**.

Heterotrophic organisms utilize the organic substances produced by autotrophic organisms for energy and as raw materials for the synthesis of their own biomass.

Decomposers (or **reducers**) are a subclass of the heterotrophic organisms and consist of chiefly bacteria and fungi, which ultimately break down material of biological origin to the simple compounds originally fixed by the autotrophic organisms.

Microorganisms in Water

Microorganisms compose a diverse group of organisms generally capable of existing as single cells that can be seen only under a microscope. Microscopically small single-celled microorganisms, consisting of bacteria, fungi, and algae are of the utmost importance in water for a number of reasons as listed below:

- Through their ability to fix inorganic carbon, algae and photosynthetic bacteria are the predominant producers of the biomass that supports the rest of the food chain in bodies of water.
- As catalysts of aquatic chemical reactions, bacteria mediate most of the significant oxidation-reduction processes that occur in water.
- By breaking down biomass and mineralizing essential elements, especially nitrogen and phosphorus, aquatic microorganisms play a key role in nutrient cycling.
- Aquatic microorganisms are essential for the major biogeochemical cycles.
- Aquatic bacteria are responsible for the breakdown and detoxification of many xenobiotic pollutants that get into the hydrosphere.

From the viewpoint of environmental chemistry, the small size of microorganisms is particularly significant because it gives them a very high surface/volume ratio, enabling very rapid exchange of nutrients and metabolic products with their surroundings, and resulting in exceptionally high rates of metabolic reactions. This, combined with the spectacularly fast geometric increase in population of single-celled microorganisms by fission during the log phase of growth (see discussion of bacterial growth rates later in this chapter and Figure 11.12) enables microganisms to multiply very rapidly on environmental chemical substrates, such as biodegradable organic matter.

Microorganisms function as living catalysts that enable a vast number of chemical processes to occur in water and soil. Most of the important chemical reactions that take place in water and soil, particularly those involving organic matter and oxidation-reduction processes, occur through bacterial intermediaries. Algae are the primary producers of biological organic matter (biomass) in water. Microorganisms are responsible for the formation of many sediment and mineral deposits; they also play the dominant role in secondary wastewater treatment. Pathogenic microorganisms must be eliminated from water purified for domestic use.

Algae

For the purposes of discussion here, **algae** can be considered as generally microscopic organisms that subsist on inorganic nutrients and produce organic matter from

carbon dioxide by photosynthesis. In a highly simplified form, the production of organic matter by algal photosynthesis is described by the reaction

$$CO_2 + H_2O \xrightarrow{h} \{CH_2O\} + O_2(g) \tag{11.11.1}$$

where $\{CH_2O\}$ represents a unit of carbohydrate and h stands for the energy of a quantum of light.

Fungi

Fungi are nonphotosynthetic organisms. The morphology (structure) of fungi covers a wide range, and is frequently manifested by filamentous structures. Discovered in 1992, the largest and oldest organism known (as verified by DNA analysis) is a huge fungus covering about 40 acres of northern Michigan forest land. Fungi are aerobic (oxygen-requiring) organisms and generally tolerate more-acidic media and higher concentrations of heavy metal ions than bacteria.

Although fungi do not grow well in water, they play an important role in determining the composition of natural waters and wastewaters because of the large amount of their decomposition products that enter water from the breakdown of cellulose in wood and other plant materials. To accomplish this, fungal cells secrete an extracellular enzyme (exoenzyme), *cellulase*. An environmentally important byproduct of fungal decomposition of plant matter is humic material (Section 11.9), which interacts with hydrogen ions and metals.

11.12 BACTERIA

Bacteria are single-celled prokaryotic microorganisms shaped as rods (**bacillus**), spheres (**coccus**), or spirals (**vibrios**, **spirilla**, **spirochetes**) that are uniquely important in environmental chemistry. Characteristics of most bacteria include a semirigid cell wall, motility with flagella for those capable of movement, unicellular nature (although clusters of cloned bacterial cells are common), and multiplication by binary fission in which each of two daughter cells is genetically identical to the parent cell.

Bacteria obtain the energy and raw materials needed for their metabolic processes and reproduction by mediating chemical reactions. Nature provides a large number of such reactions, and bacterial species have evolved that utilize many of them. Because of their participation in such reactions, bacteria are involved in many biogeochemical processes and elemental transitions and cycles in water and soil.

The metabolic activity of bacteria is greatly influenced by their small size, which is of the order of a micrometer in magnitude. Their surface-to-volume ratio is very large, so that the inside of a bacterial cell is highly accessible to a chemical substance in the surrounding medium. Thus, for the same reason that a finely divided catalyst is more efficient than a more coarsely divided one, bacteria may bring about very rapid chemical reactions compared with those mediated by larger organisms.

An example of autotrophic bacteria is *Gallionella*, which, like all autotrophic bacteria, employs inorganic carbon as a carbon source and derives its energy from mediating a chemical reaction:

$$4FeS(s) + 9O_2 + 10H_2O \qquad 4Fe(OH)_3(s) + 4SO_4{}^{2-} + 8H^+ \qquad\qquad (11.12.1)$$
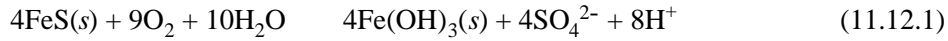
Because they consume and produce a wide range of minerals, autotrophic bacteria are involved in many geochemical transformations.

Heterotrophic bacteria are much more common in occurrence than autotrophic bacteria. They are primarily responsible for the breakdown of pollutant organic matter in water and of organic wastes in biological waste-treatment processes.

Aerobic bacteria require molecular oxygen as an electron receptor:

$$O_2 + 4H^+ + 4e^- \qquad H_2O \qquad\qquad (11.12.2)$$

Anaerobic bacteria function only in the complete absence of molecular oxygen, using substances such as nitrate ion and sulfate ion as substitutes for O_2. Frequently, molecular oxygen is quite toxic to anaerobic bacteria. A third class of bacteria, **facultative bacteria**, utilize free oxygen when it is available and use other substances as electron receptors (oxidants) when molecular oxygen is not available.

The Prokaryotic Bacterial Cell

Unicellular bacteria and cyanobacteria consist of prokaryotic cells, which differ in several major respects from the eukaryotic cells of higher organisms. Illustrated in Figure 11.11, prokaryotic bacterial cells are enclosed in a **cell wall**, which in many bacteria is frequently surrounded by a **slime layer** (capsule). The thin **cell membrane** or **cytoplasmic membrane** on the inner surface of the cell wall encloses the cellular cytoplasm, controls the nature and quantity of materials transported into and out of the cell, and is susceptible to damage from some toxic substances. Hairlike **pili**
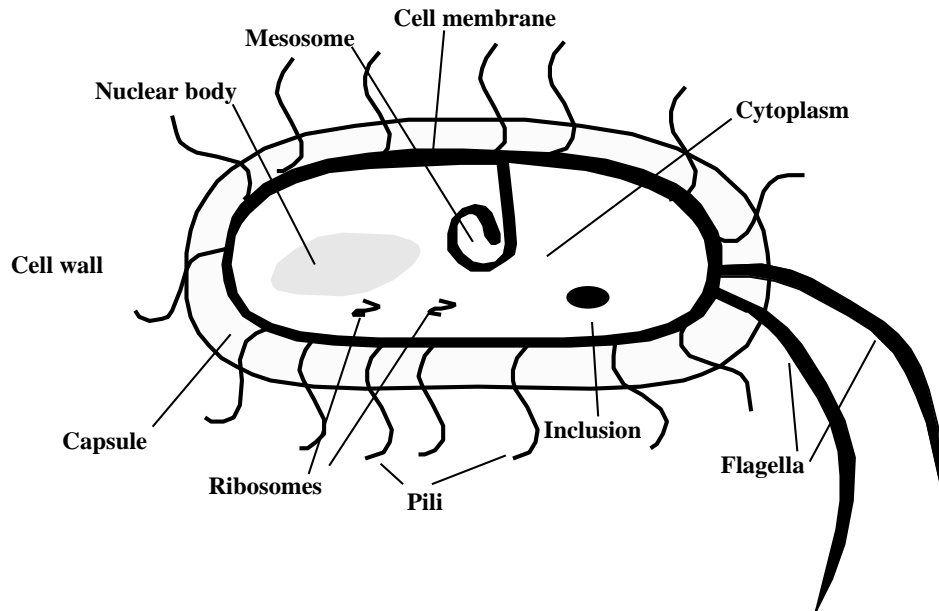

Figure 11.11 Generic prokaryotic bacterial cell illustrating major cell features.

on the surface of a bacterial cell enable the cell to stick to surfaces. **Flagella** are movable appendages that enable motile bacterial cells to move by their whipping action. Bacterial cells are filled with **cytoplasm**, an aqueous solution and suspension containing proteins, lipids, carbohydrates, nucleic acids, ions, and other materials constituting the medium in which the cell's metabolic processes are carried out. The major constituents of cytoplasm are: a **nuclear body** composed of a single DNA macromolecule that controls metabolic processes and reproduction; **inclusions** of reserve food material, usually consisting of fats and carbohydrates; and **ribosomes**, which function as sites of protein synthesis.

Rate of Bacterial Growth

The population size of bacteria and unicellular algae as a function of time in a growth culture is illustrated by Figure 11.12, which shows a **population curve** for a bacterial culture. Such a culture is started by inoculating a rich nutrient medium with a small number of bacterial cells. Bacteria multiply exponentially in the log phase.
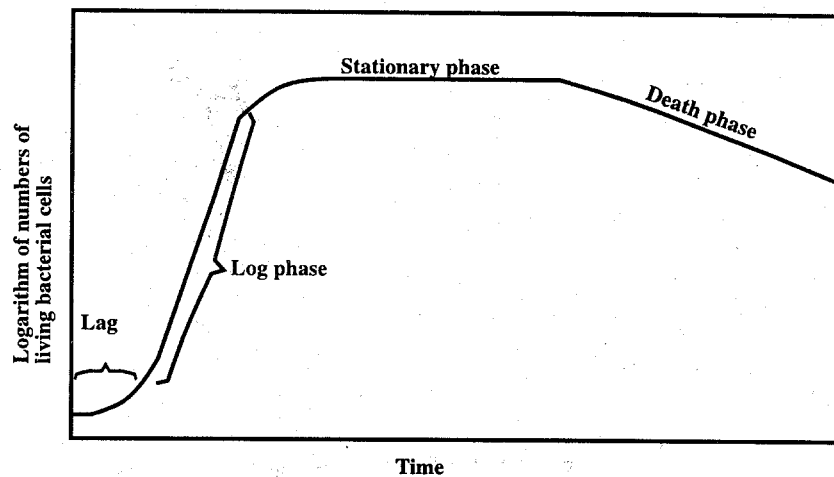
Figure 11.12 Population curve for a bacterial culture.

Bacterial Metabolism

Metabolic reactions by which bacteria break down substances and extract energy, as well as synthesizing biological materials, are mediated by enzymes (see Chapter 10). Figure 11.13 illustrates the effect of **substrate concentration** on enzyme activity. It is seen that enzyme activity increases in a linear fashion up to a value that represents saturation of the enzyme activity. Beyond this concentration, increasing substrate levels do not result in increased enzyme activity. This kind of behavior is reflected in bacterial activity and growth, which increase with available nutrients up to a saturation value. Superimposed on this plot in a bacterial system is increased bacterial population, which, in effect, increases the amount of available enzyme.
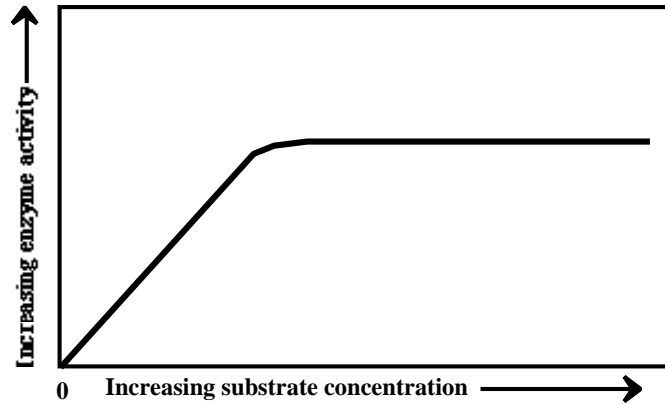
Figure 11.13 Effect of increasing substrate concentration on enzyme activity.

Figure 11.14 shows that a plot of bacterial enzyme activity as a function of temperature exhibits a maximum growth rate at an optimum temperature that is skewed toward the high temperature end of the curve. The abrupt dropoff beyond the temperature maximum occurs because enzymes are destroyed by being denatured at temperatures not far above the optimum. The temperature for optimum growth rate varies with the kind of bacteria.
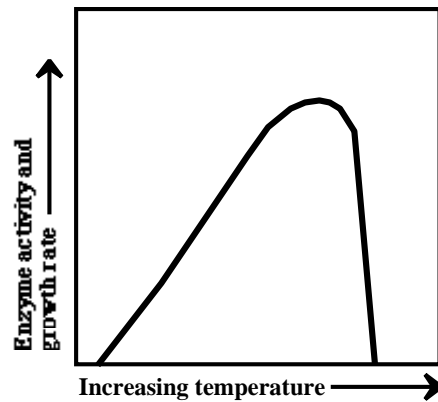

Figure 11.14 Enzyme activity as a function of temperature. A plot of bacterial growth versus temperature has the same shape.

Figure 11.15 is a plot of enzyme activity versus pH. The optimum pH may vary somewhat; for example, bacteria that are responsible for generating acid mine water (see Section 12.8) have enzymes with optimum pHs that are very low. In general, though, enzymes typically have a pH optimum around neutrality. Enzymes tend to become denatured at pH extremes. This behavior likewise is reflected in plots of bacterial metabolism as a function of pH. For some bacteria that thrive in acid, such as those that generate sulfuric acid by the oxidation of sulfide or organic acids by fermentation processes, the optimum pH may be quite low.
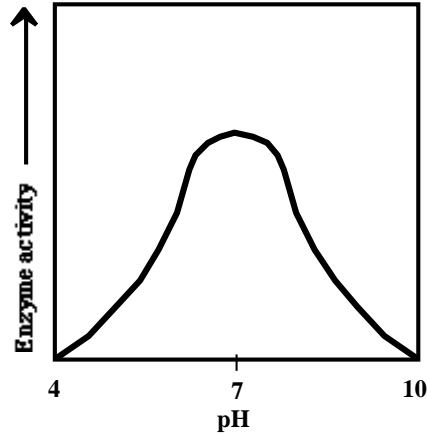
Figure 11.15 Enzyme activity as a function of pH.

## 11.13 MICROBIALLY MEDIATED ELEMENTAL TRANSISTIONS AND CYCLES

Microbially mediated transitions between elemental species and the elemental cycles resulting therefrom constitute one of the most significant aspects of geochemistry as influenced by biological processes. Such cycles involving organisms—predominantly microorganisms—are called biogeochemical cycles. This section addresses biogeochemical cycles for several important elements.

Microbial Transformations of Carbon

The carbon cycle is represented in Figure 11.16. A relatively small, but highly significant, portion of global carbon is in the atmosphere as CO_2. A very large amount of carbon is present as minerals, particularly calcium and magnesium carbonates. Another fraction of carbon is fixed as petroleum and natural gas, with a much larger amount as hydrocarbonaceous kerogen, coal, and lignite. Manufacturing processes are used to convert hydrocarbons to xenobiotic compounds with functional groups containing halogens, oxygen, nitrogen, phosphorus, or sulfur. Though a very small amount of total environmental carbon, these compounds are particularly significant because of their toxicological chemical effects.

Microorganisms are strongly involved in the carbon cycle, mediating crucial biochemical reactions discussed later in this section. Photosynthetic algae are the predominant carbon-fixing organisms in water; as they consume CO_2, the pH of the water is raised enabling precipitation of $CaCO_3$ and $CaCO_3 \cdot MgCO_3$. Organic carbon fixed by microorganisms is transformed by biogeochemical processes to fossil petroleum, kerogen, coal, and lignite. Microorganisms degrade organic carbon from biomass, petroleum, and xenobiotic sources, ultimately returning it to the atmosphere as CO_2. The following summarize the prominent ways in which microorganisms are involved in the carbon cycle:

- **Photosynthesis** in which algae, higher plants, and photosynthetic bacteria use light energy to fix inorganic carbon in a high-energy organic form:

$$CO_2 + H_2O \xrightarrow{h} \{CH_2O\} + O_2(g)$$
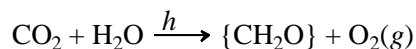
- **Respiration** in which organic matter is oxidized in the presence of molecular O_2 (**aerobic respiration**)

$$\{CH_2O\} + O_2(g) \quad CO_2 + H_2O$$
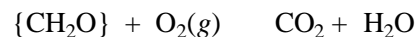
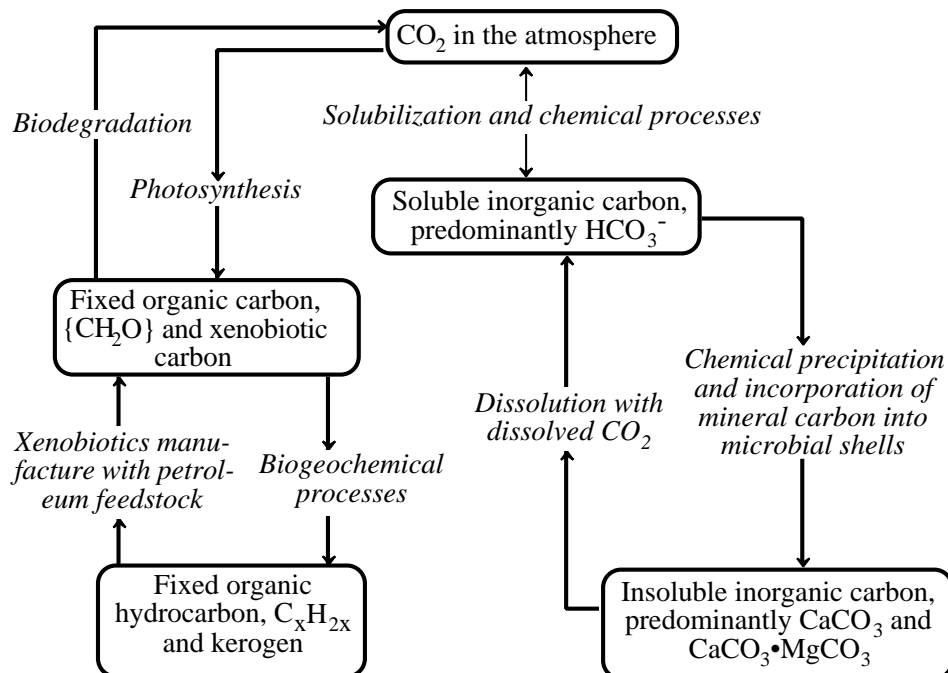or **anaerobic respiration**, which uses oxidants other than O_2, such as NO_3^- or SO_4^{2-}.

Figure 11.16 Important aspects of the biogeochemical carbon cycle.

- **Degradation of biomass** by bacteria and fungi. Biodegradation of dead organic matter consisting predominantly of plant residues prevents accumulation of excess waste residue and converts organic carbon, nitrogen, sulfur, and phosphorus to simple organic forms that can be utilized by plants. It is a key part of the biogeochemical cycles of these elements and also leaves a humus residue that is required for optimum physical condition of soil.

- **Methane production** by methane-forming bacteria, such as *Methanobacterium*, in anoxic (oxygen-less) sediments,

$$2\{CH_2O\} \quad CH_4 + CO_2$$
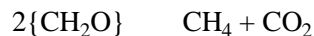
plays a key role in local and global carbon cycles as the final step in the anaerobic decomposition of organic matter. It is the source of about 80%

of the methane entering the atmosphere. Microbial methane production is a **fermentation reaction**, defined as an oxidation-reduction process in which both the oxidizing agent and reducing agent are organic substances.

- **Bacterial utilization and degradation of hydrocarbons.** The oxidation of higher hydrocarbons under aerobic conditions by *Micrococcus*, *Pseudomonas*, *Mycobacterium*, and *Nocardia* is an important environmental process by which petroleum wastes are eliminated from water and soil. The initial step in the microbial oxidation of alkanes is conversion of a terminal $-CH_3$ group to a $-CO_2$ group followed by $-$oxidation,

$$CH_3CH_2CH_2CH_2CH_2O_2H + 3O_2 \quad CH_3CH_2CH_2O_2H + 2CO_2 + 2H_2O$$

wherein carbon atoms are removed in 2-carbon fragments. The overall process leading to ring cleavage in aromatic hydrocarbons is the following in which cleavage is preceded by addition of $-OH$ to adjacent carbon atoms:
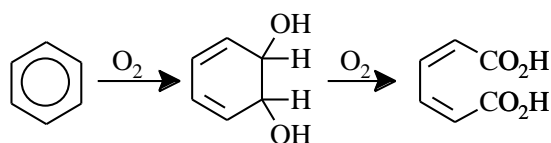

- **Biodegradation of organic matter**, such as occurs in treatment of municipal wastewater by reactions represented in a general sense by,

$$\{CH_2O\} + O_2(g) \quad CO_2 + H_2O + biomass$$

Microbial Transformations of Nitrogen

Some of the most important microorganism-mediated chemical reactions in aquatic and soil environments are those involving nitrogen compounds. They are key constituents of the **nitrogen cycle** shown in Figure 11.17, a cycle that describes the dynamic processes through which nitrogen is interchanged among the atmosphere, organic matter, and inorganic compounds. The key microbially mediated processes in the nitrogen cycle are the following:

- **Nitrogen fixation**, the binding of atmospheric nitrogen in a chemically combined form:

$$3\{CH_2O\} + 2N_2 + 3H_2O + 4H^+ \quad 3CO_2 + 4NH_4^+$$
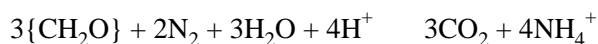
Biological nitrogen fixation is a key biochemical process in the environment and is essential for plant growth in the absence of synthetic fertilizers.

- **Nitrification**, the conversion of N(-III) to N(V) catalyzed by *Nitrosomonas* and *Nitrobacter*:
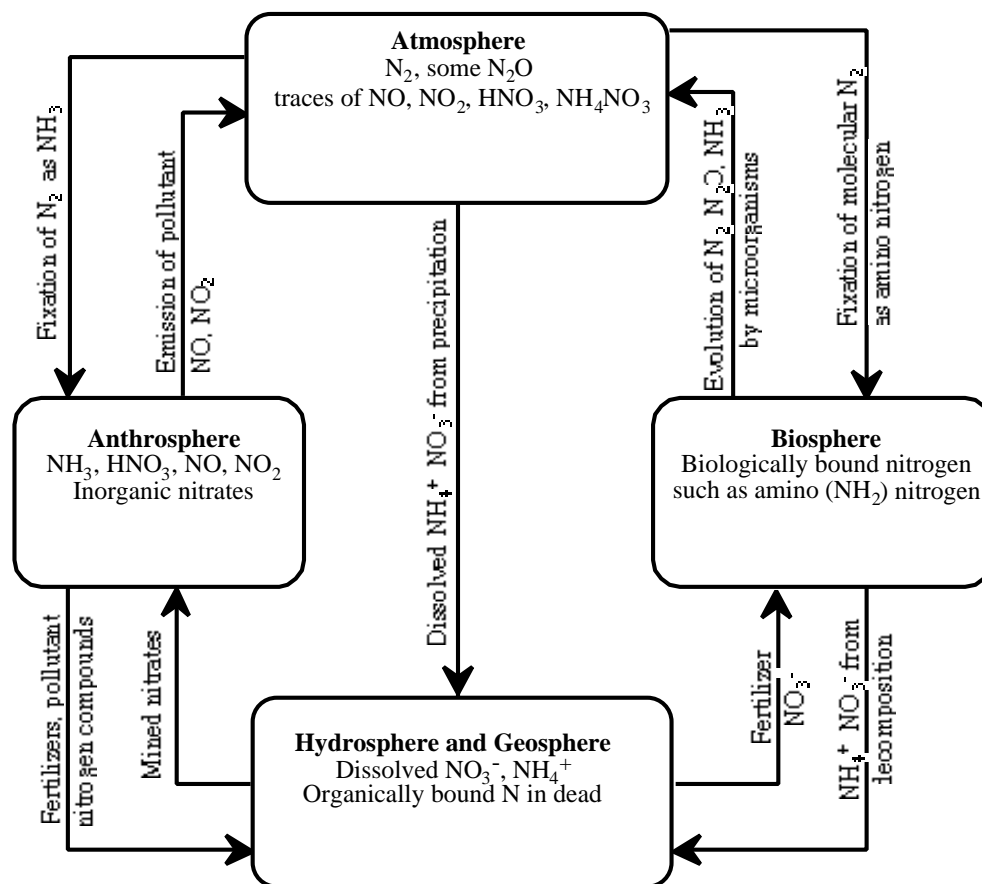
$$2O_2 + NH_4^+ \quad NO_3^- + 2H^+ + H_2O$$

Figure 11.17 Aspects of the nitrogen cycle.

Nitrification is especially important in nature because nitrogen is absorbed by plants primarily as nitrate ion, which is produced by nitrification. When fertilizers are applied in the form of ammonium salts or anhydrous ammonia, a microbial transformation to nitrate enables maximum assimilation of nitrogen by the plants.

- **Nitrate reduction** by which nitrogen in chemical compounds is reduced by microbial action to lower oxidation states in the absence of free oxygen:

$$2NO_3^- + \{CH_2O\} \quad 2NO_2^- + H_2O + CO_2$$

$$2NO_2^- + 3\{CH_2O\} + 4H^+ \quad 2NH_4^+ + 3CO_2 + H_2O$$
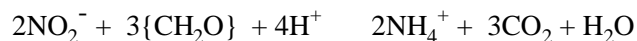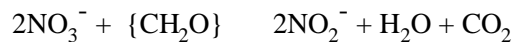
- **Denitrification**, which produces N_2 gas from chemically fixed nitrogen:

$$4NO_3^- + 5\{CH_2O\} + 4H^+ \quad 2N_2 + 5CO_2 + 7H_2O$$
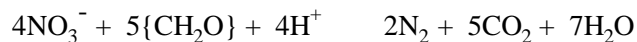
Denitrification is the mechanism by which fixed nitrogen is returned to the atmosphere and is useful in advanced water treatment for the removal of

nutrient nitrogen. Loss of nitrogen to the atmosphere may also occur through the formation of N_2O and NO by bacterial action on nitrate and nitrite catalyzed by several types of bacteria.

Microbial Transformations of Sulfur

The sulfur cycle involves interconversions among a number of sulfur species, including inorganic soluble sulfates, insoluble sulfates, soluble sulfide, gaseous hydrogen sulfide, and insoluble sulfides; biologically bound sulfur; and sulfur in synthetic organic compounds. The major microbially mediated processes in this cycle are the following:

- **Sulfate reduction** to sulfide by bacteria such as *Desulfovibrio*, which utilizes sulfate as an electron acceptor in the oxidation of organic matter:

$$SO_4^{2-} + 2\{CH_2O\} + 2H^+ \quad H_2S + 2CO_2 + 2H_2O$$
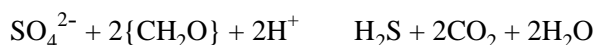
The odiferous and toxic H_2S product may cause serious problems with water quality.

- **Sulfide oxidation** by bacteria such as *Thiobacillus*:

$$2H_2S + 4O_2 \quad 4H^+ + 2SO_4^{2-}$$

Oxidation of sulfur in a low oxidation state to sulfate ion produces sulfuric acid, a strong acid. Some of the bacteria that mediate this reaction, such as *Thiobacillus thiooxidans* are remarkably acid tolerant. Acid-tolerant sulfur-oxidizing bacteria produce and thrive in acidic waters, such as acid mine water, which can be very damaging to the environment.

- **Degradation of organic sulfur compounds** by bacterially mediated processes that can result in production of strong-smelling noxious volatile organic sulfur compounds, such as methyl thiol, CH_3SH, and dimethyl disulfide, CH_3SSCH_3. The formation of these compounds, in addition to that of H_2S, accounts for much of the odor associated with the biodegradation of sulfur-containing organic compounds. Hydrogen sulfide is formed from a large variety of organic compounds through the action of a number of different kinds of microorganisms.

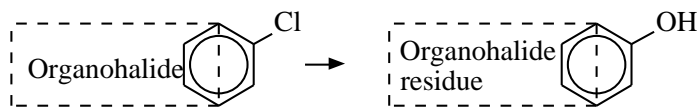## Microbial Transformations of Phosphorus

The phosphorus cycle involves natural and pollutant sources of phosphorus including biological, organic, and inorganic phosphorus. Biological phosphorus is a key constituent of cellular DNA. Organic phosphorus occurs in organophosphate insecticides. The major inorganic phosphorus species are soluble $H_2PO_4^-$ and HPO_4^{2-} and insoluble $Ca_5(OH)(PO_4)_3$. Soil and aquatic microbial processes are very important in the phosphorus cycle. Of particular importance is the fact that phosphorus is the most common limiting nutrient in water, particularly for the growth of algae. Bacteria are even more effective than algae in taking up phosphate from water, accumulating it as excess cellular phosphorus that can be released to

support additional bacterial growth, if the supply of phosphorus becomes limiting. Microorganisms that die release phosphorus that can support the growth of additional organisms.

Biodegradation of phosphorus compounds is important in the environment for two reasons. The first of these is that it is a *mineralization* process that releases inorganic phosphorus from the organic form. This process provides an important source of nutrient orthophosphate required for the growth of plants and algae. Second, biodegradation deactivates highly toxic organophosphate compounds, such as the organophosphate insecticides.

Microbial Transformations of Halogens and Organohalides

Among the more important microbial processes that operate on pollutant xenobiotic compounds in soil and water are those involving the degradation of organohalide compounds. Such compounds, particularly the organochloride compounds, are among the more abundant air and water pollutants and hazardous waste constituents. Some are relatively toxic and even carcinogenic, and they tend to accumulate in lipid tissues. The key step in biodegradation of organohalide compounds is **dehalogenation**, which involves the replacement of a halogen atom:

Microbial Transformations of Iron

Some bacteria, including *Ferrobacillus*, *Gallionella*, and some forms of *Sphaerotilus*, utilize iron compounds in obtaining energy for their metabolic needs, by oxidizing iron(II) to iron(III) with molecular oxygen:

$$4Fe(II) + 4H^+ + O_2 \qquad 4Fe(III) + 2H_2O \qquad\qquad (11.13.1)$$
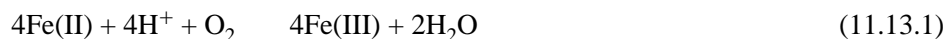
The carbon source for some of these bacteria is CO_2. Since they do not require organic matter for carbon, and because they derive energy from the oxidation of inorganic matter, these bacteria may thrive in environments where organic matter is absent. The iron(III) product is amassed as large quantities of solid $Fe(OH)_3$, so that large deposits of hydrated iron(III) oxide form in areas where iron-oxidizing bacteria thrive. Some of the iron bacteria, notably *Gallionella*, secrete large quantities of hydrated iron(III) oxide in the form of intricately branched structures that grow at the end of a twisted stalk of the iron oxide.

Acid Mine Waters

One consequence of bacterial action on metal compounds is acid mine drainage, a common and damaging water pollution problem. Acid mine water results from the presence of sulfuric acid produced by the oxidation of pyrite, FeS_2. Microorganisms are closely involved in the overall process, which consists of several reactions. Acid mine water is discussed further in Section 12.7.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The most important unique properties of water that largely determine its environmental chemical behavior are [1]_____ Thermal stratification of bodies of water results from water's [2]_____ _____. Most of the many oxidation-reduction reactions that occur in water are mediated by bacteria [3]_____. The ability of solutes in water to neutralize added strong acid is called [4]_____ and water hardness is due mostly to the presence of [5]_____. In water near neutral pH the major contributor to alkalinity is [6]_____. A major pollutant contributor to acidity is free mineral acid manifested by the presence of [7]_____ _____. The hydronium ion, H_3O^+, indicates [8]_____, and can be abbreviated simply as [9]_____. A bare metal ion cannot exist as a separate entity in water, but is present instead as [10]_____. Because they tend to lose H^+ in aqueous solution, hydrated metal ions with a charge of +3 or more, act as [11]_____. Calcium is present in water as a consequence of [12]_____ _____.The reaction $2C_{17}H_{33}COO^-Na^+ + Ca^{2+}$ $Ca(C_{17}H_{33}CO_2)_2(s) + 2Na^+$ is a manifestation of [13]_____. Oxidation-reduction reactions in water involve [14]_____ _____, and in natural water, wastewater, and soil are carried out by [15]_____. The relative oxidation-reduction tendencies of a chemical system depend upon [16]_____. The parameter pE is defined conceptually as [17]_____. In the pE-pH diagram for iron in water, the species that predominates at low pE and low pH is [18]_____, whereas at high pE and higher pH it is [19]_____. In the pE-pH diagram, the upper and lower dashed lines show [20]_____ _____, respectively. A ligand bonds to a metal ion to form a [21]_____. The NTA anion as a ligand has [22]_____ binding sites, and it forms chelates with [23]_____ rings. Some of the more significant environmental effects of complexation and chelation are. [24]_____ _____. Complexing agents in wastewater are of concern primarily because of [25]_____ _____. The most important class of complexing agents that occur naturally are, [26]_____, which are [27]_____ _____. These substances are divided into the three classes of [28]_____ and are commonly divided on the basis of [29]_____.They are most significant in drinking water supplies because of [30]_____ _____. Organometallic compounds, differ from

complexes and chelates in that [31]_____

_____.

Most of the important chemical phenomena associated with water do not occur in solution, but rather through [32]_____,

which may include [33]_____.

Sediments are [34]_____

_____ and the site of [35]_____.

Very small particles ranging from 0.001 micrometer (µm) to 1 µm in diameter have a very high surface-to-volume ratio and are called [36]_____.

Living organisms that utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms are called [37]_____, whereas heterotrophic organisms [38]_____

_____. Four reasons that microorganisms are especially important in water are [39]_____

_____

_____

_____

_____

The small size of microorganisms is particularly significant because [40]_____

_____. In a simplified sense the basic reaction by which algae produce biomass is [41]_____.

Fungi are important in the environmental chemistry of water because [42]_____

_____

_____

_____. Three classifications of bacteria based upon their requirement for oxygen are [43]_____.

The kinds of cells that bacteria have are [44]_____.

The major phases in a bacterial growth curve are [45]_____

_____.

A plot of bacterial enzyme activity as a function of temperature is shaped such that it [46]_____

_____

_____ because [47]_____

_____

_____. The prominent ways in which microorganisms are involved in the carbon cycle are [48]_____

_____

_____. The steps in the nitrogen cycle that involve bacteria are [49]_____.

Microbial transformations of sulfur involve [50]_____

_____

_____. The two reasons for which biodegradation of phosphorus compounds is important in the environment are

[51]_____

_____.

The key step in biodegradation of organohalide compounds is [52]_____.

The bacterially-catalyzed oxidation of iron(II) to iron(III) by bacteria can result in the formation of large deposits of [53]_____. Acid mine water results from the presence of [54]_____ produced by the oxidation of [55]_____ _____.

Answers to Chapter Summary

1. Properties of water as listed in Table 11.1.
2. unique temperature-density relationship
3. bacteria
4. alkalinity
5. Ca^{2+} ion
6. HCO_3^- ion
7. strong acids such as H_2SO_4 and HCl in water
8. H^+ ion bound to H_2O
9. H^+
10. the hydrated metal cation $M(H_2O)_x^{n+}$
11. Brönsted acids
12. equilibria between calcium and magnesium carbonate minerals and CO_2 dissolved in water
13. water hardness
14. the transfer of electrons between chemical species
15. bacteria
16. the activity of the electron e^-
17. the negative log of the electron activity
18. Fe^{2+}
19. solid $Fe(OH)_3$
20. the oxidizing and reducing limits of water stability
21. complex or coordination compound
22. four
23. three
24. reactions of both ligands and metals, changes in oxidation state of the metal, and effects on life processes.
25. their ability to solubilize heavy metals
26. humic substances
27. degradation-resistant materials formed during the decomposition of vegetation
28. fulvic acid, humic acid, and humin
29. solubility, particularly in acid and base
30. their potential to form trihalomethanes
31. the organic portion is bonded to the metal by a carbon-metal bond and the organic ligand is frequently not capable of existing as a stable separate species
32. interaction of solutes in water with other phases
33. solids, immisicible liquids, and gases
34. repositories of a wide variety of chemical species
35. many chemical and biochemical processes
36. colloids
37. autotrophic organisms

38. utilize the organic substances produced by autotrophic organisms as energy sources and as the raw materials for the synthesis of their own biomass
39. They are the predominant producers of the biomass in water, they mediate most of the significant oxidation-reduction processes that occur in water, they play a key role in nutrient cycling, they are essential for the major biogeochemical cycles, and they are responsible for the breakdown and detoxication of many xenobiotic pollutants that get into the hydrosphere.
40. it gives them a very high surface/volume ratio
41. $CO_2 + H_2O \xrightarrow{h} \{CH_2O\} + O_2(g)$
42. they play an important role in determining the composition of natural waters and wastewaters due to the large amount of their decomposition products that enter water from the breakdown of cellulose in wood and other plant materials
43. aerobic, anaerobic, and facultative
44. prokaryotic cells
45. lag phase, log phase, stationary phase, and death phase
46. exhibits a maximum growth rate at an optimum temperature that is skewed toward the high temperature end of the curve
47. enzymes are destroyed by being denatured at temperatures not far above the optimum
48. photosynthesis, respiration, degradation of biomass, methane production, bacterial utilization and degradation of hydrocarbons, and biodegradation of organic matter
49. nitrogen fixation, nitrification, nitrate reduction, and denitrification
50. sulfate reduction, sulfide oxidation, and biodegradation of organic sulfur compounds
51. mineralization, which releases inorganic phosphorus from the organic form, and deactivation of highly toxic organophosphate compounds
52. dehalogenation
53. iron(III) hydroxide
54. sulfuric acid
55. pyrite, FeS_2

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QUESTIONS AND PROBLEMS

1. A sample of groundwater heavily contaminated with soluble inorganic iron is brought to the surface and the alkalinity is determined without exposing the sample to the atmosphere. Why does a portion of such a sample exposed to the atmosphere for some time exhibit a decreased alkalinity?

2. What indirect role is played by bacteria in the formation of limestone caves?

3. Over the long term, irrigation must be carried out so that there is an appreciable amount of runoff, although a much smaller quantity of water would be sufficient to wet the ground. Why must there be some runoff?

4. Of the following, the true statement is that the specific species H_2CO_3 (a) is the predominant form of CO_2 dissolved in water; (b) exists only at pH values above 9; (c) makes up only a small fraction of CO_2 dissolved in water, even at low pH; (d) is not known to exist at all; (e) is formed by the reaction between CO_2 and OH^-.

5. Although algae release oxygen by photosynthesis, why may oxygen levels become rather low at night in water supporting a heavy growth of algae?

6. Alkalinity is **not** (a) a measure of the degree to which water can support algal growth, (b) the capacity of water to neutralize acid, (c) a measure of the capacity of water to resist a decrease in pH, (d) a direct measure of pH, (e) important in considerations of water treatment.

7. What is the molar concentration of O_2 in water in equilibrium with atmospheric air at 25°C?

8. Explain why a solution of $Fe_2(SO_4^{2-})_3$ in water is acidic.

9. How does the ionic radius of ions such as Ca^{2+}, Fe^{2+}, and Mn^{2+} correlate with their relative tendencies to be acidic?

10. An individual measured the pH of a water sample as 11.2 and reported it to be "highly alkaline." Is that statement necessarily true?

11. Match the following pertaining to properties of water (left) and their effects and significance (right):

A. Highest dielectric constant of any common liquid	1. Stabilization of temperatures of organisms and geographical regions
B. Higher surface tension than any other liquid	2. Controlling factor in physiology; governs drop and surface phenomena
C. Maximum density as a liquid	3. High solubility of ionic substances and their ionization in aqueous solution
D. Higher heat capacity than any liquid other than ammonia	4. Ice floats

12. How does the temperature-density relationship of water influence the presence of oxidized and reduced species in a body of water?

13. What is a particularly unique aspect of oceanographic chemistry?

14. Explain with appropriate chemical reactions how the fixation of inorganic carbon by algal photosyntheis in water can result in the eventual precipitation of $CaCO_3$.

15. The chemical species that is the predominant contributor to water alkalinity is _____ and the predominant contributor to water hardness is _____.

16. In what sense is pH an *intensity* factor, and alkalinity a *capacity* factor? How do the comparative pHs and alkalinities of 1.00×10^{-3} M NaOH and 0.100 M HCO_3^- illustrate this point?

17. Illustrate with a chemical reaction how the addition of $Al(H_2O)_6^{3+}$ might reduce alkalinity in water.

18. Explain what the chemical formula Mg^{2+}, used to represent magnesium ion dissolved in water, really means.

19. Explain what the following chemical formulas have to do with speciation of metals dissolved in water: $Fe(H_2O)_6^{3+}$, $Fe(CN)_6^{3-}$, $Pb(C_2H_5)_4$, where C_2H_5 is an ethyl group bound to lead through a carbon atom.

20. What does the reaction below show about water chemistry, hardness, and alkalinity? How is microbial degradation of organic matter tied in with the phenomenon illustrated?

$$CaCO_3(s) + CO_2(aq) + H_2O \quad Ca^{2+} + 2HCO_3^-$$
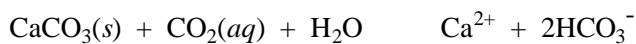
21. Explain how the reaction below illustrates a detrimental aspect of water hardness.

$$2C_{17}H_{33}COO^-Na^+ + Ca^{2+} \quad Ca(C_{17}H_{33}CO_2)_2(s) + 2Na^+$$

22. Explain what the two reactions below show about oxidation-reduction phenomena in water. How are they tied in with pE in water? How is pE conceptually defined?

$$2H_2O + 2e^- \quad H_2(g) + 2OH^-$$

$$2H_2O \quad O_2(g) + 4H^+ + 4e^-$$
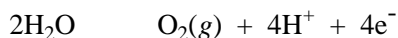
23. Define ligand, complex, and chelating agent. Why is a chelate often so stable? How are "electron pairs" involved in complexation and chelation? What is a unidentate ligand?

24. Explain in what sense the species $Fe(H_2O)_6^{2+}$ is a complex ion.

25. Explain some of the major environmental implications of complexation and chelation. What is the particular environmental harm that might come from codisposal of a toxic heavy metal salt and a chelating compound?

26. In what sense does an organometallic compound differ from a complex compound?

27. What are the three classes of humic substances? What is the source of humic substances? What are their chelating properties?

28. What are some of the unique characteristics of colloidal particles that make them so important in water? What is the approximate size of colloidal particles?

29. How are sediments formed? Discuss the significance of sediments in aquatic chemistry.

30. Define the following terms as applied to aquatic organisms and give an example of each: Autotrophic organisms, heterotrophic organisms, producers, decomposers, aerobic bacteria, anaerobic bacteria.

31. List and discuss the reasons that microorganisms are of particular importance in water.

32. Give the name and significance of each of the following compounds or microbially-mediated reactions involving sulfur: (1) $SO_4^{2-} + 2\{CH_2O\} + 2H^+$ $H_2S + 2CO_2 + 2H_2O$, (2) $2H_2S + 4O_2 \quad 4H^+ + 2SO_4^{2-}$, (3) CH_3SH.

33. What are the important implications for environmental chemistry of the fact that aquatic bacteria are extremely small and may reproduce very rapidly?

34. Define algae and fungi. Give a simplified biochemical reaction characteristic of algae and one characteristic of fungi. In what sense are fungi and algae "opposites"? Why is *cellulase* particularly important in environmental chemical processes?

35. Define each of the following applied to aquatic bacteria: Cell wall, slime layer, cell membrane, flagella, cytoplasm, nuclear body, inclusions.

36. Offer plausible explanations for the four regions shown in a bacterial growth curve. What are the special implications of the log region?

37. In the pE-pH diagram below, suppose that the upper dashed line represents equilibrium of the system shown with atmospheric oxygen and that the lower dashed line represents equilibrium with an anaerobic system, such as in the sediment of a body of water. That being the case, use arrows and reactions to explain the following in a system in which some iron is available: (1) Acid mine water typically contains dissolved iron in equilibrium with air. Which region on the diagram might represent acid mine water? (2) What is observed as the pH of iron-containing acid mine water is raised by dilution or exposure to base? (3) Explain the presence of soluble iron in anaerobic groundwater at pH 7. (4) Explain what might happen, and why a precipitate might be observed, as acid mine water is raised to the surface and exposed to air.
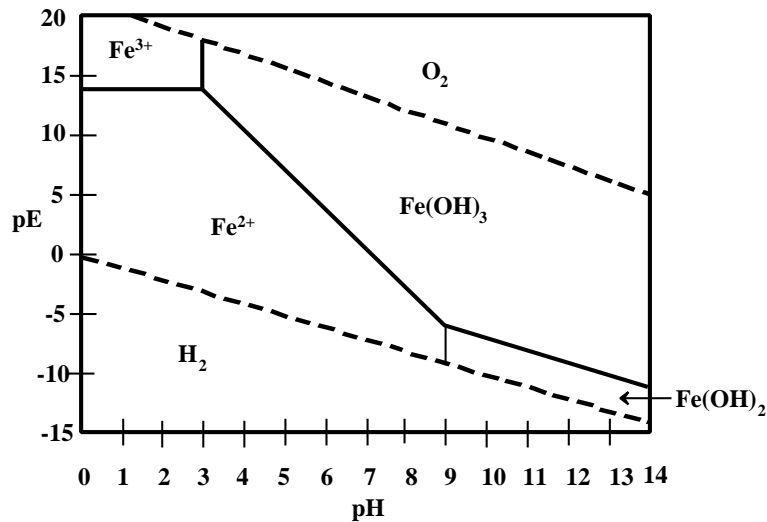
38. Explain the plot showing the effect of increasing substrate concentration on enzyme activity.

39. Explain the plot showing the effect of temperature on bacterial enzyme activity and growth. Why is it unsymmetrical?

39. Explain the significance of each of the following in the carbon cycle: Photo-synthesis, the biochemical reaction $\{CH_2O\}$ + $O_2(g)$ CO_2 + H_2O, methane production, –oxidation.

40. What is an important characteristic of *Thiobacillus thiooxidans* that make it responsible for adverse conditions that it may, itself, create through its metabolic action on species in water? Explain.

41. Give the name and significance of each of the following microbially-mediated reactions involving nitrogen: (1) $3\{CH_2O\} + 2N_2 + 3H_2O + 4H^+ \rightarrow 3CO_2 + 4NH_4^+$, (2) $2O_2 + NH_4^+ \rightarrow NO_3^- + 2H^+ + H_2O$, (3) $2NO_3^- + \{CH_2O\} \rightarrow 2NO_2^- + H_2O + CO_2$, (4) $2NO_2^- + 3\{CH_2O\} + 4H^+ \rightarrow 2NH_4^+ + 3CO_2 + H_2O$, (5) $4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$

42. Give two reasons why biodegradation of phosphorus compounds in the environment is important.