CHAPTER 2

REFRIGERANTS AND MIXTURES

2.1 INTRODUCTION

Any substance that absorbs heat through expansion or vaporization may be termed a refrigerant. In the broadest sense of the word the term "refrigerant" is also applied to such secondary cooling mediums as brine solutions or cold water. As commonly interpreted, however, refrigerants include only those working mediums which pass through the cycle of evaporation, recovery, compression, condensation, and liquefaction. Thus, circulating cold mediums are not primary refrigerants, nor are cooling mediums such as ice and solid carbon dioxide.

2.2 COMMON REFRIGERANTS

It should be recognized at the onset that there is no "ideal" refrigerant and that, because of the wide differences in the conditions and requirements of the various applications, there is no one refrigerant that is universally suitable for all applications. Hence, a refrigerant approaches the "ideal" only to the extent that its properties meet the conditions and requirements of the application for which it is to be used.

Some common refrigerants and their chemical formulas and a few of their more important thermal and physical properties are shown in Table 2.2.

TABLE 2.2 [1,8] Physical and Thermal Properties of Some Common Refrigerants

Refrigerant	Chemical Formula	Odor	Toxicity	Flamm- ability	Boiling point F	Freezing point F	Critical point temp. F	Critical point press. psia	spec. gravity at atm. (liquid)	spec. ht at avg. 5F-86F (liquid)
Ammonia	NH_3	Pungent	High	Slight	-28.0	-107.9	271.4	1657.0	0.684	1.12
Carbon dioxide	CO_2	Non	Medium	Non	-109.3	-69.9	87.8	1069.9	1.560	0.77
Freon - 12	CCl_2F_2	Sweet	Low	Non	-21.6	-252.0	233.6	596.9	1.480	0.23
Freon - 22	$CHClF_2$	Sweet	Low	Non	-41.4	-256.0	204.8	716.0	1.411	0.30
Methyl chloride	CH_3Cl	Sweet	Medium	Slight	-10.8	-144.0	289.4	968.7	1.002	0.38
Freon - 113	$CCl_2F-CClF_2$	Sweet	Low	Non	117.6	-31.0	417.4	495.0	1.559	0.21

2.3 DESIRABLE PROPERTIES FOR AN IDEAL REFRIGERANT

The ideal refrigerant should have, at least, the following characteristics:

1. Positive evaporating pressure - to prevent posible leakage of air and moisture into the system during operation.

2. Moderately low condensing pressure - to permit the use of light weight equipment and piping on the high-pressure side of the system.

3. Relatively high critical temperature - to prevent unduly large power requirements.

4. Low freezing temperature - to prevent that solidification of the refrigerant occurs during normal operation.

5. Low cost of refrigerant.

6. High latent heat of vaporization - for a high refrigerating effect.

7. Inertness and stability - should be inert to reaction with materials of the system. It should be non-corrosive in the presence of water. It should be entirely stable in its chemical make-up through the entire range of operating conditions.

8. High dielectric strength of vapor - it is important if it is to be used in a hermetically sealed unit with the motor exposed to the refrigerant.

9. High heat transfer characteristics.

10. Satisfactory oil solubility - the ability of the refrigerant to be dissolved into the oil and vice versa.

11. Low water solubility - two principal effects resulting from moisture in a refrigeration system are corrosion and freeze-up of expansion devices.

12. Non-toxicity - the toxicity of a refrigerant may be of prime or secondary importance, depending upon the application.

13. Non-irritability - the vapor should not irritate the eyes, nose, lungs, or skin.

14. Non-flammability - should prevent no danger of explosion or fire, either in combination with air or association with lubricating oils.

15. Easy leakage detection.

2.4 FREON 12 (DICHLORODIFLUOROMETHANE)

"Freon-12" is used in a wide range of applications, including very large tonnage centrifugal refrigeration and air conditioning systems, household and commercial refrigeration and air conditioning, refrigerators, frozen food cabinets, ice cream cabinets, food locker plants, water coolers, room and window air conditioners and other equipment.

It is generally used in reciprocating compressors ranging in size from fractional to 100 or more horsepower and in rotary-type compressors in the smaller sizes

(1/8 to 2 horsepower).

The whole "Freon" family of refrigerants has low toxicity, "Freon-12" of the group having about the lowest toxicityof all. This refrigerant has no odor and can be breathed with no apparent harm when its concentration in air is as high as 20% by volume. As for physiological action, it apparently acts as an inert material which is breathed in and exhaled and merely acts as an additional diluent for the oxygen in the air. Observation of its formula will indicate that it is actually a halogenated hydrocarbon, and such chemicals, in the presence of open flames or extremelyhot surfaces, may break down and cause objectionable or toxic decomposition products. For lubrication, mineral oil, free of water, is required. Oil and the "Freon" family are mutually soluble, and an excess of "Freon" may dilute the lubricating oil to a point where it loses its lubricating effectiveness. It is necessary to observe caution in operation to see that not too much oil from the compressor is carried over into the evaporator, and proper provision must be made for returning carry-over oil back to the compressor. Water must be completely removed from a "Freon" system to prevent freezing up of the expansion valve. Corrosion of metals by "Freon" is trivial or nonexistent except in the presence of water.

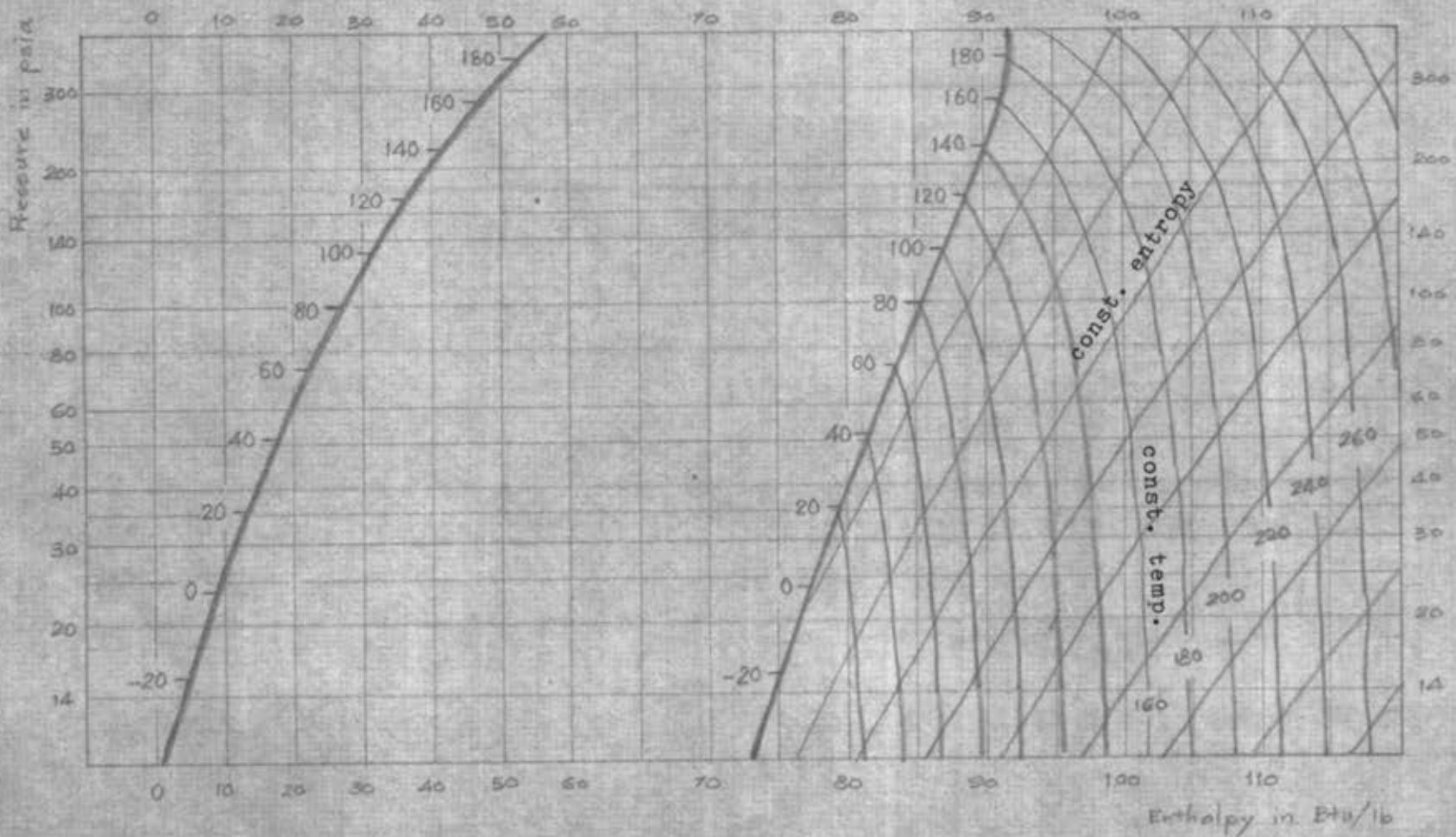Pressure-enthalpy chart of "Freon-12" is shown in Figure 2.4.

FIGURE 2.4[8] "Freon-12" refrigerant pressure-enthalpy diagram.

2.5 FREON 22 (MONOCHLORODIFLUOROMETHANE)

The "Freon-22" refrigerant is a synthetic che-
mical specially developed for those refrigeration instal-
lations that have a very low temperature cooling unit,be-
cause of it is not necessary to operate at below atmos-
pheric pressure in order to obtain these low temperature.
It also finds wide use in packaged air conditioners,where,
because of space limitation, the relatively small compres-
sor displacement required is a decided advantage. It is
also used in food freezing, and industrial process equip-
ment with either reciprocating or centrifugal compressors.

Although miscible with oil at temperatures found
in the condensing section, "Freon-22" will often separate
from the oil in the evaporator. The exact temperature at
which separation occurs varies considerably with the type
of oil and the amount of oil mixed with the refrigerant.
However, no difficulty is usually experienced with oil re-
turn from the evaporator when a properly designed serpen-
tine evaporator is used and when the suction piping is
properly designed. When flooded evaporators are employed,
oil separators should be used and special provisions
should be made to insure the return of oil from the eva-
porator. Oil separators should always be used on low tem-
perature applications.

The ability of "Freon-22" to absorb moisture is
considerably greater than that of "Freon-12" and therefore
less trouble is experienced with freeze-up in "Freon-22"

systems. Although some consider this to be an advantage, the advantage gained is questionable, since any amount of moisture in a refrigerating system is undesirable.

Pressure-enthalpy chart of "Freon-22" is shown in Figure 2.5.

2.6 COMPARATIVE REFRIGERATION PERFORMANCE

Table 2.6 shows the comparative refrigeration performance of "Frion-12" and "Freon-22" based on one ton of refrigeration at 5 F evaporator temperature and 85 F condenser temperature.

TABLE 2.6[4] Comparative Refrigeration Performance
of "Freon-12" and "Freon-22"

Performance	Freon-12	Freon-22
Evaporator pressure psig	11.8	28.3
Condensing pressure psig	93.3	159.8
Ratio of compression	4.08	4.06
Refrigeration effect Btu/lb	50.0	69.3
Refrigerant circulated lb/min-ton	4.00	2.89
Specific volume of vapor cuft/lb	1.458	1.246
Horsepower per ton hp	1.002	1.011
Compressor displacement cuft/min	5.83	3.60
Coefficient of performance	4.71	4.66
Compressor discharge temperature F	101.0	131.0
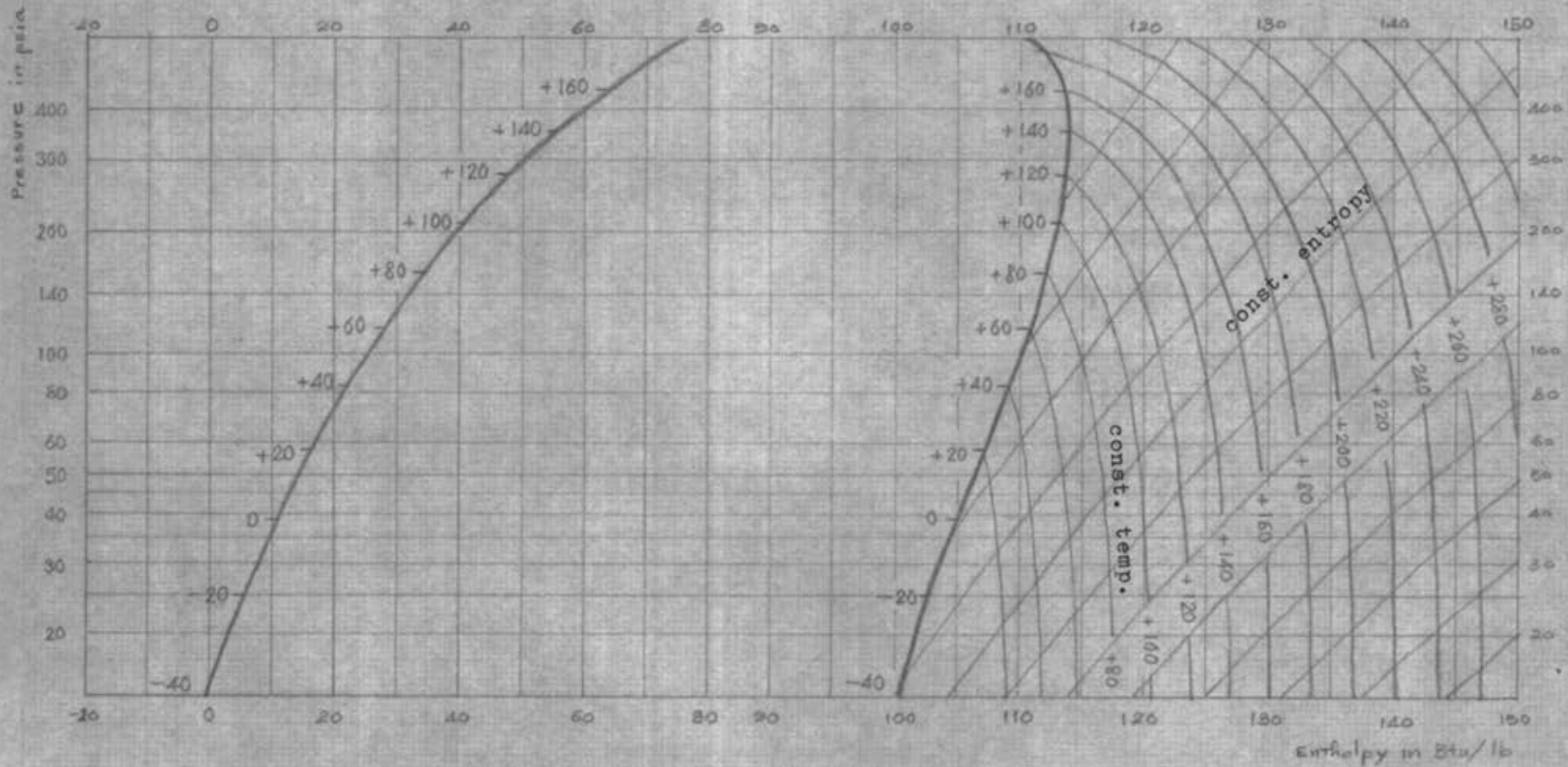
FIGURE 2.5 "Freon-22" refrigerant pressure-enthalpy diagram.

2.7 CHEMICAL COMPOUNDS OF HALOGENATED HYDROCARBON REFRIGERANTS

Most halogenated refrigerants are derived from either methane (CH_4) or ethane (C_2H_6) by Substitution of hydrogen with fluorine, chlorine and bromine. The large number of compounds possible is shown in Figure 2.7.1.

The American Society of Refrigerating Engineer (ASRE) has adopted a specific disignation system for refrigerants, the number assigned to the hydrocarbon and halocarbon have special meaning.

The first digit on the right is the number of fluorine (F) atoms in the refrigerant.

The second digit from the right is one more than the number of hydrogen (H) atoms present.

The third digit from the right is one less than the number of carbon (C) atoms, but when this digit is zero it is omitted.

In another word, a compound having the formular

$$C_cH_hF_fCl_{2c-2-h-f}$$
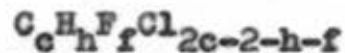
is assigned the number $\underline{(c-1)}\underline{(h+1)}\underline{f}$

when $(c-1) = 0$ it is omitted.

thus

CH_3CH_3	has the number	170
CF_2Cl_2	has the number	12
$C_2F_4Cl_2$	has the number	114

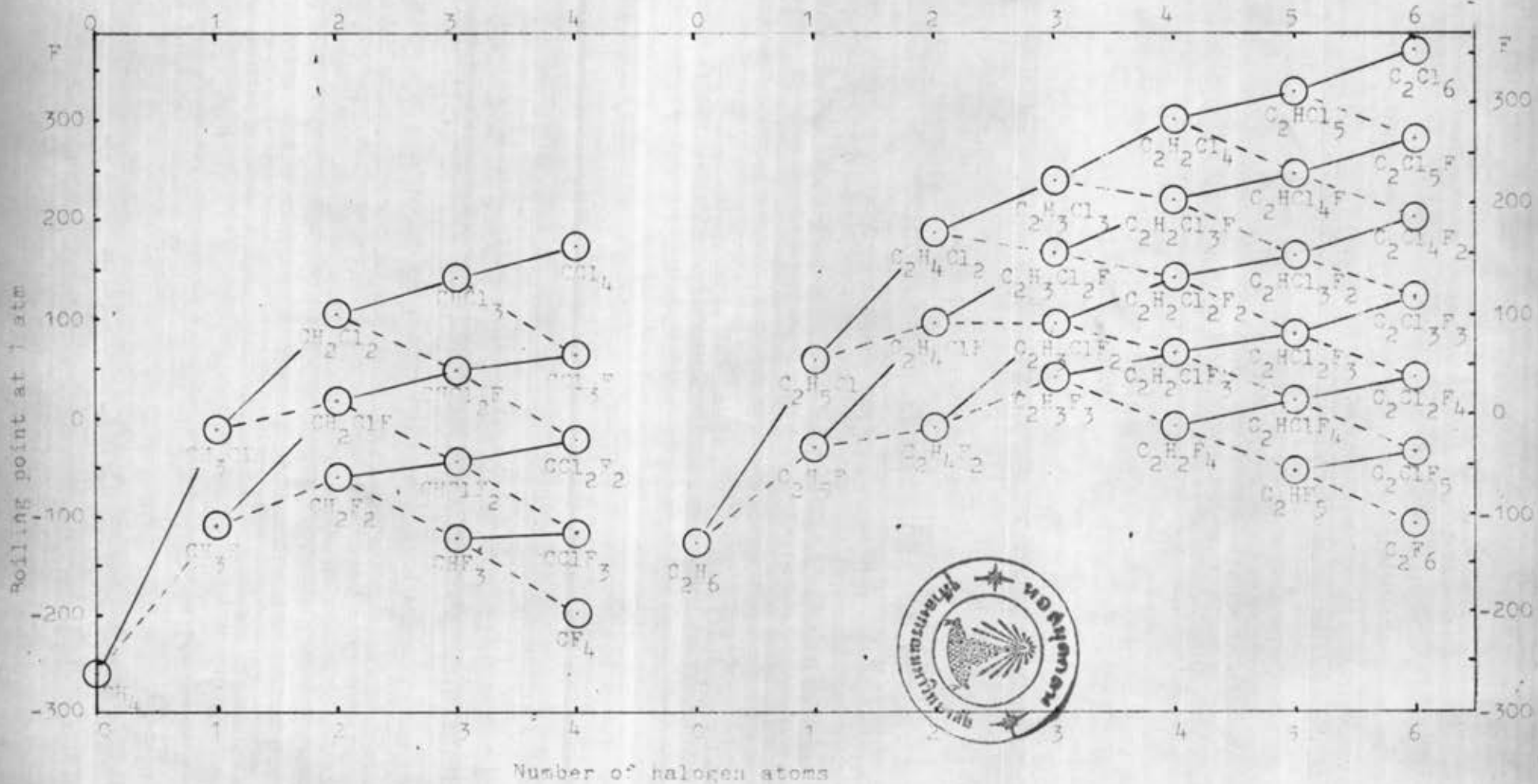The number is preceded by the maker's trade name "Freon", "Arcton", "Isceon", etc., or by the letter

FIGURE 2.7.1[5] Halogenated derivatives of methane and ethane. The full lines join compounds having equal numbers of fluorine atoms: the broken lines join compounds having equal numbers of chlorine atoms.

R, there are additional to the designation to allow for unsaturated and cyclic compounds, and brominated compounds.
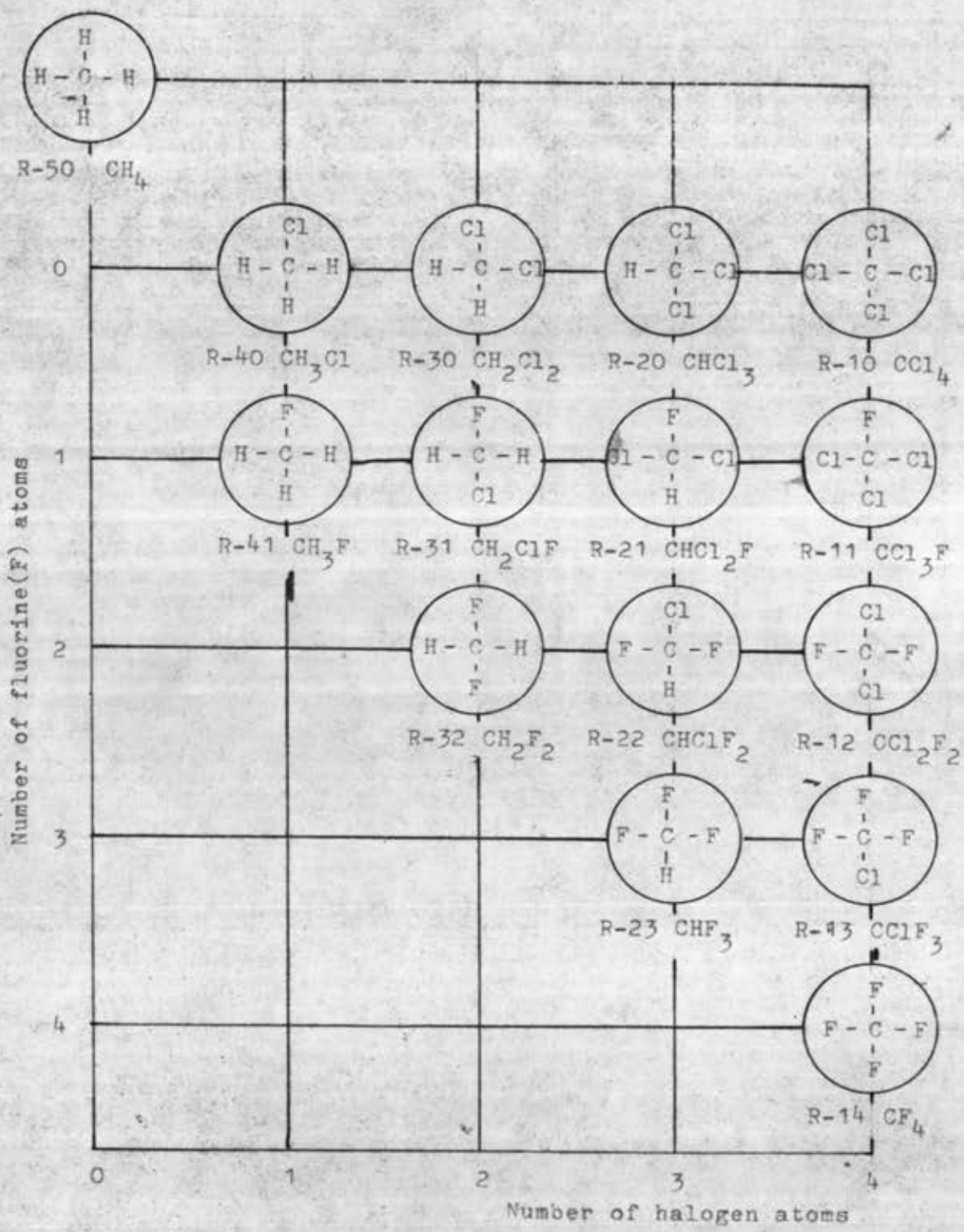
Figure 2.7.2 shows the molecular structure of the methane series halocarbons.

Figure 2.7.3 shows the molecular structure of the ethane series halocarbons.

Not all of those compounds are suitable as refrigerants.

Figure 2.7.4 shows the different molecular structures of $C_2Cl_2F_4$ and $C_2H_3ClF_2$.
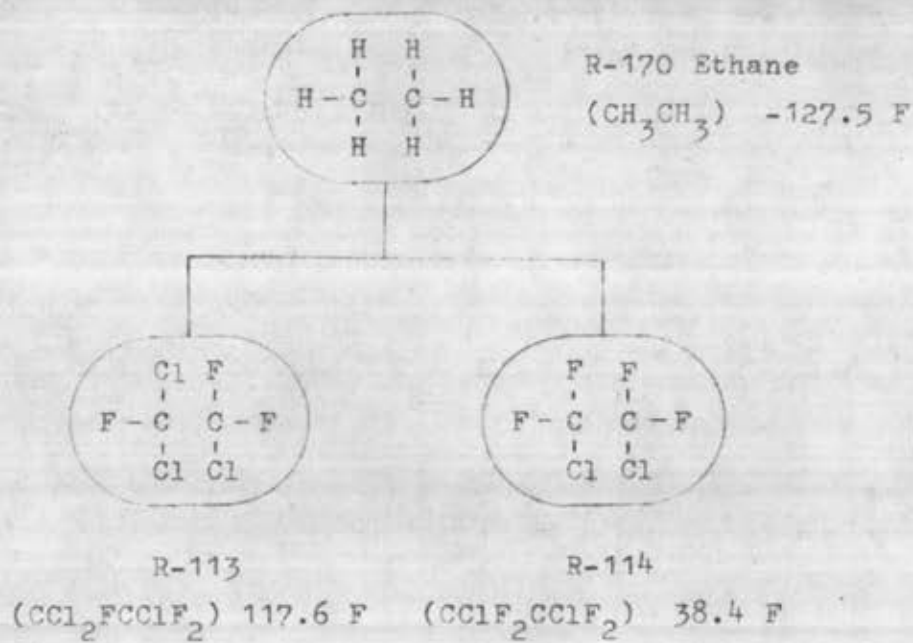
FIGURE 2.7.2 **3,8** Methane series refrigerants.

H   H
H - C   C - H
    H   H

R-170 Ethane

(CH_3CH_3) -127.5 F

Cl F
F - C C - F
Cl Cl

R-113

(CCl_2FCClF_2) 117.6 F

F   F
F - C C - F
Cl Cl

R-114

$(CClF_2CClF_2)$ 38.4 F

FIGURE 2.7.3[3].   Ethane series refrigerants.

$C_2Cl_2F_4$ R-114

F   F
Cl - C C - Cl
F   F

R-114a

Cl F
Cl - C C - F
F   F

or

Cl F
F - C C - F
Cl F

$C_2H_3ClF_2$ R- 142

H   F
H - C C - F
Cl H

R-142a

H   F
H - C C - Cl
F   H

R-142b

H   F
H - C C - F
H   Cl
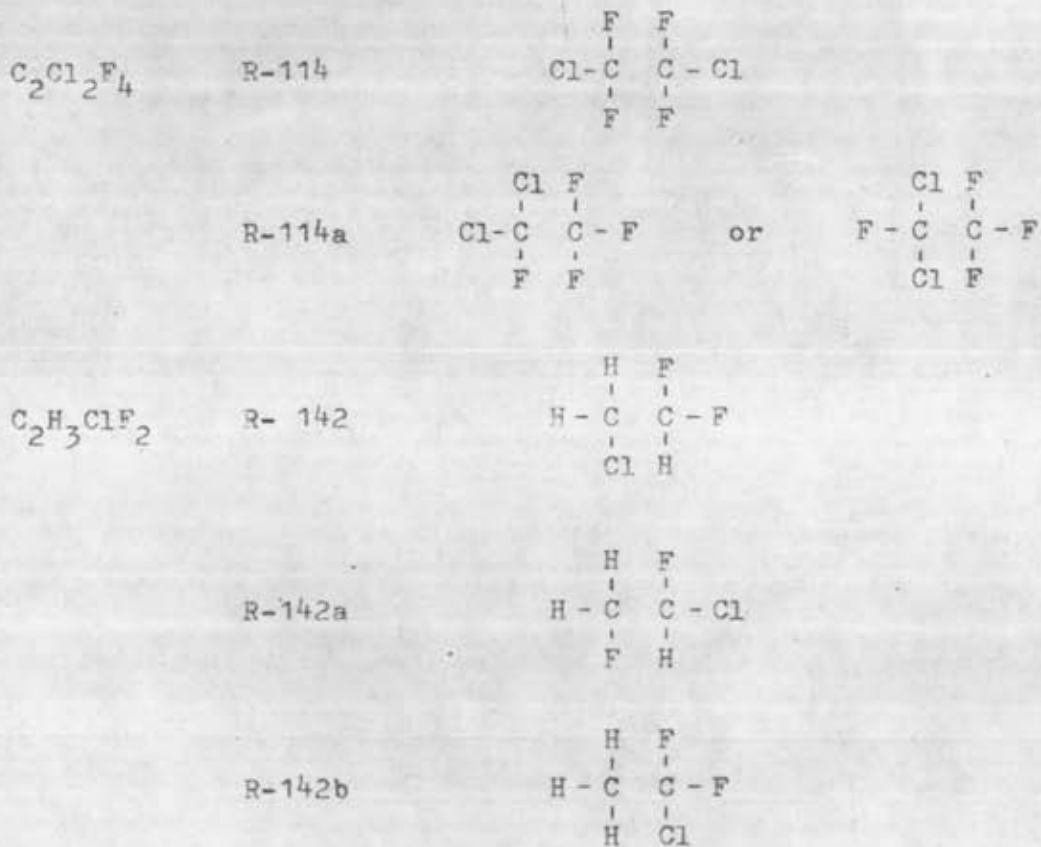
FIGURE 2.7.4 The different molecular structures of $C_2Cl_2F_4$ and $C_2H_3ClF_2$.

2.8   MIXTURES AND SOLUTIONS

Mixtures are formed by combining two or more substances, they fall into two categories:

1.   A Homogeneous Mixture. A homogeneous mixture is uniform in composition and properties, regardless of how small the particles are. It can not be separated into its constituents by pure mechanical means. All gaseous mixtures and dry air-water vapor are examples of this type.

2.   A Heterogeneous Mixture. A heterogeneous mixture is non-uniform in composition and can be separated by ordinary mechanical means.

This work will concern only with binary homogeneous liquid and homogeneous vapor mixtures of non-reacting materials.

2.8.1   THE COMPOSITION OF SOLUTIONS

The composition of a solution can be expressed in a variety of different ways, each of which has advantages for a particular purpose.

A mixture consist of two components A and B

Let m_A, m_B = mass of substance A and B

N_A, N_B = mass fraction of substance A and B

n_A, n_B = number of moles of substance A and B

x_A, x_B = mole fraction of substance A and B

M_A, M_B = molecular weight of substance A and B

Total mass $\sum m$;   A   = m_A

$$B = m_B$$

$$\Sigma m = m_A + m_B$$

The sum of mass fraction; $\quad N_A = \dfrac{m_A}{\Sigma m}$

$$N_B = \dfrac{m_B}{\Sigma m}$$

$$\Sigma N = 1$$

Total moles Σn ; $\quad n_A = \dfrac{m_A}{M_A}$

$$n_B = \dfrac{m_B}{M_B}$$

$$\Sigma n = n_A + n_B$$

The sum of mole fraction; $\quad x_A = \dfrac{n_A}{\Sigma n}$

$$x_B = \dfrac{n_B}{\Sigma n}$$

$$\Sigma x = 1$$

From the above expressions, we can conclude that

$$N_A + N_B = 1$$

$$x_A + x_B = 1$$

The mass fraction and mole fraction can be converted by

$$x_A = \dfrac{N_A/M_A}{\Sigma(N/M)} \quad ; \quad x_B = \dfrac{N_B/M_B}{\Sigma(N/M)}$$

$$N_A = \dfrac{x_A M_A}{\Sigma(xM)} \quad ; \quad N_B = \dfrac{x_B M_B}{\Sigma(xM)}$$

In general, the subscript A and B of a binary mixture can be dropt out, that is we express the mole fraction or mass fraction of a component only.

Let component A has a mass fraction of N

then component B has a mass fraction of 1 - N

where N is the concentration or mass fraction of component A in the mixture.

2.8.2 VAPOR PRESSURE OF IDEAL SOLUTIONS

As the concept of an ideal gas is helpful in the study of gases, the concept of an ideal solution is helpful in the discussion of solutions.

The partial vapor pressure of a component above the solution is a measure of the constituent's "tendency to escape" from the solution. A solution is said to be ideal if the vapor pressure of each component is proportional to the mole fraction of that component in the solution.

Consider a liquid mixture of two components, A and B, with mole fraction of x_A and x_B. If the solution is ideal, a molecule of A will have the same tendency to escape into the vapor, whether it is surrounded by other A molecules, entirely by B molecules, or partly by A and partly by B molecules. Since the intermolecular forces between all molecules are the same, it is immaterial to the behavior of a molecule what sort of neighbour it has.

Under these circumstances, the partial vapor pressure of component A is the same as that of the pure

liquid A, except that it is proportionately reduced on account of the lowered fraction of A molecules in the solution. This is expressed by

$$p_A = x_A p_A^\bullet$$

where p_A = the partial vapor pressure of A above the solution

x_A = the mole fraction of A

$p_A^\bullet$ = the vapor pressure of pure liquid A at the same temperature

The equation above is known as Raoult's Law. A similar equation applies to component B.

Raoult's law does not hold exactly for all combination of liquids. Never the less, it is a useful idealization that can be applied to some combinations, e.g. mixtures of hydrocarbons.

A binary liquid mixture obeying Raoult's law, the relationship of vapor pressures and mole fractions is shown in Figure 2.8.2. The vapor pressure against mole fraction of each component is a straight line from zero to the vapor pressure of pureliquid. The total pressure is the sum of each partial vapor pressure. The lines refer to pressures observed at a given temperature. The slopes of the partial pressure lines will change as the temperature is changed.

Solutions which obey Raoult's law are distinguished by the fact that there is no heat solution and no volume change on making of the pure liquids.
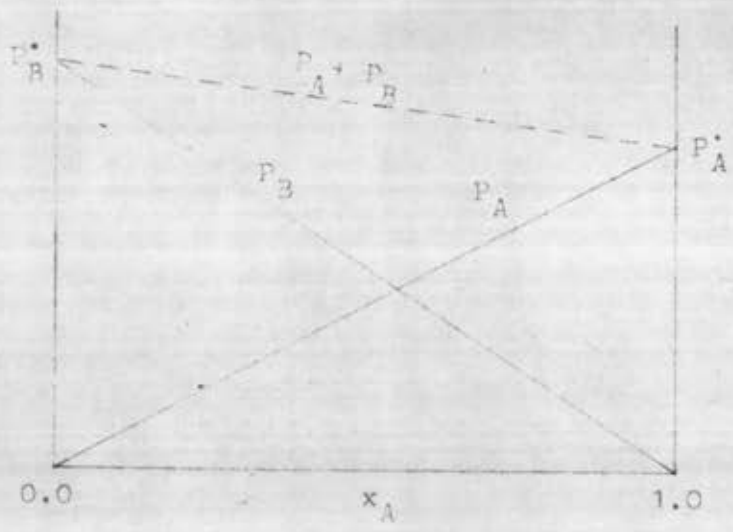
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FIGURE 2.8.2 **10** . . . . . Representation
of Raoult's law.

(a)

(b)

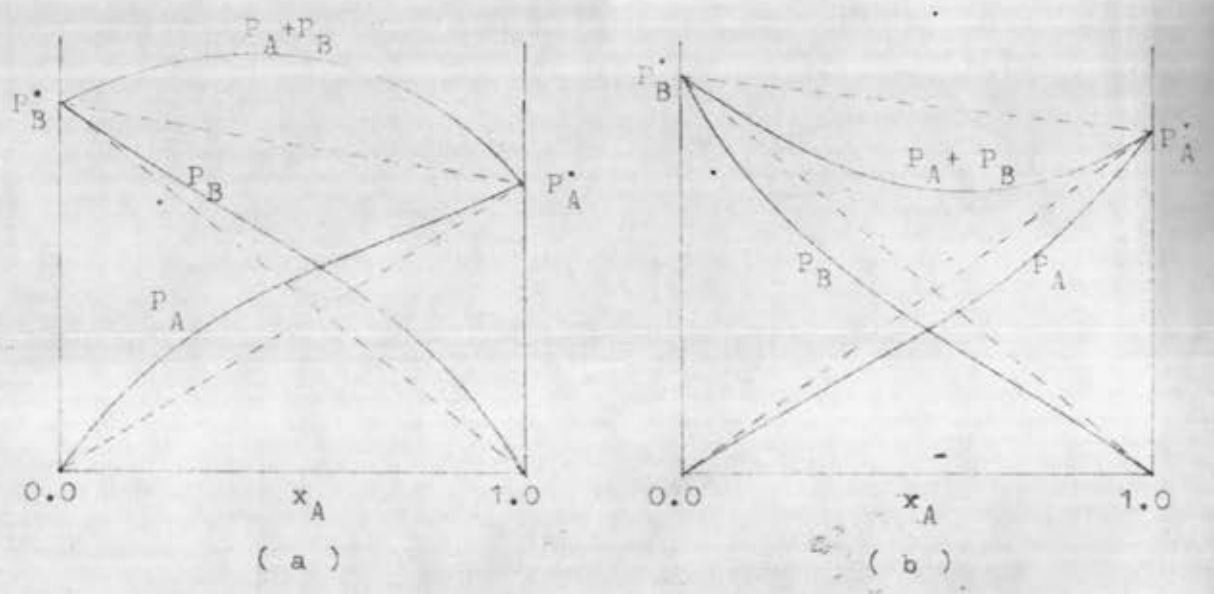FIGURE 2.8.3 **10** . . . . . Deviations from Raoult's law.

2.8.3 VAPOR PRESSURE OF NON-IDEAL SOLUTIONS

Not many solutions obey Raoult's law over the complete range of concentrations. In actual liquid mixtures, the departure from Raoult's law fall in to two general types:

1. A mixture which exhibits positive deviations from Raoult's law. The partial pressure of this mixture are in excess of those predicted for ideal solutions, as shown in Figure 2.8.3 (a). An example of such a mixture is the system of acetone-carbondisulphide.

2. A mixture which exhibits negative deviations from Raoult's law. The partial pressure of this mixture are less than expected from ideal solutions, as shown in Figure 2.8.3 (b). Such negative deviations mixture is acetone - chloroform.

Regardless of the type of departure conclusions can be taken from the experimental curves as follow:

a. As the composition approaches that of a pure liquid, the partial pressure of the nearly pure compound becomes tangent to the line representing Raoult's law.

b. The partial pressure of the dilute component is a straight line with a slope different from Raoult's law.

The vapor pressure of the dilute component is said to obey "Henry's law", which is

$$p_B = kx_B$$

A dilute solution consists of the solvent A and the solute B, the escaping tendency of B from its uniform environment is proportional to its mole fraction. For dilute solutions, the solvent obeys Raoult's law, and the solute obeys Henry's law.

2.8.4 VAPORIZATION AND CONDENSATION OF MIXTURES

When binary liquid solution are distilled at constant pressure, their behavior falls into three types:

1. Solution whose boiling points are intermediate between the boiling points of the pure components. A temperature-composition diagram is shown in Figure-2.8.4(a). The lower curve represents the boiling temperatures of all mixtures of A and B for a given pressure.The upper curve represents the composition of the vapor in equilibrium with the solution.

2. Solutions whose boiling points show a maximum which is greater than the boiling point of either pure component. A temperature-composition diagram is shown in Figure 2.8.4(b).

3. Solution whose boiling points show a minimum which is less than the boiling point of either pure component. A temperature-composition diagram is shown in Figure 2.8.4(c).

Solution of type (2) and (3), both liquid and vapor have the same composition at a concentration (point C and D), and the distillation of them at that point will proceed until all mixture has boiled away. A solution
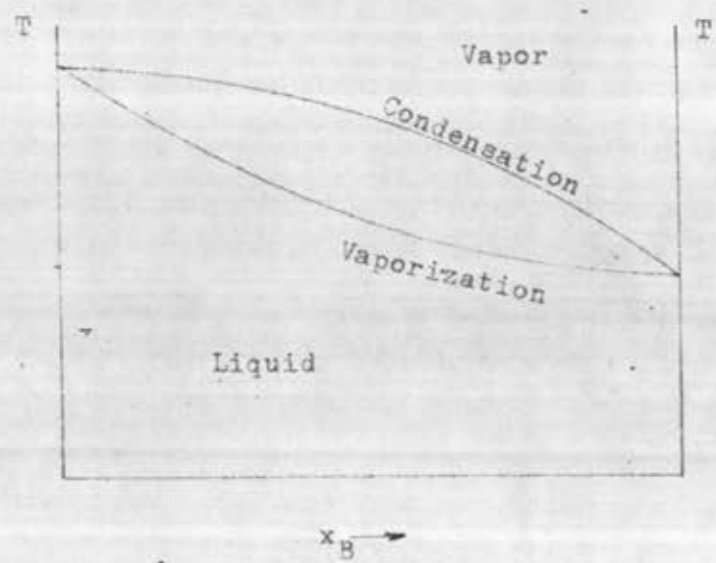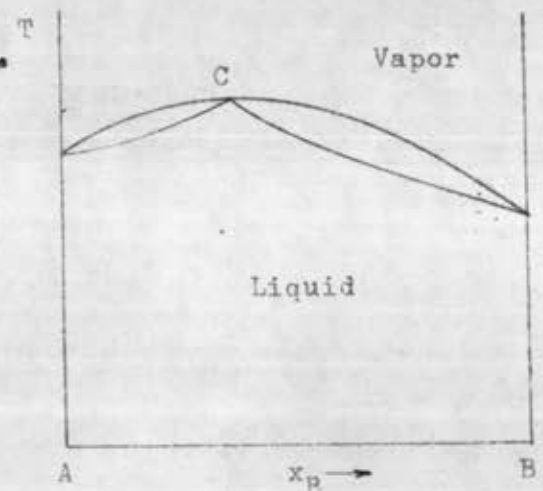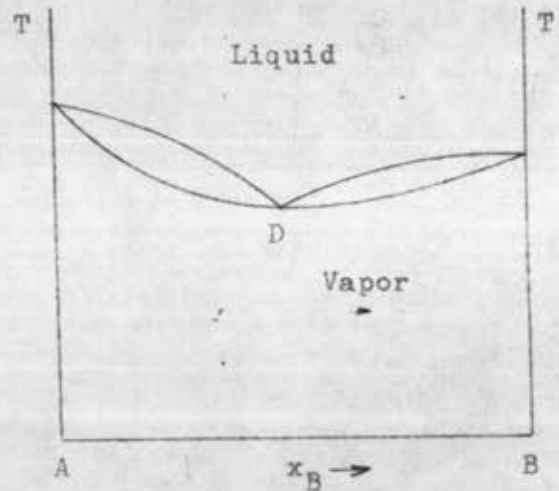
FIGURE 2.8.4 (a) (...) Temperature
-composition diagram for ideal solu-
tion.

(b)   (c)

FIGURE 2.8.4 (b),(c) (...) Temperature-composition diagrams
for solutions deviating from Raoult's law.

that distills without change in composition and tempera-
ture is called an AZEOTROPE, and the concentration at that
point is called an AZEOTROPIC COMPOSITION.

2.8.5 MISCIBILITY OF SOLUTIONS

Three general cases of miscibility arise in li-
quid-vapor equilibrium.

(a) Completely Immiscible. The two components
are immiscible in the liquid phase. There are probably no
pairs of actual liquids that are entirely immiscible; but
there are many pairs, particularly many organic liquids
with water, that are so slightly miscible as to be regard-
ed as immiscible for all practical purposes. Immiscibili-
ty is therefore a limiting case that actual systems ap-
proach more or less closely but never quite reach. Proba-
bly a system such as mercury-water comes as near to this
limiting case as any, and certainly for all practical pur-
poses these two liquids are immiscible.

(b) Completely Miscible. The commonest and most
important case is that in which the liquid components are
completely miscible over the whole range of composition
and hence only one liquid phase can exist.

For non-ideal solutions that deviate markedly
from the ideal may be classified into four different types,
according to the form of their isothermal p-x diagrams as
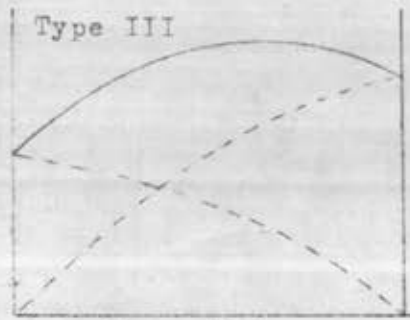shown in Figure 2.8.5 (a),(b),(c),and (d).
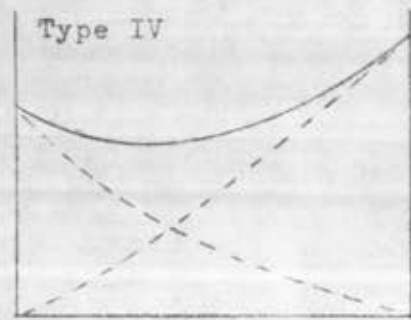
(c) Partly Miscible. Intermediate between those

Type I	Type II
Composition	Composition
(a)	(b)
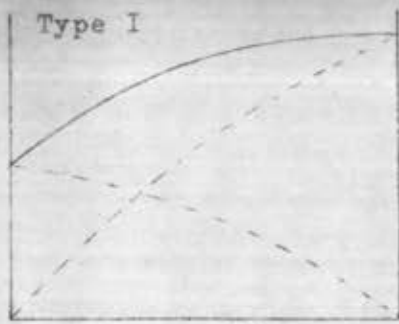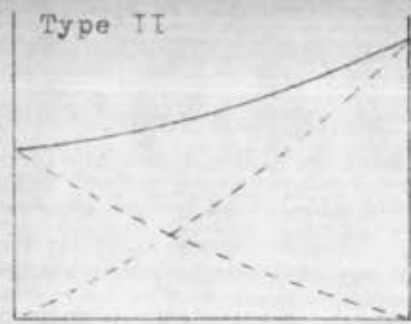
Type III	Type IV
Composition	Composition
(c)	(d)

FIGURE 2.8.5[2]   Pressure-composition diagrams of solutions that are not ideal. Type III and IV are AZEOTROPIC characters.

A —— B —— A'

87.56 psi

— Total pressure

— Partial pressure of R-12 in mixture

— Partial pressure of H_2O in mixture

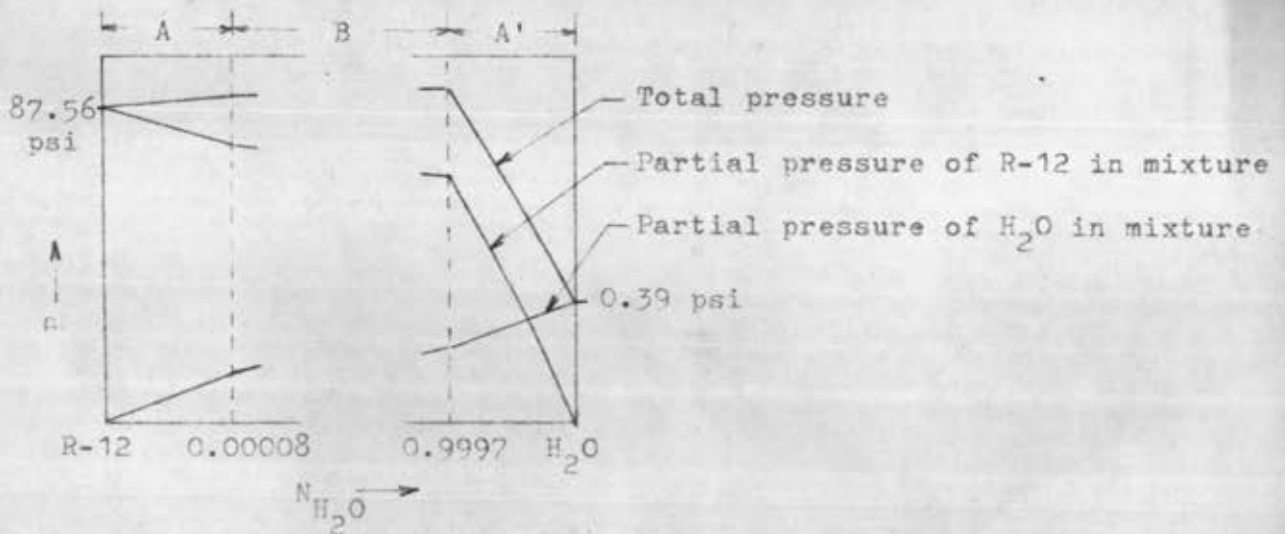0.39 psi

R-12   0.00008   0.9997 H_2O

N_{H_2O} →

FIGURE 2.8.5(e) "R-12' and water system at 72 F. A,A' are homogeneous region, and B is two layers mixture. (Ref. Elsey & Flowers, Refrigeration Engineer, Feb, 1949.)

two limiting cases is that of partial miscibility in which
there is only one liquid phase over a portion of the con-
centration range and two over the remainder. Figure 2.8.5
(e) shows a typical system presented by Elsey & Flowers.