Lesson 26

Refrigerants

The specific objectives of this lecture are to:

1. Discuss the importance of selection of suitable refrigerant in a refrigeration system (*Section 26.1*)
2. Classify refrigerants into primary and secondary, and discuss the important differences between primary and secondary refrigerants (*Section 26.2*)
3. Discuss refrigerant selection criteria based on thermodynamic, thermophysical, environmental and economic properties (*Section 26.3*)
4. Describe the numbering system used for designating refrigerants (*Section 26.4*)
5. Present a comparison between different refrigerants (*Section 26.5*)

At the end of the lecture, the student should be able to:

1. Explain the importance of refrigerant selection
2. Differentiate between primary and secondary refrigerants
3. List the criteria used in selecting refrigerants
4. List important thermodynamic and environmental properties influencing refrigerant selection
5. Write the chemical formula of a refrigerant from its number
6. Compare different refrigerants and suggest replacements for CFCs and HCFCs

26.1. Introduction:

The thermodynamic efficiency of a refrigeration system depends mainly on its operating temperatures. However, important practical issues such as the system design, size, initial and operating costs, safety, reliability, and serviceability etc. depend very much on the type of refrigerant selected for a given application. Due to several environmental issues such as ozone layer depletion and global warming and their relation to the various refrigerants used, the selection of suitable refrigerant has become one of the most important issues in recent times. Replacement of an existing refrigerant by a completely new refrigerant, for whatever reason, is an expensive proposition as it may call for several changes in the design and manufacturing of refrigeration systems. Hence it is very important to understand the issues related to the selection and use of refrigerants. In principle, any fluid can be used as a refrigerant. Air used in an air cycle refrigeration system can also be considered as a refrigerant. However, in this lecture the attention is mainly focused on those fluids that can be used as refrigerants in vapour compression refrigeration systems only.

26.2. Primary and secondary refrigerants:

Fluids suitable for refrigeration purposes can be classified into primary and secondary refrigerants. Primary refrigerants are those fluids, which are used directly as working fluids, for example in vapour compression and vapour absorption refrigeration systems. When used in compression or absorption systems, these fluids provide refrigeration by undergoing a phase change process in the evaporator. As the name implies, secondary refrigerants are those liquids, which are used for transporting thermal energy from one location to other. Secondary refrigerants are also known under the name brines or antifreezes. Of course, if the operating temperatures are above 0^oC, then pure water can also be used as secondary refrigerant, for example in large air conditioning systems. Antifreezes or brines are used when refrigeration is required at sub-zero temperatures. Unlike primary refrigerants, the secondary refrigerants do not undergo phase change as they transport energy from one location to other. An important property of a secondary refrigerant is its freezing point. Generally, the freezing point of a brine will be lower than the freezing point of its constituents. The temperature at which freezing of a brine takes place its depends on its concentration. The concentration at which a lowest temperature can be reached without solidification is called as eutectic point. The commonly used secondary refrigerants are the solutions of water and ethylene glycol, propylene glycol or calcium chloride. These solutions are known under the general name of brines.

In this lecture attention is focused on primary refrigerants used mainly in vapour compression refrigeration systems. As discussed earlier, in an absorption refrigeration system, a refrigerant and absorbent combination is used as the working fluid.

26.3. Refrigerant selection criteria:

Selection of refrigerant for a particular application is based on the following requirements:

i. Thermodynamic and thermo-physical properties
ii. Environmental and safety properties, and
iii. Economics

26.3.1. Thermodynamic and thermo-physical properties:

The requirements are:

a) Suction pressure: At a given evaporator temperature, the saturation pressure should be above atmospheric for prevention of air or moisture ingress into the system and ease of leak detection. Higher suction pressure is better as it leads to smaller compressor displacement

b) Discharge pressure: At a given condenser temperature, the discharge pressure should be as small as possible to allow light-weight construction of compressor, condenser etc.

c) Pressure ratio: Should be as small as possible for high volumetric efficiency and low power consumption

d) Latent heat of vaporization: Should be as large as possible so that the required mass flow rate per unit cooling capacity will be small

The above requirements are somewhat contradictory, as the operating pressures, temperatures and latent heat of vaporization are related by Clausius-Clapeyron Equation:

$$\ln(P_{sat}) = -\frac{h_{fg}}{RT} + \frac{s_{fg}}{R} \qquad (26.1)$$

In the above equation, P_{sat} is the saturation pressure (in atm.) at a temperature T(in Kelvin), h_{fg} and s_{fg} are enthalpy and entropy of vaporization and R is the gas constant. Since the change in entropy of vaporization is relatively small, from the above equation it can be shown that:

$$\frac{P_c}{P_e} = \exp\left[\frac{h_{fg}}{R}\left(\frac{1}{T_e} - \frac{1}{T_c}\right)\right] \tag{26.2}$$

In the above equation, P_c and P_e are the condenser and evaporator pressures, T_c and T_e are condenser and evaporator temperatures. From the above equation, it can be seen that for given condenser and evaporator temperatures as the latent heat of vaporization increases, the pressure ratio also increases. Hence a trade-off is required between the latent heat of vaporization and pressure ratio.

In addition to the above properties; the following properties are also important:

e) Isentropic index of compression: Should be as small as possible so that the temperature rise during compression will be small

f) Liquid specific heat: Should be small so that degree of subcooling will be large leading to smaller amount of flash gas at evaporator inlet

g) Vapour specific heat: Should be large so that the degree of superheating will be small

h) Thermal conductivity: Thermal conductivity in both liquid as well as vapour phase should be high for higher heat transfer coefficients

i) Viscosity: Viscosity should be small in both liquid and vapour phases for smaller frictional pressure drops

The thermodynamic properties are interrelated and mainly depend on normal boiling point, critical temperature, molecular weight and structure.

The normal boiling point indicates the useful temperature levels as it is directly related to the operating pressures. A high critical temperature yields higher COP due to smaller compressor superheat and smaller flash gas losses. On the other hand since the vapour pressure will be low when critical temperature is high, the volumetric capacity will be lower for refrigerants with high critical temperatures. This once again shows a need for trade-off between high COP and high volumetric capacity. It is observed that for most of the refrigerants the ratio of normal boiling point to critical temperature is in the range of 0.6 to 0.7. Thus the normal boiling point is a good indicator of the critical temperature of the refrigerant.

The important properties such as latent heat of vaporization and specific heat depend on the molecular weight and structure of the molecule. Trouton's rule shows that the latent heat of vaporization will be high for refrigerants having lower molecular weight. The specific heat of refrigerant is related to the structure of the molecule. If specific heat of refrigerant vapour is low then the shape of the vapour dome will be such that the compression process starting with a saturated point terminates in the superheated zone (**i.e, compression process will be dry**). However, a small value of vapour specific heat indicates higher degree of superheat. Since vapour and liquid specific heats are also related, a large value of vapour specific heat results in a higher value of liquid specific heat, leading to higher flash gas losses. Studies show that in general the optimum value of molar vapour specific heat lies in the range of **40 to 100 kJ/kmol.K**.

The freezing point of the refrigerant should be lower than the lowest operating temperature of the cycle to prevent blockage of refrigerant pipelines.

26.3.2. Environmental and safety properties:

Next to thermodynamic and thermophysical properties, the environmental and safety properties are very important. In fact, at present the environment friendliness of the refrigerant is a major factor in deciding the usefulness of a particular refrigerant. The important environmental and safety properties are:

a) Ozone Depletion Potential (ODP): According to the Montreal protocol, the ODP of refrigerants should be zero, i.e., they should be non-ozone depleting substances. Refrigerants having non-zero ODP have either already been phased-out (e.g. R 11, R 12) or will be phased-out in near-future(e.g. R22). Since ODP depends mainly on the presence of chlorine or bromine in the molecules, refrigerants having either chlorine (i.e., CFCs and HCFCs) or bromine cannot be used under the new regulations

b) Global Warming Potential (GWP): Refrigerants should have as low a GWP value as possible to minimize the problem of global warming. Refrigerants with zero ODP but a high value of GWP (e.g. R134a) are likely to be regulated in future.

c) Total Equivalent Warming Index (TEWI): The factor TEWI considers both direct (due to release into atmosphere) and indirect (through energy consumption) contributions of refrigerants to global warming. Naturally, refrigerants with as a low a value of TEWI are preferable from global warming point of view.

d) Toxicity: Ideally, refrigerants used in a refrigeration system should be non-toxic. However, all fluids other than air can be called as toxic as they will cause suffocation when their concentration is large enough. Thus toxicity is a relative term, which becomes meaningful only when the degree of concentration and time of exposure required to produce harmful effects are specified. Some fluids are toxic even in small concentrations. Some fluids are mildly toxic, i.e., they are dangerous only when the concentration is large and duration of exposure is long. Some refrigerants such as CFCs and HCFCs are non-toxic when mixed with air in normal condition. However, when they come in contact with an open flame or an electrical heating element, they decompose forming highly toxic elements (e.g. phosgene-$COCl_2$). In general the degree of hazard depends on:

- Amount of refrigerant used vs total space
- Type of occupancy
- Presence of open flames
- Odor of refrigerant, and
- Maintenance condition

Thus from toxicity point-of-view, the usefulness of a particular refrigerant depends on the specific application.

e) Flammability: The refrigerants should preferably be non-flammable and non-explosive. For flammable refrigerants special precautions should be taken to avoid accidents.

Based on the above criteria, ASHRAE has divided refrigerants into six safety groups (A1 to A3 and B1 to B3). Refrigerants belonging to Group A1 (e.g. R11, R12, R22, R134a, R744, R718) are least hazardous, while refrigerants belonging to Group B3 (e.g. R1140) are most hazardous.

Other important properties are:

f) Chemical stability: The refrigerants should be chemically stable as long as they are inside the refrigeration system.

g) Compatibility with common materials of construction (both metals and non-metals)

h) Miscibility with lubricating oils: Oil separators have to be used if the refrigerant is not miscible with lubricating oil (e.g. ammonia). Refrigerants that are completely miscible with oils are easier to handle (e.g. R12). However, for refrigerants with limited solubility (e.g. R 22) special precautions should be taken while designing the system to ensure oil return to the compressor

i) Dilelectric strength: This is an important property for systems using hermetic compressors. For these systems the refrigerants should have as high a dielectric strength as possible

j) Ease of leak detection: In the event of leakage of refrigerant from the system, it should be easy to detect the leaks.

26.3.3. Economic properties:

The refrigerant used should preferably be inexpensive and easily available.

26.4. Designation of refrigerants:

Figure 26.1 shows the classification of fluids used as refrigerants in vapour compression refrigeration systems. Since a large number of refrigerants have been developed over the years for a wide variety of applications, a numbering system has been adopted to designate various refrigerants. From the number one can get some useful information about the type of refrigerant, its chemical composition, molecular weight etc. All the refrigerants are designated by R followed by a unique number.

i) Fully saturated, halogenated compounds: These refrigerants are derivatives of alkanes (C_nH_{2n+2}) such as methane (CH_4), ethane (C_2H_6). These refrigerants are designated by R XYZ, where:

X+1 indicates the number of Carbon (C) atoms

Y-1 indicates number of Hydrogen (H) atoms, and

Z indicates number of Fluorine (F) atoms

The balance indicates the number of Chlorine atoms. Only 2 digits indicates that the value of X is zero.

Ex: R 22

$X = 0 \Rightarrow$ No. of Carbon atoms = 0+1 = 1 $\Rightarrow$ derivative of methane (CH_4)

$Y = 2 \Rightarrow$ No. of Hydrogen atoms = 2-1 = 1

$Z = 2 \Rightarrow$ No. of Fluorine atoms = 2

The balance = 4 – no. of (H+F) atoms = 4-1-2 = 1 $\Rightarrow$ No. of Chlorine atoms = 1

$\therefore$ The chemical formula of R 22 = $CHClF_2$

Similarly it can be shown that the chemical formula of:

R12	=	CCl_2F_2
R134a	=	$C_2H_2F_4$ (derivative of ethane)

(letter a stands for isomer, e.g. molecules having same chemical composition but different atomic arrangement, e.g. R134 and R134a)

ii) Inorganic refrigerants: These are designated by number 7 followed by the molecular weight of the refrigerant (rounded-off).

Ex.: Ammonia:	Molecular weight is 17, $\therefore$ the designation is R 717
Carbon dioxide:	Molecular weight is 44, $\therefore$ the designation is R 744
Water:	Molecular weight is 18, $\therefore$ the designation is R 718

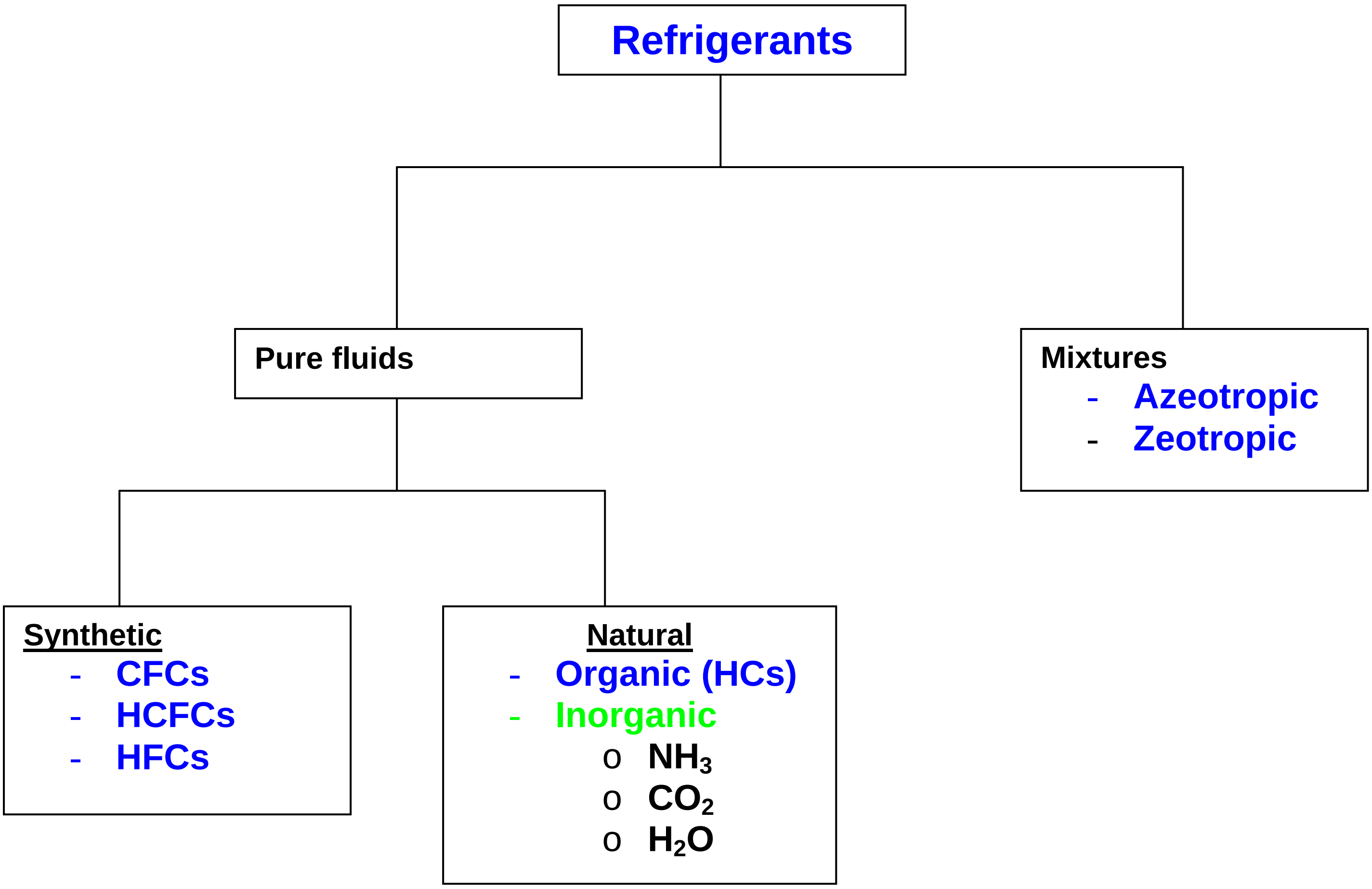

Fig.26.1*: Classification of fluids used as refrigerants*

iii) Mixtures: Azeotropic mixtures are designated by 500 series, where as zeotropic refrigerants (e.g. non-azeotropic mixtures) are designated by 400 series.

Azeotropic mixtures:

R 500: Mixture of R 12 (73.8 %) and R 152a (26.2%)

R 502: Mixture of R 22 (48.8 %) and R 115 (51.2%)

R503: Mixture of R 23 (40.1 %) and R 13 (59.9%)

R507A: Mixture of R 125 (50%) and R 143a (50%)

Zeotropic mixtures:

R404A : Mixture of R 125 (44%), R 143a (52%) and R 134a (4%)

R407A : Mixture of R 32 (20%), R 125 (40%) and R 134a (40%)

R407B : Mixture of R 32 (10%), R 125 (70%) and R 134a (20%)

R410A : Mixture of R 32 (50%) and R 125 (50%)

iv) Hydrocarbons:

Propane (C_3H_8)	:	R 290
n-butane (C_4H_{10})	:	R 600
iso-butane (C_4H_{10})	:	R 600a

Unsaturated Hydrocarbons: R1150 (C_2H_4)
R1270 (C_3H_6)

26.5. Comparison between different refrigerants:

Synthetic refrigerants that were commonly used for refrigeration, cold storage and air conditioning applications are: R 11 (CFC 11), R 12 (CFC 12), R 22 (HCFC 22), R 502 (CFC 12+HCFC 22) etc. However, these refrigerants have to be phased out due to their Ozone Depletion Potential (ODP). The synthetic replacements for the older refrigerants are: R-134a (HFC-134a) and blends of HFCs. Generally, synthetic refrigerants are non-toxic and non-flammable. However, compared to the natural refrigerants the synthetic refrigerants offer lower performance and they also have higher Global Warming Potential (GWP). As a result, the synthetic refrigerants face an uncertain future. The most commonly used natural refrigerant is ammonia. This is also one of the oldest known refrigerants. Ammonia has good thermodynamic, thermophysical and environmental properties. However, it is toxic and is not compatible with some of the common materials of construction such as copper, which somewhat restricts its application. Other natural refrigerants that are being suggested are hydrocarbons (HCs) and carbon di-oxide (R-744). Though these refrigerants have some specific problems owing to their eco-friendliness, they are being studied widely and are likely to play a prominent role in future.

Prior to the environmental issues of ozone layer depletion and global warming, the most widely used refrigerants were: R 11, R 12, R 22, R 502 and ammonia. Of these, R 11 was primarily used with centrifugal compressors in air conditioning applications. R 12 was used primarily in small capacity refrigeration and cold storage applications, while the other refrigerants were used in large systems such as large air conditioning plants or cold storages. Among the refrigerants used, except ammonia, all the other refrigerants are synthetic refrigerants and are non-toxic and non-flammable. Though ammonia is toxic, it has been very widely used due to its excellent thermodynamic and thermophysical properties. The scenario changed completely after the discovery of ozone layer depletion in 1974. The depletion of stratospheric ozone layer was attributed to chlorine and bromine containing chemicals such as Halons, CFCs, HCFCs etc. Since ozone layer depletion could lead to catastrophe on a global level, it has been agreed by the global community to phase out the ozone depleting substances (ODS). As a result except ammonia, all the other refrigerants used in cold storages had to be phased-out and a search for suitable replacements began in earnest. At the same time, it was also observed that in addition to ozone layer depletion, most of the conventional synthetic refrigerants also cause significant global warming. In view of the environmental problems caused by the synthetic refrigerants, opinions differed on replacements for conventional refrigerants. The alternate refrigerants can be classified into two broad groups:

i) Non-ODS, synthetic refrigerants based on Hydro-Fluoro-Carbons (HFCs) and their blends
ii) Natural refrigerants including ammonia, carbon dioxide, hydrocarbons and their blends

It should be noted that the use of natural refrigerants such as carbon dioxide, hydrocarbons is not a new phenomena, but is a revival of the once-used-and-discarded technologies in a much better form. Since the natural refrigerants are essentially making a comeback, one advantage of using them is that they are familiar in terms of their strengths and weaknesses. Another important advantage is that they are completely environment friendly, unlike the HFC based refrigerants, which do have considerable global warming potential. The alternate synthetic refrigerants are normally non-toxic and non-flammable. It is also possible to use blends of various HFCs to obtain new refrigerant mixtures with required properties to suit specific applications. However, most of these blends are non-azeotropic in nature, as a result there could be significant temperature glides during evaporation and condensation, and it is also important take precautions to prevent leakage, as this will change the composition of the mixture. Table 26.1 shows a list of refrigerants being replaced and their replacements.

Refrigerant	Application	Substitute suggested Retrofit(R)/New (N)
R 11(CFC) NBP = 23.7°C h_{fg} at NBP=182.5 kJ/kg T_{cr} =197.98°C Cp/Cv = 1.13 ODP = 1.0 GWP = 3500	Large air conditioning systems Industrial heat pumps As foam blowing agent	R 123 (R,N) R 141b (N) R 245fa (N) n-pentane (R,N)
R 12 (CFC) NBP = -29.8°C h_{fg} at NBP=165.8 kJ/kg T_{cr} =112.04°C Cp/Cv = 1.126 ODP = 1.0 GWP = 7300	Domestic refrigerators Small air conditioners Water coolers Small cold storages	R 22 (R,N) R 134a (R,N) R 227ea (N) R 401A,R 401B (R,N) R 411A,R 411B (R,N) R 717 (N)
R 22 (HCFC) NBP = -40.8°C h_{fg} at NBP=233.2 kJ/kg T_{cr} =96.02°C Cp/Cv = 1.166 ODP = 0.05 GWP = 1500	Air conditioning systems Cold storages	R 410A, R 410B (N) R 417A (R,N) R 407C (R,N) R 507,R 507A (R,N) R 404A (R,N) R 717 (N)
R 134a (HFC) NBP = -26.15°C h_{fg} at NBP=222.5 kJ/kg T_{cr} =101.06°C Cp/Cv = 1.102 ODP = 0.0 GWP = 1200	Used as replacement for R 12 in domestic refrigerators, water coolers, automobile A/Cs etc	**No replacement required** * Immiscible in mineral oils * Highly hygroscopic
R 717 (NH_3) NBP = -33.35°C h_{fg} at NBP=1368.9 kJ/kg T_{cr} =133.0°C Cp/Cv = 1.31 ODP = 0.0 GWP = 0.0	Cold storages Ice plants Food processing Frozen food cabinets	**No replacement required** * Toxic and flammable * Incompatible with copper * Highly efficient * Inexpensive and available
R 744 (CO_2) NBP = -78.4°C h_{fg} at 40°C=321.3 kJ/kg T_{cr} =31.1°C Cp/Cv = 1.3 ODP = 0.0 GWP = 1.0	Cold storages Air conditioning systems Simultaneous cooling and heating (Transcritical cycle)	**No replacement required** * Very low critical temperature * Eco-friendly * Inexpensive and available

***Table 26.1**: Refrigerants, their applications and substitutes*

Refrigerant	Application	Substitute suggested Retrofit(R)/New (N)
R718 (H_2O) NBP = 100.^{o}C h_{fg} at NBP=2257.9 kJ/kg T_{cr} =374.15^{o}C Cp/Cv = 1.33 ODP = 0.0 GWP = 1.0	Absorption systems Steam jet systems	**No replacement required** * High NBP * High freezing point * Large specific volume * Eco-friendly * Inexpensive and available
R600a (iso-butane) NBP = -11.73^{o}C h_{fg} at NBP=367.7 kJ/kg T_{cr} =135.0^{o}C Cp/Cv = 1.086 ODP = 0.0 GWP = 3.0	Replacement for R 12 Domestic refrigerators Water coolers	**No replacement required** * Flammable * Eco-friendly

***Table 26.1**: Refrigerants, their applications and substitutes (contd.)*

Questions and answers:

1. Which of the following statements are TRUE?

a) A primary refrigerant does not undergo phase change in a refrigeration cycle
b) A secondary refrigerant does not undergo phase change in a refrigeration cycle
c) The freezing point of a brine is generally lower than the freezing point of its constituents
d) The freezing point of a brine is generally higher than the freezing point of its constituents

Ans.: b) and c)

2. Which of the following statements are TRUE?

a) The suction pressure of a refrigerant should be as high as possible

b) The suction pressure of a refrigerant should be as low as possible

c) The discharge pressure of a refrigerant should be as high as possible

d) The discharge pressure of a refrigerant should be as low as possible

Ans.: a) and d)

3. Which of the following statements are TRUE?

a) At a given temperature, as the latent heat of vaporization increases, the saturation pressure decreases
b) For given evaporator and condenser temperatures, as the latent heat of vaporization increases, the pressure ratio decreases
c) As the latent heat of vaporization increases, the required mass flow rate of refrigerant, becomes smaller for a given capacity
d) For a given pressure ratio, as the isentropic index of compression increases, the compressor discharge temperature increases

Ans.: a), c) and d)

4. Which of the following statements are TRUE?

a) A refrigerant having high critical temperature yields high COP and high volumetric capacity
b) A refrigerant having high critical temperature yields low COP and high volumetric capacity
c) A refrigerant having high critical temperature yields low COP and low volumetric capacity
d) A refrigerant having high critical temperature yields high COP and low volumetric capacity

Ans.: d)

5. Which of the following statements are TRUE?

a) Low molecular weight refrigerants have high latent heat of vaporization
b) Low molecular weight refrigerants have low latent heat of vaporization
c) For saturated state at the inlet to the compressor, a refrigerant having high vapour specific heat may give rise to wet compression
d) For saturated state at the inlet to the compressor, a refrigerant having low vapour specific heat may give rise to wet compression

Ans.: a) and c)

6. The chemical formula of refrigerant R11 is:

a) CCl_3F
b) $CClF_3$
c) CClHF
d)CHF

Ans.: a)

7. The chemical formula of R141 is:

a) $C_2H_3ClF_3$
b) $C_2H_2Cl_3F$
c) $C_2H_3Cl_2F$
d) $C_2H_2ClF_3$

Ans.: c)

8. Which of the following statements is TRUE?

a) Evaporation process is non-isothermal for zeotropic mixtures
b) Evaporation process is non-isothermal for azeotropic mixtures
c) Composition of azeotropic mixture changes in the event of a leak
d) Composition of zeotropic mixture changes in the event of a leak

Ans.: a) and d)

9. Which of the following refrigerants are phased-out due to Montreal protocol on ozone layer depletion

a) R11
b) R21
c) R12
d) R32

Ans.: a), b) and c)

10. Which of the following refrigerants replace R12 in domestic refrigerators?

a) R22
b) R11
c) R134a
d) R141b

Ans.: c)

11. Which of the following refrigerants are suggested as replacements for R22 in large air conditioning and cold storage systems?

a) R134a
b) R21
c) R410A
d) R407C

Ans.: c) and d)