4

Refrigerants

A refrigerant is any body or substance, which acts as a cooling agent by absorbing heat from another body or substance. With regard to the vapour compression cycle, the refrigerant is the working fluid of the cycle, which alternately vaporises and condenses as it absorbs and gives off heat. Theoretically, any reasonably volatile substance which is liquid at the temperature desired in the evaporator can be used as a refrigerant, but in practice the choice is limited by factors such as toxicity, cost, flammability, chemical stability, etc.

A *primary refrigerant* is one, which is used in a recirculating cycle and is accompanied by a change in state. During the cyclic process it undergoes compression, condensation, expansion, and evaporation. A *secondary refrigerant* is one, which is used as a heat transfer medium without a change of state but with a change in temperature. Chilled water used in a conventional air-conditioning plant and circulated through the air-cooling coils is an example of a secondary refrigerant. Figure 4.1 shows an air-conditioning system that uses both primary and secondary refrigerants.

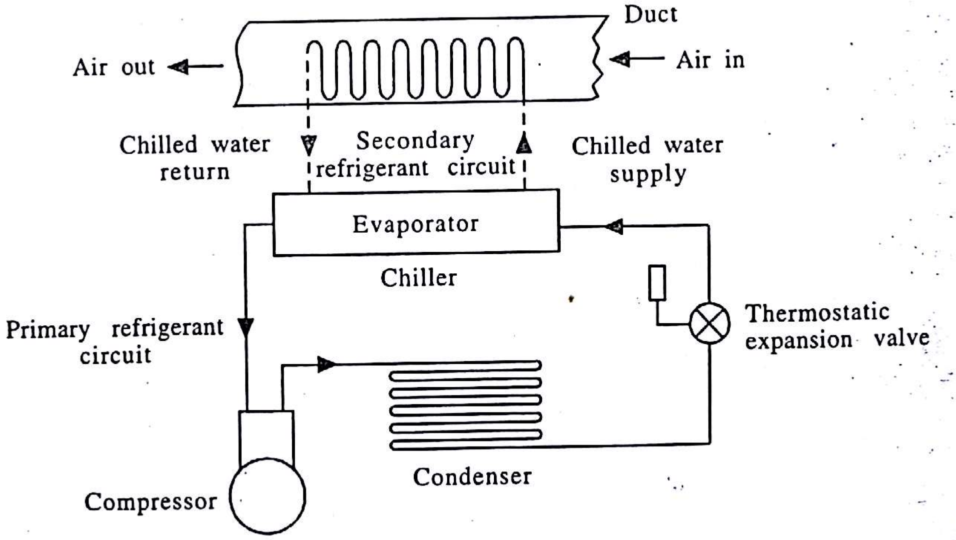

FIGURE 4.1 Air-conditioning system using both primary and secondary refrigerants.

4.1 CLASSIFICATION

Many refrigerants have been used over the years and some of them have become obsolete and since replaced by newer refrigerants. Some currently popular refrigerants are being phased out due to their damaging effect on ozone layer.

The generic classification of refrigerants is shown in Figure 4.2. Based on this classification, some of the popular refrigerants have been listed in Tables 4.1 to 4.4. The detailed properties of some of these refrigerants have been discussed at length later in this chapter.

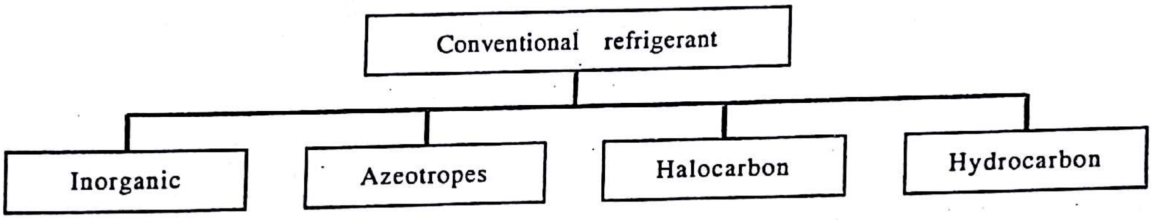

FIGURE 4.2 Classification of refrigerants.

TABLE 4.1 Halocarbon refrigerants

Designation	Chemical name	Chemical formula	Use	Remarks
R11	Trichloromonofluoromethane	CCl_3F	Air conditioning	
R12	Dichlrodifluoromethane	CCl_2F_2	Do	Being phased out
R22	Monochlorodifluoromethane	$CHClF_2$	Refrigeration and air conditioning	Still acceptable
R134a	Tetrafluoroethane	CF_3CH_2F	Air conditioning	Substituting R12
R40	Methyl chloride	CH_3Cl	Refrigeration	Obsolete

TABLE 4.2 Inorganic refrigerants

Designation	Chemical name	Chemical formula	Use	Remarks
R717	Ammonia	NH_3	Industrial refrigeration	Still popular
R718	Water	H_2O	Absorption cycles	–
R729	Air		Refrigeration and air conditioning	Still acceptable
R744	Carbon dioxide	CO_2	Marine refrigeration, Ice making	Discontinued
R764	Sulphur dioxide	SO_2	Air conditioning	Discontinued

TABLE 4.3 Hydrocarbon refrigerants

Designation	Chemical name	Chemical formula	Use	Remarks
R50	Methane	CH_4	No direct use	–
R170	Ethane	C_2H_6	Gas liquefaction	–
R290	Propane	$CH_3CH_2CH_3$	Gas liquefaction	–

TABLE 4.4 Common azeotropes

Group	Designation	Composition		Chemical formula	Use	Remarks
Azeotropes	R500	R12	73.8%	CCl_2F_2		–
		R115	26.2%	CH_3CHF_2		–
	R501	R22	75%	$CHClF_2$	Cascade systems	–
		R12	25%	CCl_2F_2		–
	R502	R22	48.8%	$CHClF_2$		–
		R115	51.2%	$CClF_2CF_3$		–

Halocarbon refrigerants, listed in Table 4.1, contain one or more of the three halogens—chlorine, fluorine, and bromine. These refrigerants are obtained by replacing one or more hydrogen atoms in a hydrocarbon molecule such as ethane or methane with the above-mentioned halogens. The halocarbon family is comprised of refrigerants which are non-flammable and most of them are non-toxic too. Thus a refrigerant can be found in this group to fit practically any application. Because of their overall performance, these اصطناعي synthetic refrigerants have replaced the classic refrigerants like NH_3, CO_2, and water etc. listed in Table 4.2.

However, in recent years some of the refrigerants in the halocarbon family have lost favour because of their negative impact on environmental issues. Because of their great stability, fully halogenated compounds, such as chlorofluorocarbons (**CFCs**) persist in the atmosphere for many years and eventually diffuse into the stratosphere. The molecules of CFCs, such as R11 and R12, contain only carbon and the halogens contain chlorine and fluorine. Once in the upper atmosphere, the CFC molecules break down releasing chlorine, which destroys ozone and causes **ozone depletion**. In the lower atmosphere, the CFC molecules absorb تحت الاحمر infrared radiation, which may contribute to the warming of the earth, i.e. **global warming**. Substitution of a hydrogen atom by one or more of the halogens in a CFC molecule greatly reduces its lifetime in atmosphere and consequently its negative impact. These compounds are referred to as hydrochlrofluorocarbons (**HCFCs**). The ozone depleting CFC refrigerants will be phased out as per the decision of the Montreal protocol, an international treaty.

Like halocarbon refrigerants, many *hydrocarbon refrigerants*, listed in Table 4.3, are suitable as refrigerants. They are commonly used as refrigerants in liquefaction of gases.

Azeotropes, listed in Table 4.4 are those mixtures of two or more substances which behave as if they were compounds, for they cannot be separated into their components by distillation. An azeotrope evaporates and condenses as a single substance with properties that are different from those of its constituents.

4.2 DESIRABLE PROPERTIES OF REFRIGERANTS

No single refrigerant satisfies all the attributes desired of a refrigerant for all operating conditions. So a refrigerant is chosen that has the greatest number of advantages and the least number of disadvantages for the specific application involved. Obviously, in most cases there must be a compromise. The best refrigerant for producing low temperatures is not necessarily the best one for producing moderate temperatures. Similarly, the refrigerant chosen for a reciprocating compressor is usually different from the one that is chosen for a centrifugal compressor.

The important properties that relate to the overall performance of a refrigeration system are tabulated in Table 4.5, followed by a review of some of the refrigerant properties which affect the refrigerant cycle performance.

TABLE 4.5 Comparative refrigerant performance per kilowatt of refrigeration[a]

Refrigerant		Evaporator pressure, MPa	Condenser pressure, MPa	Compression ratio	Net refrigerating effect, kJ/kg	Refrigerant circulated, kg/s	Liquid circulated, L/s	Specific volume of suction gas, m^3/kg	Compressor displacement, L/s	Power consumption, kW	Coefficient of performance	Comp. discharge temperature, K
No.	Chemical name or composition (% by mass)											
744	Carbon dioxide	2.291	7.208	3.15	134.24	0.00745	0.0123	0.0087	0.065	0.338	2.96	343
290	Propane	0.291	1.077	3.71	279.88	0.00357	0.0074	0.1542	0.551	0.211	4.74	320
502	R22/115 (48.8/51.2)	0.349	1.319	3.78	104.39	0.00958	0.0080	0.0500	0.479	0.226	4.43	310
22	Dichlorodifluromethane	0.296	1.192	4.03	162.46	0.00616	0.0053	0.0774	0.476	0.210	4.75	326
717	Ammonia	0.236	1.164	4.94	1102.23	0.00091	0.0015	0.5106	0.463	0.207	4.84	371
500	R12/152a (73.8/26.2)	0.214	0.879	4.11	140.95	0.00709	0.0062	0.0938	0.665	0.213	4.69	314
12	Dichlorodifluoromethane	0.183	0.745	4.07	116.58	0.00858	0.0066	0.0914	0.784	0.213	4.69	311
134a	Tetrafluoroethane	0.160	0.770	4.81	150.71	0.00664	0.0056	0.1224	0.812	0.226	4.42	316
600	Butane	0.056	0.283	5.05	292.01	0.00342	0.0060	0.6641	2.274	0.214	4.68	318

Adapted by permission from *ASHRAE Fundamentals* 1989. Notes: [a]Based on 258 K evaporation and 303 K condensation.

Evaporator and condenser pressure

It is desirable that both these pressures be positive, yet not too high above the atmospheric pressure. Positive pressure prevents leakage of air and moisture into the system and also makes it easier to detect leaks. The pressure at which the refrigerant vapour will condense at ordinary air or water temperatures should be low. A high condensing pressure would require heavy material for compressors, piping and coils, and also increase the tendency to leakage.

Critical temperature

High critical temperature is desirable as it is impossible to condense the refrigerant at a temperature above the critical, no matter how much the pressure is increased. The critical temperature of all refrigerants except CO_2 is sufficiently high and such refrigerants, therefore, present no problem. In the case of CO_2 the pressure at the end of compression would be too large, necessitating heavy construction to withstand such high pressure. The critical temperatures and pressures of some common refrigerants are listed in Table 4.6.

TABLE 4.6 Critical temperature and pressure of various refrigerants

Refrigerants	Critical temperature (°C)	Critical pressure in bar
R11	197.96	44.0
R12	111.78	41.24
R22	96.14	49.90
R134a	101.03	40.56
R502	82.20	40.75
NH_3	132.22	113
H_2O	373.99	220
CO_2	30.98	74
CH_4	190.55	45.9

Boiling and freezing temperatures

A refrigerant should have a low boiling temperature, otherwise it would become necessary to operate the compressor at high vacuums with the resulting lowered efficiency and capacity. The refrigerant chosen must have a freezing point well below any temperature that would be encountered in operation.

Density

Low refrigerant densities are usually preferable, since they permit the use of small suction and discharge lines without excessive pressure drops. For larger capacity machines, however, a high vapour density is desirable since this results in a need for a smaller compressor and a smaller gas piping.

Latent heat of vaporization

A high latent heat at the evaporator temperature is desirable because it is usually associated with a high refrigerating effect per unit mass of refrigerant circulated. The values of enthalpy of vaporization of a number of common refrigerants are listed in Table 4.7.

TABLE 4.7 Enthalpy of vaporization at 1 atmosphere pressure (1.01 bar)

Refrigerant	Saturation temperature (°C) at 1 atm.	Enthalpy of vaporisation (kJ/kg)
R11	23.71	181.36
R12	–29.80	165.91
R22	–40.80	233.79
R134a	–26.07	216.83
R114	3.6	131.45
R502	–45.42	172.48
R717	–33.33	1369
R744	–78.4	571.5
R718	100	2257

جمود / خمول.

Stability and inertness

تفكك يواجه

An ideal refrigerant should not decompose at any temperature normally encountered. Disintegration of refrigerants may result in non-condensable gases in the system as well as sludge.

Corrosive properties

The refrigerant should not react with any of the materials normally used in system construction. Any such reaction would lead to corrosion products, contaminating the system and possibly resulting in leakages.

Specific volume

A refrigerant should have low volume per kg when in gaseous state. This not only reduces the size of the equipment but also means higher compressor efficiency. Figure 4.3 shows the relative displacement volume required by different refrigerants. As high displacement volume of

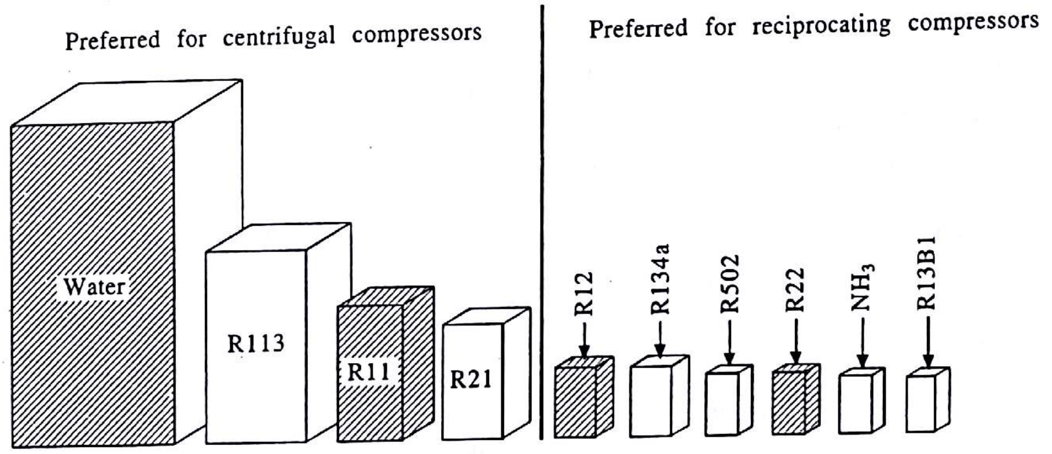

FIGURE 4.3 Graphic representation of displacement volume required by different refrigerants.

refrigerants is desirable for centrifugal compressors, the refrigerants shown on the left-hand side of the vertical line are preferred for this duty. Likewise, the refrigerants on the right of the vertical line are desirable for use in reciprocating compressors.

Viscosity

It is desirable that both the liquid and the vapour refrigerants have low viscosities because of the lower pressure drops in passing through liquid and suction lines. Heat transfer is also improved in the evaporator and the condenser due to low viscosity.

Thermal conductivity

For efficient use of evaporator and condenser surfaces, a refrigerant should possess a high value of thermal conductivity.

Dielectric strength

The electrical resistance of a refrigerant is important if it is to be used in a hermetically sealed unit with the motor exposed to the refrigerant.

Oil effect and miscibility with oil

The refrigerant should have no chemical reaction with the lubricating oil. Such reaction would modify the lubricating properties, and hence, affect lubrication. Certain reactions can even acidify oils. As regards miscibility, oil miscible refrigerants are advantageous in that they give better lubrication because the refrigerant acts as a carrier of oil to the moving parts. They also eliminate oil separation problems and aid in the return of oil from the evaporator.

السمية الانفجار

Toxicity and explosive properties

غير سام غير متهيج

The refrigerant should be non-poisonous and non-irritating. In any air-conditioning application, particularly, there should be no odour. An ideal refrigerant should present no danger of explosion or fire, either in combination with air or in association with lubricating oil.

القابل للتلف

Effects on perishable products

In case of leakage, an ideal refrigerant should have no effect on any perishable materials with which it may come into contact.

Leak detection

قابل

A leak should be susceptible to detection by some mechanical or chemical means. The detection of leaks just by odour can be very dangerous as well as deceiving.

خداع

Cost

In very small plants requiring a small charge of refrigerant, the cost factor is unimportant. But the cost factor assumes significance in large plants, and the tightness of the construction and leakage minimization are looked after with much care. The rate of leakage is inversely proportional to the square root of molecular weight. It also depends on the pressure differential, velocity, density, and capillarity.

4.3 COMMON REFRIGERANTS

The characteristics and properties of a number of commonly used refrigerants are discussed below.

Ammonia

Ammonia is one of the oldest and most widely used of all refrigerants. It is extensively used in large refrigeration plants such as ice plants, breweries بيرة, and industrial processing plants. Ammonia gives a large amount of refrigeration per cubic metre of compressor displacement, which results in low compressor cost. The cost of ammonia itself is less than that of any refrigerant except that of carbon dioxide and water. Ammonia is a low-density refrigerant which creates smaller pressure drops for a given size line. For these reasons, an ammonia system is the most economical system available for large-sized reciprocating refrigerating systems. The freezing point of ammonia, –60°C, is low enough so that there is no problem with ordinary refrigeration temperatures. The odour of ammonia gives instant warning of a leak. A small amount of sulphur dioxide causes a dense white smoke to appear at an ammonia leak, indicating the source of leak. Sulphur candles made of wood or metal pieces dipped in molten sulphur are used for leak detection.

Against the above-mentioned advantages, ammonia is highly toxic and highly irritating. Ammonia is flammable in mixtures of between 16 and 25 per cent in air. Because of its affinity for water, it is difficult to keep ammonia perfectly dry. When ammonia contain any water, it is corrosive to copper and most copper alloys. Accordingly, copper, brass or bronze should not be used in pipes, fittings and bearings in ammonia systems.

At high discharge temperature of ammonia, unless controlled, discharge temperatures can carbonize or otherwise damage lubricating oil. At the high discharge temperatures generated by ammonia, there is a tendency for ammonia to dissociate, i.e. breakdown into its constituents of nitrogen and hydrogen. These gases, unless disposed off, collect in the condenser. Their pressures are added to the normal condensing pressure, which increases the total head pressure and power required. Because of high discharge temperatures, the cylinders of ammonia compressors are water-jacketed. Water-cooling is necessary to keep the cylinder walls cool enough to make satisfactory lubrication possible.

In spite of these disadvantages, ammonia gives excellent economical service in large compression refrigeration systems when the systems are under the supervision of competent مختص operating personnel. Ammonia is used fairly extensively in semi-automatic and automatic refrigeration plants like cold stores, fish freezing plants, etc. Because of the negative impact of CFC refrigerants on the environment, the industry is showing renewed تجديد interest in environmentally safe refrigerants like ammonia.

Carbon dioxide

Carbon dioxide is one of the first refrigerants to be used in mechanical refrigerating systems. It is odourless, non-toxic, non-flammable, non-explosive, and non-corrosive. Because of its safe properties, it has been widely used in the past for marine service and for air conditioning in hospitals, theatres, and hotels and in other places where safety is the prime consideration. At the present time, the use of carbon dioxide is limited to some extremely low temperature applications, particularly in the production of dry ice, i.e. solid CO_2.

One of the main disadvantages of carbon dioxide is its high operating pressure, which under standard conditions of –15°C and 30°C is 22.2 bar and 71 bars respectively. The high suction pressure gives a small piston displacement resulting in smaller compressors, but this requires the use of extra heavy equipment and piping. Normal condensing temperatures are near the critical temperature of 31°C for carbon dioxide. This leads to excessive power costs, nearly three times those of other refrigerants. Carbon dioxide is non-miscible in oil and, therefore, does not dilute the oil in the crankcase of the compressor. Like ammonia, carbon dioxide is lighter than oil.

Next to water, carbon dioxide is the cheapest refrigerant. But its high pressure, and the difficulty in leak detection, results in higher replacement cost compared to that associated with ammonia. Because of these disadvantages, carbon dioxide was replaced when other safe refrigerants became available. Leak detection is carried out by soap solution only.

Water

The principal advantage of water as a refrigerant is its availability at virtually no cost. Another obvious advantage of water is that it is non-toxic and non-flammable. The two disadvantages of water are its high freezing point and high vacuum required. The very large volume of water vapour at such low operating pressures makes the use of ordinary compression equipment impossible.

In the past the steam-jet system with water as the refrigerant has had some use in large air-conditioning systems. The lithium bromide absorption refrigeration system, using water as refrigerant, is extensively used in large air-conditioning applications.

Sulphur dioxide

Sulphur dioxide was the most used domestic refrigerant in the 1920s and 1930s, having been replaced first by methyl chloride and later by the more desirable fluorocarbon refrigerants. It is highly toxic, but non-flammable and nonexplosive. As sulphur dioxide is not oil miscible, it simplifies the problem of oil return, which accounts for the relative popularity of sulphur dioxide for small automatic equipment used in the earlier days.

Like most common refrigerants, sulphur dioxide in the pure state is non-corrosive to metals normally used in the refrigerating systems. However, it combines with moisture to form sulphurous acids (H_2SO_3) and sulphuric acid (H_2SO_4), both of which are highly corrosive.

Methyl chloride

Methyl chloride is a halocarbon of the methane series. It has many of the properties desirable in a refrigerant, which accounts for its wide use in the past in both domestic and commercial applications. Methyl chloride is corrosive to aluminium, zinc, magnesium and the compounds formed in combinations with these materials. It is also both flammable and explosive. In the presence of moisture, methyl chloride forms a weak hydrochloric acid, which is corrosive to both ferrous and non-ferrous metals. Since natural rubber and synthetic neoprene are dissolved by methyl chloride, neither is a suitable gasket material for use in methyl chloride systems.

يأكل
النيوبرين الصناعي
الحديدية
لا يوجد

Halocarbon refrigerants

Due to limitations of the other refrigerants, studies were made to investigate the possibility of using synthetic chemicals as refrigerants. The outcome of these studies was the development of the halocarbon group of refrigerants. The refrigerants of this group are non-flammable and most of them are non-toxic. They are available with evaporating temperature at atmospheric pressure from approximately 100°C below zero to 100°C above zero. Thus, a refrigerant can be chosen from this group that will fit practically any application.

All refrigerants in this family are derivatives of the hydrocarbons, methane and ethane. Refrigerants of this family are called halogenated hydrocarbons, or more simply halocarbons, because chlorine and fluorine are part of a family of chemicals called halogens.

Leaks in halocarbon systems may be detected in two ways—by a special torch or by an electronic leak detector. The presence of any halogen will change the colour of a blue gas flame in the presence of copper to green or purple. Another halogen leak detection device depends on a cell whose electrical characteristics change in the presence of halocarbon gases. A change in electric current through this cell triggers a relay, which operates a light or buzzer to indicate a leak. One unsafe characteristic of all halocarbons is, that they break down at high temperature to give very irritating and toxic compounds. The temperature at which this happens is high enough and does not occur in an operating system.

Refrigerant-11 (CCl_3F): It is non-corrosive, non-toxic and non-flammable refrigerant. The low operating pressures and the relatively high compressor displacement required necessitate the use of a centrifugal compressor. Like other fluorocarbon refrigerants, Refrigerant-11 dissolves natural rubber. Refrigerant-11 is used mainly in the air-conditioning of small office buildings, factories, stores, theatres, etc. A halide torch may be used for leak detection.

Refrigerant-12: It has been by far the most widely used refrigerant until recent years. It is a completely safe refrigerant in that it is non-toxic, non-flammable, and non-explosive. Moreover, it is a highly stable compound and, therefore, difficult to break down even under extreme operating conditions. Refrigerant-12 condenses at moderate pressures under normal atmospheric conditions and is a suitable refrigerant for use in high, medium and low temperature applications and with all the three types of compressors. Refrigerant-12 is oil miscible under all operating conditions that not only simplifies the problem of oil return but also tends to increase the efficiency and capacity of the system. The horsepower required per kilowatt of capacity compares favourably with that required for other commonly used refrigerants. However, this refrigerant is being phased out because of its damaging effect on ozone layer.

Refrigerant-22: This refrigerant was developed primarily as a low temperature refrigerant and it is extensively used in domestic and farm freezers and in commercial and industrial low temperature systems down to evaporator temperatures as low as –70°C. It is also widely used in packaged air conditioners, where, because of space limitations, the relatively small compressor displacement required is a definite advantage. Both the operating pressures and the adiabatic discharge temperature are higher for Refrigerant-22 than for Refrigerant-12. Horsepower requirements are approximately the same. Although miscible with oil at temperatures prevailing in the condensing sections, Refrigerant-22 will often separate from the oil in the evaporator. With proper piping design this problem may be surmounted. Oil separators should always be used in low temperature applications.

The ability of Refrigerant-22 to absorb moisture is considerably greater than that of Refrigerant-12 and therefore less trouble is experienced with freeze ups in Refrigerant-22 systems. Being a fluorocarbon, Refrigerant-22 is a safe refrigerant. A halide torch may be used for leak detection. This refrigerant is also being phased out.

Refrigerant-134a: Due to phasing out of Refrigerant-12, which was the most widely used refrigerant up to recent years, there was frantic search for a suitable replacement. At this point in time, R134a is considered to be the most direct substitute for R12 and as a replacement in higher temperature applications. Its net refrigerating effect (based on –15°C evaporator and 30°C condenser temperature) is 151 kJ/kg against 116.58 kJ/kg for R12.

BIBLIOGRAPHY

American Society of Heating, Refrigerating and Air-Conditioning Engineers, *ASHRAE Handbook of Fundamentals*, 1993.

American Society of Heating, Refrigerating and Air-Conditioning Engineers, *ASHRAE Handbook of Fundamentals*, 1997.

ASHRAE Standard 62-1989, *Ventilation for Acceptable Indoor Air Quality*, Atlanta: American Society of Heating, Refrigerating and Air Conditioning Engineers.

Chemical Engineer's Handbook, 5th edition, 1973. McGraw-Hill, New York.

McLinden M.O., Thermodynamic properties of CFC alternatives: A survey of available data, *Int. Journal of Refrigeration*, Vol. **13**, May, 1990.

Sand, J.R. et al., Experimental performance of ozone-safe alternative refrigerants, *ASHRAE Transactions, Part 2*, Vol. **96**, pp. 173–182, 1990.

Stewart, R.B., R.T. Jacobse, and S.G. Penoncello, *ASHRAE Thermodynamic properties of refrigerants*, ASHRAE, 1986.

REVIEW EXERCISES

4.1 Describe the desirable and undesirable features of ammonia for use as a refrigerant.

4.2 Why is it that most of the currently popular halocarbon refrigerants are being phased out?

4.3 What piping material would you recommend for ammonia systems?

4.4 What is an azeotrope? Which popular halocarbon refrigerant is an azeotrope? For what reason it is often used instead of R22?

4.5 Why are positive condenser and evaporator pressures desirable?

4.6 Briefly describe the damages done to ozone layers by chlorofluorocarbon (CFC) refrigerants.