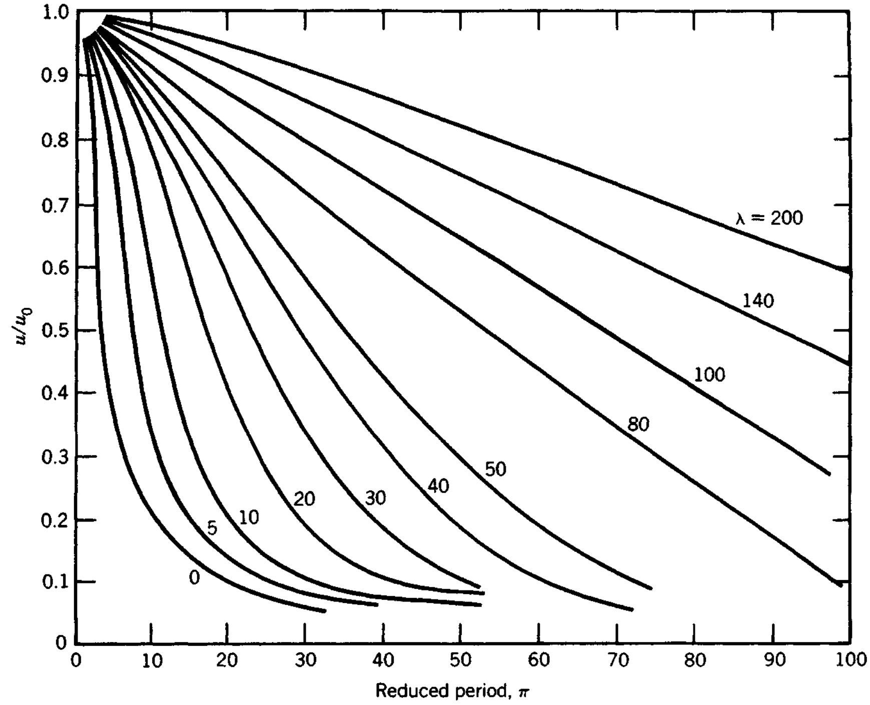


Fig. 63.26 End correction for regenerator heat transfer calculation using symmetrical cycle theory[27] (courtesy Plenum Press):

$$\lambda = \frac{4H_0S(T_c + T_w)}{C_cT_c + C_wT_w} = \text{reduced length}$$

$$\pi = \frac{12H_0(T_c + T_w)}{c\rho_s d} = \text{reduced period}$$

$$U_0 = \frac{1}{4}\left[\frac{1}{h} + \frac{0.1d}{k}\right]$$

where T_w, T_c = switching times of warm and cold streams, respectively, hr
S = regenerator surface area, m^2
U_0 = overall heat transfer coefficient uncorrected for hysteresis, kcal/m^2 · hr · °C
U = overall heat transfer coefficient
C_w, C_c = heat capacity of warm and cold stream, respectively, kcal/hr · °C
c = specific heat of packing, kcal/kg · °C
d = particle diameter, m
ρ_s = density of solid, kg/m^3

phases are well distributed in the flow stream approaching the distribution point. Streams that cool during passage through an exchanger are likely to be modestly self-compensating in that the viscosity of a cold gas is lower than that of a warmer gas. Thus a stream that is relatively high in temperature (as would be the case if that passage received more than its share of fluid) will have a greater flow resistance than a cooler system, so flow will be reduced. The opposite effect occurs for streams being warmed, so that these streams must be carefully balanced at the exchanger entrance.

63.4 INSULATION SYSTEMS

Successful cryogenic processing requires high-efficiency insulation. Sometimes this is a processing necessity, as in the Joule–Thomson liquefier, and sometimes it is primarily an economic requirement, as in the storage and transportation of cryogens. For large-scale cryogenic processes, especially those operating at liquid nitrogen temperatures and above, thick blankets of fiber or powder insulation, air

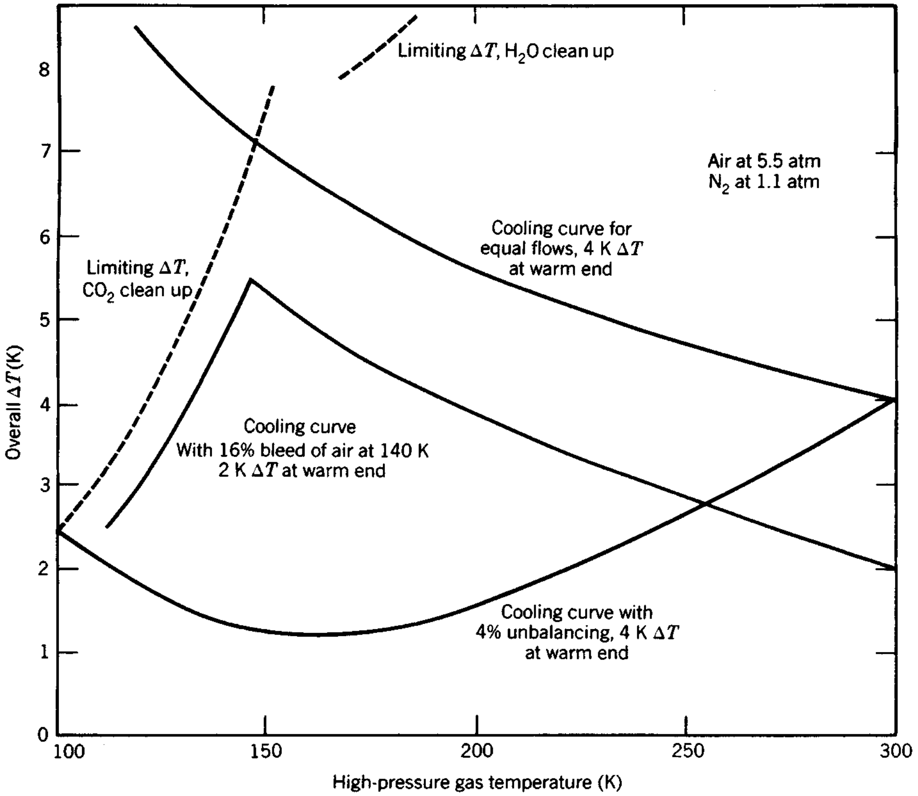


Fig. 63.27 ΔT limitation for contaminant cleanup in a regenerator.

or N_2 filled, have generally been used. For lower temperatures and for smaller units, vacuum insulation has been enhanced by adding one or many radiation shields, sometimes in the form of fibers or pellets, but often as reflective metal barriers. The use of many radiation barriers in the form of metal-coated plastic sheets wrapped around the processing vessel within the vacuum space has been used for most applications at temperatures approaching absolute zero.

63.4.1 Vacuum Insulation

Heat transfer occurs by convection, conduction, and radiation mechanisms. A vacuum space ideally eliminates convective and conductive heat transfer but does not interrupt radiative transfer. Thus heat transfer through a vacuum space can be calculated from the classic equation:

$$q = \sigma A F_{12}(T_1^4 - T_2^4) \tag{63.10}$$

where q = rate of heat transfer, J/sec
σ = Stefan-Boltzmann constant, 5.73×10^{-8} J/sec · m^2 · K
F_{12} = combined emissivity and geometry factor
T_1, T_2 = temperature (K) of radiating and receiving body, respectively

In this formulation of the Stefan–Boltzmann equation it is assumed that both radiator and receiver are gray bodies, that is, emissivity ϵ and absorptivity are equal and independent of temperature. It is also assumed that the radiating body loses energy to a totally uniform surroundings and receives energy from this same environment.

The form of the Stefan–Boltzmann equation shows that the rate of radiant energy transfer is controlled by the temperature of the hot surface. If the vacuum space is interrupted by a shielding surface, the temperature of that surface will become T_s, so that

$$q/A = F_{1s}\,(T_1^4 - T_s^4) = F_{s2}\,(T_s^4 - T_2^4) \tag{63.11}$$

Since q/A will be the same through each region of this vacuum space, and assuming $F_{1s} = F_{s2} = F_{12}$

$$T_s = \sqrt[4]{\frac{T_1^4 + T_2^4}{2}} \tag{63.12}$$

For two infinite parallel plates or concentric cylinders or spheres with diffuse radiation transfer from one to the other,

$$F_{12} = 1 \Bigg/ \frac{1}{\epsilon_1} + \frac{A_1}{A_2}\left(\frac{1}{\epsilon_2} - 1\right) \tag{63.13}$$

If A_1 is a small body in a large enclosure, $F_{12} = \epsilon_1$. If radiator or receiver has an emissivity that varies with temperature, or if radiation is spectral, F_{12} must be found from a detailed statistical analysis of the various possible radiant beams.[30]

Table 63.5 lists emissivities for several surfaces of low emissivity that are useful in vacuum insulation.[31]

It is often desirable to control the temperature of the shield. This may be done by arranging for heat transfer between escaping vapors and the shield, or by using a double-walled shield in which is contained a boiling cryogen.

It is possible to use more than one radiation shield in an evacuated space. The temperature of intermediate streams can be determined as noted above, although the algebra becomes clumsy. However, mechanical complexities usually outweigh the insulating advantages.

63.4.2 Superinsulation

The advantages of radiation shields in an evacuated space have been extended to their logical conclusion in superinsulation, where a very large number of radiation shields are used. A thin, low emissivity material is wrapped around the cold surface so that the radiation train is interrupted often. The material is usually aluminum foil or aluminum-coated Mylar. Since the conductivity path must also be blocked, the individual layers must be separated. This may be done with glass fibers, perlite bits, or even with wrinkles in the insulating material; 25 surfaces/in. of thickness is quite common. Usually the wrapping does not fill in the insulating space. Table 63.6 gives properties of some available superinsulations.

Superinsulation has enormous advantages over other available insulation systems as can be seen from Table 63.6. In this table insulation performance is given in terms of effective thermal conductivity

$$k_e = \frac{q/A}{T/L} \tag{63.14}$$

where k_e = effective, or apparent, thermal conductivity
L = thickness of the insulation
$T = T_1 - T_2$

This insulating advantage translates into thin insulation space for a given rate of heat transfer, and into low weight. Hence designers have favored the use of superinsulation for most cryogen containers

Table 63.5 Emissivities of Materials Used for Cryogenic Radiation Shields

Material	Emissivity at 300 K	77.8 K	4.33 K
Aluminum plate	0.08	0.03	
Aluminum foil (bright finish)	0.03	0.018	0.011
Copper (commercial polish)	0.03	0.019	0.015
Monel	0.17	0.11	
304 stainless steel	0.15	0.061	
Silver	0.022		
Titanium	0.1		

Table 63.6 Properties of Various Multilayer Insulations (Warm Wall at 300 K)

Sample Thickness (cm)	Shields per Centimeter	Density (g/cm^3)	Cold Wall T (K)	Conductivity (μW/cm · K)	Material[a]
3.7	26	0.12	76	0.7	1
3.7	26	0.12	20	0.5	1
2.5	24	0.09	76	2.3	2
1.5	76	0.76	76	5.2	3
4.5	6	0.03	76	3.9	4
2.2	6	0.03	76	3.0	5
3.2	24	0.045	76	0.85	5
1.3	47	0.09	76	1.8	5

[a] 1. Al foil with glass fiber mat separator.
2. Al foil with nylon net spacer.
3. Al foil with glass fabric spacer.
4. Al foil with glass fiber, unbonded spacer.
5. Aluminized Mylar, no spacer.

built for transport, especially where liquid H_2 or liquid He is involved, and for extraterrestrial space applications.

On the other hand, superinsulation must usually be installed in the field, and hence uniformity is difficult to achieve. Connections, tees in lines, and bends are especially difficult to wrap effectively. Present practice requires that layers of insulation be overlapped at a joint to ensure continuous coverage. Some configurations are shown in Fig. 63.28. Also, it has been found that the effectiveness

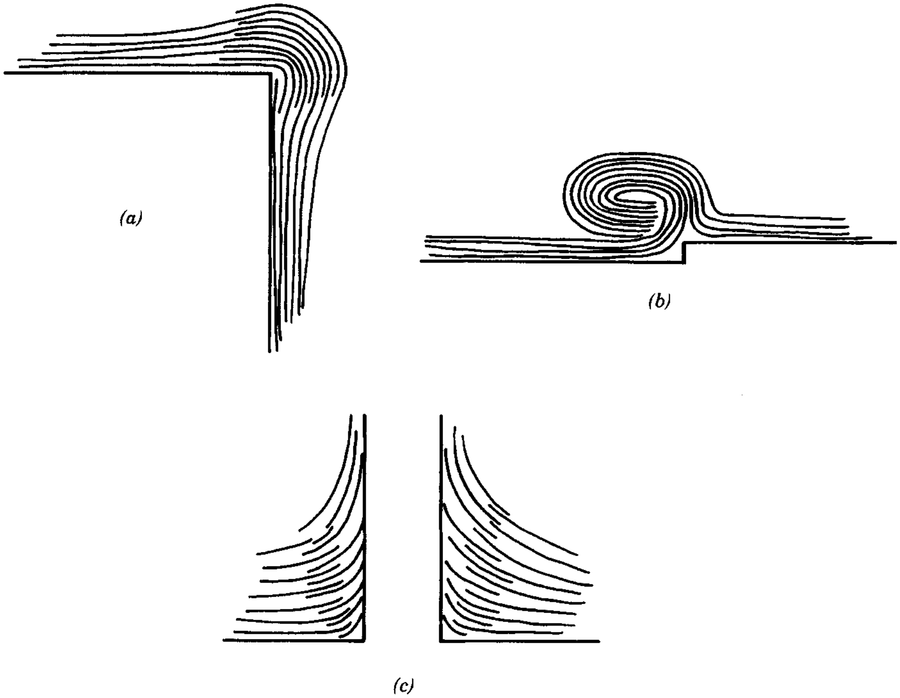


Fig. 63.28 Superinsulation coverage at joints and nozzles: (*a*) Lapped joint at corner. Also usable for nozzle or for pipe bend. (*b*) Rolled joint used at surface discontinuity, diameter change, or for jointure of insulation sections. (*c*) Multilayer insulation at a nozzle.

of superinsulation drops rapidly as the pressure increases. Pressures must be kept below 10^{-3} torr; evacuation is slow; a getter is required in the evacuated space; and all joints must be absolutely vacuum tight. Thus the total system cost is high.

63.4.3 Insulating Powders and Fibers

Fibers and powders have been used as insulating materials since the earliest of insulation needs. They retain the enormous advantage of ease of installation, especially when used in air, and low cost. Table 63.7 lists common insulating powders and fibers along with values of effective thermal conductivity.[32] Since the actual thermal conductivity is a function of temperature, these values may only be used for the temperature ranges shown.

For cryogenic processes of modest size and at temperatures down to liquid nitrogen temperature, it is usual practice to immerse the process equipment to be insulated in a cold box, a box filled with powder or fiber insulation. Insulation thickness must be large, and the coldest units must have the thickest insulation layer. This determines the placing of the process units within the cold box. Such a cold box may be assembled in the plant and shipped as a unit, or it can be constructed in the field. It is important to prevent moisture from migrating into the insulation and forming ice layers. Hence the box is usually operated at a positive gauge pressure using a dry gas, such as dry nitrogen. If rock wool or another such fiber is used, repairs can be made by tunneling through the insulation to the process unit. If an equivalent insulating powder, perlite, is used, the insulation will flow from the box through an opening into a retaining bag. After repairs are made, the insulation may be poured back into the box.

Polymer foams have also been used as cryogenic insulators. Foam-in-placed insulations have proven difficult to use because as the foaming takes place cavities are likely to develop behind process units. However, where the shape is simple and assembly can be done in the shop, good insulating characteristics can be obtained.

In some applications powders or fibers have been used in evacuated spaces. The absence of gas in the insulation pores reduces heat transfer by convection and conduction. Figure 63.29 shows the effect on a powder insulation of reducing pressure in the insulating space. Note that the pressures may be somewhat greater than that needed in a superinsulation system.

63.5 MATERIALS FOR CRYOGENIC SERVICE

Materials to be used in cryogenic service must operate satisfactorily in both ambient and cryogenic temperatures. The repeated temperature cycling that comes from starting up, operating, and shutting down this equipment is particularly destructive because of expansion and contraction that occur at every boundary and jointure.

63.5.1 Materials of Construction

Metals

Many of the normal metals used in equipment construction become brittle at low temperatures and fail with none of the prewarning of strain and deformation usually expected. Sometimes failure occurs at very low stress levels. The mechanism of brittle failure is still a topic for research. However, those metals that exhibit face-centered-cubic crystal lattice structure do not usually become brittle. The austenitic stainless steels, aluminum, copper, and nickel alloys are materials of this type. On the other hand, materials with body-centered-cubic crystal lattice forms or close-packed-hexagonal lattices are usually subject to a brittle transformation as the temperature is lowered. Such materials include the low-carbon steels and certain titanium and magensium alloys. Figure 63.30 shows these crystal forms and gives examples of notch toughness at room temperature and at liquid N_2 temperature for several example metals. In general carbon acts to raise the brittle transition temperature, and nickel lowers

Table 63.7 Effective Thermal Conductivity of Various Common Cryogenic Insulating Materials (300 to 76 K)

Material	Gas Pressure (mm Hg)	P (g/cm^2)	K (W/cm · K)
Silica aerogel (250A)	$<10^{-4}$	0.096	20.8×10^{-6}
	N_2 at 628	0.096	195.5×10^{-6}
Perlite (+30 mesh)	$<10^{-5}$	0.096	18.2×10^{-6}
	N_2 at 628	0.096	334×10^{-6}
Polystyrene foam	Air, 1 atm	0.046	259×10^{-6}
Polyurethane foam	Air, 1 atm	0.128	328×10^{-6}
Foamglas	Air, 1 atm	0.144	346×10^{-6}

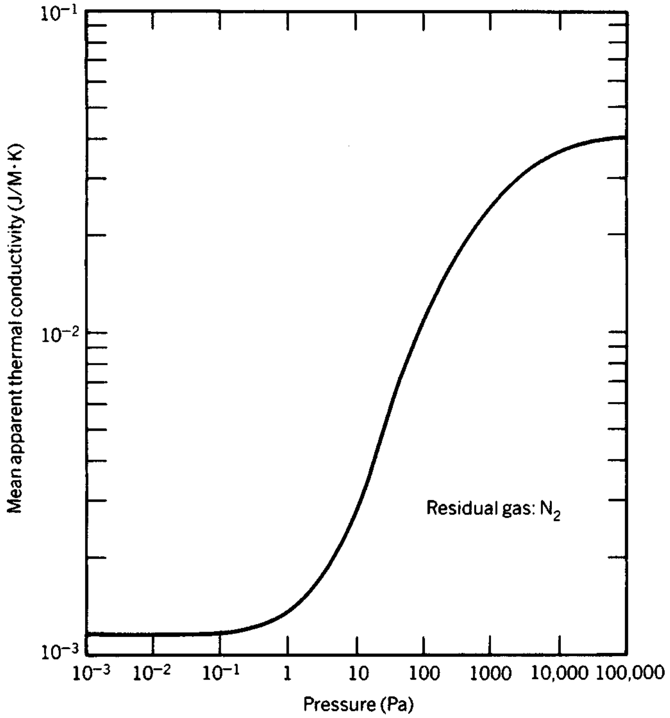
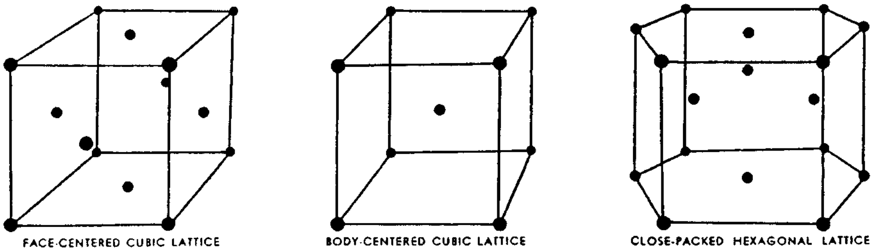


Fig. 63.29 Effect of residual gas pressure on the effective thermal conductivity of a powder insulation—perlite, 30–80 mesh, 300 to 78 K.



Metal	Crystal Lattice	Energy to Break, Foot-pounds Keyhole Room Temperature	 —320°F
Austenitic Stainless Steel	Face-centered Cubic	43	50
Aluminum	Face-centered Cubic	19	27
Copper	Face-centered Cubic	43	50
Nickel	Face-centered Cubic	89	99
Iron	Body-centered Cubic	78	1.5
Titanium	Close-packed Hexagonal	14.5	6.6
Magnesium	Close-packed Hexagonal	4	(3 at —105° F)

(Courtesy—American Society for Metals)

Fig. 63.30 Effect of crystal structure on brittle impact strengths of some metals. (Courtesy American Society for Metals.)

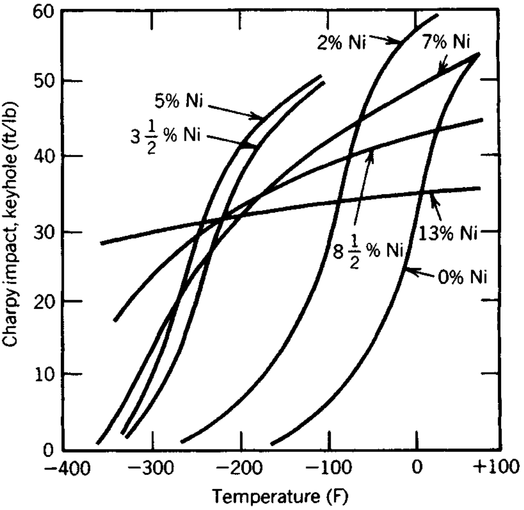


Fig. 63.31 Effect of nickel content in steels on Charpy impact values. (Courtesy American Iron and Steel Institute.)

it. Additional lowering can be obtained by fully killing steels by deoxidation with silicon and aluminum and by effecting a fine grain structure through normalizing by addition of selected elements.

In selecting a material for cryogenic service, several significant properties should be considered. The toughness or ductibility is of prime importance. Actually, these are distinctively different properties. A material that is ductile, as measured by elongation, may have poor toughness as measured by a notch impact test, particularly at cryogenic temperatures. Thus both these properties should be examined. Figures 63.31 and 63.32 show the effect of nickel content and heat treatment on Charpy impact values for steels. Figure 63.33 shows the tensile elongation before rupture of several materials used in cryogenic service.

Tensile and yield strength generally increase as temperature decreases. However, this is not always true, and the behavior of the particular material of interest should be examined. Obviously if the material becomes brittle, it is unusable regardless of tensile strength. Figure 63.34 shows the tensile and yield strength for several stainless steels.

Fatigue strength is especially important where temperature cycles from ambient to cryogenic are frequent, especially if stresses also vary. In cryogenic vessels maximum stress cycles for design are

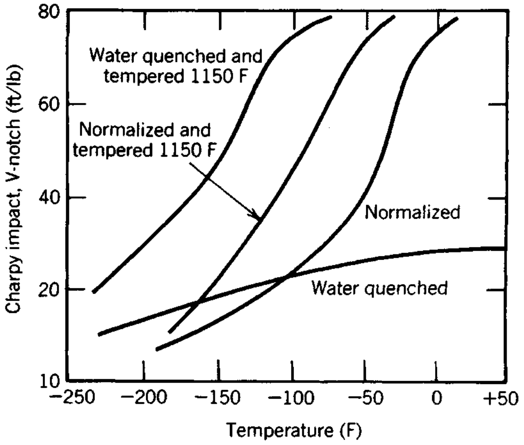


Fig. 63.32 Effect of heat treatment on Charpy impact values of steel. (Courtesy American Iron and Steel Institute.)

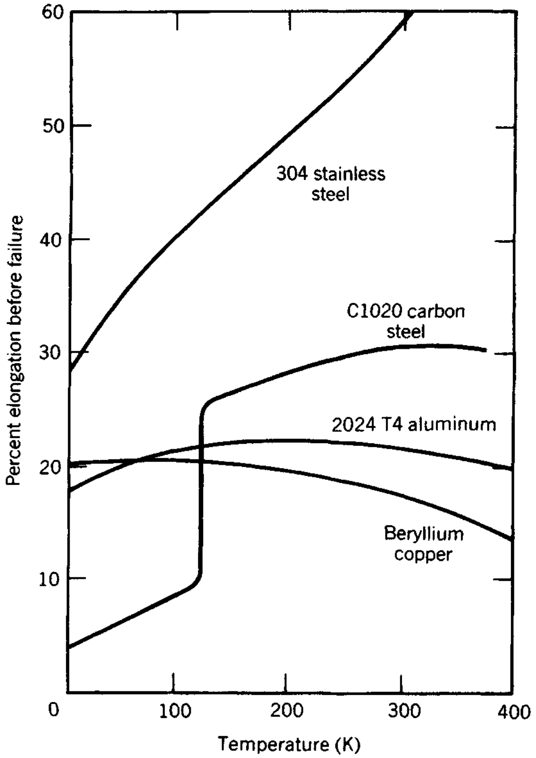


Fig. 63.33 Percent elongation before rupture of some materials used in cryogenic service.[33]

about 10,000–20,000 rather than the millions of cycles used for higher-temperature machinery design. Because fatigue strength data for low-temperature applications are scarce, steels used in cryogenic rotating equipment are commonly designed using standard room-temperature fatigue values. This allows a factor of safety because fatigue strength usually increases as temperature decreases.

Coefficient of expansion information is critical because of the stress that can be set up as temperatures are reduced to cryogenic or raised to ambient. This is particularly important where dissimilar materials are joined. For example, a 36-ft-long piece of 18-8 stainless will contract more than an inch in cooling from ambient to the boiling point of liquid H_2. And stainless steel has a coefficient of linear expansion much lower than that of copper or aluminum. This is seen in Fig. 63.35.

Thermal conductivity is an important property because of the economic impact of heat leaks into a cryogenic space. Figure 63.36 shows the thermal conductivity of some metals in the cryogenic temperature range. Note that pure copper shows a maximum at very low temperatures, but most alloys show only modest effect of temperature on thermal conductivity. One measure of the suitability of a material for cryogenic service is the ratio of tensile strength to thermal conductivity. On this basis stainless steel looks very attractive and copper much less so.

The most common materials used in cryogenic service have been the austenitic stainless steels, aluminum alloys, copper alloys, and aluminum-alloyed steels. Fine grained carbon-manganese steel and aluminum-killed steel and the 2.5% Ni steels can be used to temperatures as low as −50°C. A 3.5% Ni steel may be used roughly to −100°C; 5% Ni steels have been developed especially for applications in liquified natural gas processing, that is, for temperatures down to about −170°C. Austenitic stainless steels with about 9% Ni such as the common 304 and 316 types are usable well into the liquid H_2 range (−252°C). Aluminum and copper alloys have been used throughout the cryogenic temperature range. However, in selecting a particular alloy for a given application the engineer should consider carefully all of the properties of the material as they apply to that application.

Stainless steel may be joined by welding. However, the welding rod chosen and the joint design must both be selected for the material being welded and the expected service. For example, 9% nickel steel can be welded using nickel-based electrodes and a 60–80° single V joint design. Inert gas welding using Inconel-type electrodes is also acceptable. Where stress levels will not be high types

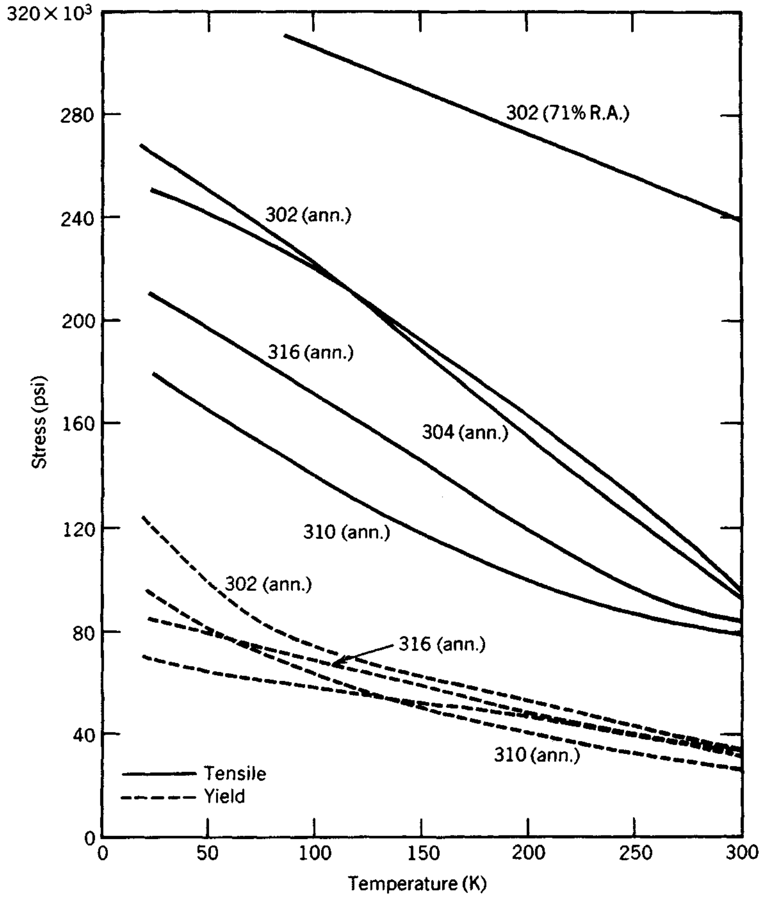


Fig. 63.34 Yield and tensile strength of several AISI 300 series stainless steels.[33] (Courtesy American Iron and Steel Institute.)

309 and 310 austenitic-stainless-steel electrodes can be used despite large differences in thermal expansion between the weld and the base metal.

Dissimilar metals can be joined for cryogenic service by soft soldering, silver brazing, or welding. For copper-to-copper joints a 50% tin/50% lead solder can be used. However, these joints have little ductility and so cannot stand high stress levels. Soft solder should not be used with aluminum, silicon-bronze, or stainless steel. Silver soldering is preferred for aluminum and silicon bronze and may also be used with copper and stainless steel.

Polymers

Polymers are frequently used as structural materials in research apparatus, as windows into cryogenic spaces, and for gaskets, O-rings, and other seals. Their suitability for the intended service should be as carefully considered as metals. At this point there is little accumulated, correlated data on polymer properties because of the wide variation in these materials from source to source. Hence properties should be obtained from the manufacturer and suitability for cryogenic service determined case by case.

Tables 63.8 and 63.9 list properties of some common polymeric materials. These are not all the available suitable polymers, but have been chosen especially for their compatibility with liquid O_2. For this service chemical inertness and resistance to flammability are particularly important. In addition to these, nylon is often used in cryogenic service because of its machinability and relative strength. Teflon and similar materials have the peculiar property of losing some of their dimensional stability at low temperatures; thus they should be used in confined spaces or at low stress levels.

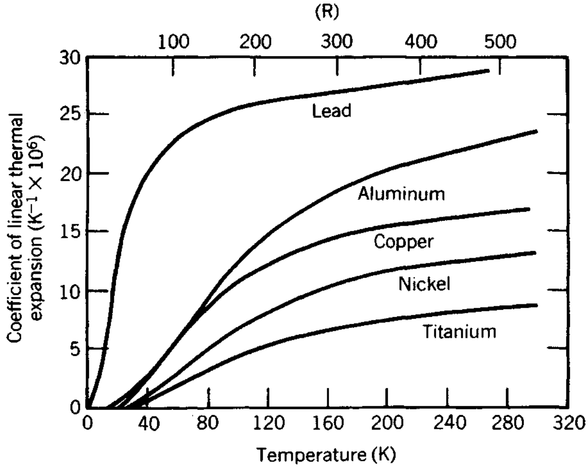


Fig. 63.35 Coefficient of linear thermal expansion of several metals as a function of temperature. (Courtesy American Institute of Chemical Engineers.)

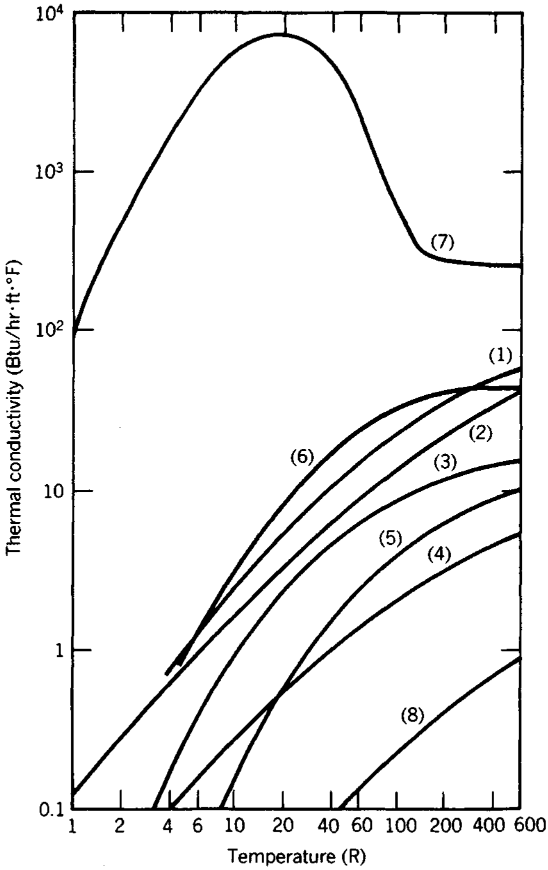


Fig. 63.36 Thermal conductivity of materials useful in low-temperature service. (1) 2024TA aluminum; (2) beryllium copper; (3) K-Monel; (4) titanium; (5) 304 stainless steel; (6) C1020 carbon steel; (7) pure copper; (8) Teflon.[35]

Table 63.8 Properties of Polymers Used in Cryogenic Service

Elastomer Type	Silicone Rubber	Vinylidene Fluoride Hexafluoropropylene	Fluorosilicone	Polytrifluorochloroethylene
Trade Name	Silastic[a] Silicone Rubber[e,f]	Viton[b] Fluore[c]	Silastic LS-53[a]	Kel-F[c,d]
Physical and Mechanical Properties				
Durometer range (shore A)	45–60	55–90	50–60	55–90
Specific gravity (base elastomer)	1.17–1.46	1.4–1.85	1.41–1.46	1.4–1.85
Density, lb/in.^{3} (base elastomer)	0.045	0.051–0.067	0.051	0.051–0.067
Tensile strength; psi:				
Pure gum	Under 400	>2000	1000	350–600
Reinforced	600–1500	—	—	—
Elongation, percent:				
Pure gum	Under 200	>350	200	500–800
Reinforced	200–800	—	—	—
Thermal conductivity, g, Btu/hr/ft^2/(°F/ft)	0.13	—	0.13	—
Coefficient of thermal expansion, cubical, in.^{3}/in.^{3}/°F	45 × 10^{-5}	27 × 10^{-5}	45 × 10^{-5}	—
Electrical insulation	Excellent	Excellent	Good	Excellent
Rebound				
Cold	Very good	Good	Very good	—
Hot	Very good	Excellent	Very good	—
Compression set	Good to excellent	Good to excellent	Good	Good to excellent
Resistance Properties				
Temperature:				
Tensile strength at 250°F, psi	850	300–800	—	300–800
Tensile strength at 400°F, psi	400	150–300	—	150–300
Elongation at 250°F, percent	350	100–350	—	100–350
Elongation at 400°F, percent	200	50–160	—	50–160
Low temperature brittle point, °F	−90 to −200	10 to −60	−90	10 to −60
Low temperature range of rapid stiffening, °F	−60 to −120	20 to −30	—	−20 to −30
Drift, room temperature	Poor to excellent	Good	—	Good
Drift, elevated temperature (158° to 212°F)	Excellent	Good to excellent	Excellent	Good to excellent

Table 63.8 (*Continued*)

Elastomer Type	Silicone Rubber	Vinylidene Fluoride Hexafluoropropylene	Fluorosilicone	Polytrifluorochloroethylene
Trade Name	Silastic[a] Silicone Rubber[e,f]	Viton[b] Fluore[c]	Silastic LS-53[a]	Kel-F[c,d]
Heat aging (212°F)	Excellent	Excellent	Excellent	Excellent
Maximum recommended continuous service temperature, °F	480	450	500	400
Minimum recommended service temperature, °F	−178	−50	−90	−60
Mechanical:				
Tear resistance	Poor	Poor to good	—	Poor to good
Abrasion resistance	Poor	Good	Poor	Good
Impact resistance (fatigue)	Poor	Poor to good	Poor	Poor to good
Chemical:				
Sunlight aging	Excellent	Excellent	Excellent	Excellent
Weather resistance	Excellent	Excellent	Excellent	
Oxidation	Excellent	Excellent	Excellent	↓
Acids:				
Dilute	Very good	Excellent	Excellent	
Concentrated	Good	Good	Very good	
Alkali	Fair to excellent	Poor to fair	Fair to excellent	Poor to fair
Alcohol	Good	Excellent	Poor to good	Excellent
Petroleum products, resistance	Poor to fair	Good to excellent	Excellent	Good to excellent
Coal tar derivatives, resistance	Poor	Excellent	—	Excellent
Chlorinated solvents, resistance	Good	Good	—	Good
Hydraulic oils:				
Silicates	Poor	Good	—	Good
Phosphates	Good	Poor	—	Poor
Water swell resistance	Good	Good	Excellent	Good
Permeability to gases	Good	Excellent	Fair	Excellent

[a] Dow Corning Corp.

[b] E. I. duPont de Nemours.

[c] Minnesota Mining and Manufacturing Co.

[d] CTFE compounded with vinylidine fluoride.

[e] General Electric.

[f] Union Carbon and Carbide.

Table 63.9 Properties of Polymers Used in Cryogenic Service

Common Name	Fluorinated Ethylene Propylene	Polychlorotrifluoroethylene	Polyvinylidene Fluoride	Polytetrafluoroethylene	Polyimide
Trade Name	Teflon FEP[a]	Kel-F[b]	Kynar[c]	Fluorosint[d,e] Teflon TFE[a] Halon TFE[f]	Kapton H[a] Kapton F[a] Vespel[a] Polymer SP-1[a]
Physical and Mechanical Properties					
Specific gravity	2.14–2.17	2.1–2.2	1.76–1.77	2.13–2.22	1.42
Tensile strength, psi	2700–3100	4500–6000	7000	2000–4500	25,000[g]; 10,500
Elongation, percent	250–330	30–250	100–300	200–400	70[g]; 6–8
Tensile modulus, psi	0.5×10^5	$1.5 \times 10^5 - 3 \times 10^5$	1.2×10^5	0.58×10^5	4.3×10^5
Compressive strength, psi	2200	32,000–80,000	10,000	1700	24,400
Flexural strength, psi	—	7400–9300	—	—	14,000
Impact strength, ft-lb/in. of notch	No break	0.8–5.0	3.5	3.0	0.9
Rockwell hardness	R25	R110–R115	D80 (Shore)	D50–D65 (Shore)	H85–H95
Thermal conductivity, Btu/hr/ft^2/(°F/in.)	1.75	0.9	0.9	1.75	2.2
Specific heat, Btu/lbm/°F	0.28	0.22	0.33	0.25	0.27
Coefficient of linear expansion, in./in./°F $\times 10^{-5}$	4.7×10^{-5} to 5.8×10^{-5}	5×10^{-5} to 15×10^{-5}	6.7×10^{-5}	5.5×10^{-5}	28×10^{-5} to 35×10^{-5}
Volume resistivity, ohm-cm	$>2 \times 10^{18}$	1.2×10^{18}	2×10^{14}	$>10^{18}$	10^{18}
Clarity	Transparent to translucent	transparent to translucent	Transparent to translucent	Opaque	Opaque
Processing Properties					
Molding qualities	Excellent	Excellent	Excellent	—	—
Injection molding temperature, °F	625–760	440–600	450–550	—	—
Mold shrinkage, in./in.	0.03–0.06	0.005–0.010	0.030	—	—
Machining qualities	Excellent	Excellent	Excellent	Excellent	—

Table 63.9 (*Continued*)

Common Name	Fluorinated Ethylene Propylene	Polychlorotri-fluoroethylene	Polyvinylidene Fluoride	Polytetra-fluoro-ethylene	Polyimide
Trade Name	Teflon FEP[a]	Kel-F[b]	Kynar[c]	Fluorosint[d,e] Teflon TFE[a] Halon TFE[f]	Kapton H[a] Kapton F[a] Vespel[a] Polymer SP-1[a]
Resistance Properties					
Mechanical abrasion and wear Tabor CS 17 wheel mg, loss/ 1000 cycles	—	0.01	17.6	—	—
Temperature:					
Flammability	None	None	Self-extinguishing	None	—
Low temperature brittle point, °F	−420	−400	−80	−420	—
Resistance to heat, °F (continuous)	400	350–390	300	550	500
Deflection temperature under load, °F	—	258 (66 psi)	300 (66 psi), 195 (264 psi)	250 (66 psi)	—
Chemical:					
Effect of sunlight	None	None	Slight bleaching on long exposure	None	Degrades after prolonged exposure
Effect of weak acids	↓	↓	None	↓	None
Effect of strong acids	↓	↓	Attacked by fuming sulfuric	↓	
Effect of weak alkalies	↓	↓	None	↓	—
Effect of strong alkalies	↓	↓	None	↓	Attacked
Effect of organic solvents	↓	Halogenated compounds cause slight swelling	Resists most solvents	↓	Resistant to most organic solvents

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[a] E. I. duPont de Nemours.

[b] Minnesota Mining and Manufacturing Co.

[c] Pennsalt Chemicals Corp.

[d] Polymer Corp. of Pennsylvania.

[e] Polypenco, Inc.

[f] Allied Chemical Corp.

[g] Film.

Glass

Glasses, especially Pyrex and quartz, have proven satisfactory for cryogenic service because of their amorphous structure and very small coefficient of thermal expansion. They are commonly used in laboratory equipment, even down to the lowest cryogenic temperatures. They have also successfully been used as windows into devices such as hydrogen bubble chambers that are built primarily of metal.

63.5.2 Seals and Gaskets

In addition to careful selection of materials, seals must be specially designed for cryogenic service. Gaskets and O-rings are particularly subject to failure during thermal cycling. Thus they are best if confined and/or constructed of a metal-polymer combination. Such seals would be in the form of metal rings with C or wedge cross sections coated with a sealant such as Kel-F, Teflon, or soft metal. Various designs are available with complex cross sections for varying degrees of deflection. The surfaces against which these seal should be ground to specified finish. Elastomers such as neoprene and Viton-A have proven to be excellent sealants if captured in a space where they are subjected to 80% linear compression. This is true despite the fact that they are both extremely brittle at cryogenic temperatures without this stress.

Adhesive use at low temperatures is strictly done on an empirical basis. Still, adhesives have been used successfully to join insulating and vapor barrier blankets to metal surfaces. In every case the criteria are that the adhesive must not become crystalline at the operating temperature, must be resistant to aging, and must have a coefficient of contraction close to that of the base surface. Polyurethane, silicone, and various epoxy compounds have been used successfully in various cryogenic applications.

63.5.3 Lubricants

The lubrication of cryogenic machinery such as valves, pumps, and expanders is a problem that has generally been solved by avoidance. Valves usually have a long extension between the seat and the packing gland. This extension is gas filled so that the packing gland temperature stays close to ambient. For low-speed bearings babbitting is usually acceptable, as is graphite and molybdenum sulfide. For high-speed bearings, such as those in turboexpanders, gas bearings are generally used. In these devices some of the gas is leaked into the rotating bearing and forms a cushion for rotation. If out-leakage of the contained gas is undesirable, N_2 can be fed to the bearing and controlled so that leakage of N_2 goes to the room and not into the cryogenic system. Bearings of this sort have been operated at speeds up to 100,000 rpm.

63.6 SPECIAL PROBLEMS IN LOW-TEMPERATURE INSTRUMENTATION

Cryogenic systems usually are relatively clean and free flowing, and they often exist at a phase boundary where the degrees of freedom are reduced by one. Although these factors ease measurement problems, the fact that the system is immersed in insulation and therefore not easily accessible, the desire to limit thermal leaks to the system, and the likelihood that vaporization or condensation will occur in instrument lines all add difficulties.

Despite these differences all of the standard measurement techniques are used with low-temperature systems, often with ingenious changes to adapt the device to low-temperature use.

63.6.1 Temperature Measurement

Temperature may be measured using liquid-in-glass thermometers down to about −40°C, using thermocouples down to about liquid H_2 temperature, and using resistance thermometers and thermistors down to about 1 K. Although these are the usual devices of engineering measurement laboratory measurements have been done at all temperatures using gas thermometers and vapor pressure thermometers.

Table 63.10 lists the defining fixed points of the International Practical Temperature Scale of 1968. This scale does not define fixed points below the triple point of equilibrium He.[36] Below that range the NBS has defined a temperature scale to 1 K using gas thermometry.[37] At still lower temperatures measurement must be based on the fundamental theories of solids such as paramagnetic and superconducting phenomena.[38]

The usefulness of vapor pressure thermometry is limited by the properties of available fluids. This is evident from Table 63.11. For example, in the temperature range from 20.4 to 24.5 K there is no usable material. Despite this, vapor pressure thermometers are accurate and convenient. The major problem in their use is that the hydraulic head represented by the vapor line between point of measurement and the readout point must be taken into account. Also, the measurement point must be the coldest point experienced by the device. If not, pockets of liquid will form in the line between the point of measurement and the readout point greatly affecting the reading accuracy.

Standard thermocouples may be used through most of the cryogenic range, but, as shown in Fig. 63.37 for copper–constantan, the sensitivity with which they measure temperature drops as the tem-

Table 63.10 Defining Fixed Points of the International Practical Temperature Scale, 1968

Equilibrium Point	T (K)
Triple point of equilibrium H_2	13.81
Boiling point of equilibrium H_2 (P = 33330.6 N/m^2)	17.042
Boiling point of equilibrium H_2 (P = 1 atm)	20.28
Boiling point of neon (P = 1 atm)	27.102
Triple point of O_2	54.361
Boiling point of O_2 (P = 1 atm)	90.188
Triple point of H_2O (P = 1 atm)	273.16
Freezing point of Zn (P = 1 atm)	692.73
Freezing point of Ag (P = 1 atm)	1235.08
Freezing point of Au (P = 1 atm)	1337.58

perature decreases. At low temperatures heat transfer down the thermocouple wire may markedly affect the junction temperature. This is especially dangerous with copper wires, as can be seen from Fig. 63.36. Also, some thermocouple materials, for example, iron, become brittle as temperature decreases. To overcome these difficulties special thermocouple pairs have been used. These usually involve alloys of the noble metals. Figure 63.37 shows the thermoelectric power, and hence sensitivity of three of these thermocouple pairs.

Resistance thermometers are also very commonly used for cryogenic temperature measurement. Metal resistors, especially platinum, can be used from ambient to liquid He temperatures. They are extremely stable and can be read to high accuracy. However, expensive instrumentation is required because resistance differences are small requiring precise bridge circuitry. Resistance as a function of temperature for platinum is well known.[36]

At temperatures below 60 K, carbon resistors have been found to be convenient and sensitive temperature sensors. Since the change in resistance per given temperature difference is large (580 ohms/K would be typical at 4 K) the instrument range is small, and the resistor must be selected and calibrated for use in the narrow temperature range required.

Germanium resistors that are single crystals of germanium doped with minute quantities of impurities are also used throughout the cryogenic range. Their resistance varies approximately logarithmically with temperature, but the shape of this relation depends on the amount and type of dopant. Again, the germanium semiconductor must be selected and calibrated for the desired service.

Thermistors, that is, mixed, multicrystal semiconductors, like carbon and germanium resistors, give exponential resistance calibrations. They may be selected for order-of-magnitude resistance changes over very short temperature ranges or for service over wide temperature ranges. Calibration is necessary and may change with successive temperature cycling. For this reason they should be temperature-cycled several times before use. These sensors are cheap, extremely sensitive, easily read, and available in many forms. Thus they are excellent indicators of modest accuracy but of high sensitivity, such as sensors for control action. They do not, however, have the stability required for high accuracy.

Table 63.11 Properties of Cryogens Useful in Vapor Pressure Thermometers

Substance	Triple Point (K)	Boiling Point (K)	Critical Point (K)	dP/dT (mm/K)	Hydraulic Heat at Boiling Point (K/cm^2)
^{3}He	—	3.19	3.32	790	0.000054
^{4}He	—	4.215	5.20	715	0.00013
p-H_2 (20.4 K equilibrium)	13.80	20.27	32.98	224	0.00023
Ne	24.54	27.09	44.40	230	0.0039
N_2	63.15	77.36	126.26	89	0.0067
Ar	83.81	87.30	150.70	80	0.013
O_2	54.35	90.18	154.80	79	0.011

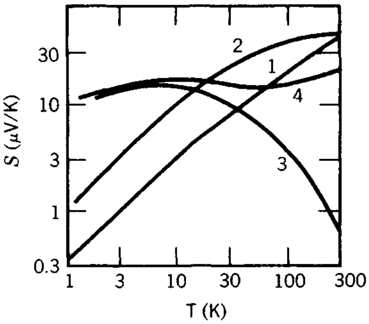

Fig. 63.37 Thermoelectric power of some thermocouples useful for cryogenic temperature measurement (courtesy Plenum Press): (1) Copper versus constantan; (2) Au + 2 at % Co versus silver normal (Ag + 0.37 at % Au); (3) Au + 0.03 at % Fe versus silver normal; (4) Au + 0.03 at % Fe versus Chromel.

63.6.2 Flow Measurement

Measurement of flow in cryogenic systems is often made difficult because of the need to deal with a liquid at its boiling point. Thus any significant pressure drop causes vaporization, which disrupts the measurement. This may be avoided by subcooling the liquid before measurement. Where this is possible, most measurement problems disappear, for cryogenic fluids are clean, low-viscosity liquids. Where subcooling is not possible, flow is most often measured using turbine flow meters or momentum meters.

A turbine meter has a rotor mounted axially in the flow stream and moved by the passing fluid. The rate of rotation, which is directly proportional to the volumetric flow rate, is sensed by an electronic counter that senses the passage of each rotor blade. There are two problems in the use of turbine meters in cryogenic fluids. First, these fluids are nonlubricating. Hence the meter rotor must be self-lubricated. Second, during cool-down or warm-up slugs of vapor are likely to flow past the rotor. These can flow rapidly enough to overspeed and damage the rotor. This can be avoided by locating a bypass around the turbine meter shutting off the meter during unsteady operation.

Momentum meters have a bob located in the flow stream to the support of which a strain gage is attached. The strain gage measures the force on the bob, which can be related through drag calculations or correlation to the rate of fluid flow past the bob. These meters are flexible and can be wide of range. They are sensitive to cavitation problems and to overstrain during upsets. Generally, each instrument must be calibrated.

63.6.3 Tank Inventory Measurement

The measurement of liquid level in a tank is made difficult by the cryogenic insulation requirements. This is true of stationary tanks, but even more so when the tank is in motion, as on a truck or spaceship, and the liquid is sloshing.

The simplest inventory measurement is by weight, either with conventional scales or by a strain gage applied to a support structure.

The sensing of level itself can be done using a succession of sensors that read differently when in liquid than they do in vapor. For instance, thermistors can be heated by a small electric current. Such devices cool quickly in liquid, and a resistance meter can "count" the number of thermistors in its circuit that are submerged.

A similar device that gives a continuous reading of liquid depth would be a vertical resistance wire, gently heated, while the total wire resistance is measured. The cold, submerged, fraction of the wire can be easily determined.

Other continuous reading devices include pressure gages, either with or without a vapor bleed, that read hydrostatic head, capacitance probes that indicate the fraction of their length that is submerged, ultrasonic systems that sense the time required for a wave to return from its reflectance off the liquid level, and light-reflecting devices.

63.7 EXAMPLES OF CRYOGENIC PROCESSING

Here three common, but greatly different, cryogenic technologies are described so that the interaction of the cryogenic techniques discussed above can be shown.

63.7.1 Air Separation

Among the products from air separation, nitrogen, oxygen, and argon are primary and are each major items of commerce. In 1994 nitrogen was second to sulfuric acid in production volume of industrial inorganic chemicals, with 932 billion standard cubic feet produced. Oxygen was third at 600 billion standard cubic feet produced. These materials are so widely used that their demand reflects the general trend in national industrial activity. Demand generally increases by 3 to 5%/year. Nitrogen is widely used for inert atmosphere generation in the metals, electronics and semiconductor, and chemical industries, and as a source of deep refrigeration, especially for food freezing and transporation. Oxygen is used in the steel industry for blast furnace air enrichment, for welding and scarfing, and for alloying operation. It is also used in the chemical industry in oxidation steps, for wastewater treatment, for welding and cutting, and for breathing. Argon, mainly used in welding, in stainless steel making, and in the production of specialized inert atmospheres, has a demand of only about 2% of that of oxygen. However, this represents about 25% of the value of oxygen shipments, and the argon demand is growing faster than that of oxygen or nitrogen.

Since all of the industrial gases are expensive to ship long distances, the industry was developed by locating a large number of plants close to markets and sized to meet nearby market demand. Maximum oxygen plant size has now grown into the 3000 ton/day range, but these plants are also located close to the consumer with the product delivered by pipe line. Use contracts are often long-term take-or-pay rental arrangements.

Air is a mixture of about the composition shown in Table 63.12. In an air separation plant O_2 is typically removed and distilled from liquified air. N_2 may also be recovered. In large plants argon may be recovered in a supplemental distillation operation. In such a plant the minor constituents (H_2–Xe) would have to be removed in bleed streams, but they are rarely collected. When this is done the Ne, Kr, Xe are usually adsorbed onto activated carbon at low temperature and separated by laboratory distillation.

Figure 63.38 is a simplified flow sheet of a typical small merchant oxygen plant meeting a variety of O_2 needs. Argon is not separated, and no use is made of the effluent N_2. Inlet air is filtered and compressed in the first of four compression stages. It is then sent to an air purifier where the CO_2 is removed by reaction with a recycling NaOH solution in a countercurrent packed tower. Usually the caustic solution inventory is changed daily. The CO_2-free gas is returned to the compressor for the final three stages after each of which the gas is cooled and water is separated from it. The compressed gas then goes to an adsorbent drier where the remaining water is removed onto silica gel or alumina. Driers are usually switched each shift and regenerated by using a slip stream of dry, hot N_2 and cooled to operating temperature with unheated N_2 flow.

The compressed, purified air is then cooled in the main exchanger (here a coiled tube type, but more usually of the plate-fin type) by transferring heat to both the returning N_2 and O_2. The process is basically a variation of that invented by Georges Claude where part of the high-pressure stream is withdrawn to the expansion engine (or turbine). The remainder of the air is further cooled in the main exchanger and expanded through a valve.

The combined air stream, nearly saturated or partly liquefied, enters the bottom of the high-pressure column. This distillation column condenses nearly pure N_2 at its top using boiling O_2 in the low-pressure column as heat sink. If the low-pressure column operates at about 140 kN/m^2 (20 psia), the high-pressure column must operate at about 690 kN/m^2 (100 psia). The bottom product, called crude O_2, is about 65 mole % N_2. The top product from the high-pressure column, nearly pure N_2, is used as N_2 reflux in the low-pressure column.

The crude O_2 is fed to an activated carbon bed where hydrocarbons are removed, is expanded to low-pressure column pressure, goes through a subcooler in which it supplies refrigeration to the

Table 63.12 Approximate Composition of Dry Air

Component	Composition (mole %)
N_2	78.03
O_2	20.99
Ar	0.93
CO_2	0.03
H_2	0.01
Ne	0.0015
He	0.0005
Kr	0.00011
Xe	0.000008

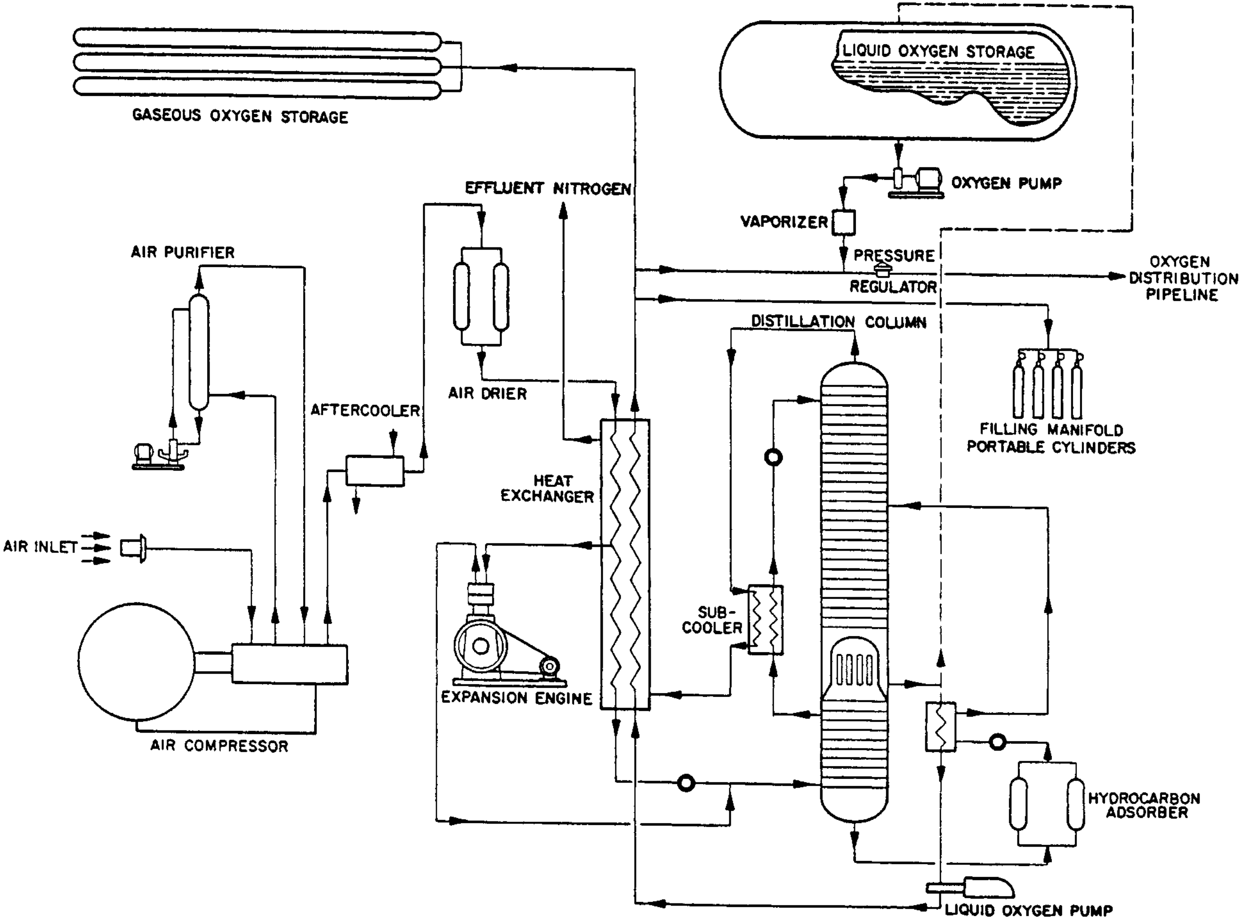

Fig. 63.38 Flow sheet of a merchant oxygen plant. (Courtesy Air Product and Chemicals, Inc.)

liquid O_2 product, and is fed to the low-pressure column. The hydrocarbons removed in the adsorber may come in as impurities in the feed or may be generated by decomposition of the compressor oil. If they are not fully removed, they are likely to precipitate in the liquid O_2 at the bottom of the low-pressure column. They accumulate there and can form an explosive mixture with oxygen whenever the plant is warmed up. Acetylene is especially dangerous in this regard because it is so little soluble in liquid oxygen.

The separation of O_2 and N_2 is completed in the low-pressure column. In the column, argon accumulates below the crude O_2 feed and may be withdrawn at about 10 mole % for further distillation. If it is not so removed, it leaves as impurity in the N_2 product. Light contaminants (H_2 and He) must be removed periodically from the top of the condenser/reboiler. Heavy contaminants are likely to leave as part of the O_2 product.

This plant produces O_2 in three forms: liquid, high-pressure O_2 for cylinder filling, and lower-pressure O_2 gas for pipe line distribution. The liquid O_2 goes directly from the low-pressure column to the storage tank. The rest of the liquid O_2 product is pumped to high pressure in a plunger pump after it is subcooled so as to avoid cavitation. This high-pressure liquid is vaporized and heated to ambient in the main heat exchanger. An alternate approach would be to warm the O_2 to ambient at high-pressure column pressure and then compress it as a gas. Cylinder pressure is usually too great for a plate-and-fin exchanger, so if the option shown in this flow sheet is used, the main exchanger must be of the coiled tube sort.

The nitrogen product, after supplying some refrigeration to the N_2 reflux, is warmed to ambient in the shell of the main exchanger. Here the N_2 product is shown as being vented to atmospheric. However, some of it would be required to regenerate the adsorbers and to pressurize the cold box in which the distillation columns, condenser/reboiler, main exchanger, hydrocarbon adsorber, subcoolers, throttling valves, and the liquid end of the liquid oxygen pump are probably contained.

This process is self-cooling. At startup refrigeration needed to cool the unit to operating temperatures is supplied by the expansion engine and the three throttling valves. During that time the unit is probably run at maximum pressure. During routine operation that pressure may be reduced. The lower the liquid O_2 demand, the less refrigeration is required and the lower the operating pressure may be.

63.7.2 Liquefaction of Natural Gas

Natural gas liquefaction has been commercially done in two very different situations. Companies that distribute and market natural gas have to meet a demand curve with a sharp maximum in midwinter. It has been found to be much more economic to maintain a local supply of natural gas liquid that can be vaporized and distributed at peak demand time than to build the gas pipe line big enough to meet this demand and to contract with the supplier for this quantity of gas. Thus the gas company liquefies part of its supply all year. The liquid is stored locally until demand rises high enough to require augmenting the incoming gas. Then the stored liquid is vaporized and added to the network. These "peak-shaving" plants consist of a small liquefier, an immense storage capacity, and a large capacity vaporizer. They can be found in most large metropolitan areas where winters are cold, especially in the northern United States, Canada, and Europe.

The second situation is that of the oil/gas field itself. These fields are likely to be at long distances from the market. Oil can be readily transported, since it is in a relatively concentrated form. Gas is not. This concentration is done by liquefaction prior to shipment, thus reducing the volume about 600-fold. Subsequently, revaporization occurs at the port near the market. These "base-load" LNG systems consist of a large liquefaction plant, relatively modest storage facilities near the source field, a train of ships moving the liquid from the field to the port near the market, another storage facility near the market, and a large capacity vaporizer. Such a system is a very large project. Because of the large required investment, world political and economic instability, and safety and environmental concerns in some developed nations, especially the United States, only a few such systems are now in operation or actively in progress. See Table 63.13 for data on world LNG trade.

Peak-Shaving Plants

The liquefaction process in a peak-shaving installation is relatively small capacity, since it will be operating over the bulk of the year to produce the gas required in excess of normal capacity for two to six weeks of the year. It usually operates in a region of high energy cost but also of readily available mechanical service and spare parts, and it liquefies relatively pure methane. Finally, operating reliability is not usually critical because the plant has capacity to liquefy the required gas in less time than in the maximum available.

For these reasons efficiency is more important than system reliability and simplicity. Cascade and various expander cycles are generally used, although a wide variety of processes have been used including the Stirling cycle.

Figure 63.39 shows a process in which an N_2 expander cycle is used for low-temperature refrigeration, whereas the methane itself is expanded to supply intermediate refrigeration. This is done because of the higher efficiency of N_2 expanders at low temperature and the reduced need for methane purification. The feed natural gas is purified and filtered and then split into two streams. The larger

Table 63.13 Data on World LNG Trade

World's LNG Plants, 1994			World's LNG Imports, 1994		World's LNG Trade	
Location	Capacity, Million Metric Tons/yr	Parallel Liq. Trains	Country	Quantity, Million Metric Tons/yr	Year	Amount, Million Metric Tons/yr
Kenai, Alaska	2.9	2	Japan	38.9	1980	22
Skikda, Algeria	6.2	8	S. Korea	4.4	1990	65
Arzew, Algeria	16.4	12	Taiwan	1.7	2000	90–95 (est)
Camel, Algeria	1.3	1	France	6.6	2010	130–160 (est)
Mersa, Libya	3.2	4	Other Europe	7.8		
Das Is., Abu Dhabi	4.3	2	U.S.A.	1.7		
Arun, Indonesia	9.0	5				
Bontang, Indonesia	13.2	7				
Lamut, Brunei	5.3	5				
Bintulu, Malaysia	7.5	3				
Barrup, Australia	6.0	3				

is cooled in part of the main exchanger, expanded in a turboexpander, and rewarmed to supply much of the warm end refrigeration, after which it is sent to the distribution system. The smaller fraction is cooled both by methane and by N_2 refrigeration until it is largely liquid, whereupon it goes to storage. Heavier liquids are removed by phase separation along the cooling path. Low-temperature refrigeration is supplied by a two-stage Claude cycle using N_2 as working fluid.

The LNG is stored in very large, insulated storage tanks. Typically such a tank might be 300 ft in diameter and 300 ft high. The height is made possible by the low density of LNG compared to other hydrocarbon liquids. LNG tanks have been built in ground as well as aboveground and of concrete as well as steel. However, the vast majority are aboveground steel tanks.

In designing and building LNG tanks the structural and thermal requirements added to the large size lead to many special design features. A strong foundation is necessary, and so the tank is often set on a concrete pad placed on piles. At the same time the earth underneath must be kept from freezing and later thawing and heaving. Thus electric cables or steam pipes are buried in the concrete to keep the soil above freezing. Over this pad a structurally sound layer of insulation, such as foam glass, is put to reduce heat leak to the LNG. The vertical tank walls are erected onto the concrete pad. The inner one is of stainless steel, the outer one is usually of carbon steel, and the interwall distance would be about 4 ft. The walls are field erected with welders carried in a tram attached to the top of the wall and lifted as the wall proceeds. The wall thickness is, of course, greater at the bottom than it is higher up.

The floor of the tank is steel laid over the foam glass and attached to the inner wall with a flexible joint. This is necessary because the tank walls will shrink upon cooling and expand when reheated. The dish roof is usually built within the walls over the floor. When the walls are completed, a flexible insulating blanket is put on the inside wall and the rest of the interwall space is filled with perlite. The blanket is necessary to counter the wall movement and prevent settling and crushing the perlite. At the end of construction the roof is lifted into position with slight air pressure. Usually this roof has hanging from it an insulated subroof that also rises and protects the LNG from heat leak to the roof. When this structure is in place, it is welded in and cover plates are put over the insulated wall spaces.

For safety considerations these tanks are usually surrounded by a berm designed to confine any LNG that escapes. LNG fire studies have shown such a fire to be less dangerous than a fire in an equivalent volume of gasoline. Still, the mass of LNG is so large that opportunities for disaster are seen as equally large. The fire danger will be reduced if the spill is more closely confined, and hence these berms tend to be high rather than large in diameter. In fact, a concrete tank berm built by the Philadelphia Gas Works is integral with the outside tank wall. That berm is of prestressed concrete thick enough to withstand the impact of a major commercial airliner crash.

Revaporization of LNG is done in large heat exchangers using air or water as heat sink. Shell and tube exchangers, radiators with fan-driven air for warming, and cascading liquid exchangers have all been used successfully, although the air-blown radiators tend to be noisy and subject to icing.

Base-Load LNG Plant

Table 63.13 lists the base-load LNG plants in operation in 1994. Products from these plants produce much of the natural gas used in Europe and in Japan, but United States use has been low, primarily because of the availability of large domestic gas fields.

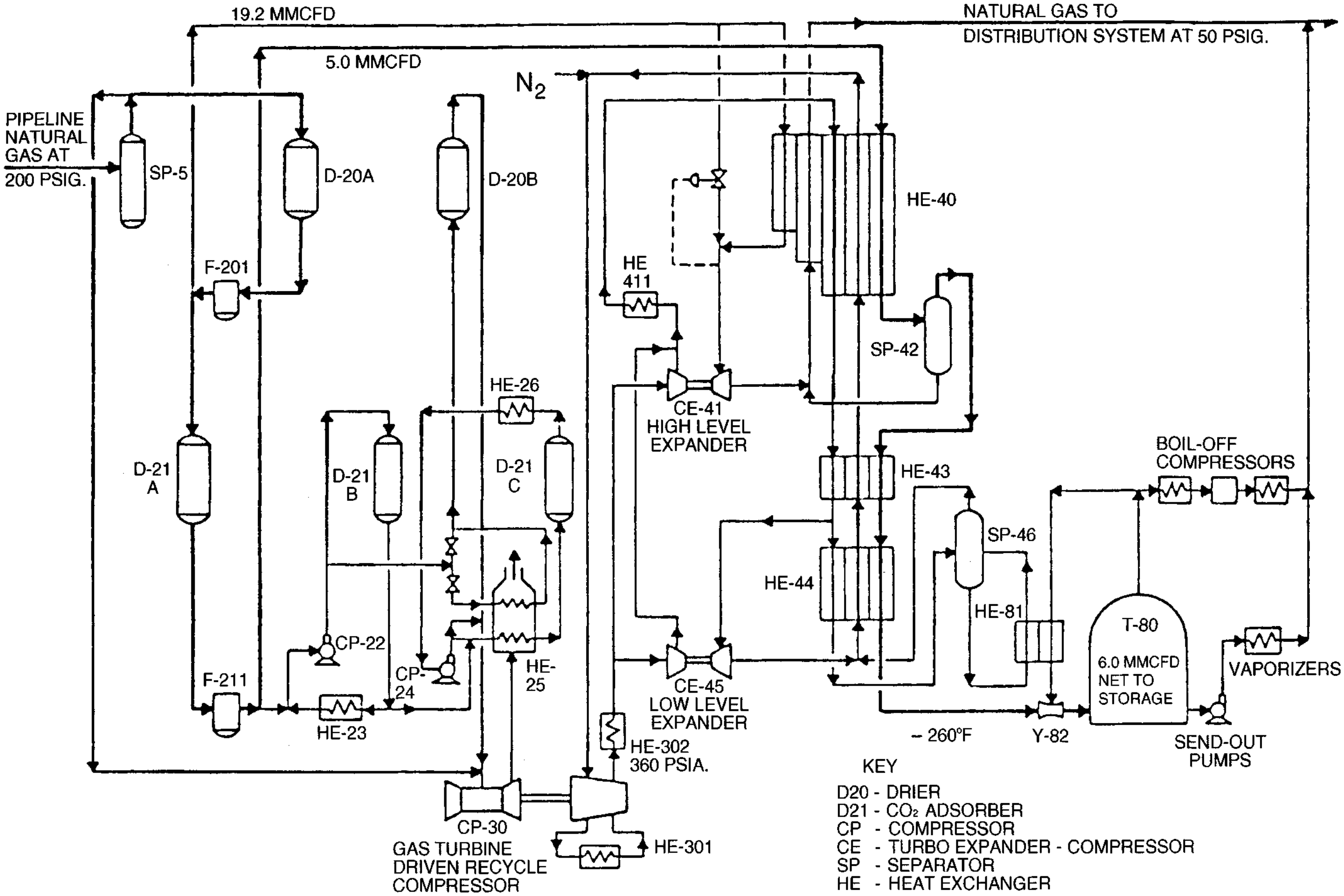

Fig. 63.39 Flow sheet of an LNG process using N_2 refrigeration.

In contrast to peak-shaving plants, liquefiers for these projects are large, primarily limited by the size of compressors and heat exchangers available in international trade. Also, these plants are located in remote areas where energy is cheap but repair facilities expensive or nonexistent. Thus, only two types of processes have been used: the classic cascade cycle and the mixed refrigerant cascade. Of these the mixed refrigerant cascade has gradually become dominant because of its mechanical simplicity and reliability.

Figure 63.40 shows a simplified process flow sheet of a mixed refrigerant cascade liquefier for natural gas. Here the natural gas passes through a succession of heat exchangers, or of bundles in a single heat exchanger, until liquified. The necessary refrigeration is supplied by a multicomponent refrigeration loop, which is essentially a Joule-Thomson cycle with successive phase separators to remove liquids as they are formed. These liquid streams are subcooled, expanded to low pressure, and used to supply the refrigeration required both by the natural gas and by the refrigerant mixture.

The success of this process depends on a selection of refrigerant composition that gives a cooling curve with shape closely matching the shape of the natural gas cooling curve. Thus all heat transfer will be across small ΔTs. This is shown in Fig. 63.41, a cooling curve for a mixed refrigerant cycle. The need to deal with a mixed refrigerant and to control the composition of the refrigerant mixture are the major difficulties with these processes. They complicate design, control, and general operation. For instance, a second process plant, nearly as large as the LNG plant, must be at hand to separate refrigerant components and supply makeup as needed by the liquefier.

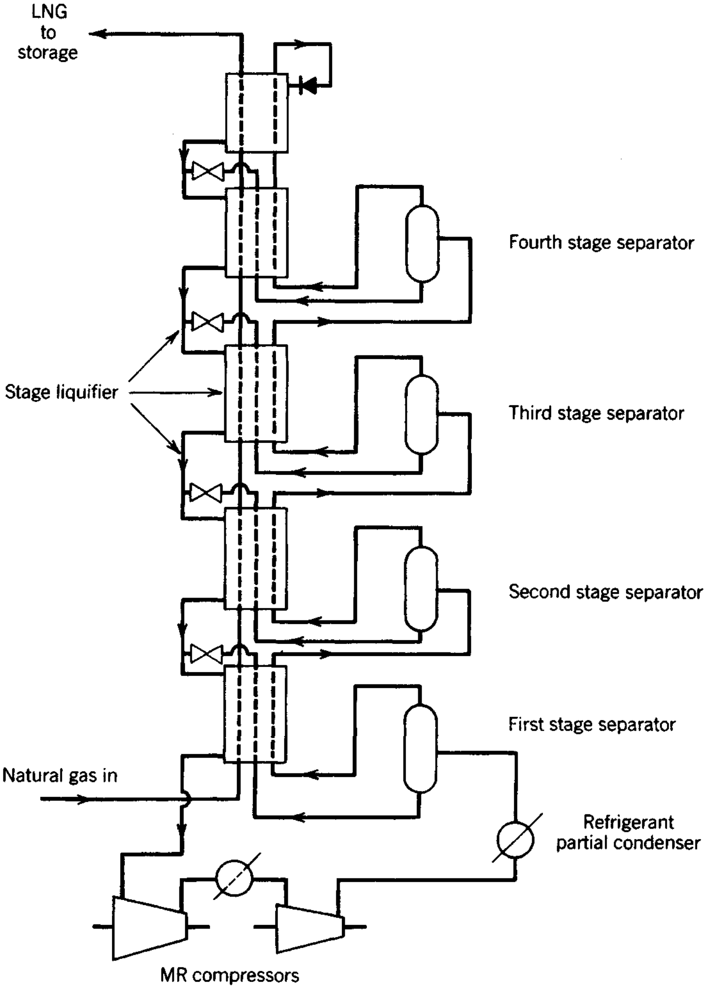

Fig. 63.40 Mixed refrigerant LNG process flow sheet. (Courtesy Plenum Press.)

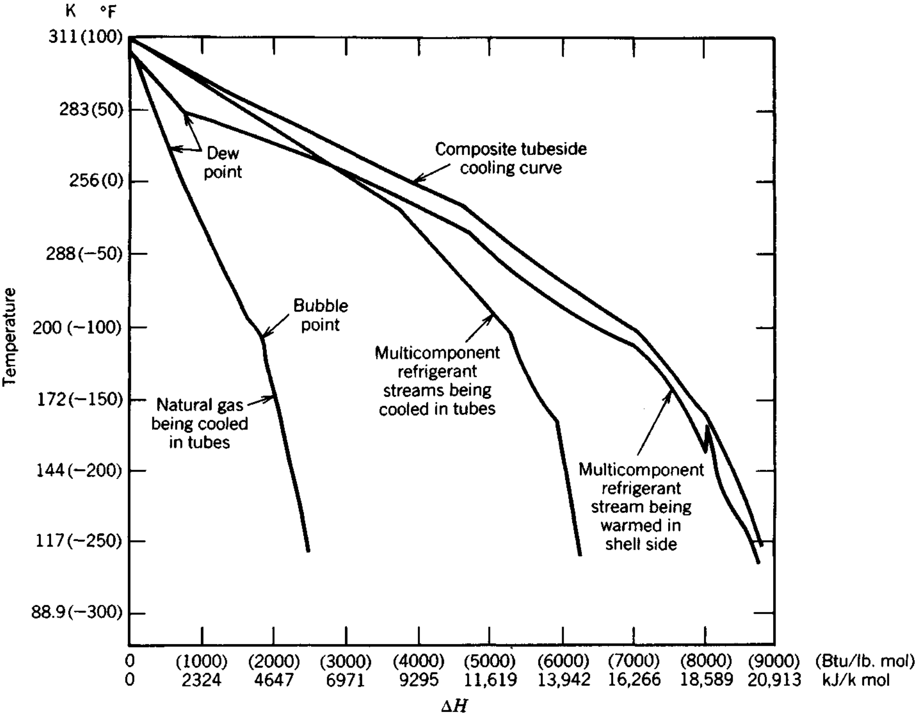

Fig. 63.41 Mixed refrigerant process cooling curve. (Courtesy Plenum Press.)

Also not shown in this flow sheet is the initial cleanup of the feed natural gas. This stream must be filtered, dried, purified of CO_2 before it enters the process shown here.

As noted above, both compressors and heat exchangers will be at the commercial maximum. The heat exchanger is of the coiled-tube-in-shell sort. Typically it would have ¾-in. aluminum tubes wrapped on a 2–3 ft diameter mandrel to a maximum 14-ft diameter. The exchanger is probably in two sections totaling about 120 ft in length. Shipping these exchanger bundles across the world challenges rail and ship capacities.

Ships used to transport LNG from the terminal by the plant to the receiving site are essentially supertankers with insulated storage tanks. These tanks are usually built to fit the ship hull. There may be four or five of them along the ship's length. Usually they are constructed at the shipyard, but in one design they are built in a separate facility, shipped by barge to the shipyard, and hoisted into position. Boiloff from these tanks is used as fuel for the ship. On long ocean hauls 6–10% of the LNG will be so consumed. In port the evaporated LNG must be reliquefied, for which purpose a small liquefier circuit is available onboard.

63.7.3 Helium Recovery and Liquefaction

Helium exists in minute concentrations in air (see Table 63.12). However, this concentration is well below the 0.3 vol % that is considered to be the minimum for economic recovery. It exists at higher concentrations in a few natural gas deposits in the United States, as shown in Table 63.14, and in like concentrations in some deposits in Russia, Poland, and Venezuela. This fossil material is apparently the total world supply.

The vital role that helium plays in welding, superconductivity applications, space program operations, medicine, in certain heat transfer and inert atmosphere needs, and in a wide variety of research requirements lead to the demand that helium be conserved. This was undertaken by the Bureau of Mines after World War II. A series of helium-separation plants was built in the Southwest. Generally these produced an 80% helium stream from high He-content steams of natural gas that would otherwise have gone directly to the municipal markets. The processes used a modified Joule-Thompson cooling system that depended on the methane accompanying the He. This crude He was stored in the Cliffside Field, a depleted gas reservoir, from which it could be withdrawn and purified. Most of

Table 63.14 Helium in Natural Gases in the United States

A. Composition of Some He-Rich Natural Gases in the United States

	Typical Composition (vol %)					
Location	CH_4	C_2H_6	N_2	CO_2	O_2	He
Colorado (Las Animas Co.)	0		77.6	14.7	0.3	7.4
Kansas (Waubaunsee, Elk, McPherson Cos.)	30	30	66.4	0.2	0	3.4
Michigan (Isabella Co.)	57.9	25.5	14.3	0	0.3	2.0
Montana (Musselshell)			54	30		16
Utah (Grand)	17		1.0	3.5		7.1

B. Estimated Helium Reserves (1994)

Location		Estimated Reserve (SCF)
Rocky Mountain area (Arizona, Colorado, Montana, New Mexico, Utah, Wyoming)		25×10^9
Midcontinent area (Kansas, Oklahoma, Texas)		169×10^9
He stored in the cliffside structure		30×10^9
	Total	224×10^9

these plants shut down during the 1970s because of shifting government policies and budgetary limitations. In 1995 the last of these plants was closed down, as was the Bureau of Mines itself. The fate of the stored crude helium is being debated now (1996).

There are now about 30 billion standard cubic feet of crude He stored in the Cliffside reservoir, more than enough to supply the U.S. government needs estimated, at 10 Bcf through 2015. Total demand for U.S. helium is nearly constant at about 3 Bcf/yr (in 1994). Private industry supplies about 89% of this market, the rest coming from the stored government supply. The estimated He resources in helium-rich natural gas in the United States is about 240 Bcf as of 1994. With the stored He, this makes a total supply of about 270 Bcf, probably enough to supply the demand until the middle of the 21st century. Eventually technology will be needed to economically recover He from more dilute sources.

The liquefaction of He, or the production of refrigeration at temperatures in the liquid He range, requires special techniques. He, and also H_2, have negative Joule–Thomson coefficients at room temperature. Thus cooling must first be done with a modified Claude process to a temperature level of 30K or less. Often expanders are used in series to obtain temperatures close to the final temperature desired. An expansion valve may then be used to effect the actual liquefaction. Such a process is shown in Fig. 63.42. The goal of this process is the maintenance of a temperature low enough to sustain superconductivity (see below) using a conventional low-temperature superconductor. Since such processes are usually small, and since entropy gains at very low temperature are especially damaging to process efficiency, these processes must use very small ΔT's for heat transfer, require high-efficiency expanders, and must be insulated nearly perfectly. Note that in heat exchanger X4 the ΔT at the cold end is 0.55K.

63.8 SUPERCONDUCTIVITY AND ITS APPLICATIONS

For normal electrical conductors the resistance decreases sharply as temperature decreases, as shown in Fig. 63.42. For pure materials this decrease tends to level off at very low temperatures. This results from the fact that the resistance to electron flow results from two factors: the collision of electrons with crystal lattice imperfections and electron collisions with the lattice atoms themselves. The former effect is not temperature dependent, but the latter is. This relationship has, itself, proven of interest to engineers, and much thought and development has gone toward the building of power transmission lines operating at cryogenic temperatures and taking advantage of the reduced resistance.

63.8.1 Superconductivity

In 1911 Dr. Onnes of Leiden was investigating the electrical properties of metals at very low temperatures, helium having just been discovered and liquefied. He was measuring the resistance of frozen mercury as the temperature was reduced into the liquid He range. Suddenly the sample showed

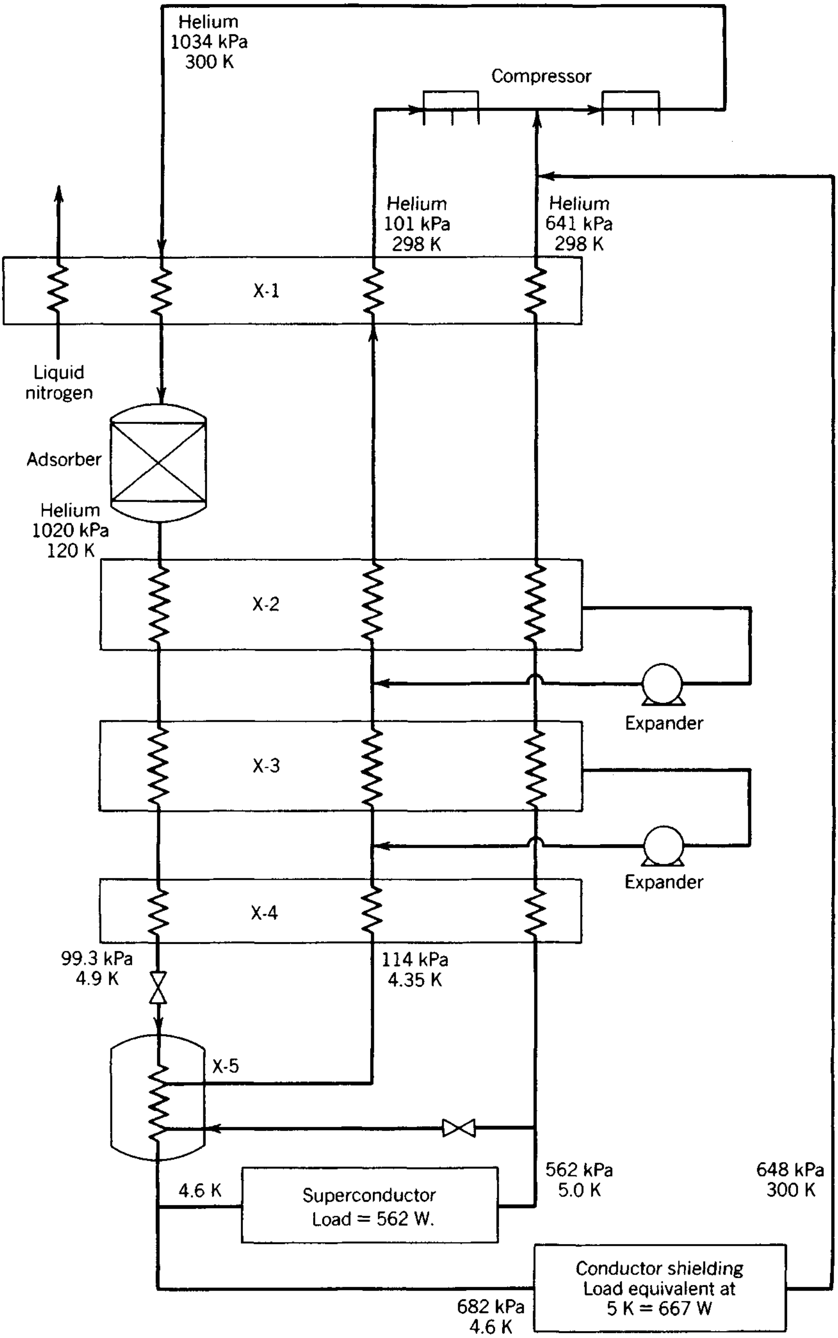

Fig. 63.42 Helium liquefier flow sheet.

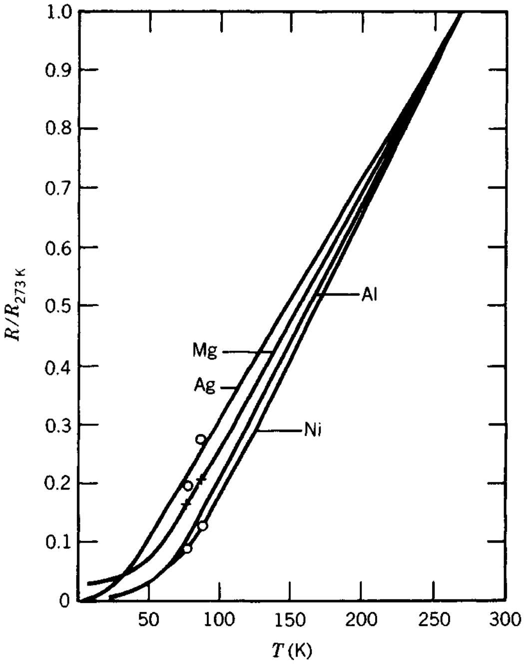

Fig. 63.43 Variation of resistance of metals with temperature.

zero resistance. At first a short circuit was suspected. However, very careful experiments showed that *the electrical conductivity of the sample had dropped discontinuously to a very low value.* The phenomenon of superconductivity has since been found to occur in a wide range of metals and alloys. The resistance of a superconductor has been found to be smaller than can be measured by the best instrumentation available. Possibly it is zero. Early on this was demonstrated by initiating a current in a superconducting ring which could then be maintained, undiminished, for months.

The phenomenon of superconductivity has been studied ever since in attempts to learn the extent of the phenomena, to develop a theory that will explain the basic mechanism and predict superconductive properties, and to use superconductivity in practical ways.

On an empirical basis it has been found that superconductors are diamagnetic, that is, they exclude a magnetic field, and that they exist within a region bounded by temperature and magnetic field strength. This is shown in Fig. 63.44. In becoming superconductive a material also changes in specific heat and in thermal conductivity.

The theory of supercoductivity developed after the discovery in 1933 by Meissner of the magnetic field exclusion. This led to a qualitative "two-fluid" model analogous to the theory underlying HeII. Since then this theory has been recast in quantum mechanical theory terms, most completely and successfully by J. Bardeen, L. N. Cooper, and R. Schrieffer of the University of Illinois in 1957 (BCS theory).

The BCS theory accounts for the Meissner effect and for other physical behavior phenomena of superconductors. It does not yet allow the prediction of superconductive transition points for new materials. The theory predicts an energy gap between normal and superconductive states existing simultaneously and visualizes the flow of paired electrons through the crystal lattice and the quantization of the magnetic flux. The quantized flux lines are fundamental to the explanation of the difference between type I superconductors that exhibit perfect Meissner effects, and which have relatively low transition temperatures and field tolerance, and type II superconductors that have imperfect Meissner effects, higher transition temperatures, and greater tolerance of magnetic fields. For example, Nb_3Sn, which is a type II superconductor, can be used for generation of magnetic fields of 100,000 gauss. These materials allow the penetration of magnetic field above a lower critical field strength, H_{c1}, but remain superconductive to a much greater field strength, H_{c2}. At fields above H_{c1}, flux enters the material in the form of quantized bundles that are pinned by dislocations so that the flux does not move easily and lead to normalization of the material.

Thus both HeII and superconductors may be considered examples of superfluids. Each exhibits a nondissipative process for mass transfer. In HeII the mass transferred is the fluid itself in inviscid

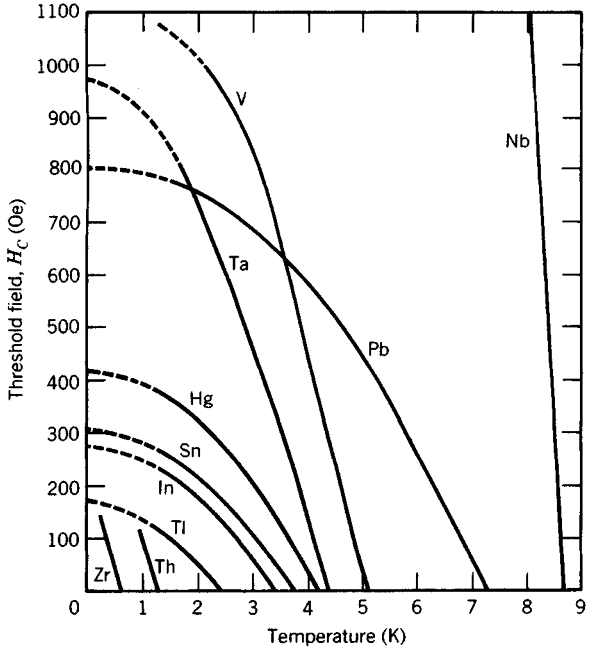

Fig. 63.44 Limits to superconductive behavior of some elements.

flow; with a superconductor it is the electrons flowing without encountering resistance. In both cases a flow velocity greater than a critical value restores normality. In superconductors circulating currents are set up in the penetration layer at the surface to cancel the applied magnetic field. When this field is increased to a critical value, the critical current is reached and the material reverts to the normal state.

63.8.2 Applications of Superconductivity

Development of applications of superconductivity has proceeded very rapidly over the past decade. However, by far the widest use of superconductivity has been in magnet applications. Superconductive magnets were constructed and tested soon after such practical superconductors as Nb_3Sn and rhodium–zirconium were discovered about 1960. Field strengths as high as 7 T were predicted then. Since then magnets in a wide range of sizes and shapes have been made, tested, and used with field strengths approaching 20 T.

The first three Nb alloys listed in Table 63.16 are ductile to the point that they are readily fabricated by conventional wire-drawing techniques. These form the cheapest finished product, but cannot be used at high field strengths. The Nb_3Sn, which is the most widely used superconductive

Table 63.15 Superconductive Elements with Zero-Field Transition Temperatures

Mg											Al 1.20°	Si	P
Co	Sc	Ti 0.40°	V 4.9°	Cr	Mn	Fe	Co	Ni	Cu	Zn 0.88°	Ga 1.10°	Ge	As
Sr	Y	Zr 0.75°	Nb 9.5°	Mo 0.95°	Tc 11.2°	Ru 0.47°	Rh	Pd	Ag	Cd 0.56°	In 3.40°	Sn 3.73°	Sb
Ba	La 5.4°	Hf 0.35°	Ta 4.5°	W	Re 1.7°	Os 0.71°	Ir 0.15°	Pt	Au	Hg 4.15°	Tl 2.39°	Pb 7.22°	Bi
Ra	Ac	Th 1.37°	Pa	U-β 1.8°									

Table 63.16 Some Commercially Available Superconductive Materials[a]

Material	T_c (K)	H_c 2 (T) at 4.2 K	J_c (10^5 A/cm^2 at 4.2 K) 2.5 T	5 T	10 T	15 T	Fabrication
Nb–25 wt% Zr	11	7.0	1.1	0.8	0	0	Fairly ductile
Nb–33 wt% Zr	11.5	8.0	0.9	0.8	0	0	Fairly ductile
Nb–48 wt% Ti	9.5	12.0	2.5	1.5	0.3	0	Ductile
Nb_3Sn	18.0	22.0	17.0	10.0	4.0	0.5	CVD diffusion bronze
V_3Ga	15.0	23.0	5.0	2.5	1.4	0.9	Diffusion bronze

[a] Courtesy Plenum Press.

material, and V_3Ga are formed into tape by chemical vapor deposition. The tape is clad with copper for stability and stainless steel for strength. Materials for multifilament conductor formation are produced by the bronze process. In this process filaments of Nb or V are drawn down in a matrix of Sn–Cu or Sn–Ga alloy, the bronze. Heat treatment then produces the Nb_3Sn or V_3Ga. The residual matrix is too resistive for satisfactory stabilization. Hence copper filaments are incorporated in the final conductors.

Multifilament conductors are then made by assembling superconductive filaments in a stabilizing matrix. For example, in one such conductor groups of 241 Ni–Ti filaments are sheathed in copper and cupronickel and packed in a copper matrix to make a 13,255-filament conductor. Such a conductor can be wound into an electromagnet or other large-scale electrical device.

Superconductive magnets have been used, or are planned to be used for particle acceleration in linear accelerators, for producing the magnetic fields in the plasma step of magnetohydrodynamics, for hydrogen bubble chambers, for producing magnetic "bottles" for nuclear fusion reactors such as the Tokomak, for both levitation and propulsion of ultra high speed trains, for research in solid-state physics, for field windings in motors, and for a host of small uses usually centered on research studies. In fact superconductive magnetics with field strength approaching 10 T are an item of commerce. They are usable where liquid helium temperatures are available and produce magnetic fields more conveniently and cheaply than can be done with a conventional electromagnet. Table 63.18 lists the superconductive magnets in use for various energy related applications.

Perhaps the most interesting of these applications is in high-speed railroads. Studies in Japan, Germany, Canada, and the United States are aimed at developing passenger trains that will operate at 300 mph and above. The trains would be levitated over the track by superconductive magnets, sinking to track level only at start and stop. Propulsion systems vary but are generally motors often with superconductive field windings. Such railroads are proposed for travel from Osaka to Tokyo and from San Diego to Los Angeles. Design criteria for the Japanese train are given in Table 63.19.

Superconductive electrical power transmission has been seriously considered for areas of high density use. Superconductors make it possible to bring the capacity of a single line up to 10,000–30,000 MW at a current density two orders of magnitude greater than conventional practice. The resulting small size and reduced energy losses reduce operating costs of transmission substantially.

The economic attraction of a superconductive transmission line depends on the cost of construction and the demand for power, but also on the cost of refrigeration. Thus a shield is built in and kept at liquid N_2 temperature to conserve on helium. Also, superinsulation is used around the liquid N_2 shield.

Other applications of superconductivity have been found in the microelectronics field. Superconductive switches have been proposed as high-speed, high-density memory devices and switches for computers and other electronic circuits. The ability of the superconductor to revert to normal and

Table 63.17 Composition on Critical Temperature of Some HTS Materials

Formula	a–b–b–d Values Reported	Critical Temp, T_c, K
$Y_a Ba_b Cu_c O_n$	1–2–3, 1–2–4	80–92
$Bi_a Sr_b Ca_c Cu_d O_n$	2–2–1–2, 2–2–2–3	80–110
$Tl_a Ba_b Ca_c Cu_d O_n$	Several	–125
$Hg_a Ba_b Ca_c Cu_d O_n$	1–2–0–1, 1–2–2–3	95–155*

* High temperature obtained while subjecting the sample to external pressure.

Table 63.18 General Characteristics of Superconductive Magnets for Energy Conversion and Storage Systems[40,a]

Application	Magnet Type	Typical Stored Energy in the Winding (MJ)	Operated			Largest Prototype So Far
			dc	Pulsed	Transients	
MHD generators	Dipole magnet with warm aperature, possibly tapered	500–5000	Yes	No	Yes, from the MHD fluid	60-MJ magnet
Homopolar machines	Solenoid	10–100	Yes	No	No	3-MW generator
Synchronous machines	Rotating dipole or quadrupole winding	Power plant machines, 50–100; airborne systems, 0.5–1	Yes	No	Yes, in case of unbalanced load	5-MVA generator
Fusion magnets Tokamak or similar low-β confinement	Toroidal field coils	$\geq 10^5$	Yes	Yes, in case of fast voltage control	Yes, pulsed field harmonic components of poloidal field	—
	Poloidal field coils	$\geq 10^3$	No	Yes, with rise times of seconds	Yes, dc field components from the toroidal field	—
Mirror confinement	Baseball coils	$\geq 10^5$	Yes	No	No	Baseball coils with 9 MJ
Energy storage; operation of pulsed fusion magnets						
Theta pinch	No optimal shape defined yet	≥ 100 per unit	No	Yes, transfer time about 30 msec	—	300 kJ
Tokamak	No optimal shape defined yet	$\geq 10^4$	No	Yes, transfer time about seconds	—	
Load leveling in the grid	No optimal shape defined yet	$\geq 10^8$	No	Yes, transfer time about hours	—	—

[a] Courtesy Plenum Press.

Table 63.19 Design Criteria for Japanese High Speed Train[41,a]

Maximum number of coaches/train	16
Maximum operation speed	550 km/hr
Maximum acceleration and deceleration:	
Acceleration	3 km/hr/sec
Deceleration, normal brake	5 km/hr/sec
Deceleration, emergency brake	10 km/hr/sec
Starting speed of levitation	100 km/hr
Effective levitation height (between coil centers)	250 mm
Accuracy of the track	±10 mm/10 m
Hours of operation	From 6 AM to 12 PM at 15-min intervals
Period of operation without maintenance service	18 hr
Number of superconduction magnets	
Levitation	4 × 2 rows/coach
Guiding and drive	4 × 2 rows/coach
Carriage weight	30 tons
dimensions	25 m × 3.4 m × 3.4 m
Propulsion	Linear synchronous motor

[a] Courtesy Plenum Press.

again to superconductive in the presence or absence of a magnetic field makes an electric gate or a record of the presence of an electric current. However, these devices have been at least temporarily overshadowed by the rapid development of the electronic chip. Ultimately, of course, these chips will be immersed in a cryogen to reduce resistance and dissipate resistive heat.

63.9 CRYOBIOLOGY AND CRYOSURGERY

Cryogenics has found applications in medicine, food storage and transportation, and agriculture. In these areas the low temperature can be used to produce rapid tissue freezing and to maintain biological materials free of decay over long periods.

The freezing of food with liquid N_2 has become commonplace. Typically the loose, prepared food material is fed through an insulated chamber on a conveyor belt. Liquid N_2 is sprayed onto the food, and the evaporated N_2 flows countercurrent to the food movement to escape the chamber at the end in which the food enters. The required time of exposure depends on the size of individual food pieces and the characteristics of the food itself. For example, hamburger patties freeze relatively quickly because there is little resistance to nitrogen penetration. Conversely, whole fish may freeze rapidly on the surface, but the enclosing membranes prevent nitrogen penetration, so internal freezing occurs by conductive transfer of heat through the flesh. Usually a refrigerated holding period is required after the liquid N_2 spray chambers to complete the freezing process.

The advantages of liquid N_2 food freezing relative to more conventional refrigeration lie in the speed of freezing that produces less tissue damage and less chance for spoilage, and the inert nature of nitrogen, which causes no health hazard for the freezer plant worker or the consumer.

Liquid N_2 freezing and storage has also been used with parts of living beings such as red blood cells, bull semen, bones, and various other cells. Here the concern is for the survival of the cells upon thawing, for in the freezing process ice crystals form which may rupture cell walls upon freezing and thawing. The rate of survival has been found to depend on the rate of cooling and heating, with each class of material showing individual optima. Figure 63.45 shows the survival fractions of several cell types as a function of cooling velocity. Better than half the red blood cells survive at cooling rates of about 3000 K/min. Such a cooling rate would kill all of the yeast cells.

The mechanism of cell death is not clearly understood, and may result from any of several effects. The cell-wall rupture by crystals is the most obvious possibility. Another is the dehydration of the cell by water migration during the freezing process. In any case the use of additives such as glycerol, dimethyl sulfoxide, pyridine *n*-oxide, and methyl and dimethyl acetamide has greatly reduced cell mortality in various specific cases. The amount and type of additive that is most effective depends upon the specific cell being treated.

Controlled freezing has proven useful in several surgical procedures. In each of these the destruction of carefully selected cells and/or their removal has been the goal of the operation.

In treating Parkinson's disease destruction of some cells in the thalmus can lead to sharp reduction in tremors and muscular rigidity. The operation is done under local anesthetic using a very fine probe consisting of three concentric tubes. Liquid N_2 flows in through the center tube, returning as vapor through the central annulus. The outer annulus is evacuated and insulates all but the probe tip. The

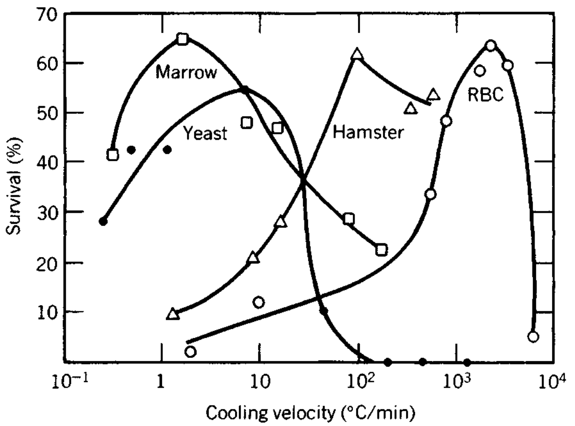

Fig. 63.45 Survival rate for various cells frozen to liquid N_2 temperature.[42] (Courtesy Plenum Press.)

surgeon inserts the probe using X-ray pictures for guidance. He or she gently cools that probe tip using temperatures just below freezing. If the patient's tremors subside without other side effects, the right location has been found. Freezing of a quarter inch sphere around the probe tip can proceed.

In ophthalmic surgery cryogenic probes are used to lift cataracts from the lens of the eye. Here the cataract is frozen to the cryo-probe tip and carefully separated from the eye. Liquid N_2 is not needed and Freons or Joule–Thomson cooling is sufficient.

Malignant or surface tumors can also be removed cryogenically. The freezing of such a cell mass helps to prevent the escape of some of the cells into the blood stream or the body cavity.

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