ULTRALOW-TEMPERATURE REFRIGERATION

ULTRALOW-TEMPERATURE refrigeration is defined here as refrigeration in the temperature range of −50 to −100°C. What is considered low temperature for an application depends on the temperature range for that specific application. Low temperatures for air conditioning are around 0°C; for industrial refrigeration, −35 to −50°C; and for cryogenics, approaching 0 K. Applications such as freeze-drying, as well as the pharmaceutical, chemical, and petroleum industries, use refrigeration in the temperature range designated low in this chapter.

The −50 to −100°C temperature range is treated separately because design and construction considerations for systems that operate in this range differ from those encountered in the two fields bracketing it, namely, industrial refrigeration and cryogenics. Designers and builders of cryogenic facilities are rarely active in the low-temperature refrigeration field. One major type of low-temperature system is the **packaged type**, which often serves such applications as environment chambers. The other major category is **custom-designed and field-erected** systems. Industrial refrigeration practitioners are the group most likely to be responsible for these systems, but they may deal with low-temperature systems only occasionally; the experience of a single organization does not accumulate rapidly. The objective of this chapter is to bring together available experience for those whose work does not require daily contact with low-temperature systems.

The refrigeration cycles presented in this chapter may be used in both standard packaged and custom-designed systems. Cascade systems are emphasized, both autocascade (typical of the packaged units) and two-refrigerant cascade (encountered in custom-engineered low-temperature systems).
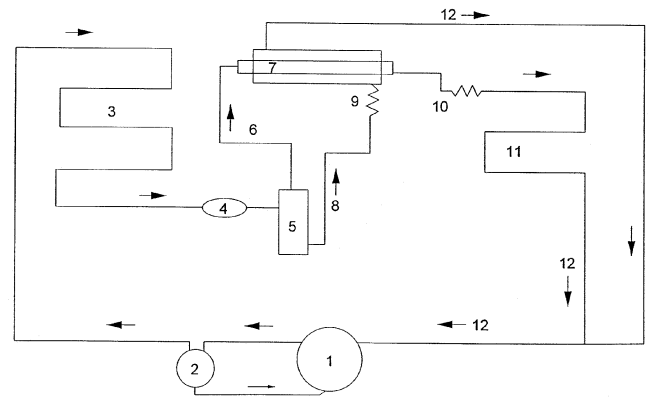
AUTOCASCADE SYSTEMS

An autocascade refrigeration system is a complete, self-contained refrigeration system in which multiple stages of cascade cooling effect occur simultaneously by means of vapor-liquid separation and adiabatic expansion of various refrigerants. Physical and thermodynamic features, along with a series of counterflow heat exchangers and an appropriate mixture of refrigerants, make it possible for the system to reach low temperature.

Autocascade refrigeration systems offer many benefits, such as a low compression ratio and relatively high volumetric efficiency. However, system chemistry and heat exchangers are complex, refrigerant compositions are sensitive, and compressor displacement is large.

Operational Characteristics

Components of an autocascade refrigeration system typically include a vapor compressor, an external air- or water-cooled condenser, a mixture of refrigerants with descending boiling points, and a series of insulated heat exchangers. Figure 1 is a schematic diagram of a simple system illustrating a single stage of autocascade effect.

The preparation of this chapter is assigned to TC 10.4, Ultralow-Temperature Systems and Cryogenics.

1. Compressor
2. Oil separator
3. Condenser
4. Filter drier
5. Phase separator
6. Vapor tube to second condenser
7. Heat exchanger (evaporator of first refrigerant, cooling second refrigerant)
8. First refrigerant liquid line to metering device
9. First refrigerant metering device feeding heat exchanger, cooling second refrigerant
10. Second refrigerant metering device
11. Evaporator
12. Suction lines to compressor

Fig. 1   Simple Autocascade Refrigeration System

In this system, two refrigerants, which have significantly different boiling points, are compressed and circulated by one vapor compressor. Assume that one refrigerant is R-23 (normal boiling point, −82°C) and the second refrigerant is R-404a (normal boiling point, −46.7°C). Assume that ambient temperature is 25°C and that the condenser is 100% efficient.

With properly sized components, this system should be able to achieve −60°C in the absorber while the compression ratio is maintained at 5.1 to 1. As the refrigerant mixture is pumped through the main condenser and cooled to 25°C at the exit, compressor discharge pressure is maintained at 1524 kPa (gage). At this condition, virtually all R-404a is condensed at 35°C and then further chilled to subcooled liquid. Although R-23 molecules are present in both liquid and vapor phases, the R-23 is primarily vapor due to the large difference in the boiling points of the two refrigerants. A phase separator located at the outlet of the condenser therefore collects the liquid by gravitational effect, and the R-23-rich vapor is removed from the outlet of the phase separator to the heat exchanger.

At the bottom of the phase separator, an expansion device adiabatically expands the collected R-404a-rich liquid such that the outlet of the device produces a low temperature of −19°C at 220 kPa (gage) (Weng 1995). This cold stream is immediately sent back to the heat exchanger in a counterflow pattern such that the R-23-rich vapor is condensed to liquid at −18.5°C and 1524 kPa (gage). The R-23-rich liquid is then adiabatically expanded by a second expansion device to −60°C. As it absorbs an appropriate amount of heat in the absorber, the R-23 mixes with the expanded R-404a and evaporates in the heat exchanger, providing a cold source for condensing R-23 on the high-pressure side of the heat
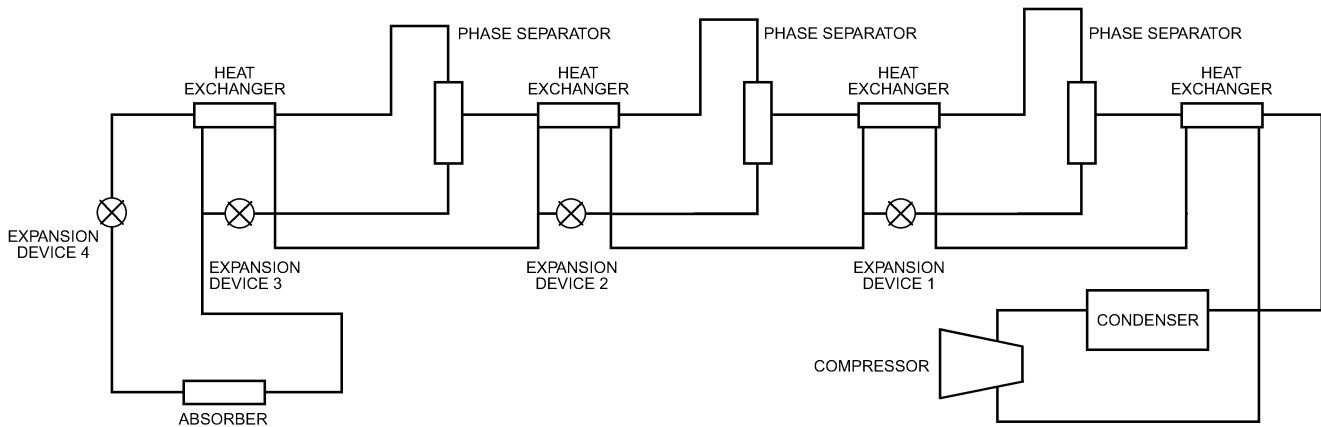
Fig. 2   Four-Stage Autocascade System

exchanger. Leaving the heat exchanger at superheated conditions, the vapor mixture then returns to the suction of the compressor for the next cycle.

As can be seen from this simple example, the autocascade effect derives from a **short cycle** of the refrigerant circuit within the system that performs only internal work to condense the lower boiling point refrigerant.

The concept of the single-stage cycle can be extended to multiple stages. Figure 2 shows the flow diagram of a four-stage system. The condensation and subsequent expansion of one refrigerant provides the cooling necessary to condense the next refrigerant in the heat exchanger downstream. This process continues until the last refrigerant with the lowest boiling point is expanded to achieve extremely low temperature.

Design Considerations

Compressor Capacity. As can be seen from Figures 1 and 2, a significant amount of compressor work is used for internal evaporating and condensing of refrigerants. The final gain of the system is therefore relatively small. Compressor capacity must be sufficient to produce an appropriate amount of final refrigerating effect.

Heat Exchanger Sizing. Because there is a significant amount of refrigerant vapor in each stage of the heat exchanger, the overall heat-transfer coefficients on both the evaporating side and the condensing side are rather small compared to those of pure components at phase-changing conditions. Therefore, generous heat-transfer area should be provided for energy exchange between refrigerants on the high- and low-pressure sides.

Expansion Devices. Each expansion device is sized to provide sufficient refrigerating effect for the adjacent downstream heat exchanger.

Compressor Lubrication. General guidelines for lubrication of refrigeration systems should be adopted.

CUSTOM-DESIGNED AND FIELD-ERECTED SYSTEMS

If the refrigeration assignment is to maintain a space at a low temperature to store a modest quantity of product in a chest or cabinet, the packaged low-temperature system is probably the best choice. Prefabricated walk-in environmental chambers are also practical solutions when they can accommodate space needs. When the required refrigeration capacity exceeds that of packaged systems, or when a fluid must be chilled, a custom-engineered system should be considered.

The refrigeration requirement may be to chill a certain flow rate of a given fluid from one temperature to another. Part of the design process is to choose the type of system, which may be a multistage

plant using a single refrigerant or a two-circuit cascade system using a high-pressure refrigerant for the low-temperature circuit. The compressor(s) and condenser(s) must be selected, and the evaporator and interstage heat exchanger (in the case of the cascade system) must be either selected or custom-designed.

The design process includes selection of (1) metal for piping and vessels and (2) insulating material and method of application. The product to be refrigerated may actually pass through the evaporator, but in many cases a secondary coolant transfers heat from the final product to the evaporator. Brines and antifreezes that perform satisfactorily at higher temperatures may not be suitable at low temperatures. Compressors are subjected to unusual demands when operating at low temperatures, and because they must be lubricated, oil selection and handling must be addressed.

SINGLE-REFRIGERANT SYSTEMS

Single-refrigerant systems are contrasted with the cascade system, which consists of two separate but thermally connected refrigerant circuits, each with a different refrigerant (Stoecker and Jones 1982).

In the industrial refrigeration sector, the traditional refrigerants have been R-22 and ammonia (R-717). Because R-22 will ultimately be phased out, various hydrofluorocarbon (HFC) refrigerants and blends are proposed as replacements. Two that might be considered are R-507 and R-404a.

Two-Stage Systems

In systems where the evaporator operates below about −20°C, two-stage or compound systems are widely used. These systems are explained in Chapter 3 of this volume and in Chapter 1 of the ASHRAE Handbook—Fundamentals. Advantages of two-stage compound systems that become particularly prominent when the evaporator operates at low temperature include

- Improved energy efficiency due to the removal of flash gas at the intermediate pressure and desuperheating of the discharge gas from the low-stage compressor before it enters the high-stage compressor.
- Improved energy efficiency because the two-stage compressors are more efficient operating against discharge-to-suction pressure ratios that are lower than for a single-stage compressor.
- Avoidance of high discharge temperatures typical of single-stage compression. This is important in reciprocating compressors but of less concern with oil-injected screw compressors.
- Possibility of a lower flow rate of liquid refrigerant to the evaporator because the liquid is at the saturation temperature of the intermediate pressure rather than the condensing pressure, as is true of single-stage operation.

Table 1 Low-Temperature Characteristics of Several Refrigerants at Three Evaporating Temperatures

Refrigerant	Freezing Point	Pressure Ratio with Two-Stage System			Volumetric Flow of Refrigerant, L/s per kW		
		Evaporating Temp.			Evaporating Temp.		
		−50°C	−70°C	−90°C	−50°C	−70°C	−90°C
R-22	−160°C	4.6	8.14	17.9	1.57	4.81	19.8
R-507	<−100°C	4.4	7.8	16.1	1.29	4.08	17.5
R-717	−77.8°C	5.75	11.1	25.4	2.05	7.24	—
R-404a	<−100°C	4.36	7.58	15.2	1.34	4.13	16.75

Refrigerant and Compressor Selection

The compound, two-stage (or even three-stage) system is an obvious possibility for low-temperature applications. However, at very low temperatures, certain limitations of the refrigerant itself appear. These limitations include the freezing point, the pressure ratios required of the compressors, and the volumetric flow at the suction of the low-stage compressor per unit refrigeration capacity. Table 1 shows some key values for four candidate refrigerants, illustrating some of the concerns that arise when considering refrigerants that are widely applied in industrial refrigeration systems. Refrigerants not included in Table 1 are hydrocarbons (HCs), which are candidates particularly in the petroleum and petrochemical industry, where the entire plant is geared toward working with flammable gases.

The first factor shown in Table 1 is the **freezing point.** It is not a limitation for the halocarbon refrigerants, but ammonia freezes at –78°C, so its use must be restricted to temperatures safely above that temperature.

The next data shown are **pressure ratios** the compressors must operate against in two-stage systems. A condensing temperature of 35°C is assumed, with the intermediate pressure being the geometric mean of the condensing and evaporating pressures. Many low-temperature systems may be small enough that a reciprocating compressor would be favorable, but the limiting pressure ratio with reciprocating compressors is usually about 8, a value chosen to limit the discharge temperature. An evaporating temperature of –70°C is about the lowest permissible for systems using reciprocating compressors. For evaporating temperatures lower than –70°C, a three-stage system should be considered. An alternative to the reciprocating compressor is the screw compressor, which operates with lower discharge temperatures because it is oil flooded. The screw compressor can therefore operate against larger pressure ratios than the reciprocating compressor; in larger systems, it is the favored compressor type.

The third characteristic shown in Table 1 is the required **volumetric pumping capacity** of the compressor, measured at the compressor suction. This value is an indicator of the physical size of the compressor; the values become huge at the –90°C evaporating temperature.

Some conclusions from Table 1 are

• A single-refrigerant, two-stage system can adequately serve a plant in the higher-temperature portion of the range considered here, but it becomes impractical in the lower-temperature portion.
• Ammonia, which has many favorable properties for industrial refrigeration, has little appeal for low-temperature refrigeration because of its relatively high freezing point and pressure ratios.

Special Multistage Systems

Special high-efficiency operations to recover volatile compounds such as hydrocarbons use the **reverse Brayton cycle**. This consists of one or two conventional compressor refrigeration cycles with the lowest stage ranging from −60 to −100°C. This final stage
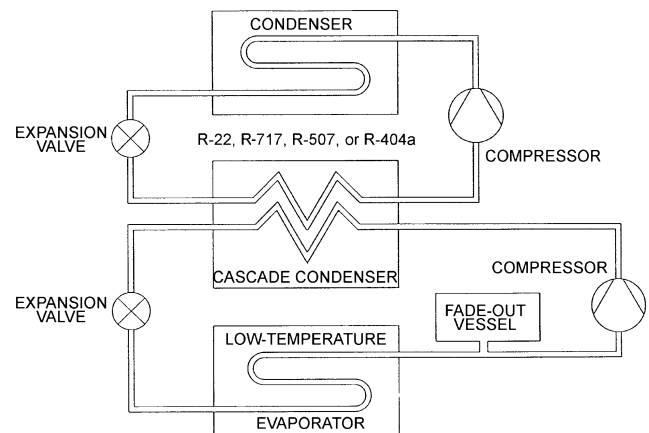
Fig. 3 Simple Cascade System

is achieved by using a turbo compressor/expander and enables the collection of liquefied hydrocarbons (Emhö 1997; Jain and Enneking 1995; Enneking and Priebe 1993).

CASCADE SYSTEMS

The cascade system, illustrated in Figure 3, confronts some of the problems of single-refrigerant systems. The system consists of two separate circuits, each using a refrigerant appropriate for its temperature range. The two circuits are thermally connected by the cascade condenser, which is the condenser of the low-temperature circuit and the evaporator of the high-temperature circuit. Refrigerants typically chosen for the high-temperature circuit include R-22, ammonia, R-507, R-404a, and so forth. For the low-temperature circuit, a high-pressure refrigerant with a high vapor density (even at low temperatures) is chosen. For many years, R-503, an azeotropic mixture of R-13 and R-23, has been a popular choice, but R-503 is no longer available because R-13 is an ozone-depleting chlorofluorocarbon (CFC). R-23 could be and has been used alone, but R-508b, an azeotrope of R-23 and R-116, has superior properties. R-508b is discussed further in the section on Refrigerants for Low-Temperature Circuit.

The cascade system possesses some of the thermal advantages of two-stage, single-refrigerant systems in that it approximates the flash gas removal process and also permits each compressor to take a share of the total pressure ratio between the low-temperature evaporator and the condenser. The cascade system has the thermal disadvantage of needing to provide an additional temperature lift in the cascade condenser because the condensing temperature of the low-temperature refrigerant is higher than the evaporating temperature of the high-temperature refrigerant. There is an optimum operating temperature of the cascade condenser for minimum total power requirement, just as there is an optimum intermediate pressure in two-stage, single-refrigerant systems.

Figure 3 shows a fade-out vessel, which limits the pressure in the low-temperature circuit when the system shuts down. At room temperature, the pressure of R-23 or R-508b in the system would exceed 4000 kPa if liquid were present. The entire low-temperature system must be able to accommodate this pressure. The process taking place in the fade-out vessel is at constant volume, as shown on the pressure-enthalpy diagram of Figure 4. When the system operates at low temperature, the refrigerant in the system is a mixture of liquid and vapor, indicated by point A. When the system shuts down, the refrigerant begins to warm and follows the constant-volume line, with the pressure increasing according to the saturation curve. When the saturated vapor line is reached at point B, further increases in temperature result in only slight increases in pressure because the refrigerant is superheated vapor.

The larger cascade systems are field engineered, but packaged systems are also available. Figure 5 shows a two-stage system with the necessary auxiliary equipment. Figure 6 shows a three-stage cascade system.

Refrigerants for Low-Temperature Circuit

R-503 is no longer available for general use. R-23 can be used, but R-508b, an azeotropic mixture of two non-ozone-depleting refrigerants, R-23 and R-116, is superior. It is nonflammable and has zero ozone depletion potential (ODP). Table 2 lists some properties of R-508b.
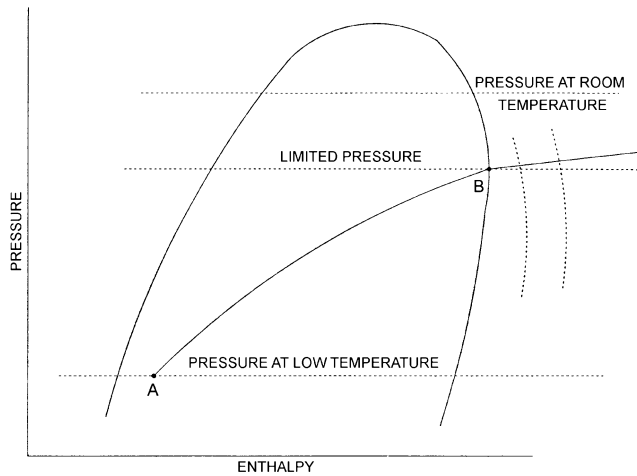

Fig. 4   Simple Cascade Pressure-Enthalpy Diagram

R-508b offers excellent operating characteristics compared to R-503 and R-13. Capacity and efficiency values are nearly equivalent to R-503's and superior to R-13's. The compressor discharge temperature is lower than for R-23; lower discharge temperatures may equate to longer compressor life and better lubricant stability. The estimated operating values of a cascade system running with R-508b are shown in Table 3. Performance parameters of R-503, R-13, and R-23 are shown for comparison.

Table 4 shows calculated data for R-23 and R-508b for two operating ranges. The volumetric efficiency is 100%. Actual compressor performance varies with pressure ratios and would yield lower capacity and efficiencies and higher discharge temperatures and flow requirements than shown.

Compressor Lubrication

The criteria for selecting a lubricant for use with R-508b in an existing low-temperature system should include (1) refrigerant/lubricant miscibility, (2) chemical stability, (3) materials compatibility,

Table 2   Properties of R-508b

Boiling point (101.325 kPa)	$-88°C$
Critical temperature	$13.7°C$
Critical pressure	3935 kPa
Latent heat of vaporization at boiling point	168.4 kJ/kg
Ozone depletion potential (R-12 = 1)	0
Flammability	Nonflammable
Exposure limit (8- and 12-hour) [a]	1000 ppm

[a]The exposure limit is a calculated limit determined from the DuPont airborne exposure limit (AEL) of the individual components. The AEL is the maximum amount to which nearly all workers can be repeatedly exposed during a working lifetime without adverse effects.
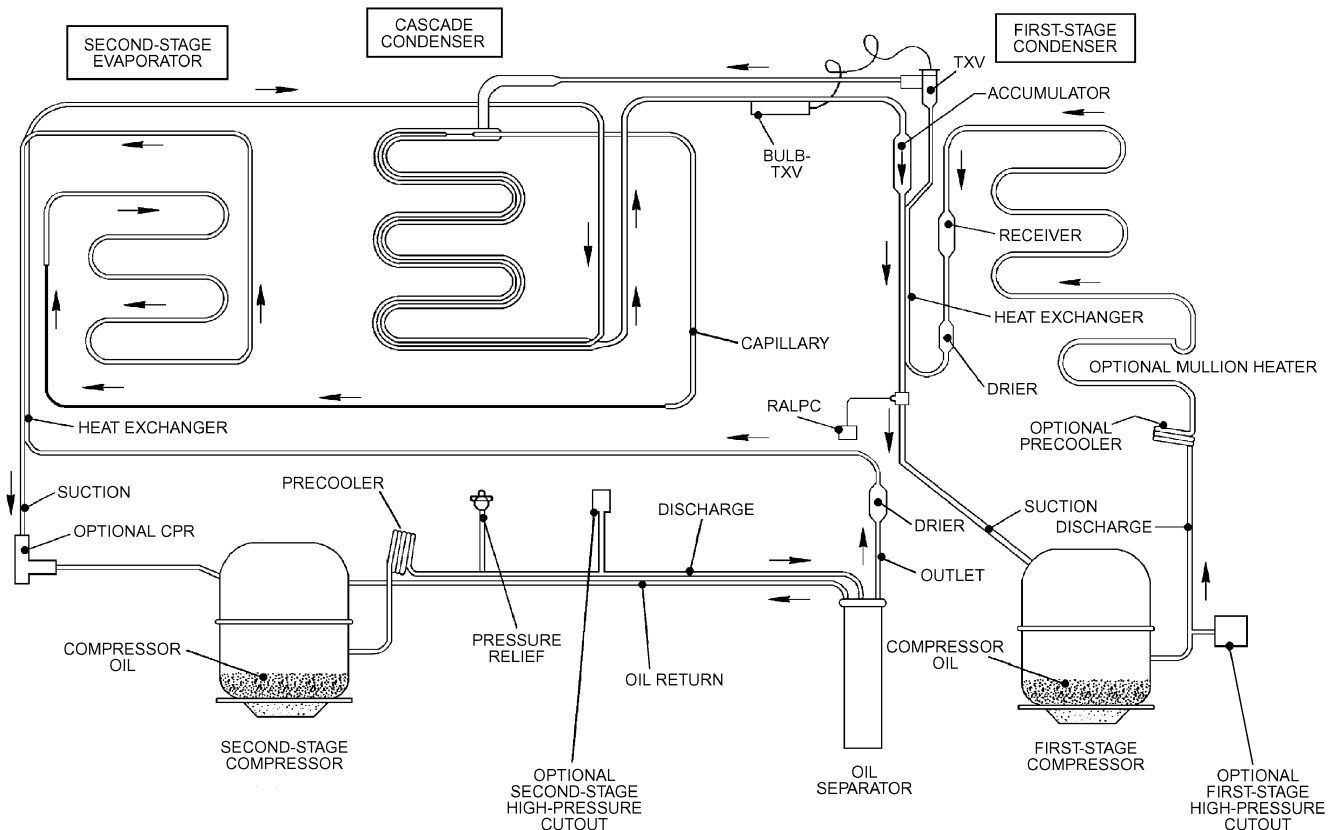

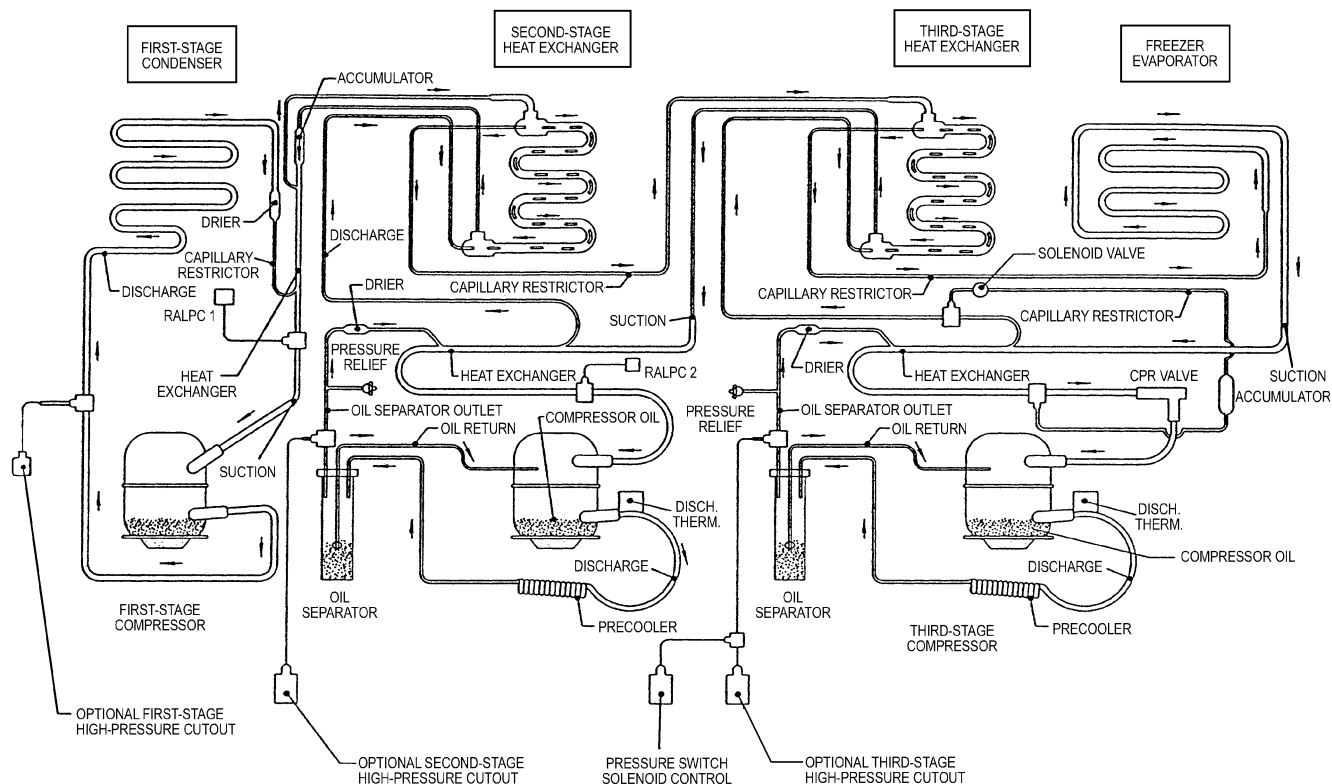**Fig. 5   Two-Stage Cascade System**

Fig. 6   Three-Stage Cascade System

Table 3   Theoretical Performance of a Cascade System Using R-13, R-503, R-23, or R-508b

	R-503	R-13	R-23	R-508b
Capacity (R-503 = 100)	100	71	74	98
Efficiency (R-503 = 100)	100	105	95	103
Discharge pressure, kPa	999	717	848	1013
Suction pressure, kPa	110	83	90	110
Discharge temperature, °C	107	92	138	87

Note: Operating conditions are −84.4°C evaporator, −35°C condenser; 5.6 K subcooling; −17.8°C suction temperature; 70% isentropic compression efficiency, 4% volumetric clearance.

Table 4   Theoretical Compressor Performance Data for Two Different Evaporating Temperatures

Refrigerant	Evaporating Temperature, °C	Pressure Ratio	Discharge Temperature, °C	Volumetric Flow, L/s per kW
R-23	−80	7.49	58	1.10
R-508b	−80	6.51	32	0.866
R-23	−100	26.88	72	3.85
R-508b	−100	21.88	39	2.94

Basis: −35°C condensing temperature; compressor efficiency of 70%; volumetric efficiency of 100%; 10 K subcooling, and 50 K suction superheat.

and (4) refrigeration system design. Original equipment manufacturers and compressor suppliers should be consulted.

It has been long-standing practice in the low-temperature industry to use additives to enhance system performance, and this practice may be applied to R-508b. The miscibility of R-508b with certain polyol esters (POEs) is slightly better than the limited miscibility of R-13 and R-503 with mineral oil and alkylbenzene, which helps oil circulation at the low evaporator temperatures. Even with the increased miscibility, additives may enhance performance. Certain POE oils designed for use in very low temperature systems have been used successfully with R-508b in equipment retrofits. Compressor manufacturers and suppliers should be consulted before a final decision on the lubricants and any additives is made.

Compressors

Larger cascade systems typically use standard, positive-displacement compressors in the dual refrigeration system. The evaporator of the higher temperature refrigerant system serves as the condenser for the lower temperature refrigerant system. This permits rather normal application of the compressors on both systems in relation to the pressures, compression ratios, and oil and discharge temperatures within the compressors. However, several very important items must be considered for both the high and low sides of the cascade system in order to avoid operational problems. Commercially available compressors must be analyzed for both sides of the cascade system to determine the best combination for a suitable intermediate high-side evaporator/low-side condenser and minimum (or economical) system power usage.

High-Temperature Circuit. The higher temperature system is generally a single- or two-stage system using a commercial refrigerant (R-134a, R-22, R-404a, or R-717); evaporating temperature is approximately −23 to −45°C, and condensing is at normal ambient conditions. Commercially available reciprocating and screw compressors are suitable for this duty. If the compressor evaporating temperature is below −45°C, it becomes necessary to provide a suction-line heat exchanger to superheat the compressor suction gas to at least −43°C to avoid the low-temperature metal brittleness associated with lower temperatures at the compressor suction valve and body. Suction piping materials and the evaporator/condenser (evaporator side) must also be suitable for these low temperatures per American Society of Mechanical Engineers (ASME) code requirements.

The lubricant for the higher temperature system must be compatible with the refrigerant employed and suitable for the type of system, considering oil carryover and return from the evaporator and the low-temperature conditions within the evaporator.

Low-Temperature Circuit. The compressor for this duty may also be a standard refrigeration compressor, provided that the compressor suction gas is superheated to at least −43°C to avoid low-temperature metal brittleness. Operation is typically well within standard pressure, oil temperature, and discharge temperature limits. The refrigerant is usually R-23 or R-508b. Because the temperatures in the low side are below −45°C, all piping, valves, and vessels must be of materials in compliance with the ASME codes pertaining to these temperatures.

It may be difficult to obtain compressor rating data for low-temperature applications with these refrigerants because few actual test data are available, and the manufacturer may be reluctant to be specific. Therefore, the low side should not be designed too close to the required specification. A good practice is to calculate the actual volumetric flow rate to be handled by the compressor (at the expected superheat) to be certain that it can perform as required.

The capacity loss from the high superheat is more than recouped (for a net capacity gain) from the liquid subcooling obtained by the suction-line heat exchanger. In rare cases, it may be necessary to inject a small quantity of hot gas into the suction to ensure maximum suction temperature.

The lubricant selected for the low side of the cascade must be compatible with the specific refrigerant employed and also suitable for the low temperatures expected in the evaporator. It is important that adequate coalescing oil separation (5 ppm) is provided to minimize oil carryover from the compressor to the evaporator.

In direct-expansion evaporators, any oil is forced through the tubes, but the velocity in the return lines must be high enough to keep this small amount of oil moving back to the compressor. If the system has capacity control, then multiple suction risers or alternative design procedures may be required to prevent oil logging in the evaporator and ensure oil return. At these ultralow temperatures, it is imperative to select a lubricant that remains fluid and does not plate out on the evaporator surfaces, where it can foul heat transfer.

Choice of Metal for Piping and Vessels

The usual construction metal for use with thermal fluids is carbon steel. However, at temperatures below −29°C, carbon steel should not be used due to its loss of ductility. The designer should consider the use of 304 or 316 stainless steel because of their good low-temperature ductility. Another alternative is to use carbon steel that has been manufactured specifically to retain good ductility at low temperatures (Dow Corning USA 1993). For example,

Carbon steel	Down to −29°C
SA - 333 - GR1	−29 to −46°C
SA - 333 - GR7	−46 to −73°C
SA - 333 - GR3	−59 to −101°C
SA - 333 - GR6	To −46°C

LOW-TEMPERATURE MATERIALS

Choosing material for a specific low-temperature use is often a compromise involving several factors:

• Cost
• Stress level at which the product will operate
• Manufacturing alternatives
• Operating temperature
• Ability to weld and stress-relieve welded joints
• Possibility of excessive moisture and corrosion

• Thermal expansion and modulus of elasticity characteristics for bolting and connection of dissimilar materials
• Thermal conductivity and resistance to thermal shock

Effect of Low Temperature on Materials. When the piping and vessels are to contain refrigerant at low temperature, special materials must usually be chosen because of the effect of low temperature on material properties. Chemical interactions between the refrigerant and containment material must also be considered. Mechanical and physical properties, fabricability, and availability are some of the important factors to consider in selecting a material for low-temperature applications. Few generalizations can be made, except that decreased temperature increases hardness, strength, and modulus of elasticity. The effect of low temperatures on ductility and toughness can vary considerably between materials. With a decrease in temperature, some metals show an increase in ductility; others show an increase to some limiting low temperature, followed by a decrease at lower temperatures. Still other metals show a decrease in toughness and ductility as the temperature is decreased below room temperature.

The effect of temperature reduction on polymers depends on the type of polymer. Thermoplastic polymers, which soften when heated above their glass transition temperature T_g, become progressively stiffer and finally brittle at low temperatures. Thermosetting plastics, which are highly cross-linked and do not soften when heated, are brittle at ambient temperatures and remain so at lower temperatures. Elastomers (rubbers) are lightly cross-linked and stiffen like thermoplastics as the temperature is lowered, becoming fully brittle at very low temperatures.

Although polymers become brittle and may crack at low temperatures, their unique combination of properties—excellent thermal and electrical insulation capability, low density, low heat capacity, and nonmagnetic character—make them attractive for a variety of lower-temperature applications. At extremely low temperatures, all plastic materials are very brittle and have low thermal conductivity and low strength relative to metals and composites, so selection and use must be carefully evaluated.

Fiber composite materials have gained widespread use at low temperatures, despite their incorporation of components that are often by themselves brittle. A factor that must be considered in the use of composites is the possibility of **anisotropic** behavior, in which they exhibit properties with different values when measured along axes in different directions. Composites with aligned fibers are highly anisotropic.

Metals

The relation of tensile strength to temperature for metals commonly used for structural applications at low temperatures is shown in (Askeland 1994). The slopes of the curves indicate that the increase in strength with decrease in temperature varies among the different metals. However, tensile strength is not the best criterion for determining the suitability of a material for low-temperature service because most failures result from a loss of ductility.

Lower temperatures can have a dramatic effect on the **ductility** of metal; the effect depends to a large extent on crystal structure. Metals and alloys that are face-centered cubic (FCC) and ductile at ambient temperatures remain ductile at low temperatures. Metals in this category include aluminum, copper, copper-nickel alloys, nickel, and austenitic stainless steels. Metals and alloys that are body-centered cubic (BCC), such as pure iron, carbon steel, and many alloy steels, become brittle at low temperatures. Many BCC metals and alloys exhibit a ductile-to-brittle transition at lower temperatures (see 1020 steel in). This loss of ductility comes from a decrease in the number of operating slip systems, which accommodate dislocation motion. Hexagonal close-packed (HCP) metals and alloys occupy an intermediate place between FCC and BCC materials and may remain ductile or become brittle at low
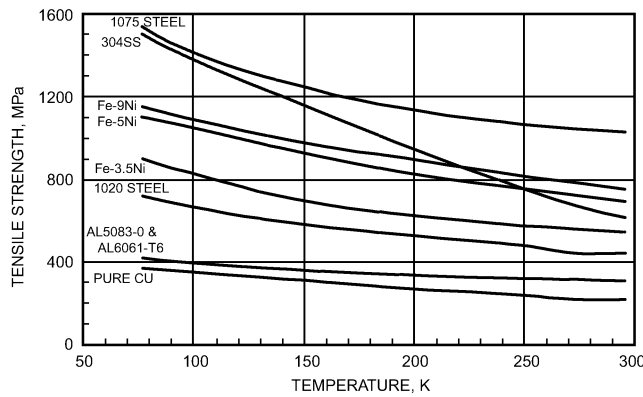
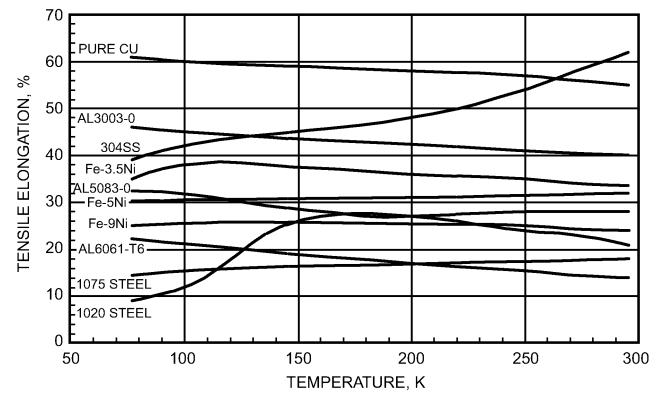**Fig. 7 Tensile Strength Versus Temperature of Several Metals**

Fig. 8 Tensile Elongation Versus Temperature of Several Metals

Table 5   Several Mechanical Properties of Aluminum Alloys at −196°C

Aluminum Alloy	Modulus of Elasticity, GPa	Yield Strength, MPa	Ultimate Tensile Strength, GPa	Percent Elongation at Failure, %	Plane Strain Fracture Toughness, MPa·m$^{1/2}$
1100-0	78	50	190	—	—
2219-T851	85	440	568	14	45
5083-0	80	158	434	32	62
6061-T651	77	337	402	23	42

temperatures. Zinc becomes brittle, whereas pure titanium (Ti) and many Ti alloys remain ductile.

Ductility values obtained from the **static tensile test** may give some clue to ductility loss, but the **notched-bar impact test** gives a better indication of how the material performs under dynamic loading and how it reacts to complex multidirectional stress. Figure 8 shows ductility, as measured by percent elongation in the tensile test, in relation to temperature for several metals. As temperature drops, the curves for copper and aluminum show an increase in ductility, while AISI 304 stainless steel and Ti-6%Al-4%V show a decrease.

Aluminum alloys are used extensively for low-temperature structural applications because of cost, weldability, and toughness. Although their strength is considered modest to intermediate, they remain ductile at lower temperatures. Typical mechanical properties at −196°C are listed in Table 5. Property values between ambient (21°C) and −196°C are intermediate between those at these temperatures.

Aluminum 1100 (relatively pure at 99% Al) has a low yield strength but is highly ductile and has a high thermal conductivity. It is used in nonstructural applications such as thermal radiation shields. For structural purposes, alloys 5083, 5086, 5454, and 5456 are often employed. Alloys such as 5083 have a comparatively high strength in the annealed (0) condition and can be readily welded with little loss of strength in the heat-affected zone; post-welding heat treatments are not necessary. These alloys are used in the storage and transportation areas. Alloy 3003 is widely used for plate-fin heat exchangers because it is easily brazed with an Al-7%Si filler metal. Aluminum-magnesium alloys (6000 series) are used as extrusions and forgings for such components as pipes, tubes, fittings, and valve bodies.

Copper alloys are rarely used for structural applications because of joining difficulties. Copper and its alloys behave similarly to aluminum alloys as temperature decreases. Strength is typically inversely proportional to impact resistance; high-strength alloys have low impact resistance. Silver soldering and vacuum brazing are the most successful methods for joining copper. Brass is useful for small components and is easily machined.

Nickel and **nickel alloys** do not exhibit a ductile-to-brittle transition as the temperature decreases and can be welded successfully, but their high cost limits use. High-strength alloys can be used at very low temperatures.

Iron-based alloys that are body-centered cubic usually exhibit a ductile-to-brittle transition as the temperature decreases. The BCC phase of iron is ferromagnetic and easily identified because it is attracted to a magnet. Extreme brittleness is often observed at lower temperatures. Thus, BCC metals and alloys are not normally used for structural applications at lower temperatures. Notable exceptions are iron alloys with a high nickel content.

Nickel and manganese are added to iron to stabilize the austenitic phase (FCC), promoting low-temperature ductility. Depending on the amount of Ni or Mn added, a great deal of low-temperature toughness can be developed. Two notable high-nickel alloys for use below ambient temperature include 9% nickel steel and austenitic 36% Ni iron alloy. The 9% alloy retains good ductility down to 100 K (−173°C). Below 100 K, ductility decreases slightly, but a clear ductile-to-brittle transition does not occur. Iron containing 36% Ni possesses the unusual feature of nearly zero thermal contraction during cooling from room temperature to near absolute zero. It is therefore an attractive metal for subambient use where the thermal stress associated with differential thermal contraction is to be avoided. Unfortunately, this alloy is quite expensive and therefore sees limited use.

Lesser amounts of Ni can be added to Fe to lower cost and depress the ductile-to-brittle transition temperature. Iron with 5% Ni can be used down to 150 K (−123°C), and Fe with 3.5% Ni remains ductile to 170 K (−102°C). The high-nickel steels are usually heat treated before use by water quenching from 800°C, followed by tempering at 580°C. The 580°C heat treatment tempers martensite formed during quenching and produces 10 to 15% stable austenite, which is responsible for the improved toughness of the product.

The austenitic stainless steels (300 series) are widely used for low-temperature applications. Many retain high ductility down to 4 K (−269°C) and below. Their attractiveness is based on good strength, stiffness, toughness, and corrosion resistance, but cost is high compared to that of Fe-C alloys. A stress relief heat treatment

is generally not required after welding, and impact strengths vary only slightly with decreasing temperature. A popular, readily available steel with moderate strength for low-temperature service is AISI type 304, with the low-carbon grade preferred. Where higher strengths are needed and welding can be avoided, strain-hardened or high-nitrogen grades are available. Castable austenitic steels are also available; a well-known example (14-17%Cr, 18-22%Ni, 1.75-2.75%Mo, 0.5%Si max, and 0.05%C max) retains excellent ductility and strength to extremely low temperatures.

Titanium alloys have high strength, low density, and poor thermal conductivity. Two alloys often used at low temperatures are Ti-5%Al-2.5%Sn and Ti-6%Al-4%V. The Ti-6-4 alloy has the higher yield strength, but it loses ductility below about 80 K (−193°C). The low-temperature properties are dramatically affected by oxygen, carbon, and nitrogen content. Higher levels of these interstitial elements increase strength but decrease ductility. Extra-low interstitial (ELI) grades containing about half the normal levels are usually specified for low-temperature applications. Both Ti-6-4 and Ti-5-2.5 are easily welded but expensive and difficult to form. They are used where a high strength-to-mass or strength-to-thermal conductivity ratio is attractive. Titanium alloys are not recommended for applications where an oxidation hazard exists.

Thermoplastic Polymers

Reducing the temperature of thermoplastic polymers restricts molecular motion (bond rotations and molecules sliding past one another), so that the material becomes less deformable. A rapid change in behavior normally takes place over a narrow temperature range beginning at the material's glass transition temperature T_g.

Figure 9 shows the general mechanical response of linear amorphous thermoplastics to temperature. At or above the melting temperature T_m, bonding between polymer chains is weak, the material flows easily, and the modulus of elasticity is nearly zero. Just below T_m, the polymer becomes rubbery; with applied stress, the material deforms by elastic and plastic strain. The combination of these deformations is related to the applied stress by the shear modulus. At still lower temperatures, the polymer becomes stiffer, exhibiting "leathery" behavior and a higher stress at failure. Many commercially available polymers (e.g., polyethylene) are used in this condition. T_g is located at the transition between the leathery and glassy regions. T_g is usually 0.5 to 0.75 times the absolute melting temperature T_m. Table 6 lists T_g and T_m values for common polymers. In the glassy state, at temperatures below T_g, the polymer is hard, brittle, and glass-like. Although polymers in the glassy region have poor ductility and formability, they are strong, stiff, and creep-resistant.

For thermoplastic polymers, the temperature at which stress is applied and the rate of stress application are interdependent based on time-temperature superposition. This relationship allows different types of tests, such as creep or stress relaxation, to be related through a single curve that describes the viscoelastic response of the material to time and temperature. Applying stress more rapidly has an effect equivalent to applying stress at lower temperatures.

Figure 10 shows tensile strength versus temperature for plastic and polymer composites.

Thermoplastic polymers such as polyethylene and polyvinyl chloride (PVC) may be used for plastic films and wire insulation but are not generally suitable for structural applications because of their brittle nature at temperatures below T_g. The only known polymer that exhibits appreciable ductility at temperatures substantially below T_g is polytetrafluoroethylene (PTFE). Because of their large thermal contraction coefficients, thermoplastic polymers should not be restrained during cool-down. Large masses should be cooled slowly to ensure uniform thermal contraction; the coefficient of thermal contraction decreases with temperature. Contractions of 1 to 2% in cooling from ambient to −196°C are common. For instance, nylon, PTFE, and polyethylene contract 1.3, 1.9, and 2.3%, respectively. These values are large compared to those for metals, which contract 0.2 to 0.3% over the same temperature range.

Table 6 Approximate Melting and Glass Transition Temperatures for Common Polymers

Polymer	Melting Temperature T_m		Glass Transition Temperature T_g	
	K	**°C**	**K**	**°C**
Addition polymers				
Low-density polyethylene	390	115	155	−120
High-density polyethylene	415	140	155	−120
Polyvinyl chloride	—	—	365	90
Polypropylene	445	170	260	−15
Polystyrene	—	—	380	105
Polytetrafluoroethylene	605	330	—	—
Polymethyl methacrylate (acrylic)	—	—	370	95
Condensation polymers				
6-6 Nylon	540	265	320	50
Polycarbonate	—	—	420	145
Polyester	530	255	350	75
Elastomers				
Silicone	—	—	150	−125
Polybutadiene	395	115	185	−90
Polychloroprene	355	80	220	−50
Polyisoprene	305	30	200	−70

Source: Askeland (1994). Derived from Table 15-2, p. 482.
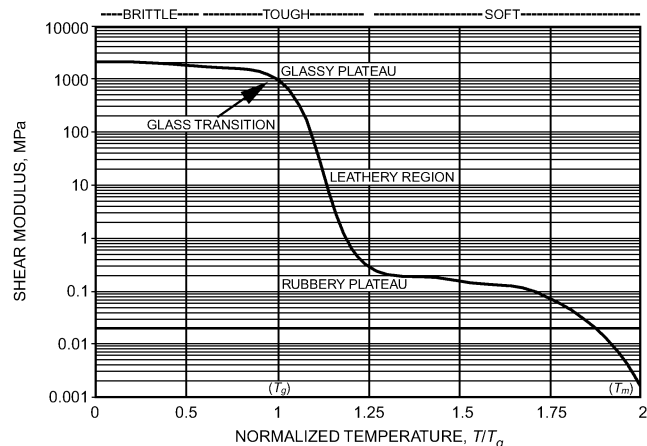

Fig. 9   Shear Modulus Versus Normalized Temperature (T/T_g) for Thermoplastic Polymers
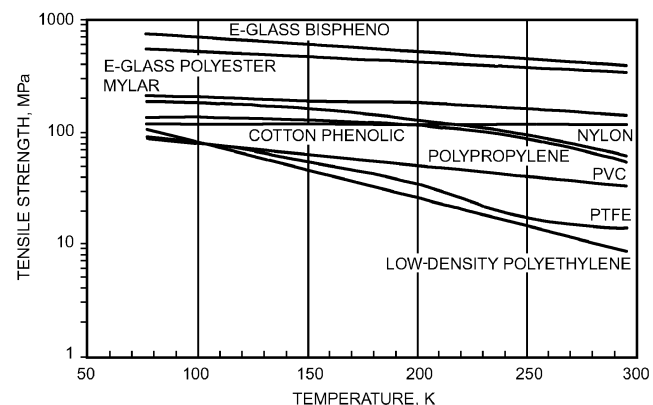

Fig. 10   Tensile Strength Versus Temperature of Plastics and Polymer Matrix Laminates

Thermosetting Plastics

Thermosetting plastics such as epoxy are relatively unaffected by changes in temperature. The materials as a class are brittle and generally used in compression and not tension. Care must be taken in changing their temperature to avoid thermally induced stress, which could lead to cracking. Adding particulate fillers such as silica (SiO_2) to thermosetting resins can increase elastic modulus and decrease strength. The main reasons for adding fillers are to reduce the coefficient of thermal expansion and to improve thermal conductivity. Filled thermosetting resins such as epoxy and polyester can be made to have coefficients of thermal expansion that closely match those of metal. Such materials may be used as insulation and spacers but are not generally used for load-bearing structural applications.

Fiber Composites

Nonmetallic filamentary reinforced composites have gained wide acceptance for low-temperature structural applications because they have good strength, low density, and low thermal conductivity. Nonmetallic insulating composites are usually formed by laminating together layers of fibrous materials in a liquid thermosetting resin such as polyester or epoxy. The fibers are often but not necessarily continuous; they can take the form of bundles, mats, yarns, or woven fabrics. The most frequently used fiber materials include glass, aramid, and carbon. The reinforcing fibers add considerable mechanical strength to otherwise brittle matrix material and can lower the thermal expansion coefficient to a value comparable to that of metals. High figures of merit (ratio of thermal conductivity to elastic modulus or strength) can reduce refrigeration costs substantially from those obtained with fully metallic configurations. Nonmetallic composites can be used for tanks, tubes, struts, straps, and overlays in low-temperature refrigeration systems. These materials perform well in high loading environments and under cyclic stress; they do not degrade chemically at low temperatures.

Different combinations of fiber materials, matrices, loading fractions, and orientations yield a range of properties. Material properties are often anisotropic, with maximum properties in the fiber direction. Failure of composites is caused by cracking in the matrix layer perpendicular to the direction of stress. The cracking may propagate along the fibers but does not generally lead to debonding. Maximum elongations at failure for glass-reinforced composites are usually 2 to 5%; the material is generally elastic all the way to failure.

A major advantage of using glass fibers with a thermosetting binder matrix is the ability to match thermal contraction of the composite to that of most metals. Aramid fibers produce laminates with lower density but higher cost. With carbon fibers, it is possible to produce components that show virtually zero contraction on cooling.

Typical tensile mechanical property data for glass-reinforced laminates are given in Table 7. Under compressive loading, strength and modulus values are generally 60 to 70% of those for tensile loading because of shrinkage of the matrix away from fibers and microbuckling of fibers.

Adhesives

Adhesives for bonding composite materials to themselves or to other materials include epoxy resins, polyurethanes, polyimides, and polyheterocyclic resins. Epoxy resins, modified epoxy resins (with nylon or polyamide), and polyurethanes apparently give the best overall low-temperature performance. The joint must be properly designed to account for the different thermal contractions of the components. It is best to have the adhesives operate under compressive loads. Before bonding, surfaces to be joined should be free of contamination, have uniform fine scale

Table 7 Tensile Properties of Unidirectional Fiber-Reinforced Composites

Composite	Test Temperature, °C	Tensile Strength, MPa	Tensile Modulus, GPa
E Glass (50%)			
Longitudinal	22	1050	41
	−196	1340	45
Transverse	22	9	11
	−196	8	12
Aramid fibers (63%)			
Longitudinal	25	1130	71
	−196	1150	99
Transverse	25	4.2	2.5
	−196	3.6	3.6

Source: Hands (1986). Table 11.3.

roughness, and preferably be chemically cleaned and etched. An even bond gap thickness of 0.1 to 0.2 mm is usually best.

INSULATION

Refrigerated pipe insulation, by necessity, has become an engineered element of the refrigeration system. The complexity and cost of this element now rival that of the piping system. This is especially true of systems operating at the depressed temperatures considered in this chapter.

Some factory-assembled, close-coupled systems that operate intermittently can function with a relatively simple installation of flexible sponge/foam rubber pipe insulation. Larger systems that operate continuously require much more investment in design and installation. Higher-technology materials and techniques, which are sometimes waived (at risk of invested capital) for systems operating at warmer temperatures, are critical for low-temperature operation. Also, the nature of the application does not usually permit shutdown for repair.

Pipe insulation systems are distinctly different from cold room construction. Cold room construction vapor leaks can be neutral if they reach equilibrium with the dehumidification effect of the refrigeration unit. Moisture entering the pipe insulation can only accumulate and form ice, destroying the insulation system. At these low temperatures, it is proper to have redundant vapor retarders (e.g., reinforced mastic plus membrane plus sealed jacket). Insulation should be multilayer to allow expansion and contraction, with inner plies allowed to slide and the outer ply joint sealed. Sealants are placed in the warmest location because they may not function properly at the lower temperature of inner plies. Insulation should be thick enough to prevent condensation (above dew point) at the outside surface.

The main components of a low-temperature refrigerated pipe insulation system are shown in Table 8.

HEAT TRANSFER

The heat-transfer coefficients of boiling and condensing refrigerant and the convection heat-transfer coefficients of secondary coolants are the most critical heat-transfer issues in low-temperature refrigeration. In a cascade system, for example, the heat-transfer coefficients in the high-temperature circuit are typical of other refrigeration applications at those temperatures. In the low-temperature circuit, however, the lower temperatures appreciably alter the properties of the refrigerant and therefore the boiling and condensing coefficients.

The expected changes in properties with a decrease in temperature are as follows. As the temperature drops,

- Density of liquid increases
- Specific volume of vapor increases

Table 8   Components of a Low-Temperature Refrigerated Pipe Insulation System

Insulation System Component	Primary Roles	Secondary Roles	Typical Materials
Insulation	Efficiently insulate the pipe Provide external hanger support	Limit water movement toward pipe Reduce rate of moisture/vapor transfer toward pipe Protect vapor retarder from external damage	Polyurethane-modified polyisocyanurate foams Extruded polystyrene foams Cellular glass
Elastomeric joint sealant	Limit liquid water movement through insulation cracks Reduce rate of moisture/vapor transfer toward pipe		Synthetic rubbers Resins
Vapor retarder	Severely limit moisture transfer toward pipe Eliminate liquid water movement toward pipe		Mastic/fabric/mastic Laminated membranes
Protective jacket	Protect vapor retarder from external damage Limit water movement toward pipe	Reduce moisture/vapor transfer toward pipe	Aluminum Stainless steel PVC
Protective jacket joint sealant	Prevent liquid water movement through gaps in protective jacket	Limit rate of moisture/vapor transfer toward pipe	
Vapor stops	Isolate damage caused by moisture penetration		Mastic/fabric/mastic

- Enthalpy of evaporation increases
- Specific heat of liquid decreases
- Specific heat of vapor decreases
- Viscosity of liquid increases
- Viscosity of vapor decreases
- Thermal conductivity of liquid increases
- Thermal conductivity of vapor decreases

In general, increases in liquid density, enthalpy of evaporation, specific heats of liquid and vapor, and thermal conductivity of liquid and vapor cause an increase in the boiling and condensing heat-transfer coefficients. Increases in specific volume of vapor and viscosities of liquid and vapor decrease these heat-transfer coefficients.

Data from laboratory tests or even field observations are scarce for low-temperature heat-transfer coefficients. However, heat-transfer principles indicate that in most cases lowering the temperature level at which the heat transfer occurs reduces the coefficient. The low-temperature circuit in a custom-engineered cascade system encounters lower temperature boiling and condensation than are typical of industrial refrigeration. In some installations, refrigerant boiling is within the tubes; in others, it is outside the tubes. Similarly, the designer must decide whether condensation at the cascade condenser takes place inside or outside the tubes.

Some relative values based on correlations in Chapter 4 of the ASHRAE Handbook—Fundamentals may help the designer determine which situations call for conservative sizing of heat exchangers. The values in the following subsections are based on changes in properties of R-22 because data for this refrigerant are available down to very low temperatures. Other halocarbon refrigerants used in the low-temperature circuit of the cascade system are likely to behave similarly. Predictions are complicated by the fact that in a process inside tubes, the coefficient changes constantly as the refrigerant passes through the circuit. For both boiling and condensing, temperature has a more moderate effect when the process occurs outside the tubes than when it occurs inside the tubes.

A critical factor in the correlations for boiling or condensing inside the tubes is the mass velocity G in g/(s·m^2). The relative values given in the following subsections are based on keeping G in the tubes constant. The result is that G drops significantly because the specific volume of vapor experiences the greatest rel-

Table 9   Overview of Some Secondary Coolants

Coolant	Flash Point, °C	Freezing Point, °C	Boiling Point, °C	Temperature at Which Viscosity > 10 mm^2/s
Polydimethyl-siloxane	46.7	−111.1	175	−60
d-Limonene	46.1	−96.7	154.4	−80
Diethylbenzene[a]	58	<−84	181	−80
Diethylbenzene[a]	58	−75	181	−70
Hydrofluoroether	not flamm.	−130	60	−30
Ethanol	12	−117	78	−60
Methanol	11	−98	64	−90

[a]Two proprietary versions containing different additives.

ative change of all the properties. As the vapor becomes less dense, the linear velocity can be increased and still maintain a tolerable pressure drop of the refrigerant through the tubes. So G would not drop to the extent used in the comparison below, and the reductions shown for tube-side boiling and condensing would not be as severe as shown.

Condensation Outside Tubes. Based on Nusselt's film condensation theory, the condensing coefficient at −20°C, a temperature that could be encountered in a cascade condenser, would actually be 17% higher than the condensing coefficient in a typical condenser at 30°C. The increase is due to higher latent heat, liquid density, and thermal conductivity. The penalizing influence of the increase in specific volume of vapor is not present because this term does not appear in the Nusselt equation.

Condensation Inside Tubes. Using the correlation of Ackers and Rosson (Table 3, Chapter 4 of the ASHRAE Handbook—Fundamentals) with a constant velocity and thus decreasing the value of G by one-fifth, the condensation coefficient at −20°C is one-fourth that at 30°C.

Boiling Inside Tubes. Using the correlation of Pierre [Equation (1) in Table 2, Chapter 4 of the ASHRAE Handbook—Fundamentals] and maintaining a constant velocity, when the temperature

Table 10   Refrigerant Properties of Some Low-Temperature Secondary Coolants

Temperature, °C	Viscosity, mPa·s	Density, kg/m³	Heat Capacity, kJ/(kg·K)	Thermal Conductivity, W/(m·K)
Polydimethylsiloxane[a]				
−100	78.6	978	1.52	0.1340
−90	33.7	968	1.54	0.1323
−80	20.1	958	1.56	0.1305
−70	13.3	948	1.58	0.1288
−60	9.4	937	1.60	0.1269
−50	6.4	927	1.62	0.1250
d-Limonene[b]				
−80	1.8	929.6	—	0.139
−70	1.7	921.0	—	0.137
−60	1.6	912.2	—	0.135
−50	1.5	903.5	1.39	0.133
Diethylbenzene[a, c]				
−90		Below Freezing Point		
−80	10.0	933.6	1.570	0.1497
−70	7.11	926.7	1.594	0.1475
−60	5.12	920.0	1.615	0.1454
−50	3.78	913.0	1.636	0.1435
Hydrofluoroether[d]				
−100	21.226	1814	0.933	0.093
−90	10.801	1788	0.954	0.091
−80	6.412	1762	0.975	0.089
−70	4.235	1737	0.992	0.087
−60	3.017	1711	1.013	0.085
−50	2.268	1686	1.033	0.083
Ethanol[e]				
−100	47.1	717.0	1.884	0.199
−90	28.3	726.0	1.918	0.198
−80	18.1	735.1	1.943	0.197
−70	12.4	744.1	1.964	0.195
−60	8.7	753.1	1.985	0.194
−50	6.4	762.2	2.011	0.192
Methanol[e]				
−100	16.1	720	2.178	0.224
−90	8.8	729	2.203	0.223
−80	5.7	738	2.228	0.222
−70	40.2	747	2.253	0.221
−60	2.98	756	2.278	0.220
−50	22.6	765	2.303	0.219
Acetone				
−94		Freezing point		
−90	—	—	1.996	0.150
−80	1.19	—	2.042	0.148
−70	0.89	—	2.008	0.146
−60	0.75	—	2.021	0.145
−50	0.75	—	2.029	0.143
20	—	791	—	—

Sources:
[a]Dow Corning USA (1993)
[b]Florida Chemical Co. (1994)
[c]Therminol LT (1992)
[d]3M Company (1996)
[e]Raznjevic (1997)

drops to −70°C, the boiling coefficient drops to 46% of the value at −20°C.

Boiling Outside Tubes. In a flooded evaporator with refrigerant boiling outside the tubes, the heat-transfer coefficient also drops as the temperature drops. Once again, the high specific volume of vapor is a major factor, restricting the ability of liquid to be in contact with the tube, which is essential for good boiling. Figure 4 in Chapter 4 (Perry 1950; Stephan 1963a, 1963b, 1963c) of the ASHRAE Handbook—Fundamentals shows that the heat flux has a dominant influence on the coefficient. For the range of temperatures presented for R-22, the boiling coefficient drops by 12% as the boiling temperature drops from −15°C to −41°C.

SECONDARY COOLANTS

Secondary coolant selection, system design considerations, and applications are discussed in Chapter 4 of this volume; properties of brines, inhibited glycols, halocarbons, and nonaqueous fluids are given in Chapter 21 of the ASHRAE Handbook—Fundamentals. The focus here is on secondary coolants for low-temperature applications in the range of −50 to −100°C.

An ideal secondary coolant should

- Have favorable thermophysical properties (high specific heat, low viscosity, high density, and high thermal conductivity)
- Be nonflammable, nontoxic, environmentally acceptable, stable, noncorrosive, and compatible with most engineering materials
- Possess a low vapor pressure

There are just a few fluids that meet such criteria, especially in the entire −50 to −100°C range. Some of these fluids are hydrofluoroether (HFE), diethylbenzene, d-limonene, polydimethylsiloxane, trichloroethylene, and methylene chloride. Table 9 provides an overview of these coolants. Table 10 gives refrigerant properties for the coolants at various low temperatures.

Polydimethylsiloxane, known as silicone oil, is environmentally friendly, nontoxic, and combustible and can operate in the whole range. Due to its high viscosity (greater than 10 mPa·s), its flow pattern is laminar at lower temperatures, which limits heat transfer.

d-Limonene is optically active terpene ($C_{10}H_{16}$) extracted from orange and lemon oils. This fluid can be corrosive and is not recommended for contact with some important materials (polyethylene, polypropylene, natural rubber, neoprene, nitrile, silicone, and PVC). Some problems with stability, such as increased viscosity with time, are also reported. Contact with oxidizing agents should be avoided. The values listed are based on data provided by the manufacturer in a limited temperature range. d-Limonene is a combustible liquid with a flash point of 46.1°C.

The synthetic aromatic heat transfer fluid group includes **diethylbenzene**. Different proprietary versions of this coolant contain different additives. In these fluids, the viscosity is not as strong a function of temperature. Freezing takes place by crystallization, similar to water.

Hydrofluoroether (1-methoxy-nonafluorobutane, $C_4F_9CH_3$), is a new fluid, so there is limited experience with its use. It is nonflammable, nontoxic, and appropriate for the whole temperature range. No ozone depletion is associated with its use, but its global warming potential is 500 and its atmospheric lifetime is 4.1 years.

The alcohols—**methanol and ethanol**—possess suitable low-temperature physical properties, but they are flammable and methanol is toxic, so their application is limited to industrial situations where these characteristics can be accommodated.

Another possibility for a secondary coolant is **acetone** (C_3H_6O).

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