UNIT 10 SOLUTIONS—I

Structure

10.1 INTRODUCTION

A solution may be defined as a homogeneous mixture of two or more substances, the composition of which may vary. It consists of two components, solute and solvent. The substance which is present in larger proportion is called the solvent and the substance which is present in smaller proportion is called the solute. Depending upon the number of constituents, a solution may be referred to as binary (two components), ternary (three components) or quaternary (four components). Depending upon the state of the solute and the solvent, there are nine types of solutions. The concentration of a solution could be expressed using different terms, e.g., molarity, molality, mole fraction, etc. The solubility of solids in liquids generally increases with rise in temperature. The solubility of gases in liquids is governed by Henry's law. Liquid solutions obeying Raoult's law are called ideal solutions. Solutions which do not obey Raoult's law are called non-ideal solutions. In this unit, we shall discuss the above aspects and also study fractional distillation of liquids. In the next unit, we shall study partially miscible and completely immiscible liquid pairs.

Objectives

After studying this unit, you should be able to:

- define a solution,
- list various types of solutions,
- express concentration of solutions in different ways,
- define solubility,
- explain the solubility curves,
- state Henry's law,
- state Raoult's law,
- distinguish between ideal and non-ideal solutions,
- discuss Raoult's law curves,
- explain the principle of fractional distillation, and
- define the term, azeotrope.

10.2 TYPES OF SOLUTIONS

A solution may exist in solid, liquid or gaseous state. Depending upon the physical state, a solution may be classified into the types shown in Table 10.1.

Solutions of substances in water are called aqueous solutions while solutions in other solvents are called nonaqueous solutions.

Solutions of metals in mercury are called amalgams e.g., sodium amalgam, zinc amalgam, etc. Amalgamation modifies the properties of metals. For example, sodium metal is a powerful reducing agent whereas sodium amalgam is a moderate reducing agent.

Table 10.1 : Types of Solutions

Solute	Solvent	Example
Gas	Gas	Mixture of gases (e.g., air)
Gas	Liquid	Aerated water (which is a solution of CO_2 in water under pressure)
Gas	Solid	Gas adsorbed by metals or minerals (e.g., H_2 on palladium)
Liquid	Gas	Moist air
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in zinc (zinc amalgam)
Solid	Gas	Camphor in air
Solid	Liquid	Salt in water
Solid	Solid	Alloys (e.g., brass)

A solution is always in the same physical state as the solvent. In this unit, we shall study solid-liquid, gas-liquid and liquid-liquid solutions.

SAQ 1

Classify the following into the types of solutions to which they belong :

i) A five rupee coin
ii) Sodium amalgam
iii) Soda water

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10.3 DIFFERENT WAYS OF EXPRESSING CONCENTRATION OF SOLUTIONS

The relative amounts of a solute and a solvent in a solution are expressed through concentration terms. Some of the ways of expressing the concentration of a solution are described below :

A solution containing *x* mol of a substance in 1 dm^3 of a solution is called *x* molar or *x* M solution.

i) Molarity (M)

Molarity is defined as the number of moles of the solute present in 1 dm^3 (1 L or 10^{-3} m^3) of the solution. When 0.1 mole of a solute is present in one cubic decimeter of the solution, we say that the solution is 0.1 molar (0.1 M).

$$\text{Molarity (M)} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in dm}^3} \quad \text{.... (10.1)}$$

Note that the volume of the solution should be expressed in dm^3 for expressing the concentration in terms of molarity.

ii) Molality (m)

Molality is defined as the number of moles of a solute present in one kilogram of the solvent. When one mole of a solute is dissolved in one kilogram of water, the concentration of the solution is one molal (1 m).

$$\text{Molality (m)} = \frac{\text{Number of moles of the solute}}{\text{Mass of the solvent in kg}} \quad \ldots (10.2)$$

iii) Normality (N)

The number of gram-equivalents of a solute present in 1 dm^3 of the solution is called its normality. A one normal solution contains one gram-equivalent of a solute in 1 dm^3 of solution and is denoted by 1 N.

$$\text{Normality (N)} = \frac{\text{Strength in g dm}^{-3}}{\text{Equivalent weight}} \quad \ldots (10.3)$$

iv) Mole fraction (*x*)

The mole fraction of a solute in a solution is the ratio of the number of moles of a solute to the total number of moles of the solute and the solvent in a solution. If n_2 mole of a solute is dissolved in n_1 mole of a solvent, the mole fraction of the solvent and the solute are given by the following expressions :

The sum of the mole fractions of all the components in a solution is always equal to one.

$$\text{Mole fraction of the solvent } (x_1) = \frac{n_1}{n_1 + n_2} \quad \ldots (10.4)$$

$$\text{Mole fraction of the solute } (x_2) = \frac{n_2}{n_1 + n_2} \quad \ldots (10.5)$$

v) Percentage

In terms of percentage, the concentration of a solution may be expressed in four different ways :

10 mL of alcohol present in 100 mL of solution = 10% (*V/V*)
10 g NaCl present in 100 mL of solution = 10% (*W/V*)
10 mL alcohol present in 100 g of solution = 10% (*V/W*)
10 g NaCl present in 100 g of solution = 10% (W/W)

Unless specified, a 10% solution may always be taken as weight by weight (*W/W*).

vi) Parts per million (ppm)

When a solute present in the solution is in very minute amounts, the concentration is usually expressed in parts per million (ppm). For example, the amount of oxygen dissolved in sea water is 5.8 g in 10^6 (1 million) gram of sea water. It means 5.8 parts of oxygen are present in one million parts of sea water. Hence, the concentration of oxygen in sea water is 5.8 ppm. The concentration of gases which pollute the atmosphere is also expressed in ppm.

All concentration units except mole fraction, molality, ppm and percentage (*W/W*), vary with temperature.

$$\text{One ppm} = \frac{\text{Mass of solute (g)}}{\text{Total mass of solution (g)}} \times 10^6 \quad \ldots (10.6)$$

Similar to Eq. 10.6, parts per billion (ppb) may be defined as follows:

$$\text{One ppb} = \frac{\text{Mass of solute (g)}}{\text{Total mass of solution (g)}} \times 10^9$$

Let us work out an example using the molarity expression explained above.

Example 1

Concentrated sulphuric acid contains 98% acid by weight. Its density is 1.85×10^3 kg m^{-3}. Calculate its molarity.

Solution

$1 m = 10 dm$
$1 m^3 = (10 dm)^3$
$= 10^3 dm^3$

$$\text{Molarity of sulphuric acid} = \frac{\text{Number of moles of sulphuric acid}}{\text{Volume in dm}^3}$$

$$= \frac{\text{Mass of sulphuric acid in 1 m}^3}{\text{Molar mass} \times 10^3 \text{ dm}^3}$$

$$= \frac{98 \times 1.85 \times 10^3 \text{ kg}}{100 \times 0.098 \text{ kg mol}^{-1}} \times \frac{1}{10^3 \text{dm}^3}$$

$$= 18.5 \text{ M.}$$

SAQ 2

A solution contains 0.100 kg each of water and ethanol. Find the mole fraction of each component.

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10.4 SOLUTIONS OF SOLIDS IN LIQUIDS

In solutions of solids in liquids, the liquid is referred to as the solvent and, the solid which is dissolved in it, as the solute. When a solid is added gradually to a given amount of a liquid (solvent) at constant temperature, a state is reached when some of the solid remains undissolved. The solution is then said to be saturated. The mass of the solute that can be dissolved in 0.100 kg of a solvent to form a saturated solution at a given temperature is called its **solubility**.

Solubility of a solid in a liquid varies with temperature. The plot of solubility against temperature is called the solubility curve. Some typical solubility curves are shown in Fig. 10.1.

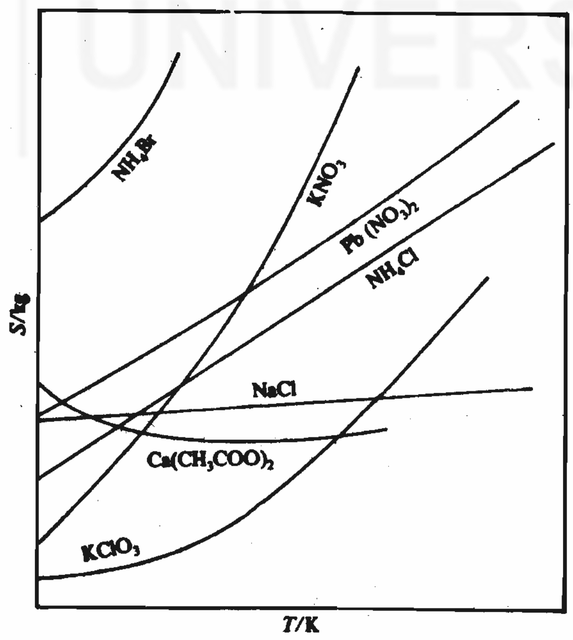

Fig. 10.1 : Solubility curves of different solutes: *S* stands for solubility and *T* for temperature.

The solubilities of many of the ionic substances in water increase with temperature. The solubility of sodium chloride increases to a very small extent with rise in temperature. The solubility of calcium acetate decreases with rise in temperature.

In many cases, when a solute is dissolved in a solvent, heat is absorbed, i.e., cooling results. Then according to Le Chatelier's principle, when the temperature of a saturated solution in contact with the solute is raised, a change will take place such that there is absorption of heat, i.e., along the direction in which cooling takes place. The solubility of the substance will, therefore, increase with rise in temperature.

The dissolution of some salts in water (e.g., calcium salts of organic acids) is accompanied by evolution of heat. Evidently, the solubility of such salts decreases with rise in temperature.

According to Le Chatelier's principle, if a system under equilibrium is subjected to a change of concentration, pres or temperature, the system shifts in such a way that tends to und the effect of that change. You study this principle in detail in Unit 14.

10.5 SOLUTIONS OF GASES IN LIQUIDS

Most of the gases dissolve in water or some other liquids to a greater or lesser extent. In a gas, the molecules are quite far apart. After dissolution in a liquid solvent, the molecules of the gas are much closer. It is just like saying that before a gas dissolves in a liquid, it must be condensed to give a liquid. The condensation of gas is an exothermic process. The enthalpy of condensation is larger than the enthalpy of solution. Thus the dissolution of a gas is an exothermic process (i.e., heat is evolved). The solubility of a gas in a liquid is measured in terms of absorption coefficient or Bunsen coefficient. This coefficient has been named after the scientist, Bunsen, who introduced it. It is denoted by α. It is defined as the volume of a gas at standard temperature and pressure (273.15 K and 1.013×10^5 Pa) dissolved by unit volume of the solvent at the temperature of the experiment and under a pressure of 1.013×10^5 Pa. The absorption coefficients of some gases are given in Table 10.2.

Table 10.2 : Absorption Coefficients at 293 K

Solvent	Carbon dioxide	Hydrogen	Oxygen	Nitrogen
Water	0.88	0.018	0.028	0.015
Ethanol	3.00	0.081	0.142	0.130
Benzene	—	0.060	0.165	0.105

Factors affecting solubility of gases

The solubility of a gas in a liquid depends upon :

- temperature
- pressure, and
- nature of the gas and the solvent.

We will consider each of these factors separately.

1. Effect of temperature

The dissolution of a gas in a liquid is an exothermic process. Hence, according to Le Chatelier's principle, the solubility of a gas in a liquid decreases with rise in temperature. This behaviour can be seen when bubbles of dissolved air escape on heating water below 373 K.

2. Effect of pressure—Henry's law

The solubility of solids in liquids is not so much affected by pressure as the volume changes are not so high. But the solubility of a gas in a liquid varies considerably with pressure. In 1803, the English Chemist, Henry found that the solubility of a gas increases as the gas pressure is increased at a given temperature. He proposed the generalisation which is known as Henry's law. It may be stated as follows :

At constant temperature, the partial pressure of a gas over a solution is directly proportional to the concentration of the gas in the solution.

For example, doubling the pressure of oxygen, doubles the amount of oxygen that will dissolve in a given amount of the solvent.

Mathematically, Henry's law is expressed as follows:

$$p = Kx \qquad \ldots (10.7)$$

where p is the partial pressure of the gas over the solution and x is the solubility of the gas in terms of its mole fraction in the solution; K is a constant, characteristic of the specific combination of the solvent and the gas. It is called Henry's law constant. The partial pressure is expressed in terms of pascal (Pa).

From Eq. 10.7, the Henry's law constant is given as

$$K = \frac{p}{x} \qquad \ldots (10.8)$$

K has the dimensions of pressure. K is not constant as expected from Eq. 10.8 because of non-ideality of the solution. Its value is obtained by plotting the ratio p/x vs x and extrapolating to $x = 0$. Such a graph is shown in Fig. 10.2.

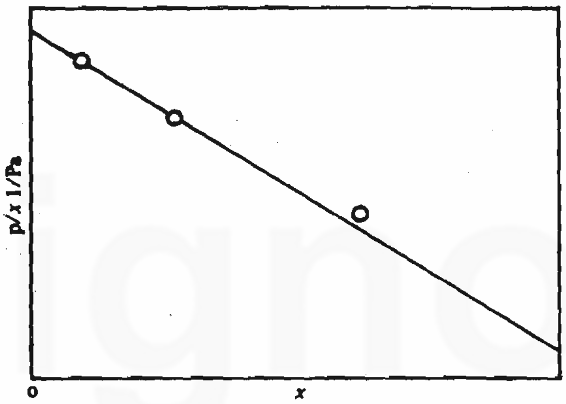

Fig. 10.2: Evaluation of Henry's law constant.

Henry's law constants for some gases are given in Table 10.3.

Table 10.3 : Henry's Law Constants at 298 K

Gas	$K/10^9$ Pa	
	In water	In benzene
H_2	7.12	0.37
N_2	8.68	0.24
O_2	4.40	—
CO	5.80	0.16
CO_2	0.17	0.01

It has been found that Henry's law is followed most closely by dilute solutions of gases that do not react with the solvent. So, the law is invalid for the solubility of hydrogen chloride and ammonia in water. Hydrogen chloride ionises in water and ammonia enters into chemical combination with water.

$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$
$$H_2O + NH_3 \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

3. Nature of the gas and the solvent

Generally, gases which react chemically with the solvent are more soluble in it than in other solvents. For example, hydrogen chloride gas is more soluble in water than in benzene. Gases which can be easily liquefied are more soluble in common solvents.

Example 2

The Henry's law constant for O_2 is 4.40×10^9 Pa. Calculate the molarity of oxygen in water at 298 K. The partial pressure of oxygen over the solution is 1.00×10^5 Pa. Assume that 1.00 dm³ of the aqueous solution weighs 1.00 kg.

Solution

$K = 4.40 \times 10^9$ Pa
$p = 1.00 \times 10^5$ Pa

Mole fraction of oxygen,

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} = \frac{n_{O_2}}{n_{O_2} + (1.00/0.018)\ \text{mol}} \approx \frac{n_{O_2}}{(1.00/0.018)\ \text{mol}} = \frac{n_{O_2}}{55.6\ \text{mol}}$$

The approximation is done above since the number of moles of O_2 is negligible in comparison to the number of moles of H_2O.

Substituting the values in Eq. 10.8, we get

$$4.40 \times 10^9\ \text{Pa} = \frac{1.00 \times 10^5\ \text{Pa}}{n_{O_2}/55.6\ \text{mol}} = \frac{1.00 \times 10^5\ \text{Pa}}{n_{O_2}} \times 55.6\ \text{mol}$$

$$\text{or } n_{O_2} = \frac{1.00 \times 10^5\ \text{Pa}}{4.40 \times 10^9\ \text{Pa}} \times 55.6\ \text{mol} = 1.26 \times 10^{-3}\ \text{mol}.$$

In other words, the solubility of oxygen in water at 298 K = 1.26×10^{-3} mol dm^{-3} since 1 kg (or 1 dm^3) of the solution contains 1.26×10^{-3} mol of oxygen.

SAQ 3

Why cannot fish live in warm water?

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10.6 SOLUTIONS OF LIQUIDS IN LIQUIDS

In the liquid-liquid type solution, we consider only binary liquid solutions, i.e., solutions containing two liquids. When two liquids A and B are mixed, we can have the following possibilities.

i) liquid A is completely miscible with liquid B in all proportions (e.g., water and ethanol, toluene and benzene, etc.).

ii) liquids A and B are only partially miscible in each other (e.g., water and phenol).

iii) liquids A and B are completely immiscible with each other (e.g., water and carbon tetrachloride). We shall study completely miscible liquid systems in this unit. The other two types will be taken up for study in Unit 11.

Raoult's Law

Consider a binary solution containing two liquids A and B which are completely miscible with each other in all proportions. In such solutions, the terms, solute and solvent, can be interchanged for the two components. In 1880, the French Chemist, Raoult found that when a non-volatile solute is dissolved in a solvent (liquid), the vapour pressure of the solvent decreases. If the solute and the solvent are both volatile, the vapour pressures of both the components are decreased. Based on these observations, he gave the following generalisation which is called **Raoult's law**.

Each component of an ideal solution is present in differing amounts in liquid and vapour phases. Remember that Raoult's law talks about the relationship between the partial pressure of a component and its mole fraction in the liquid phase.

The partial vapour pressure of any volatile component in a solution is equal to the product of the vapour pressure of the pure component and its mole fraction in the solution.

If x_A and x_B are the mole fractions of the components A and B in the liquid solution and p_A and p_B, the vapour pressures of these components, respectively, then according to Raoult's law,

$$p_A = p_A^\circ x_A \quad \ldots (10.9)$$

and $$p_B = p_B^\circ x_B \quad \ldots (10.10)$$

If the vapours behave like an ideal gas, then according to Dalton's law of partial pressures, the total vapour pressure, p, is given by

$$p = p_A + p_B = p_A^0 x_A + p_B^0 x_B \quad \ldots (10.11)$$

Ideal Solutions

A solution which obeys Raoult's law at all concentrations and at all temperatures is called an ideal solution. Two liquids A and B on mixing form an ideal solution, if

i) the molecules of A and B have similar structure and polarity, and

ii) the intermolecular attractions between A and A, B and B, and A and B are all alike.

Thermodynamically, ideal solutions are those in which there is no volume change ($\Delta V_{mixing} = 0$) and enthalpy change ($\Delta H_{mixing} = 0$) when two liquids A and B are mixed. Thus the characteristics of an ideal solution are:

i) it must obey Raoult's law

ii) $\Delta H_{mixing} = 0$

iii) $\Delta V_{mixing} = 0$

Some examples of nearly ideal liquid mixtures are :

i) ethylene bromide and ethylene chloride

ii) n-hexane and n-heptane

iii) benzene and toluene

iv) n-butyl chloride and n-butyl bromide

v) carbon tetrachloride and silicon tetrachloride

Non-ideal Solutions

Many of the completely miscible liquid pairs form non-ideal solutions. These solutions do not obey Raoult's law. They either show positive deviation (when the vapour pressure of the solution is higher than that of an ideal solution of the same concentration) or negative deviation (when the vapour pressure of the solution is lower than that of an ideal solution of the same concentration) from Raoult's law. In such solutions

$$p_A \neq p_A^\circ x_A \quad \ldots (10.12)$$

and $$p_B \neq p_B^\circ x_B \quad \ldots (10.13)$$

When the components of a non-ideal solution are mixed, a considerable change in volume and enthalpy is noticed. Thus the characteristics of non-ideal solutions are as follows :

i) they do not obey Raoult's law

ii) $\Delta H_{mixing} \neq 0$

iii) $\Delta V_{mixing} \neq 0$

Examples of non-ideal solutions showing positive and negative deviations are given in Table 10.4.

Table 10.4 : Liquid pairs showing deviation from Raoult's law

Positive deviation	Negative deviation
$H_2O + C_2H_5OH$	$H_2O + HCl$
$CH_3COCH_3 + C_2H_5OH$	$H_2O + HNO_3$
$C_2H_5OH + C_6H_{12}$	$H_2O + H_2SO_4$
$CH_3COCH_3 + CS_2$	$CH_3COCH_3 + CHCl_3$

Let us work out an example illustrating the application of Raoult's law.

Example 3

Two liquids A and B form an ideal solution at 300 K. The vapour pressure of a solution containing 1.0 mol of A and 2.0 mol of B at 300 K is 2.0×10^5 Pa. When one more mole of B is added to the solution, the vapour pressure of the solution is 2.1×10^5 Pa. Calculate the vapour pressures of A and B in the pure state.

Solution

According to Eq. 10.11, total vapour pressure of the solution is given by,

$$p = p^\circ_A x_A + p^\circ_B x_B$$

Substituting the values, we get

$$2.0 \times 10^5 \text{ Pa} = p^\circ_A \left(\frac{1.0}{1.0 + 2.0}\right) + p^\circ_B \left(\frac{2.0}{1.0 + 2.0}\right)$$

or $2.0 \times 10^5 \text{ Pa} = p^\circ_A/3.0 + 2.0\, p^\circ_B/3.0$

or $p^\circ_A + 2.0\, p^\circ_B = 6.0 \times 10^5$ Pa . . . (1)

Also $2.1 \times 10^5 \text{ Pa} = p^\circ_A \left(\frac{1.0}{1.0 + 3.0}\right) + p^\circ_B \left(\frac{3.0}{1.0 + 3.0}\right)$

or $p^\circ_A + 3.0\, p^\circ_B = 8.4 \times 10^5$ Pa . . . (2)

From (1) and (2),

$p^\circ_B = 2.4 \times 10^5$ Pa

$p^\circ_A = 1.2 \times 10^5$ Pa

SAQ 4

0.100 mol of acetone and 0.100 mol of chloroform are mixed at 308 K. At this temperature, the total vapour pressure of the solution is 3.47×10^4 Pa. The vapour pressures of pure acetone and pure chloroform at 308 K are 4.60×10^4 Pa and 3.92×10^4 Pa, respectively. Verify whether this solution is ideal or not.

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10.7 RAOULT'S LAW CURVES

According to Raoult's law, the partial vapour pressure of each component A and B of an ideal solution is given by Eqs. 10.9 and 10.10. The partial vapour pressure of each component can be plotted against its mole fraction in the liquid phase. Such vapour pressure curves for an ideal solution are shown in Fig. 10.3.

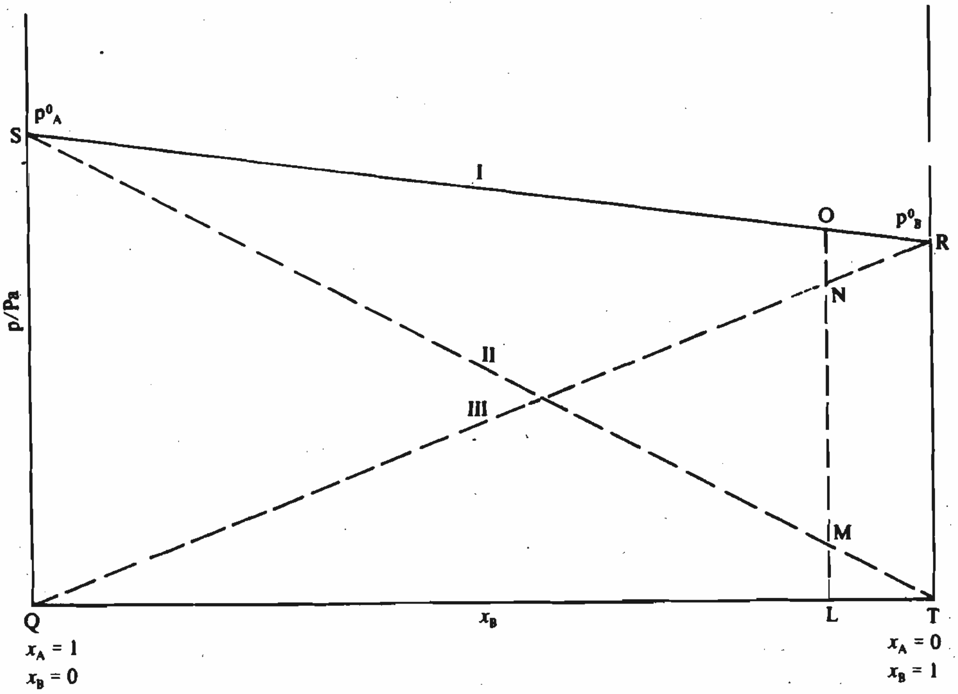


Fig. 10.3 : Vapour pressure curves for ideal solution :
Curve I : Total vapour pressure of solution;
Curve II : Partial vapour pressure of A, $p_A = p_A^\circ x_A$;
Curve III : Partial vapour pressure of B, $p_B = p_B^\circ x_B$

Note that the partial pressure curves II and III of the components A and B pass through the respective origins T and Q (where the mole fraction of a particular component and its partial pressure are zero). This is understandable since the partial pressure of a component, p_i as given by Raoult's law is $p_i = p^\circ_i x_i$. This resembles the equation $y = mx$ that represents a straight line passing through the origin. The curve I representing the total vapour pressure of an ideal solution is a straight line connecting p_A° and p_B°, since the total pressure p as per Eq. 10.11 is given by

$p = p_A^\circ$ when $x_A = 1$ and $x_B = 0$ and $p = p_B^\circ$ when $x_A = 0$ and $x_B = 1$

The dotted lines show the variation of vapour pressure of the components A and B with mole fraction in the liquid phase. Thus curve QR (III) indicates the variation of partial vapour pressure of B with its mole fraction in liquid solution and curve ST (II) indicates the variation of partial vapour pressure of A with its mole fraction in the liquid solution. The points, S and R, represent the vapour pressures (p_A^0 and p_B^0) of the pure components A and B, respectively. The variation of total vapour pressure with respect to the mole fraction of B in the liquid solution is given by the curve SR (I).

From Fig. 10.3, it can be seen that the vapour pressure of an ideal solution of composition L is given by the sum of the partial vapour pressure of A and the partial vapour pressure of B (or OL = ML + NL).

Vapour Pressure Curves of Solutions Showing Positive Deviation

If the molecular interactions between A and B are weaker than the A-A or B-B molecular interactions, then the escaping tendency of the molecules of A and B from the solution becomes more than that from the pure liquids. As a result, the vapour pressure of the solution will be greater than that of an ideal solution of the same composition. Such solutions are said to show positive deviation from Raoult's law. Mathematically,

$$p_A > p_A^\circ x_A \qquad \ldots (10.14)$$

$$p_B > p_B^\circ x_B \qquad \ldots (10.15)$$

$$\text{and } p > p_A^\circ x_A + p_B^\circ x_B \qquad \ldots (10.16)$$

In Fig. 10.4, the dotted lines are theoretical curves showing the ideal behaviour; the solid lines are curves drawn as per experimental values and show positive deviation from ideal behaviour. When ethanol and cyclohexane are mixed, the curves as shown in Fig. 10.4 are obtained.

In ethanol, there is a strong intermolecular hydrogen bonding. When cyclohexane is added to it, the cyclohexane molecules get in between the ethanol molecules thereby decreasing the intermolecular interactions. During the formation of such solutions, heat is absorbed and there is a slight increase in volume.

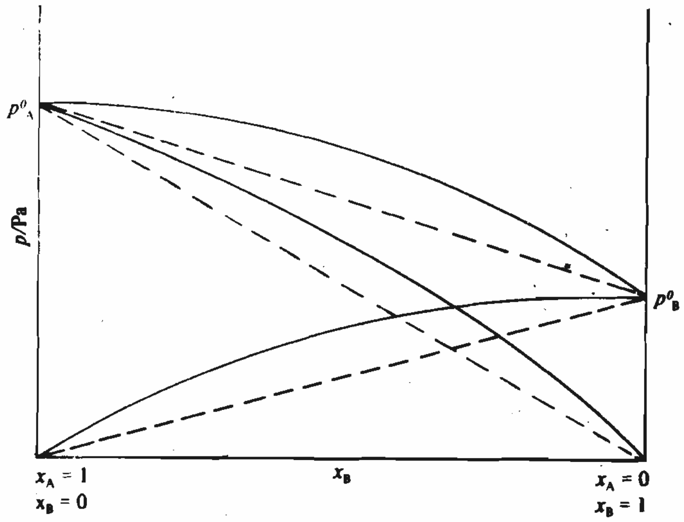


Fig. 10.4 : Curves showing positive deviation from Raoult's law.

Vapour Pressure Curves of Solutions Showing Negative Deviation

If the intermolecular forces between A and B are stronger than those of A-A and B-B, the solution formed by mixing A and B shows negative deviation from Raoult's law. Due to stronger A-B interactions, the escaping tendency of A and B from the solution becomes less than that from the pure liquids. The vapour pressure of such a solution will be less than an ideal solution of the same composition. This behaviour is shown in Fig. 10.5.

We have explained in Sec. 4.5 of Unit 4 of this course that increase of molecular attraction causes a decrease in vapour pressure of liquids.

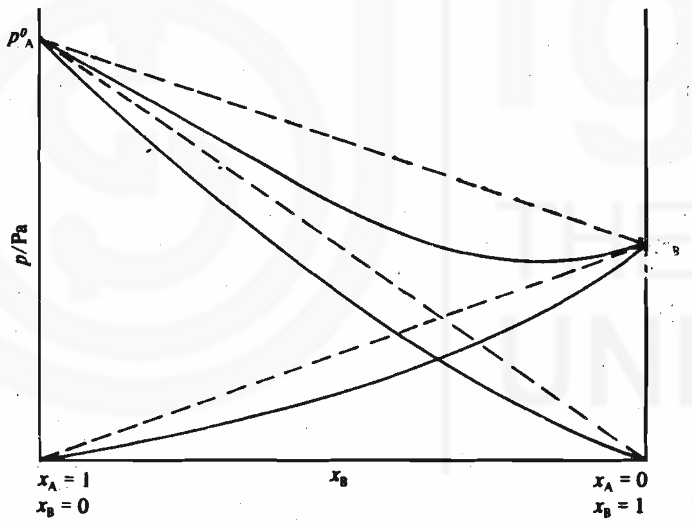


Fig. 10.5 : Curves showing negative deviation from Raoult's law.

The dotted lines are the theoretical curves representing the ideal behaviour, whereas the solid lines are the curves drawn as per experimental values and show negative deviation from ideal behaviour. When acetone and chloroform are mixed, they form hydrogen bonds with each other. As a result, the intermolecular attractions between acetone and chloroform become stronger. The tendency of the molecules to escape from the solution thus decreases. The vapour pressure, therefore, decreases. During the formation of such solutions, heat is evolved and there is a slight decrease in volume.

10.8 VAPOUR PRESSURE VARIATION WITH LIQUID AND VAPOUR COMPOSITION

Consider a solution containing one mole of benzene and one mole of toluene so that the mole fraction of each component in the solution is 0.5. The vapour pressures of pure benzene and toluene at 298 K are 1.25×10^4 Pa and 3.70×10^3 Pa, respectively. According to Raoult's law.

$$p_{C_6H_6} = p^{\circ}_{C_6H_6}\, x_{C_6H_6} = (1.25 \times 10^4 \text{ Pa}) \times 0.5 = 6.25 \times 10^3 \text{Pa}$$

$$p_{C_7H_8} = p^{\circ}_{C_7H_8}\, x_{C_7H_8}$$

$$= (3.70 \times 10^3 \text{ Pa}) \times 0.5$$

$$= 1.85 \times 10^3 \text{ Pa}$$

$$p_{\text{total}} = (6.25 \times 10^3 \text{ Pa}) + (1.85 \times 10^3 \text{ Pa}) = 8.10 \times 10^3 \text{ Pa}$$

Mole fraction of benzene in the vapour phase

$$= \frac{6.25 \times 10^3 \text{ Pa}}{8.10 \times 10^3 \text{ Pa}} = 0.77$$

Mole fraction of toluene in the vapour phase

$$= \frac{1.85 \times 10^3 \text{ Pa}}{8.10 \times 10^3 \text{ Pa}} = 0.23$$

It is quite interesting to compare the mole fractions of benzene in the vapour and liquid phase solutions. From the calculations made above, the mole fraction of benzene (0.77) in the vapour phase is more than that in the liquid phase (0.5). Again, the mole fraction of toluene in the vapour phase (0.23) is less than that in the liquid phase (0.5). Bearing in mind that benzene is more volatile than toluene, we can arrive at the following generalisation which is one of the forms of Konowaloff's rule: The mole fraction of a more volatile component in an ideal solution is more in the vapour phase than in the liquid phase.

For the purpose of comparing the compositions of the solutions in the liquid and the vapour phases at a given total vapour pressure, it is worth drawing curves of the type I and II shown in Fig. 10.6. Curve I shows the variation of total vapour pressure with respect to the mole fraction in the liquid phase. Similarly, curve II shows the variation of the total vapour pressure with respect to the mole fraction in the vapour phase. The line MN is called a **tie line** and it gives us the composition of the solution in the liquid and vapour phases in equilibrium at a particular total vapour pressure.

Note that the vapour phase curve II lies below the liquid phase curve I. This is due to the fact that the vapour phase is richer in the more volatile component than the liquid phase and this has been explained in the beginning of this section.

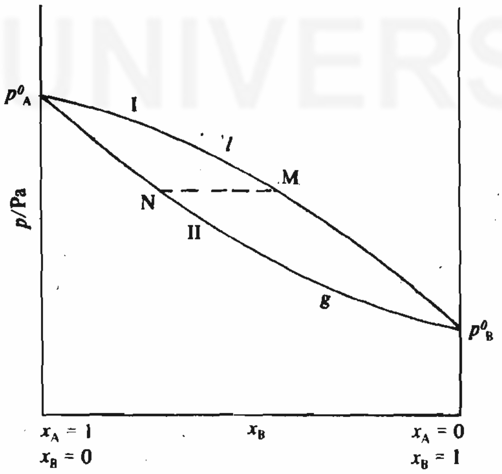


Fig. 10.6: Liquid and vapour composition curves for an ideal solution.

In Figs. 10.6 to 10.15, *g* and *l* refer to vapour phase and liquid phase curves.

The curves I and II of Fig. 10.6 are obtained in the case of solutions obeying Raoult's law. In the case of solutions showing positive deviation from Raoult's law, the liquid and vapour comporisition curves are of the type shown in Fig. 10.7. Note that there is a maximum point, M, where both the liquid and vapour phases have the same composition.

In the case of a solution showing negative deviation from Raoult's law, the liquid and vapour composition curves are of the type shown in Fig. 10.8. Note that the curves meet at the minimum point M' where both the liquid and vapour phases have the same composition.

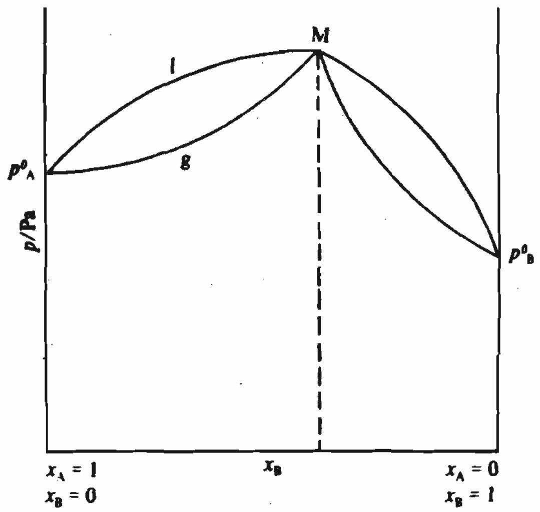


Fig. 10.7: Liquid and vapour composition curves for a liquid mixture showing positive deviation.

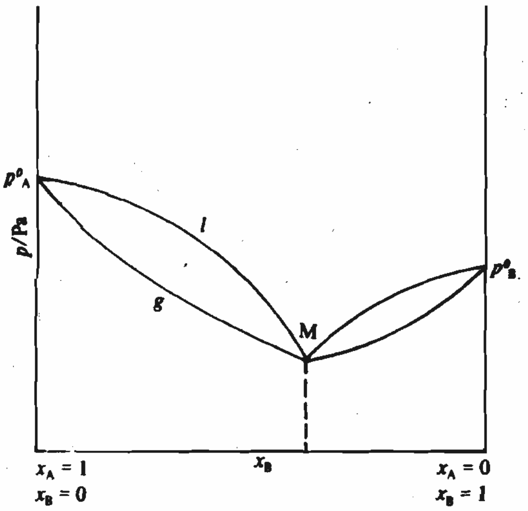


Fig. 10.8: Liquid and vapour composition curves for a liquid mixture showing negative deviation.

The curves in Figs. 10.3 to 10.8 have been drawn for vapour pressure values at constant temperature.

So far we studied the effect of composition on the vapour pressure of the completely miscible liquid system. In the next section, we will study the effect of composition on the boiling points of solutions. Such studies are helpful in understanding some of the aspects of separation of components from a binary liquid mixture. In particular, we will study the principles of fractional distillation and azeotropic distillation.

SAQ 5

In a binary solution obeying Raoult's law, can the liquid and the vapour phases have the same composition?

....

....

....

10.9 BOILING POINT DIAGRAMS

Let us consider a binary mixture consisting of two liquids A and B which are completely miscible with each other. On heating under constant pressure, say, under atmospheric pressure, it will start boiling when the total vapour pressure becomes equal to the atmospheric pressure. If p represents the atmospheric pressure, then the condition for boiling is

$$p = p_A + p_B \qquad \ldots (10.17)$$

where p_A and p_B are the partial pressures of the two components A and B. Since different compositions of a solution have different vapour pressures, the various solutions will not reach a total vapour pressure equal to the atmospheric pressure at the same temperature. Hence, the solutions of different compositions will boil at different temperatures. In general, solutions of low vapour pressure will boil at temperatures higher than those of solutions for which the vapour pressures are high. It is because solutions of high vapour pressure can have the total pressure equal to the atmospheric pressure at relatively lower temperatures as compared to solutions for which vapour pressures are low. Hence it is possible to draw temperature-composition diagrams which will correspond to the three general types of vapour pressure-composition diagrams. First we shall study boiling point-composition curves of an ideal solution:

Type I : Distillation of an Ideal Solution

Let us consider a binary mixture of liquids A and B obeying Raoult's law.

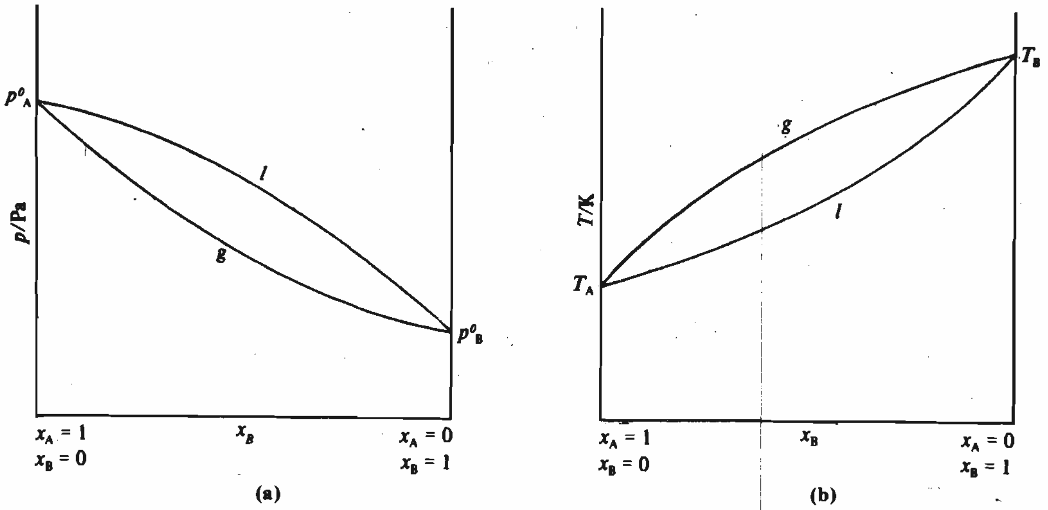


Fig. 10.9 : a) Liquid and vapour composition plotted against vapour pressure at constant temperature for an ideal solution, b) liquid and vapour composition plotted against temperature at constant pressure for an ideal solution.

Let the vapour pressure of pure A be higher than that of pure B (Fig. 10.9 a). Consequently at constant pressure, the boiling point of A (T_A) will be lower than that of B (T_B). We can get an idea about the relative composition of the vapour phase over a solution using Konowaloff's rule. Although you have studied one of the forms of this rule in the last section, this rule can also be stated as follows :

In the distillation of a binary liquid mixture, vapours coming out will be richer in that component whose addition to the liquid mixture causes an increase in vapour pressure.

In other words, as compared to the liquid mixture, the vapour is richer in the more volatile component. In the liquid mixture that we have taken, A is more volatile than B. Hence, the vapour composition at any temperature must lie closer to A than the corresponding liquid composition. In other words, in the composition against temperature plot, the vapour composition curve must lie above the liquid composition curve as shown in Fig. 10.9 b. Note the difference in the relative positions of the liquid and vapour curves between Figs. 10.9 a and b.

Using Fig. 10.10 we can understand the various stages in the separation of the components of an ideal solution.

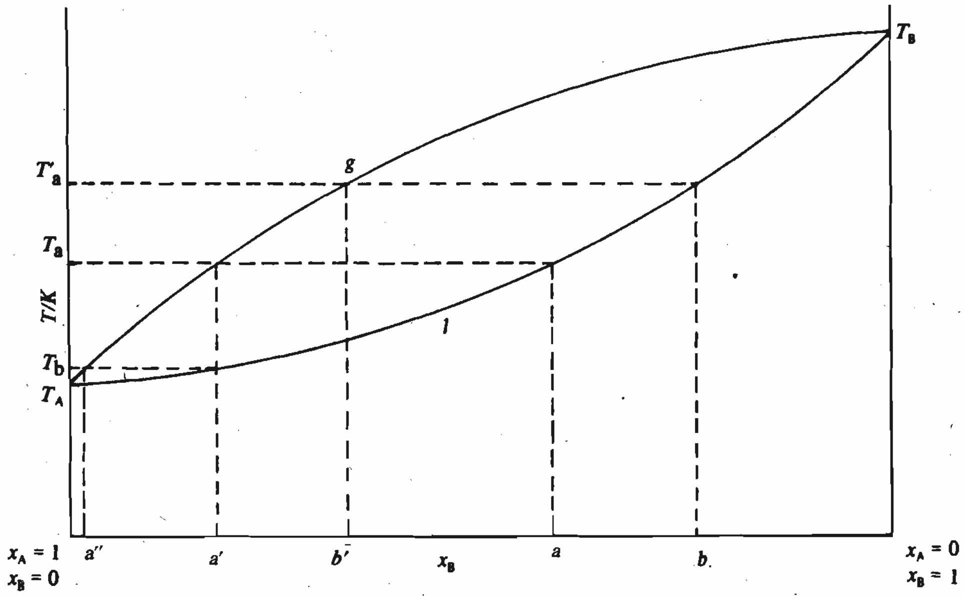


Fig. 10.10 : Separation of the components from an ideal solution at constant pressure.

Let us start with a solution of A and B having liquid composition, *a*. If this solution is heated, it boils at a temperature, T_a, when its vapour pressure is equal to the atmospheric pressure. At T_a, let the composition of the liquid and the vapour be *a* and *a*′, respectively. Since A is more volatile than B, vapours of composition *a*′ will be richer in A than liquid of composition *a*. Assume that these vapours coming out of the liquid are collected and condensed to obtain the liquid. The liquid so obtained by cooling the vapours of composition *a*′ also will have the same composition. As the vapours of composition *a*′ (which are richer in A than the liquid of composition *a*) are removed, the composition of the residual liquid changes to *b*; note that the liquid of composition *b* is richer in B than the liquid of composition *a*. The boiling point of this residual liquid (T_a') is higher than T_a. At this temperature, vapours coming out of the boiling tube have composition *b*′. Again the vapours of composition *b*′ are richer in A than the liquid of composition *b*. The vapours on condensation give liquid of composition *b*′. On the removal of vapours, the boiling point rises and the residual liquid becomes richer in *B*. So, if this process is continued, the boiling point of the residual solution will rise from initial boiling point T_a towards the boiling point of pure B, T_B. At the same time, the residue will become richer in B and if the process is repeated continuously, a final residue of pure B can be obtained.

Let us now consider the liquid *a*′ obtained by cooling the vapours coming out at T_a. If this liquid is heated, it boils at T_b and the vapours coming out will have the composition *a*″, which on condensation give the liquid of same composition. It is obvious from Fig. 10.10 that liquid of composition *a*″ is richer in A than that of composition *a*′. If the process of distillation and condensation is continued, we can obtain vapours of pure A. So, we can separate mixtures of type I into a residue of the less volatile component (B) and a distillate of more volatile component (A). The separation is practically more efficient using fractional distillation.

Fractional Distillation and Theoretical Plates

The several stages described for the separation of ideal solution into its pure components can be carried out in the continuous process which is called fractional distillation. In fractional distillation, the process of successive vaporization and condensation is carried out in a fractionating column. Let us understand it by taking benzene and toluene liquid mixture, having the composition *a* (Fig. 10.11).

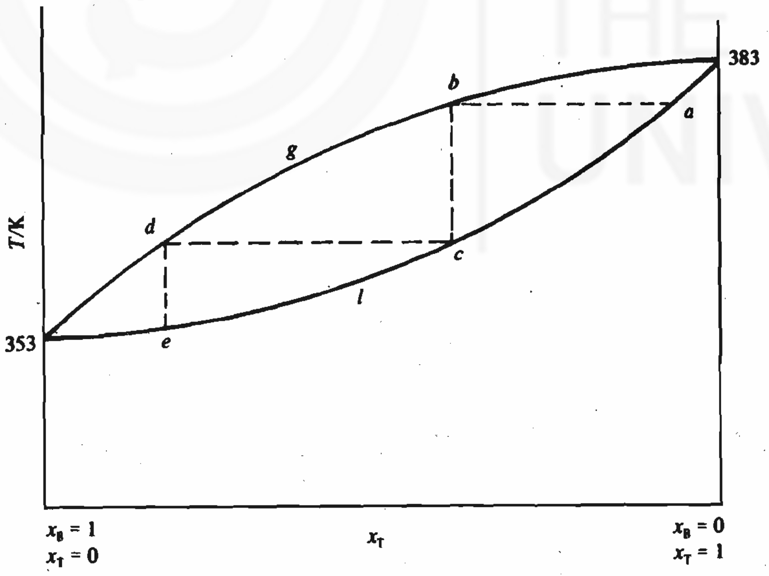
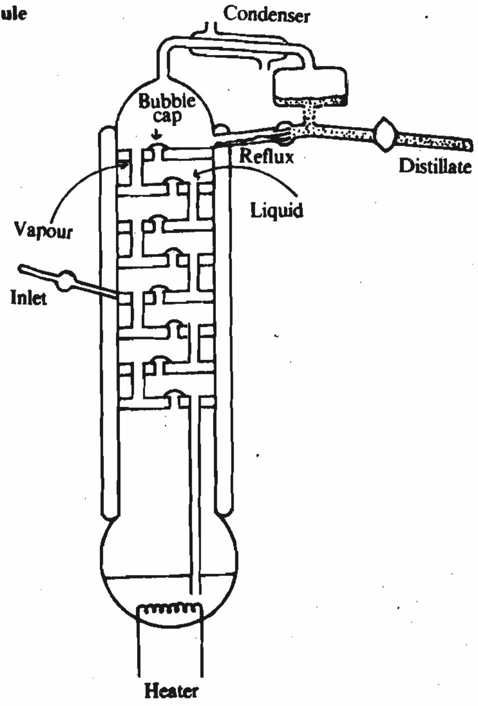


Fig. 10.11 : Liquid and vapour compositions of benzene and toluene; x_B and x_T refer to mole fractions of benzene and toluene.

The vapours in equilibrium are richer in the more volatile component, benzene, and will have the composition *b*. This vapour may be condensed by lowering the temperature along the line *bc*. If a small fraction of this condensate is vaporized, the vapours formed will have composition *d*. Finally, by repetition of vaporization and condensation, a vapour fraction rich in benzene can be obtained. Here, each vaporization and condensation represented by the path *abcde* corresponds to an idealized process in which only a small fraction of the vapour is condensed and only a small fraction of the condensate is revaporized. Practically, the fractionating column shown in Fig. 10.12 is more efficient.



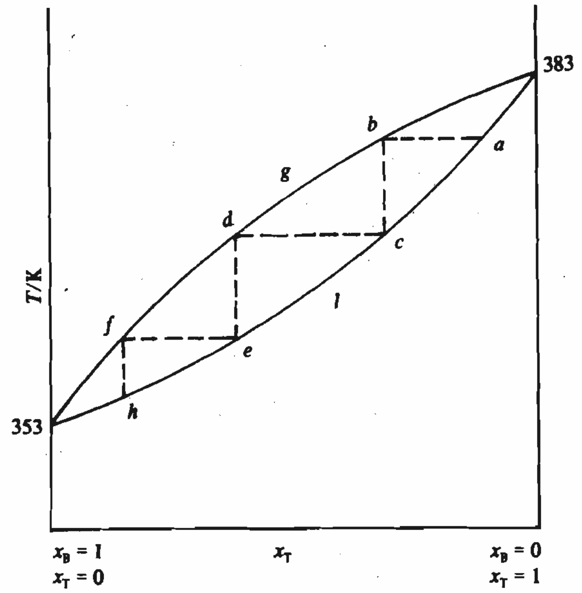


Fig. 10.12 : Fractionating column.

Fig. 10.13 : Fractionation of the components; x_B and x_T stand for mole fractions of benzene and toluene.

Each layer of the liquid on the plates of the column is equivalent to the boiling liquid in a distillation flask, and the liquid on the plate next above it is equivalent to the liquid condensed from the vapours. The vapour passes upwards through bubble caps, where it is partially condensed into the liquid and mixed with it. Part of the resulting solution is vaporized in the process and is condensed in the next higher layer, while part of the liquid overflows and runs down the tube to the next lower plate. The efficiency of a column is expressed in terms of the equivalent number of **theoretical plates.** The number of theoretical plates in a column is equal to the number of successive infinitesimal vaporizations required to give the separation to the desired extent. The number of theoretical plates in a distillation column under actual operation may be obtained by using Fig. 10.13 and counting the number of equilibrium vaporizations required to achieve the separation of the components to the required extent. Suppose that in distilling a solution of benzene and toluene of composition *a* with a certain distillation column, it is found that distillate of composition *h* is obtained (Fig. 10.13). Such a distillation is equivalent to three simple vaporizations and condensations as indicated by steps *abc, cde* and *efh*. Since the distilling pot itself corresponds to one theoretical plate, the column has two theoretical plates.

Type II : Distillation of a Solution Exhibiting Positive Deviation

Let us now take up the separation of a mixture of liquids showing positive deviation from Raoult's law. Fig. 10.14 represents the boiling point-composition diagram of such systems. Note that this system has a minimum point (C) where the liquid and vapour phases have the same composition.

Let us consider the distillation of a solution of composition, *a*, which is between X and C. The vapours coming off will have the composition *p* and will be richer in B than the liquid, *a*. Because of this, the composition of the residue will shift towards A. Hence, the residue will have to boil at a higher temperature than the original solution, *a*. If the distillation is continued (through the steps *abc, bcd* etc.), finally a residue of pure A, boiling at temperature T_A, will be obtained. Now, if the vapours of composition *p* coming out from the original solution, are condensed and redistilled repeatedly (through the steps *pqr, qrs*, etc.), vapours of composition C will eventually be obtained. Such vapours when condensed and redistilled will again yield the vapours of composition C i.e., vapours will have the same composition as that of the liquid solution. Hence, no further separation is possible by distillation. Because of this, the liquid of composition C is called the constant boiling mixture. Thus, any

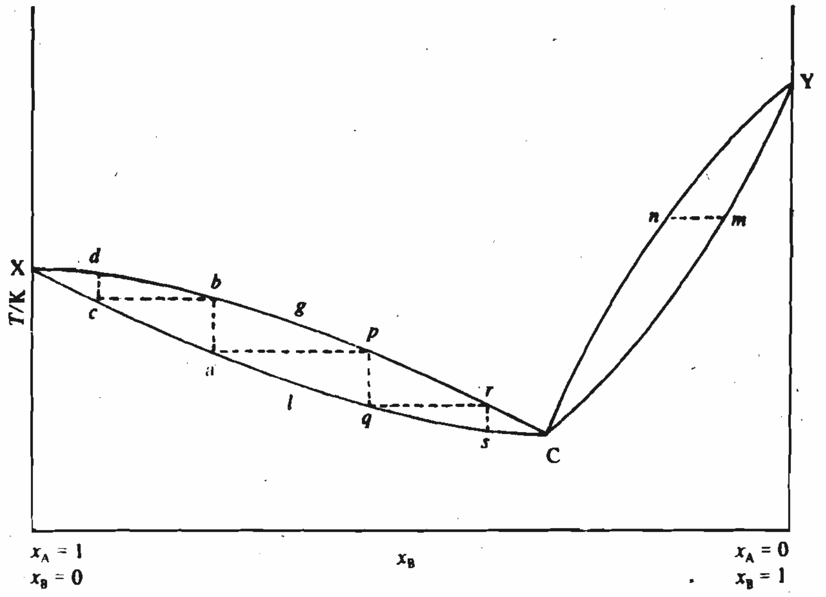


Fig. 10.14: Boiling point-composition digaram of a liquid mixture showing positive deviation.

mixture having a composition between X and C can be separated by fractional distillation only into a residue of pure A and a final distillate of composition, C, but pure B cannot be recovered.

On the other hand, if a solution of composition *m* which is between C and Y is distilled, then the vapours of composition *n*, which are coming out, will be richer in A than the original solution. Hence, on repeated distillation, the residue will tend towards pure B, while the distillate will tend towards C. Such solutions on complete distillation will yield, pure B in the residue and constant boiling mixture C in the distillate. Pure A cannot be recovered by the distillation of a liquid mixture of composition between C and Y.

Type III : Distillation of a Solution Exhibiting Negative Deviation

Now let us study the distillation behaviour of a mixture of liquids A and B showing negative deviation from Raoult's law. Fig. 10.15 represents the variation of liquid and vapour compositions of such a system at different temperatures.

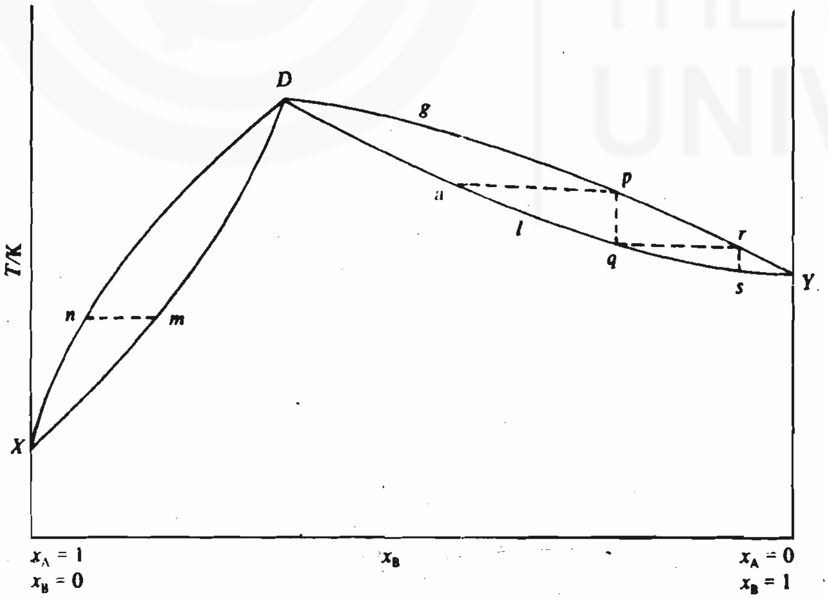


Fig. 10.15 : Boiling point-composition diagram of a liquid mixture showing negative deviation.

The behaviour of such a system on distillation is similar to the previous one. The difference is that the residues tend towards the maximum boiling mixture, while the distillates tend towards the pure constituents. If the starting mixture has a composition *a* which is between Y and D, then the vapours will have composition *p* richer in B than the solution *a*. Hence, the composition of ~~the~~ residue will shift towards D. Repeated distillation of the condensate will finally yield pure B in the vapour form. That is, repeated distillations and condensations of liquid *a* leads to a liquid residue of composition D and vapours of pure B.

A mixture of composition *m* between D and X will yield on distillation a vapour of composition *n* richer in A than the solution. Here again, the residue will shift towards D. By redistillation of the condensate, the vapours will tend towards pure A. Finally, we will have a residue of composition D and a distillate of pure A.

In general, we can separate a liquid mixture showing negative deviation into a residue of composition D, the constant maximum boiling mixture, and a distillate of either pure A or pure B, depending on whether the starting composition is between X and D or D and Y. But D cannot be separated further by distillation.

The constant boiling mixtures having composition C in type II solutions (Fig. 10.14) and composition D in type III solutions (Fig. 10.15) are called **azeotropes** (i.e., liquids boiling unchanged). They resemble pure compounds in their boiling behaviour. However, changes in pressure produce changes in the **composition** as well as the boiling point of the azeotropes (see Table 10.5). The azeotropes are not chemical compounds but are rather mixtures resulting from the interplay of intermolecular forces in solution. Table 10.6 lists some azeotropic mixtures along with their composition and boiling points. In Tables 10.5 and 10.6, T_B stands for the boiling point of a liquid.

Azeotropes are called constant boiling mixtures, since these mixtures boil at constant temperature. The vapours coming out of the azeotropic mixture have the same composition as the liquid.

Table 10.5 : Pressure Dependence of H_2O-HCl Azeotropes

Pressure/ 10^5 Pa	% HCl	T_B/K
0.658	20.92	370.7
0.921	20.36	379.5
1.00	20.22	381.7
1.05	20.16	383.1

Table 10.6 : Azeotropes with Minimum Boiling Points (at 10^5 Pa)

Component-I	T_B of I	Component-II	T_B of II	Azeotrope	
	K		K	Mass % of I	T_B/K
H_2O	373.1	C_2H_5OH	351.4	4.50	351.3
H_2O	373.1	$CH_3COC_2H_5$	352.7	11.30	346.5
CCl_4	349.9	CH_3OH	337.8	79.44	328.8
CS_2	319.4	CH_3COCH_3	329.6	67.00	312.4
$CHCl_3$	334.3	CH_3OH	337.8	87.40	326.5

SAQ 6
Can azeotropes be separated into pure components by fractional distillation? Explain.

....

....

....

SAQ 7
How many theoretical plates are there as per Fig. 10.12?

....

....

....

10.10 SUMMARY

We have learnt in this unit about the solutions and their various properties. A solution is a homogeneous mixture of two or more substances. Solutions can be formed in all the three phases, namely, solid, liquid and gaseous. Solutions can be divided into nine types depending upon the physical state of the solute and the solvent. A solution which cannot dissolve more amount of a solute at a particular temperature is called a saturated solution. Pressure has only a small effect on the solubility of solids in liquids. The solubility of a gas varies with pressure.

Completely miscible liquid pairs may be ideal or non-ideal. Ideal solutions obey Raoult's law. Non-ideal solutions either show positive or negative deviation from Raoult's law. Ideal solution can be separated into pure components by fractional distillation. Non-ideal solution can be separated into two fractions by fractional distillation—one, a pure component and, another, a constant boiling azeotropic mixture.

10.11 TERMINAL QUESTIONS

1) Fill in the blanks in the following:
   i) The solubility of a solute .... with increase in temperature when the dissolution is accompanied by absorption of heat.
   ii) One molal solution contains a mole of a solute dissolved in .... of the solvent.
   iii) In an ideal solution, partial vapour pressure of a component of a solution = mole fraction × ....
   iv) The constituents of .... solution can be separated by fractional distillation into pure components.

2) Explain why we cannot prepare absolute alcohol by fractional distillation.

3) If 0.100 kg of an aqueous solution of potassium chloride contains 7.45×10^{-3} kg of the solute, then calculate the molality of the solution.

4) The vapour pressures of pure liquids A and B at 300 K are 2.6×10^4 Pa and 6.4×10^4 Pa, respectively. Calculate the mole fractions of A and B in vapour and liquid phases of a solution when the equilibrium total vapour pressure of the binary liquid solution is 4.5×10^4 Pa at 300 K. Assume that the liquid and the vapour are ideal.

5) The solubility of carbon dioxide in water at 298 K is 3.40×10^{-2} mol dm^{-3}. The partial pressure of carbon dioxide over the solution is 1.00×10^5 Pa. Assuming that one dm^3 of the solution contains 1.00 kg of water, calculate the Henry's lalw constant for carbon dioxide.

6) State whether the following statements are true or false:
   i) Azeotropes are compounds and not mixtures.
   ii) Molality is the number of moles of solute dissolved in one kilogram of the solvent.
   iii) Raoult's law for ideal solutions is applicable both to the liquid and the vapour phase compositions.
   iv) The solubilities of all substances, i.e., solids, liquids and gases, in liquids increase with rise in temperature.

7) State Konowaloff's rule.

8) Which of the following liquid pairs can be completely separated into its pure components?
   i) Ethanol — water
   ii) Ethylene chloride — ethylene bromide
   iii) Nitric acid — water
   iv) Acetone — carbon disulphide
   v) Carbon tetrachloride — silicon tetrachloride.

9) An azeotropic mixture of hydrochloric acid and water contains 20.2% hydrochloric acid. Calculate its molality.

10.12 ANSWERS

Self Assessment Questions

1) i) Solid in solid
   ii) Liquid in solid
   iii) Gas in liquid

2) The masses of ethanol and water are 0.100 kg each.

No. of mol of ethanol $= \dfrac{0.100\ \text{kg}}{0.046\ \text{kg mol}^{-1}} = 2.17$ mol

No. of mol of water $= \dfrac{0.100\ \text{kg}}{0.018\ \text{kg mol}^{-1}} = 5.56$ mol

Mole fraction of ethanol in the solution

$$= \frac{2.17\ \text{mol}}{(2.17\ \text{mol} + 5.56\ \text{mol})}$$

$$= \frac{2.17\ \text{mol}}{7.73\ \text{mol}} = 0.28$$

Mole fraction of water in the solution = (1−0.28) = 0.72.

3) The solubility of oxygen is less in warm water and hence the amount of oxygen is not enough for the fish to survive.

4) Mole fraction of acetone (x_A) = 0.500

Mole fraction of chloroform (x_C) = 0.500

Partial vapour pressure of acetone (p_A) $= 0.500 \times 4.60 \times 10^4$ Pa
$= 2.30 \times 10^4$ Pa

Partial vapour pressure of choroform (p_C) $= 0.500 \times 3.92 \times 10^4$ Pa
$= 1.96 \times 10^4$ Pa

If this solution were to behave ideally, the total vapour pressure should be (2.30×10^4 Pa) + (1.96×10^4 Pa) = 4.26×10^4 Pa. The observed value (3.47×10^4 Pa) is less than the value for an ideal solution. That is, acetone-chloroform mixture exhibits negative deviation from Raoult's law.

5) Not possible.

6) Azeotropes are constant boiling mixtures. They cannot be separated into pure components by fractional distillation.

7) 9 (8 + pot).

Terminal Questions

1) i) increases
   ii) 1 kg
   iii) vapour pressure of the pure component
   iv) an ideal.

2) When an aqueous solution of ethyl alcohol is fractionated, it forms a constant boiling mixture (containing 95.5% ethyl alcohol and 4.5% water).

3) Mass of the solute (KCl) $= 7.45 \times 10^{-3}$ kg

Mass of the solvent $= (100-7.45) \times 10^{-3}\ \text{kg} = 92.55 \times 10^{-3}$ kg

$$\text{No. of moles of the solute} = \frac{\text{Mass of the solute}}{\text{Molar mass of the solute}}$$

$$= \frac{7.45 \times 10^{-3}\ \text{kg}}{7.45 \times 10^{-2}\ \text{kg mol}^{-1}} = 0.1\ \text{mol}$$

$$\text{Molality of solution} = \frac{\text{Number of moles of the solute}}{\text{Mass of the solvent}}$$

$$= \frac{0.1 \text{ mol}}{92.55 \times 10^{-3} \text{ kg}} = 1.08 \text{ m}$$

4) From the given data $p^0_A = 2.6 \times 10^4$ Pa and $p^0_B = 6.4 \times 10^4$ Pa.
Let the mole fractions of A and B in the liquid phase be x_A and x_B, respectively.
Applying Raoult's law,

$$p_A = p^0_A x_A \text{ and } p_B = p^\circ_B x_B$$

Total vapour pressure, $p = p_A + p_B = p^0_A x_A + p^0_B x_B$

or $4.5 \times 10^4 \text{ Pa} = (2.6 \times 10^4 \text{ Pa})\, x_A + (6.4 \times 10^4 \text{ Pa})\, x_B$

But $x_A + x_B = 1$ or $x_B = 1 - x_A$
$4.5 \times 10^4 \text{ Pa} = (2.6 \times 10^4 \text{ Pa})\, x_A + (6.4 \times 10^4 \text{ Pa})\, (1 - x_A)$

$$= 6.4 \times 10^4 \text{ Pa} - (3.8 \times 10^4 \text{ Pa})x_A$$

$$\text{or } x_A = \frac{(6.4 \times 10^4 \text{ Pa}) - (4.5 \times 10^4 \text{ Pa})}{(3.8 \times 10^4 \text{ Pa})} = \frac{1.9 \times 10^4 \text{ Pa}}{3.8 \times 10^4 \text{ Pa}} = 0.5$$

$x_B = 1 - x_A = 1 - 0.5 = 0.5$

$p_A = p^0_A x_A = 2.6 \times 10^4 \text{ Pa} \times 0.5 = 1.3 \times 10^4 \text{ Pa}$

$p_B = p^0_B x_B = 6.4 \times 10^4 \text{ Pa} \times 0.5 = 3.2 \times 10^4 \text{ Pa}$

$$\text{Mole fraction of A in vapour phase} = \frac{p_A}{p} = \frac{1.3 \times 10^4 \text{ Pa}}{4.5 \times 10^4 \text{ Pa}} = 0.29$$

Mole fraction of B in vapour phase = 1−0.29 = 0.71.

5) According to Henry's law, Henry's constant, K, is given by

$$K = \frac{p}{x_{CO_2}}$$

Number of moles of carbon dioxide in 1 dm^3 of the solution
$= 3.40 \times 10^{-2}$ mol

Number of moles of water present in 1 dm^3 of the solution

$$= \frac{1.00 \text{ kg}}{0.018 \text{ kg mol}^{-1}} = 55.6 \text{ mol}$$

$$\text{Mole fraction of } CO_2\ (x_{CO_2}) = \frac{3.40 \times 10^{-2} \text{ mol}}{(3.40 \times 10^{-2} + 55.6) \text{ mol}} \simeq \frac{3.40 \times 10^{-2}}{55.6}$$

$$= 6.12 \times 10^{-4}$$

$$K = \frac{p}{x_{CO_2}} = \frac{1.00 \times 10^5 \text{ Pa}}{6.12 \times 10^{-4}} = 1.63 \times 10^8 \text{ Pa}$$

6) (i) False (ii) True (iii) False (iv) False.

7) See Secs. 10.8 and 10.9.

8) (ii) and (v).

9) Let us consider 0.100 kg of the azeotropic mixture.

Mass of water in 0.100 kg of the solution
$= (0.100 - 0.0202) \text{ kg} = 0.0798 \text{ kg}$

$$\text{No. of moles of HCl dissolved in 0.0798 kg } H_2O = \frac{\text{Mass of HCl}}{\text{Molar mass of HCl}}$$

$$= \frac{0.0202 \text{ kg}}{0.0365 \text{ kg mol}^{-1}} = 0.553 \text{ mol}$$

$$\text{Molality of the solution} = \frac{\text{No. of moles of HCl}}{\text{Mass of water}} = \frac{0.553 \text{ mol}}{0.0798 \text{ kg}}$$

$$= 6.93 \text{ m.}$$

UNIT 11 SOLUTIONS—II

Structure

11.1 INTRODUCTION

In Unit 10, we have discussed the completely miscible liquid systems. In this unit, we shall study the partially miscible and completely immiscible liquid systems. We shall explain Nernst distribution law and use it in calculating the amount of the substances left unextracted after a given number of extractions. This will help us in understanding the principle of extraction by the solvents. In the next unit, you shall study some of the aspects of dilute solutions.

Objectives

After studying this unit, you should be able to :

- describe the effect of temperature on the miscibility of partially miscible liquid pairs,
- define consolute temperature,
- describe the effect of impurities on the consolute temperature,
- explain the principle of steam distillation,
- explain distribution law, and
- explain the principle of solvent extraction.

11.2 PARTIALLY MISCIBLE LIQUID SYSTEMS

Some liquid pairs do not give homogeneous solutions at all compositions. Such liquid pairs are said to be partially miscible liquids. However due to increased solubility with increase or decrease of temperature, these may become completely miscible. We can explain such a system of liquids using phenol and water. When a very small amount of phenol is added to water at room temperature, it dissolves completely to give a single liquid phase. However, when the addition of phenol is continued, a point is reached when phenol does not dissolve anymore. At this point, two phases, i.e., two liquid layers are formed—one consisting of water saturated with phenol and the other containing phenol saturated with water. Further addition of phenol causes water to shift from water-rich layer to phenol-rich layer. If the addition of phenol is continued, a point is reached when phenol acts as a solvent for all the water present and the two phases merge with each other to form a single phase, i.e., solution of water in phenol. Thus, on shaking equal volumes of phenol and water, two layers are formed—one of phenol in water and the other of water in phenol.

It has been experimentally found that at constant temperature, the composition of the two layers, although different from each other, remains constant as long as the two phases are present. Such solutions of different compositions coexisting with each other are termed as conjugate solutions. The addition of small amounts of phenol or water changes the volume of the two layers and not their compositions. As the temperature is increased, the behaviour remains the same except that the mutual solubility of the two phases increases. When the temperature reaches 338.8 K, the composition of the two layers becomes identical and thereafter the two liquids are completely miscible; i.e., at and above 338.8 K, phenol and water dissolve in each other in all proportions and yield only a single liquid layer on mixing. The variation of mutual solubility of water and phenol with temperature is shown in Fig. 11.1.

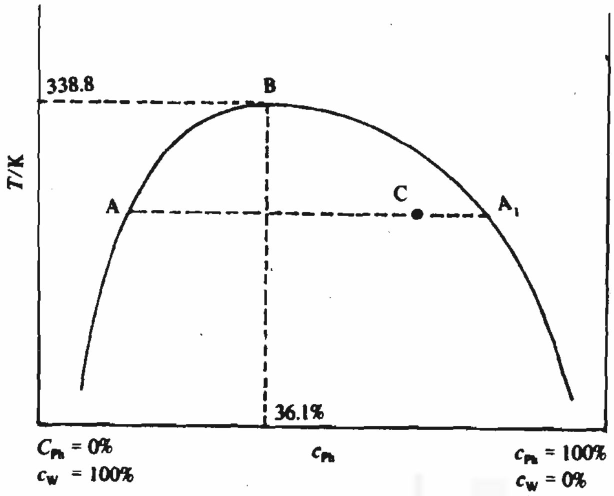


Fig. 11.1 : Phenol-water system; c_{Ph} stands for composition of phenol and c_w for composition of water.

At a particular temperature, say 325 K, point A represents the composition of water-rich layer and point A_1, represents the composition of phenol-rich layer in equilibrium with A. Between these compositions, all mixtures will yield two layers of compositions A and A_1. Outside these compositions, the two liquids are soluble mutually at 325 K. Similar behaviour is seen at other temperatures below 338.8 K. We can conclude that the dome-shaped area represents the range of existence of two liquid phases and the area outside the dome represents a single liquid phase. The temperature corresponding to the point B, i.e, the temperature at which the solubility becomes complete is called the **critical solution temperature** or the **consolute temperature.** Since the mutual solubility of phenol and water increases with rise in temperature, the critical solution temperature (CST) lies well above the room temperature. Hence, such liquid systems are said to possess an upper critical solution temperature or upper consolute temperature. Thus, the critical solution temperature, for phenol-water system is 338.8 K. At and above 338.8 K, phenol and water are completely miscible with each other in all proportions. At this temperature, the composition of the solution is 36.1% phenol and 63.9% water. At any point C, the relative weights of the two separate layers is given by the relationship,

$$\frac{\text{Mass of the first layer}}{\text{Mass of the second layer}} = \frac{A_1C}{AC} \qquad \text{... (11.1)}$$

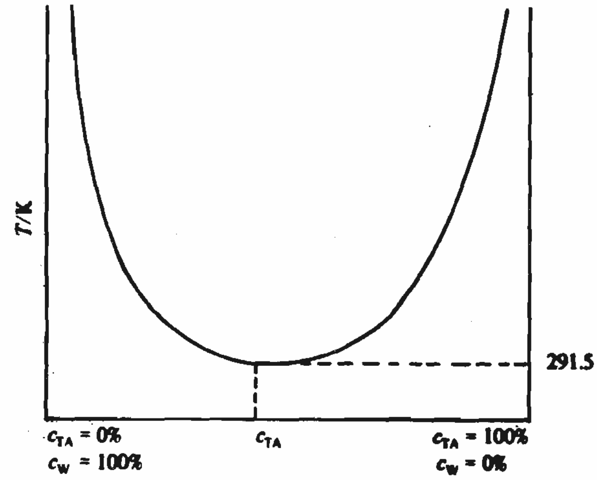


Fig. 11.2: Triethylamine-water system; c_{TA} stands for the composition of triethylamine.

There are some liquid pairs (e.g., triethylamine-water) for which mutual solubilities decrease with rise in temperature. As the temperature is decreased, the mutual solubilities increase and below the consolute temperature, the two liquids become miscible in all proportions. Such systems possess lower consolute temperatures. The variation of mutual solubility of triethylamine and water with temperature is shown in Fig. 11.2. Above 291.5 K, on shaking triethylamine and water, two layers are formed; but below 291.5 K, triethylamine and water are completely miscible with each other in all proportions.

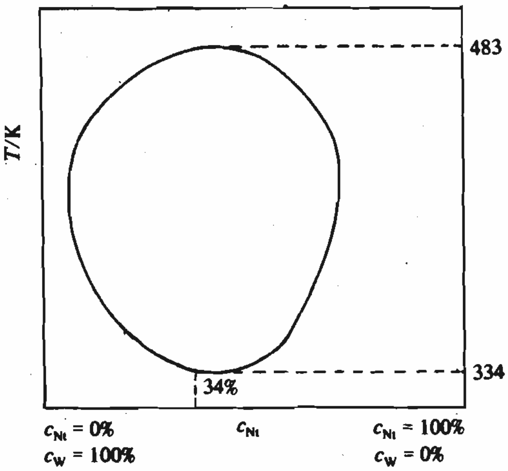


Fig. 11.3 : Nicotine-water system; c_{Nt} stands for the composition of nicotine.

Some liquid pairs, e.g., nicotine and water, show both the upper and lower consolute temperatures. These liquid pairs are completely miscible above a certain temperature (upper consolute temperature) and below a certain temperature (lower consolute temperature). The variation of mutual solubilities of nicotine and water with temperature is shown in Fig. 11.3. Within the enclosed area, the liquids are only partially miscible, while outside the enclosed area, they are completely miscible. The composition corresponding to both the upper and the lower consolute temperatures is the same, i.e., 34% nicotine. Table 11.1 lists the consolute temperatures of some liquid pairs. The two components are denoted as A and B.

Table 11.1 : Consolute Temperatures of Some Liquid Pairs

Components		Consolute temperature K	
A	B	Upper	Lower
Water	Phenol	338.8	—
Aniline	Hexane	333.6	—
Methanol	Carbon disulphide	323.5	—
Water	Diethylamine	—	316
Water	Triethylamine	—	291.5
Water	Nicotine	483	334
Glycerol	m-Toluidine	393	280

Effect of impurities on CST values

The presence of an impurity, dissolved in one or both of the phases, changes the CST values as well as the liquid phase composition at CST. Substances soluble in only one of the liquids raises the upper CST and lowers the lower CST. For example, one per cent solution of sodium chloride raises the upper CST of phenol-water system by 12°. About 0.12 molar solution of naphthalene (insoluble in water) in phenol raises the upper CST of phenol-water system by about 30°. Substances which are soluble in both the liquids tend to lower the upper CST and raise the lower CST. For example, sodium oleate is soluble in both water and phenol. Addition of 1% solution of sodium oleate to phenol-water system lowers the CST value by 45°.

As seen above, the presence of small amounts of impurities produces a very large change in the CST values. The changes in CST values is usually a linear function of concentration of impurities. Traces of water present in alcohol are estimated by measuring their CST values with cyclohexane.

As mentioned above, a very small amount of sodium oleate lowers the CST value of phenol-water system considerably. Thus, by making phenol completely miscible with water (by adding appropriate amounts of sodium oleate), lysol-like disinfectants are made.

SAQ 1

Give one example each for liquid pairs with,

a) lower critical solution temperature

b) upper critical solution temperature

c) both upper and lower critical solution temperatures.

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SAQ 2

What is the effect of adding 0.1 molar KCl on the CST of phenol-water system?

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SAQ 3

What would happen when potassium carbonate is added to a solution of water and alcohol ?

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11.3 IMMISCIBLE LIQUID PAIRS

In Sec. 11.2, we studied the partially miscible liquid pairs. In this section, we discuss the characteristics of the completely immiscible liquid pairs. We should, however, understand that there is always some solubility of a substance into the other. But this is so low that we can call it insoluble or completely immiscible.

According to Raoult's law, the vapour pressure of a liquid is lowered on the addition of another liquid, if the latter is soluble in the former. Otherwise, the vapour pressure of each component remains unaffected and each liquid exerts its own vapour pressure independent of the other. Thus, when two completely immiscible liquids A and B are mixed, the total vapour pressure (p) above the mixture will be the sum of the vapour pressures of the pure liquids at that temperature, i.e.,

$$p = p_A^0 + p_B^0 \qquad \ldots (11.2)$$

where p_A^0 and p_B^0 are respectively, the vapour pressures of pure A and B. It is known that a system starts boiling when its total vapour pressure becomes equal to the atmospheric pressure. The mixture of immiscible liquids A and B will thus start boiling at a temperature (T) at which,

$$p_A^0 + p_B^0 = \text{atmospheric pressure} \qquad \ldots (11.3)$$

This temperature will be lower than the normal boiling point of A or B. The mixed vapours thus obtained and condensed will have a composition dependent on the partial pressures of A and B at temperature T. Since the number of moles of each component present in the vapour phase is proportional to its vapour pressure, the mole ratio of A to B (n_A/n_B) in the condensate is given by

$$\frac{n_A}{n_B} = \frac{p_A^\circ}{p_B^\circ} \qquad \ldots (11.4)$$

Condensate or distillate is the liquid obtained by condensing the vapours.

If w_A and w_B are the masses of A and B in the condensate, and M_A and M_B their respective molar masses, then

$$\frac{n_A}{n_B} = \frac{w_A/M_A}{w_B/M_B} = \frac{w_A M_B}{w_B M_A} = \frac{p_A^\circ}{p_B^\circ} \qquad \ldots (11.5)$$

$$\text{or } \frac{w_A}{w_B} = \frac{p_A^\circ M_A}{p_B^\circ M_B} \qquad \ldots (11.6)$$

The fact, that a system of immiscible liquids starts boiling at temperatures less than the normal boiling points of both the liquids, is made use of in steam distillation. The steam distillation is a process of purifying organic liquids which have high boiling points and are immiscible with water. For purification by steam distillation, an impure compound

i) must be immiscible in water

ii) should not decompose at the temperature of steam

iii) should have a fairly high vapour pressure at 373 K

iv) should have non-volatile impurities.

For example, chlorobenzene has a boiling point of 405 K. A mixture of water and chlorobenzene distils at a constant temperature of 363.3 K, when the external pressure is 9.8×10^4 Pa, by passing steam through it. Let us explain the procedure for purifying an organic liquid using steam distillation. The apparatus used for steam distillation is as shown in Fig. 11.4

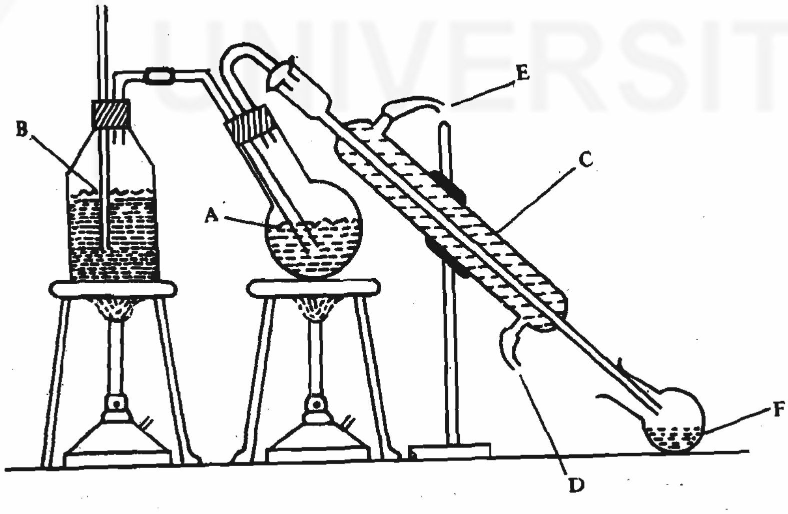

Fig. 11.4: Steam distillation.

The impure organic compound is taken in a round-bottomed flask (A) and a small quantity of water is added. The flask must be kept in a slanting position to prevent the impure liquid from splashing up into the condenser. The flask A is then heated gently on a sand bath. Now steam from flask B is bubbled through the contents in the flask. The vapours of the organic compound mix with steam and escape into the water condenser C. The condensate thus obtained in the flask F is a mixture of water and the organic compound. This mixture can be separated by means of a separating funnel.

A water condenser has a water inlet (D) and an outlet (E). This condenser is used for cooling the vapours (below 373 K) to get the liquid.

Let us illustrate the application of Eq. 11.6.

Example 1

A mixture of water and an organic liquid A, which is immiscible in water, distils at 368 K when the external pressure is 1.00×10^5 Pa. The vapour pressure of water at 368 K is 8.35×10^4 Pa. Calculate the relative molecular mass of A if the distillate contains 40% by weight of water.

Solution

Let us represent the vapour pressures of pure water and the organic liquid A at 368 K as $p^\circ_{H_2O}$ and p°_A, respectively. At a total pressure of 1.00×10^5 Pa, the liquid mixture boils, i.e.,

$$p^\circ_{H_2O} + p^\circ_A = 1.00 \times 10^5 \text{ Pa}$$

At the distillation temperature, $p^\circ_{H_2O} = 8.35 \times 10^4$ Pa

Hence $p^\circ_A = (1.00 \times 10^5 \text{ Pa} - 8.35 \times 10^4 \text{ Pa}) = 1.65 \times 10^4$ Pa

Using Eq. 11.6,

$$\frac{w_{H_2O}}{w_A} = \frac{p^\circ_{H_2O} \times M_{H_2O}}{p^\circ_A \times M_A}$$

But water is 40% by weight; hence we can write

$$\frac{40}{60} = \frac{8.35 \times 10^4 \text{ Pa}}{1.65 \times 10^4 \text{ Pa}} \times \frac{0.018 \text{ kg mol}^{-1}}{M_A}$$

$$\text{or} \quad M_A = \frac{8.35 \times 10^4 \text{ Pa}}{1.65 \times 10^4 \text{ Pa}} \times 0.018 \text{ kg mol}^{-1} \times \frac{60}{40}$$

$$= 0.137 \text{ kg mol}^{-1}$$

The relative molecular mass of A = 137.

SAQ 4

Why does a mixture of two immiscible liquids boil at a temperature which is lower than the boiling point of any of the pure liquids?

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11.4 DISTRIBUTION LAW

In this section, we discuss the effect of the addition of a solute to a pair of immiscible liquids. Water and carbon tetrachloride, for example, are practically immiscible with each other but iodine dissolves both in water and carbon tetrachloride. When iodine is added to a mixture of water and carbon tetrachloride at a certain temperature, iodine distributes itself between the two immiscible layers — water and carbon tetrachloride. Let the concentration of iodine in water and carbon tetrachloride be c_I and c_{II}, respectively, at a particular temperature. Then we have,

$$\frac{c_I}{c_{II}} = K \qquad \text{..(11.7)}$$

where K is a constant at a constant temperature.

If more of iodine is added to this system, it again distributes itself between the two layers. Now the concentration of iodine in both the layers will be more than that in the previous case. Let the concentrations be c_I' and c_{II}' in water and CCl_4 layers, respectively. Though $c_I' > c_I$ and $c_{II}' > c_{II}$, the ratio c_I'/c_{II}' is again equal to the constant, K, i.e.,

$$\frac{c_I}{c_{II}} = \frac{c'_I}{c'_{II}} = K \qquad \ldots (11.8)$$

It is evident that, in each case, I_2 distributes itself between the two immiscible layers in such a way that the ratio of its concentration in the two layers is a constant at a certain temperature. It was pointed out by Nernst that the ratio, c_I / c_{II}, is constant only when the solute exists in the same molecular form, i.e., the relative molecular mass of the solute is the same in two layers. The Nernst distribution law may be stated as follows:

At a fixed temperature, a substance X distributes itself between the two immiscible solvents A and B in equilibrium with each other in such a way that the ratio of the concentrations of X in the two solvents is constant, provided that the solute X is in the same molecular state in both the solvents.

Mathematically,

$$K = \frac{\text{Concentration of X in solvent A}}{\text{Concentration of X in solvent B}} \qquad \ldots (11.9)$$

The constant K is called the distribution or partition coefficient of the solute between the two solvents. You can see from the data given in Table 11.2 that the value of K is fairly constant in dilute solutions. As the concentration increases, there is a deviation.

Table 11.2: Distribution of I_2 between H_2O and CCl_4

$10^4 \times c_{H_2O}$ Mol dm^{-3}	$10^2 \times c_{CCl_4}$ Mol dm^{-3}	$K = \frac{c_{H_2O}}{c_{CCl_4}}$
3.22	2.745	1.17×10^{-2}
5.03	4.29	1.17×10^{-2}
7.63	6.54	1.17×10^{-2}
11.5	10.1	1.14×10^{-2}
13.4	11.96	1.12×10^{-2}

K depends upon

- nature of the solute
- nature of the solvent and
- temperature

The distribution law can be derived taking into account thermodynamic considerations.

Thermodynamic Derivation of Distribution Law

In Unit 9, Eqs. 9.83, 9.84 and 9.85 were derived by relating the chemical potential of an ideal gas to its partial pressure, concentration and mole fraction in a mixture of gases. We are going to use the modified from of Eq. 9.85 to denote the chemical potentials a solute (such as iodine) in the two immiscible liquids. Instead of mole fraction used in Eq. 9.85, we are going to use activity (a) which is an 'effective' mole fraction. In the case of an infinitely dilute solution, activity becomes equal to mole fraction. Hence using Eq. 9.85, the chemical potentials of iodine. μ_1 and μ_2 in water and carbon tetrachloride are given by the following equations.

$$\mu_1 = \mu_1^0 + RT \ln a_1 \qquad \ldots (11.10)$$
$$\mu_2 = \mu_2^0 + RT \ln a_2 \qquad \ldots (11.11)$$

where μ_1^0 and μ_2^0 are standard chemical potentials of iodine in water and carbon tetra chloride at unit activity; also a_1 and a_2 are the activities of iodine in water and carbon tetrachloride, respectively.

At equilibrium, $\mu_1 = \mu_2$

Hence $\mu_1^0 + RT \ln a_1 = \mu_2^0 + RT \ln a_2$

or $\mu_2^0 - \mu_1^0 = RT \ln a_1 - RT \ln a_2$
$= RT \ln a_1 / a_2$

At constant temperature, μ_1^0 and μ_2^0 are constants.

Also R is constant. It follows that

$$a_1 / a_2 = \text{constant} \qquad \ldots (11.12)$$

This is another form of the distribution law. At low concentrations, activities can be replaced by concentrations, and we get

$$\frac{a_1}{a_2} = \frac{c_1}{c_2}$$

Nernst first gave attention to the fact that the above statement of the distribution law is valid only when the solute undergoes no change such as dissociation or association in either of the solvents. If a solute dissociates into simple molecules or ions or if it associates to form complex molecules, then the distribution law does not apply to the total concentration of the solute in each of the two phases. It is applicable to the concentration of a particular species common to both the layers. Let us look at this in some detail taking the following cases.

Dissociation of a Solute in one of the Solvents

Let us take a solute X which remains undissociated in phase I. We assume that its concentration in phase I is c_1. In phase II, let it undergo dissociation into A and B. If c_2 is the total concentration in phase II before dissociation, and α is the degree of dissociation, then we can write

Eqs. 11.13 to 11.21 are written following the principles of chemical equilibrium which we will study in detail in Unit 14 of this course.

$$\underset{c_2(1-\alpha)}{X} \rightleftharpoons \underset{c_2\alpha}{A} + \underset{c_2\alpha}{B} \qquad .. \; (11.13)$$

Evidently, the concentration of the undissociated molecules of X in phase II is $c_2(1-\alpha)$. So as per distribution law, the distribution coefficient is given by

$$K = \frac{\text{concentration of X in phase I}}{\text{concentration of undissociated X in phase II}}$$

or $K = c_1 / c_2\,(1-\alpha)$ ...(11.14)

Example 2

An organic acid A, distributes between 1.0 dm³ each of an organic solvent, S, and water. The concentration of the acid in aqueous layer is 1.20×10^{-2} kg dm^{-3} and in the organic layer, it is 1.44×10^{-3} kg dm^{-3}. If the distribution coefficient of the acid between the organic solvent and water is 0.16, calculate the degree of dissociation of the organic acid in water. Assume that the acid does not undergo any change in its molecular state in the organic solvent, S.

Solution

Let the concentration of the acid in the organic and water layer be c_1 and c_2, respectively. Hence

$$c_1 = 1.44 \times 10^{-3}\ \text{kg dm}^{-3}$$
and $$c_2 = 1.20 \times 10^{-2}\ \text{kg dm}^{-3}$$

Using Eq. 11.14, we have

$$0.16 = \frac{1.44 \times 10^{-3}\ \text{kg dm}^{-3}}{1.20 \times 10^{-2}\ \text{kg dm}^{-3}\,(1-\alpha)} = \frac{0.12}{(1-\alpha)}$$

$$\text{or} \quad (1-\alpha) = \frac{0.12}{0.16} = 0.75$$

$$\alpha = 1 - 0.75 = 0.25$$

The percentage dissociation of the acid in water is 25%.

Association of the Solute in one of the Solvents

Let X be a solute that does not undergo dissociation or association in phase I. Let its concentration be c_1 in phase I. Let it associate in phase II as given in Eq. 11.15 to give the molecules, X_n.

Let us assume that c_2 is the concentration of the solute in phase II, if there is no association. Let α be the fraction of the molecules that is associated in phase II to give the molecules X_n.

$$\begin{array}{ccc} nX & \rightleftharpoons & X_n \\ c_2(1-\alpha) & & c_2\alpha/n \end{array} \quad \ldots (11.15)$$

Then the concentration of the associated molecules can be calculated as follows:

The concentration of the unassociated X = $c_2(1-\alpha)$

$$\left.\begin{array}{r}\text{The concentration of X used for forming}\\ \text{associated molecules}\end{array}\right\} = c_2\alpha$$

Since n moles of X give one mole of the associated species, X_n

$$\left.\begin{array}{l}\text{concentration of the}\\ \text{associated species, } X_n\end{array}\right\} = c_2\frac{\alpha}{n} \quad \ldots (11.16)$$

$$\text{Then, } K = \frac{\text{Concentration of X in phase I}}{\text{Concentration of the unassociated species in phase II}}$$

$$\text{or} \quad K = \frac{c_1}{c_2(1-\alpha)} \quad \ldots (11.17)$$

Also it is possible to calculate the equilibrium constant, K_{eq}, for equilibrium represented by Eq. 11.15, if α is known.

$$K_{eq} = \frac{c_2\frac{\alpha}{n}}{[c_2(1-\alpha)]^n} \quad \ldots (11.18)$$

$$\text{or } [c_2(1-\alpha)]^n = \frac{c_2\frac{\alpha}{n}}{K_{eq}} \quad \ldots (11.19)$$

$$c_2(1-\alpha) = \left[\frac{c_2\alpha/n}{K_{eq}}\right]^{1/n}$$

$$c_2(1-\alpha) = \left[\frac{c_2\alpha}{nK_{eq}}\right]^{1/n} \quad \ldots (11.20)$$

Substituting Eq. 11.20 in Eq. 11.17,

$$K = \frac{c_1}{\left[\frac{c_2\alpha}{nK_{eq}}\right]^{1/n}} = \frac{c_1}{c_2^{1/n}}\left[\frac{nK_{eq}}{\alpha}\right]^{1/n}$$

At constant temperature, n, K_{eq} and α are constants.

$$K = \frac{c_1}{c_2^{1/n}} \,.\, \text{constant}$$

$$K' = \frac{K}{\text{constant}} = \frac{c_1}{c_2^{1/n}} \quad \ldots (11.21)$$

Hence if c_1, c_2 and n are known, K' could be found out. The value of n could help us in finding out whether the solute remains as a dimer, trimer etc. in a particular solvent.

With the help of Eq. 11.21, it is possible to determine approximate values of n. Two important methods are illustrated below:

1) Method of Trial and Error

In Eq. 11.21, integer values starting with 1 and above are given to n. The value for which Eq. 11.21 gives a constant value for K' is adopted.

n is called the order of association.

2) Graphical Method

Eq. 11.21 can be written as,

$$c_1 = K' (c_2)^{1/n}$$

Taking logarithms on both sides, we get

$$\log c_1 = \log K' + \frac{1}{n} \log c_2$$

$$\text{or} \quad \log c_1 = \frac{1}{n} \log c_2 + \log K' \qquad \ldots(11.22)$$

Eq. 11.22 is of the type $y = mx + c$ which is an equation for a straight line. If a graph is plotted between $\log c_1$ and $\log c_2$, a straight line is obtained as shown in Fig. 11.5. The slope of the line gives the value of $1/n$ from which n can be calculated. The intercept on the Y-axis gives the value of $\log K'$ and hence K' can be calculated.

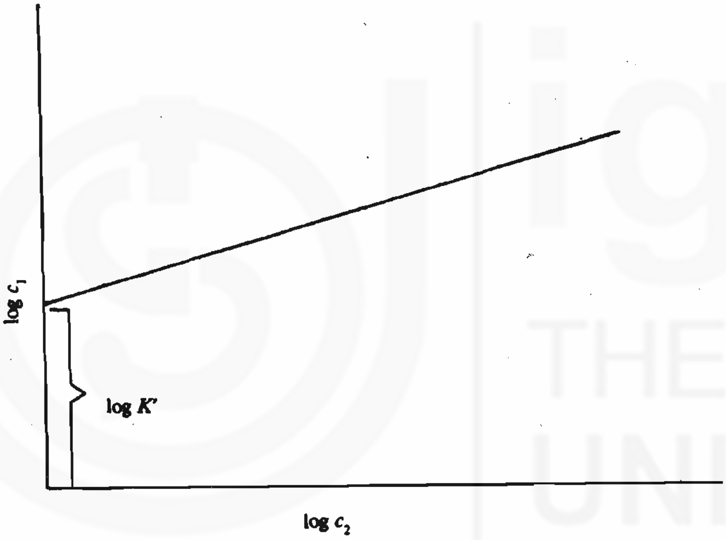

Fig. 11.5: log c_1 plotted against log c_2.

Example 3: The following results were obtained for the distribution of benzoic acid between water and benzene at 298 K:

Concentration in H_2O $(c_1)/(\text{mol dm}^{-3})$ 0.0033 0.0058 0.0075
Concentration in C_6H_6 $(c_2)/(\text{mol dm}^{-3})$ 0.0156 0.0495 0.0835

What conclusion can be drawn from these results concerning the molecular form of benzoic acid in benzene? Assume that c_1 represents the concentration of the undissociated benzoic acid in water.

Solution

It is known that benzoic acid is dissociated in water into its ions. The concentration c_1 of the undissociated benzoic acid is given above. If benzoic acid remains as normal molecules in benzene, then $\frac{c_1}{c_2}$ must be constant. Let us see whether it is so.

$$\frac{c_1}{c_2} = \frac{0.0033 \text{ mol dm}^{-3}}{0.0156 \text{ mol dm}^{-3}} = 0.211$$

$$\frac{c_1}{c_2} = \frac{0.0058 \text{ mol dm}^{-3}}{0.0495 \text{ mol dm}^{-3}} = 0.117$$

$$\frac{c_1}{c_2} = \frac{0.0075 \text{ mol dm}^{-3}}{0.0835 \text{ mol dm}^{-3}} = 0.090$$

As $\frac{c_1}{c_2}$ varies considerably, benzoic acid in benzene is not present as normal molecules. We can find the value of n using trial and error method. Substituting $n = 2$ in Eq. 11.21, let us try whether we get a constant value for $\frac{c_1}{c_2^{1/2}}$.

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0033 \text{ mol dm}^{-3}}{(0.0156 \text{ mol dm}^{-3})^{1/2}} = 0.0264\,(\text{mol dm}^{-3})^{1/2}$$

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0058 \text{ mol dm}^{-3}}{(0.0495 \text{ mol dm}^{-3})^{1/2}} = 0.0260\,(\text{mol dm}^{-3})^{1/2}$$

$$\frac{c_1}{c_2^{1/2}} = \frac{0.0075 \text{ mol dm}^{-3}}{(0.0835 \text{ mol dm}^{-3})^{1/2}} = 0.0260\,(\text{mol dm}^{-3})^{1/2}$$

It is clear from the above calculations that the values of $\frac{c_1}{c_2^{1/2}}$ are fairly constant.

Hence, benzoic acid in benzene exists as a dimer, $(C_6H_5COOH)_2$.

To understand the application of distribution law, when the solute undergoes association in one solvent and dissociation in another, let us consider the distribution of benzoic acid between water and chloroform as given in Table 11.3.

In Table 11.3, c_{w1} is the concentration of undissociated benzoic acid in aqueous layer and c_{c1} is the concentration of unassociated benzoic acid in chloroform layer.

Table 11.3 : Distribution of Benzoic Acid between Water and Chloroform at 313 K

$\frac{10^3 \times c_w}{\text{mol dm}^{-3}}$	$\frac{10^3 \times c_c}{\text{mol dm}^{-3}}$	$\frac{c_w}{c_c}$	$\frac{10^3 \times c_{w1}}{\text{mol dm}^{-3}}$	$\frac{10^3 \times c_{c1}}{\text{mol dm}^{-3}}$	$K = \frac{c_{w1}}{c_{c1}}$
2.11	7.21	0.293	1.78	4.04	0.441
2.68	10.8	0.248	2.31	5.23	0.442
3.53	16.8	0.210	3.10	7.01	0.442
7.25	57.0	0.127	6.62	15.0	0.441
12.7	167.0	0.076	11.8	26.9	0.439

In Example 3, the concentrations of undissociated benzoic acid in aqueous layer (c_1) have been given. But in Table 11.3, c_w gives the total concentration of benzoic acid in the aqueous layer and it includes the dissociated and undissociated forms. Also, c_c is the total concentration of benzoic acid in chloroform layer. You see that c_w / c_c is not constant. The observed results can be explained on the basis that the acid is partially dissociated in water into hydrogen ion and benzoate ion and partially associated in chloroform into dimers.

Since the distribution law can be applied to the common species present in both the phases (i.e., undissociated or unassociated benzoic acid), correction must be applied for association and dissociation. After applying these corrections, you see that $\frac{c_{w1}}{c_{c1}}$ is constant as given in the last column.

Applications of the Distribution Law

The study of the distribution of a solute between two immiscible solvents is quite useful in a number of ways. A few of these applications are given below:

1) By studying the distribution of acetic acid and benzoic acid between water and benzene, it is possible to show that acetic acid and benzoic acid exist as dimers in benzene.
2) If a solute dissociates in one of the solvents, then knowing the distribution coefficient, the degree of dissociation of the solute can be calculated at a particular temperature.

3) The distribution law has been used in study of many problems, e.g., solvent extraction, analysis and determination of equilibrium constants. Extraction is used both at laboratory and industrial scale in various processes. An organic compound can often be extracted economically from an aqueous solution or a suspension by,

- adding an organic solvent,
- shaking and separating the two layers, and
- finally distilling off the organic solvent to recover the purified compound.

In the process of extraction, we make use of the fact that the distribution coefficient of most of the organic compounds is very large in favour of organic solvents. It can be shown that with a given volume of an extracting liquid, the organic compound extracted is more if the extracting liquid is used in a number of instalments than if the whole of it is used in one lot. Let us derive a general formula which enables the calculation of the amount that is left unextracted after a given number of extractions.

If the distribution coefficient of a solute between ether and water is 3 in favour of ether, it means that the solute is 3 times more soluble in ether as compared to that in water.

Let us consider an aqueous solution of volume V. Let the mass of an organic compound dissolved in it be w. Let us use volume v of the organic liquid for each extraction and let the mass of the organic compound that remained unextracted in water after one extraction be w_1.

After the First Extraction

Concentration of the organic compound in the aqueous layer = $\frac{w_1}{V}$

Mass of the organic compound in the organic layer = $(w - w_1)$

Concentration of the organic compound in the organic layer = $\frac{(w - w_1)}{v}$

Distribution coefficient, K, is given by the following expression:

$$K = \frac{\text{Concentration of the compound in the aqueous layer}}{\text{Concentration of the compound in the organic layer}}$$

$$\text{or} \quad K = \frac{\frac{w_1}{V}}{\frac{(w-w_1)}{v}} = \frac{w_1 v}{(w-w_1)V}$$

$$\text{or} \quad K(w-w_1)V = w_1 v$$

$$\text{or} \quad KwV = w_1 v + Kw_1 V = w_1(v + KV)$$

$$\text{or} \quad w_1 = \frac{KwV}{(v + KV)} = w\frac{KV}{v + KV}$$

After the Second Extraction

Similarly, after the second extraction, the mass of the organic compound that remains unextracted is,

$$w_2 = w_1 \frac{KV}{v + KV} = w\left(\frac{KV}{v + KV}\right)^2$$

After *n* Extractions

In general, the mass of the organic compound that remains unextracted after *n* extractions is given by,

$$w_n = w\left(\frac{KV}{v + KV}\right)^n \quad \dots (11.23)$$

Often we have to recover the organic compounds from an aqueous solution using extraction method.

Desilverisation of Argentiferrous Lead

Desilverisation means removal of silver. Argentiferrous galena is an ore of lead containing silver.

Argentiferrous galena contains small quantities of silver which could be extracted quite economically by Parke's process. In this process, zinc is used for extracting silver from argentiferrous lead. The distribution coefficient of silver between molten Zn and molten Pb is 300 at 1073 K. Therefore, when molten zinc is added to molten argentiferrous lead, practically the whole of silver present passes into the molten zinc layer. As molten zinc and lead are immiscible, the two layers can be separated easily. Moreover, Zn-Ag alloy solidifies easily. As zinc is volatile, it can be separated from silver by distillation.

11.5 SUMMARY

When two liquids are mixed, they may be completely miscible, partially miscible or nearly completely immiscible. The miscibility of partially miscible liquid pairs varies with temperature. The miscibility of some partially miscible liquid pairs, e.g., phenol — water increases with rise in temperature. The temperature at which a pair of partially miscible liquids becomes completely miscible is called critical solution temperature. Thus phenol-water system possesses an upper CST. Some liquid pairs possess lower CST, i.e., their mutual solubility decreases with rise in temperature. Below a certain temperature, such liquid pairs are completely miscible. Some liquid pairs possess both lower and upper CST. The presence of an impurity in one or both the phases changes the CST values. Substances soluble in one of the liquids raise the upper CST and lower the lower CST. Substances soluble in both the liquids tend to lower the upper CST and raise the lower CST.

A pair of immiscible liquids boil at a temperature lower than the boiling points of any of the liquids. This fact is made use of in steam distillation. When a solute is added to a pair of immiscible liquids, it distributes itself between the two liquids in such a way that the ratio of the concentration of the solute in the two phases remains constant. This is called the distribution law. The distribution law can be used to study the state of association or dissociation of the solute in one or both the phases. It also helps in determining the degree of dissociation of a solute.

11.5 TERMINAL QUESTIONS

1) Two liquids A and B are completely immiscible with each other. Their normal boiling points are T_A and T_B, respectively and, T_A is less than T_B. The two liquids taken together will boil at

   a) T_A

   b) T_B

   c) $\frac{T_A + T_B}{2}$

   d) a temperature less than T_A

   e) none of these temperatures.

2) An immiscible mixture of an organic liquid, A and water on steam distillation boils at 372 K at pressure of 1.00×10^5 Pa. At this temperature the vapour pressure of water is 9.60×10^4 Pa. The ratio of the mass of water to the mass of A in the distillate is 4:1. Calculate the relative molecular mass of liquid A.

3) Explain the behaviour of partially miscible liquid systems with respect to change of temperature.

4) Derive distribution law thermodynamically.

5) When 1.00 dm³ of an aqueous solution containing 5.00×10^{-3} kg of a solute is shaken with 5.00×10^{-2} dm³ ether, it is found that 8.50×10^{-4} kg of the solute passes into ether. How much of the solute will be left unextracted, if the same aqueous solution is shaken with a second instalment of 5.00×10^{-2} dm³ ether? The solute exists in the same molecular state in both water and ether.

6) Succinic acid is associated in benzene. Find the order of association (n) from the following data on the distribution of succinic acid between water and benzene. Assume that c_1 is the concentration of undissociated succinic acid in water and c_2 is the total concentration of succinic acid in benzene.

$10^3 \times c_1$ in water/(kg dm^{-3})	1.10	1.95	2.90
$10^3 \times c_2$ in benzene/(kg dm^{-3})	14.2	41.2	96.5

11.7 ANSWERS

Self Assessment Questions

1) See Table 11.1.

2) Raises the critical solution temperature of phenol-water system.

3) Since potassium carbonate is highly soluble in water but not in ethanol, the solubility of ethanol in water decreases and two layers are formed.

4) The sum of the vapour pressures of the two liquids becomes equal to the atmospheric pressure at a lower temperature.

Terminal Questions

1) d)

2) Given that,

$$\frac{\text{Mass of water}}{\text{Mass of A}} = \frac{4}{1}$$

Vapour pressure of water ($p^\circ_{H_2O}$) = 9.60×10^4 Pa

Vapour pressure of liquid A (p°_A) = 1.00×10^5 Pa $- 9.60 \times 10^4$ Pa
= 4.00×10^3 Pa

Using Eq. 11.6,

$$\frac{w_{H_2O}}{w_A} = \frac{p^\circ_{H_2O} \times M_{H_2O}}{p^\circ_A \times M_A}$$

$$\text{or } M_A = \frac{p^\circ_{H_2O} \times M_{H_2O}}{p^\circ_A} \times \frac{w_A}{w_{H_2O}}$$

$$= \frac{9.60 \times 10^4 \text{ Pa} \times 0.018 \text{ kg mol}^{-1}}{4.0 \times 10^3 \text{ Pa}} \times \frac{1}{4}$$

$$= 0.108 \text{ kg mol}^{-1}$$

Hence, the relative molecular mass of A = 108

3) See Sec. 11.2.

4) See Sec. 11.4.

5) Concentration of the solute in aqueous layer
$(c_1) = (5.00 - 0.850) \times 10^{-3}$ kg/1.00 dm³
$= 4.15 \times 10^{-3}$ kg dm^{-3}

Concentration of the solute in ether layer

$$(c_2) = \frac{8.50 \times 10^{-4}\ \text{kg}}{5.00 \times 10^{-2}\ \text{dm}^3} = 1.70 \times 10^{-2}\ \text{kg dm}^{-3}$$

Distribution coefficient between water and ether

$$K = \frac{c_1}{c_2} = \frac{4.15 \times 10^{-3}\ \text{kg dm}^{-3}}{1.70 \times 10^{-2}\ \text{kg dm}^{-3}} = 0.244$$

Using Eq. 11.23, the amount of the solute left after the second extraction is

$$w_2 = w\left(\frac{KV}{v + KV}\right)^2$$

$$= 5.00 \times 10^{-3}\ \text{kg}\left[\frac{0.244 \times 1.00\ \text{dm}^3}{5.00 \times 10^{-2}\ \text{dm}^3 + (0.244 \times 1.00\ \text{dm}^3)}\right]^2$$

$$= 3.44 \times 10^{-3}\ \text{kg}$$

6) By trial and error method, let us try whether $\frac{c_1}{c_2}$ is constant keeping $n = 1$ in Eq. 11.21.

$$\frac{c_1}{c_2} = \frac{1.10 \times 10^{-3}\ \text{kg dm}^{-3}}{14.2 \times 10^{-3}\ \text{kg dm}^{-3}} = 0.077$$

$$= \frac{1.95 \times 10^{-3}\ \text{kg dm}^{-3}}{41.2 \times 10^{-3}\ \text{kg dm}^{-3}} = 0.047$$

$$= \frac{2.90 \times 10^{-3}\ \text{kg dm}^{-3}}{96.5 \times 10^{-3}\ \text{kg dm}^{-3}} = 0.030$$

As the value of $\frac{c_1}{c_2}$ is not constant, $n \neq 1$.

Let us now try for $n = 2$.

$$K = \frac{c_1}{\sqrt{c_2}} = \frac{1.10 \times 10^{-3}\ \text{kg dm}^{-3}}{\sqrt{14.2 \times 10^{-3}\ \text{kg dm}^{-3}}} = 9.23 \times 10^{-3}\ (\text{kg dm}^{-3})^{\frac{1}{2}}$$

$$= \frac{1.95 \times 10^{-3}\ \text{kg dm}^{-3}}{\sqrt{41.2 \times 10^{-3}\ \text{kg dm}^{-3}}} = 9.61 \times 10^{-3}\ (\text{kg dm}^{-3})^{\frac{1}{2}}$$

$$= \frac{2.90 \times 10^{-3}\ \text{kg dm}^{-3}}{\sqrt{96.5 \times 10^{-3}\ \text{kg dm}^{-3}}} = 9.34 \times 10^{-3}\ (\text{kg dm}^{-3})^{\frac{1}{2}}$$

As the value of $\frac{c_1}{c_2^{1/2}}$ is constant, the order of association is 2. Hence, succinic acid exists as a dimer in benzene.

UNIT 12 COLLIGATIVE PROPERTIES

Structure

12.1 INTRODUCTION

In Unit 10, we discussed the completely miscible liquid systems. In Unit 11, we discussed the partially miscible and nearly immiscible liquid systems. In this unit, we shall study colligative properties of the solutions containing non-volatile solutes. The colligative properties depend only upon the number of particles of the solute in the solution. They do not depend upon the nature of the solute. These properties help us in determining the relative molecular mass of a non-volatile solute. The colligative properties are :

- relative lowering of vapour pressure,
- elevation of boiling point,
- depression of freezing point, and
- osmotic pressure.

We shall study these properties in this unit.

Objectives

After studying this unit, you should be able to :

- explain what is meant by colligative property,
- state Raoult's law of relative lowering of vapour pressure,
- derive an expression relating the elevation of boiling point of a solution to its molality,
- define molal elevation constant,
- derive an expression relating the depression of freezing point of a solution to its molality,
- define molal depression constant,
- define osmotic pressure,
- suggest a method for determining the relative molecular mass of a non-volatile solute using osmotic pressure measurement,
- state van't Hoff laws of osmotic pressure, and
- explain van't Hoff factor.

12.2 RELATIVE LOWERING OF VAPOUR PRESSURE

If a pure liquid is placed in a closed container that is initially evacuated, the liquid evaporates to fill up the space above the liquid. At any given temperature when equilibrium is established, the pressure exerted by the vapours of a liquid is called the vapour pressure of the pure liquid (p_1^0). If a non-volatile solute is added to this liquid, the equilibrium vapour pressure (p_1) over the solution is found to be less than that of the pure liquid. According to Raoult's law, the vapour pressure (p_1) of the solvent of an ideal solution is given by $p_1 = p_1^0 x_1$ . . . (12.1)

The vapour pressure of a solution containing a non-volatile solute is less than the vapour pressure of the pure solvent.

where x_1 is the mole fraction of the solvent in the solution and p_1^0 is the vapour pressure of the pure solvent. Since the solute is non-volatile, its contribution towards the vapour pressure of the solution is negligible. Hence, the vapour pressure of solution containing a non-volatile solute is only due to the solvent. Since the mole fraction (x_1) of the solvent is less than one, it is clear from Eq. 12.1 that p_1 will also be less than p_1^0. The lowering of vapour pressure when a non-volatile solute is added to a solvent is given by ($p_1^0 - p_1$).

Substituting for p_1 from Eq.12.1, we get

$$p_1^\circ - p_1 = p_1^\circ - p_1^\circ x_1 = p_1^\circ (1 - x_1) \quad \ldots (12.2)$$

Since $x_1 + x_2 = 1$,

$$p_1^0 - p_1 = p_1^0 x_2 \quad \ldots (12.3)$$

where x_2 is the mole fraction of the solute.

According to Eq. 12.3, the lowering of vapour pressure of the solvent depends both on the vapour pressure of the pure solvent and on the mole fraction of the solute in the solution. In other words, it depends on the nature of the solvent and on the concentration of the solute and not on the nature of the solute. Eq. 12.3 can be written as

$$\frac{p_1^0 - p_1}{p_1^0} = x_2 \quad \ldots (12.4)$$

The expression on the left-hand side of Eq. 12.4 is called the **relative lowering of vapour pressure.** Eq. 12.4 also may be stated as:

It is the relative lowering of vapour pressure which is a colligative property and not the lowering of vapour pressure.

> "The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute."

The above statement is also called Raoult's law of relative lowering of vapour pressure.

Determination of Relative Molecular Mass from the Lowering of Vapour Pressure

It is possible to measure the relative molecular mass of a non-volatile solute, if the vapour pressure of a dilute solution containing the non-volatile solute is known. Thus if w_2 kg of the solute having molar mass M_2 kg mol^{-1} is dissolved in w_1 kg of the solvent having molar mass M_1 kg mol^{-1}, then from Eq. 12.4, we have -

$$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2} \quad \ldots (12.5)$$

$$\text{or} \quad \frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2} \quad \ldots (12.6)$$

For a dilute solution, the number of moles of the solute (n_2) is negligible in comparison to the number of moles of solvent (n_1). Thus Eq. 12.6 reduces to

$$\frac{p_1^\circ - p_1}{p_1^\circ} \simeq \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 M_1}{w_1 M_2} \quad \ldots (12.7)$$

Thus knowing the mass of the solvent, its relative molecular mass, mass of the solute, the vapour pressure of the solution and of the pure solvent, the relative molecular mass of the solute can be calculated from Eq. 12.7.

Measurement of Vapour Pressure Lowering

The lowering of vapour pressure of a solvent when a non-volatile solute is dissolved in it can be measured by the following methods:

i) Static Method

In this method, the difference between the vapour pressures of the solvent and the solution is determined with the help of a differential manometer. The apparatus is as shown in Fig. 12.1. It consists of two bulbs which are connected to a manometer. One arm of the manometer is connected with the bulb, A, containing the solvent and the other arm with the bulb, B, containing the solution. The manometric liquid is an inert, non-volatile, low density liquid such as β-bromonaphthalene, n-butylphthalate, etc. From the difference in the levels of the liquid in the two arms, the difference in vapour pressure between the solvent and the solution can be read directly.

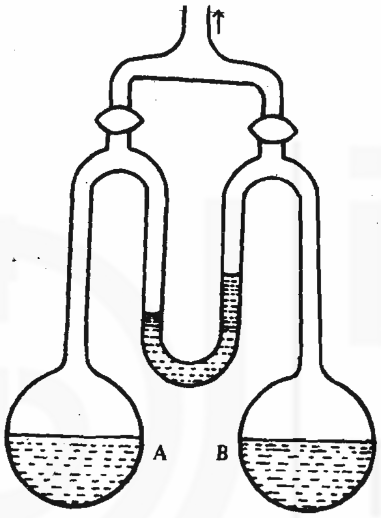

Fig. 12.1: Static method for determining the lowering of vapour pressure.

ii) Dynamic Method

This method is due to Ostwald and Walker. In this method (Fig. 12.2), a stream of dry and purified air is first passed through a pre-weighed set of bulbs containing the solution. The air coming out of the bulbs takes up an amount of vapour which is proportional to the vapour pressure of the solution. Evidently the loss in mass suffered by the bulbs containing the solution is proportional to the vapour pressure of the solution. If w_A is the loss in mass suffered by the solution-bulbs and p_1 is the vapour pressure of the solution, then we have

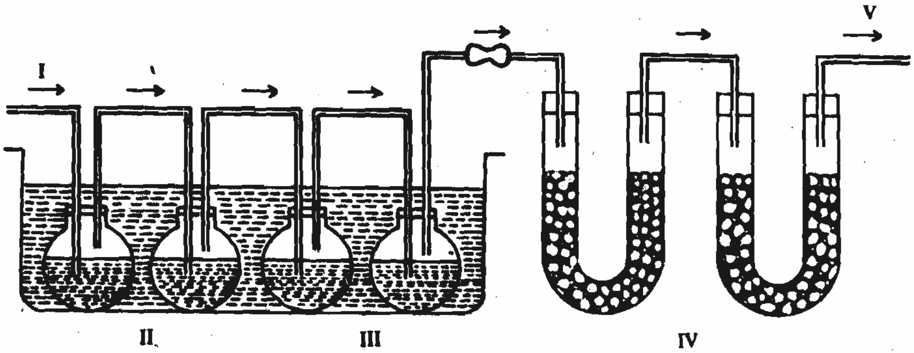

Fig. 12.2: Ostwald and Walker's apparatus for measuring the vapour pressure lowering:
I) air;
II) solution bulbs;
III) solvent bulbs; IV) weighed $CaCl_2$ tubes;
V) dry air.

$$w_A \propto p_1 \quad \ldots (12.8)$$

The air coming out of the solution bulbs is then passed through pre-weighed set of bulbs containing the solvent. As the air containing vapours of the solvent passes through the solvent, it takes up a further amount of vapour which is proportional to the difference in vapour pressures of the pure solvent and the solution. Evidently the loss in mass suffered by the solvent bulbs is proportional to the difference in vapour pressures of the pure solvent and the solution. If w_B is the loss in mass suffered by the solvent-bulbs and p_1° is the vapour pressure of the solvent, then we have

$$w_B \propto p_1^\circ - p_1 \quad \ldots (12.9)$$

From Eqs. 12.8 and 12.9 we have

$$(w_A + w_B) \propto p_1 + p_1^\circ - p_1$$

$$\text{or} \quad (w_A + w_B) \propto p_1^\circ \quad \ldots (12.10)$$

From Eqs. 12.9 and 12.10 we have,

$$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_B}{w_A + w_B} \quad \ldots (12.11)$$

Thus knowing w_A and w_B, the relative lowering of vapour pressure can be calculated using Eq. 12.11.

Fused calcium chloride is hygroscopic in nature and absorbs moisture from moist air.

If the solvent is water, the moist air coming out of the solvent bulbs may be passed through a weighed tube containing fused calcium chloride which absorbs moisture from moist air. The mass of calcium chloride tube will increase and the increase in mass will be equal to $(w_A + w_B)$.

Example 1

The vapour pressure of a solution containing 0.012 kg of a solute dissolved in 0.100 kg of water at 300 K is 3.50×10^3 Pa. Calculate the molar mass of the solute, if the vapour pressure of water at 300 K is 3.70×10^3 Pa.

Solution

$w_1 = 0.100$ kg; $w_2 = 0.012$ kg

$M_1 = 0.018$ kg mol^{-1}; $M_2 = ?$

$p_1^\circ = 3.70 \times 10^3$ Pa; $p_1 = 3.50 \times 10^3$ Pa

Using Eq. 12.7, we have

$$\frac{(3.70 \times 10^3 \text{ Pa} - 3.50 \times 10^3 \text{ Pa})}{3.70 \times 10^3 \text{ Pa}} = \frac{(0.012 \text{ kg})(0.018 \text{ kg mol}^{-1})}{(0.100 \text{ kg})(M_2)}$$

$$\text{or } M_2 = \frac{(0.012 \text{ kg})(0.018 \text{ kg mol}^{-1})}{0.100 \text{ kg}} \times \frac{3.70 \times 10^3 \text{ Pa}}{0.20 \times 10^3 \text{ Pa}}$$

$$= 0.040 \text{ kg mol}^{-1}$$

In this section, we discussed the correlation between the relative lowering of vapour pressure and the mole fraction of a non-volatile solute in a solution. In the next section, we shall study how the boiling point of a solvent is affected when a non-volatile solute is added to it.

SAQ 1

State whether the following statements are true or false:

i) Lowering of vapour pressure is not a colligative property.

ii) Relative lowering of vapour pressure is equal to the mole fraction of the solvent.
iii) Relative lowering of vapour pressure depends upon the number of particles of the solute and the solvent.

....

....

....

12.3 ELEVATION OF BOILING POINT

The temperature, at which the vapour pressure of the liquid becomes equal to the atmospheric pressure, is called the boiling point of the liquid. Since, according to Raoult's law, the vapour pressure of a solution containing a non-volatile solute is less than that of its pure solvent, the boiling point of such a solution will be higher than the boiling point of the pure solvent. This is because when a non-volatile solute is added to a solvent at a particular temperature, the vapour pressure of the solvent decreases. Thus the solution has to be heated further to make its vapour pressure equal the atmospheric pressure. This can be understood from the vapour pressure curves plotted in Fig. 12.3.

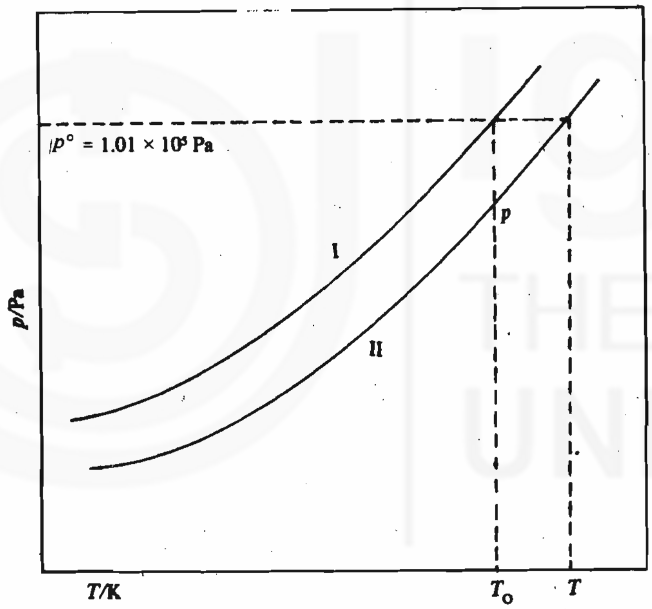

Fig. 12.3: Elevation of boiling point.

The curve I represents the variation of vapour pressure of the pure solvent with temperature. The curve II represents the variation of vapour pressure of a dilute solution of known concentration with temperature. The boiling point of the solvent is T_0 and that of the solution is T so that the elevation in boiling point is $T - T_0 = \Delta T_b$. At temperature T_0, the lowering of vapour pressure of a solvent, when a non-volatile solute is added to it, is $p^\circ - p$. From the vapour pressure curve of the solution, it is clear that the vapour pressure of the solution is p at T_0 and p° at T. Applying the integrated form of the Clausius-Clapeyron equation (Eq. 9.59), we have,

$$\ln \frac{p^\circ}{p} = \frac{\Delta H_{vap}}{R} \left[\frac{T - T_0}{TT_o} \right] \qquad \ldots (12.12)$$

where ΔH_{vap} represents the molar enthalpy of vaporization of the solvent at its normal boiling point T_0. Since, the solution is dilute, T_0 and T are not much different from each other. Eq. 12.12 may be written as

$$\ln \frac{p^\circ}{p} = \frac{\Delta H_{vap}}{R} \; \frac{\Delta T_b}{T_0^2} \qquad \ldots (12.13)$$

where, ΔT_b = Elevation in boiling point = $T - T_0$ and $T \simeq T_0$ so that $TT_0 = T_0^2$. But

$$\ln \frac{p^\circ}{p} = -\ln \frac{p}{p^\circ} = -\ln\left(1 - \frac{p^\circ - p}{p^\circ}\right)$$

$= -\ln(1 - x_2)$ (using Eq. 12.4 where x_2 is the mole fraction of the solute).

In the case of a dilute solution, x_2 is very small as compared to 1. In such cases, we can apply the approximation, $\ln(1 - x_2) = -x_2$

Hence, $\ln \frac{p^\circ}{p} = x_2$ .... (12.14)

From Eqs. 12.13 and 12.14, we have

$$x_2 = \frac{\Delta H_{\text{vap}}}{R} \quad \frac{\Delta T_b}{T_0^2} \qquad \text{... (12.15)}$$

But $x_2 = \frac{n_2}{n_1 + n_2}$ ... (12.16)

where n_1 and n_2 are the number of moles of the solvent and the solute, respectively.

When the solution is dilute, the number of moles of the solute is negligible in comparison with the number of moles of the solvent. Eq. 12.16 may be written as

$$x_2 = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} \qquad \text{... (12.17)}$$

From Eqs. 12.15 and 12.17, we have

$$\frac{\Delta H_{\text{vap}}}{R} \quad \frac{\Delta T_b}{T_0^2} = \frac{w_2/M_2}{w_1/M_1} \qquad \text{... (12.18)}$$

$$\text{or } \Delta T_b = \frac{RT_0^2}{\Delta H_{\text{vap}}} \quad \frac{w_2/M_2}{w_1/M_1} = \frac{RT_0^2 M_1}{\Delta H_{\text{vap}}} \times \frac{w_2}{w_1 M_2} \qquad \text{... (12.19)}$$

When one mole of a solute ($w_2 = M_2$) is dissolved in 1 kg of the solvent (w_1=1 kg), Eq. 12.19 reduces to

$$\Delta T_b = \frac{RT_0^2 M_1}{\Delta H_{\text{vap}}} \qquad \text{... (12.20)}$$

The right hand side of Eq. 12.20 consists of constants R, T_0, M_1 and ΔH_{vap}. Its value is a constant for a particular solvent and it is called the molal elevation constant for a particular solvent. It is denoted by K_b.

$$K_b = \frac{RT_0^2 M_1}{\Delta H_{\text{vap}}} \qquad \text{... (12.21)}$$

Using Eqs. 12.19 and 12.21, we can write

$$\Delta T_b = K_b \frac{w_2}{w_1 M_2} \qquad \text{... (12.22)}$$

$$\text{or } \Delta T_b = K_b \frac{n_2}{w_1} \qquad \text{... (12.23)}$$

$$\Delta T_b = K_b m \qquad \text{... (12.24)}$$

Molality is the number of moles of the solute dissolved in 1 kg of the solvent. If n_2 moles of a solute are dissolved in w_1 kg of the solvent, its molality is given by.

$$m = \frac{n_2}{w_1}$$

where n_2 is the number of moles of the solute and m is the molality of the solution.

Determination of Relative Molecular Mass from Elevation of Boiling Point

A known mass of a non-volatile solute, for which the relative molecular mass is to be determined, is dissolved in a known mass of the solvent. By measuring the elevation in boiling point, it is possible to calculate the relative molecular mass of the solute from Eq. 12.25 which is a rearranged form of Eq. 12.22.

$$M_2 = \frac{K_b}{\Delta T_b} \quad \frac{w_2}{w_1} \qquad \text{... (12.25)}$$

The molal elevation constants (K_b) for some liquids are given in Table 12.1.

Table 12.1: Molal Elevation Constants

Solvent	K_b K kg mol^{-1}	Solvent	K_b K kg mol^{-1}
Water	0.51	Ethyl alcohol	1.23
Acetone	1.71	Benzene	2.53
Carbon tetrachloride	4.95	Chloroform	3.90
Methyl alcohol	0.86	Cyclohexane	2.79

Determination of Boiling Point Elevation

For measuring the elevation of boiling point, a number of methods are available. In all these methods, care is taken to avoid superheating of the liquid. The most commonly used methods are given below:

Superheating means that the temperature of the liquid may rise above the boiling point of liquid and the liquid may not boil.

1) The Landsberger Method

In this method, the solvent or the solution is heated to its boiling point by passing the vapours of the solvent through them. As the vapours condense, they give up their latent heat to heat the solvent or the solution. Superheating is nearly impossible in this way because, when the boiling point is reached, the vapours will be in equilibrium with the liquid at atmospheric pressure and no more vapours will condense. The apparatus is shown in Fig. 12.4a. It consists of flask A which contains the solvent.

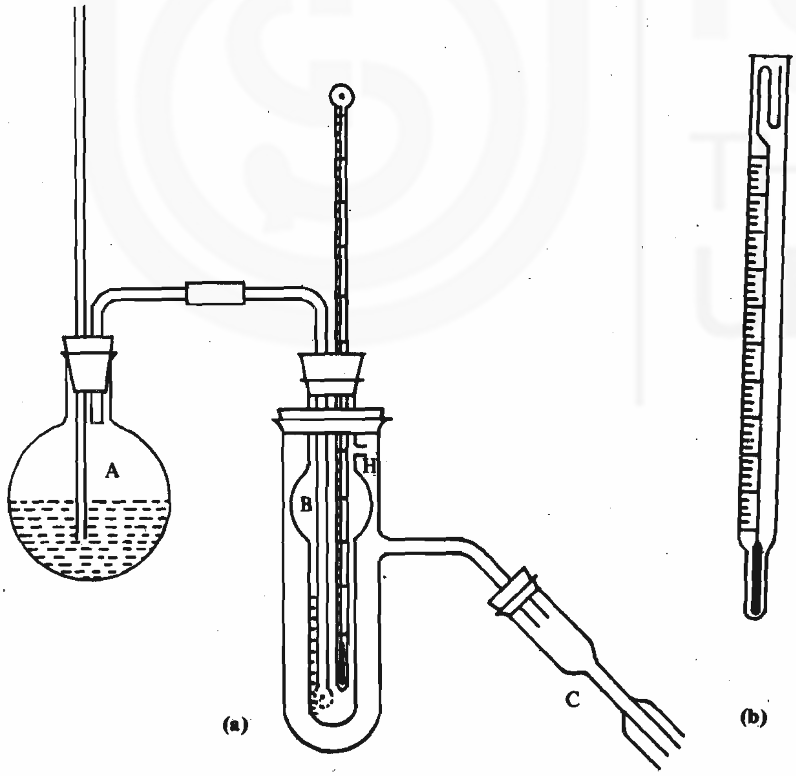

Fig. 12.4 : a) Apparatus for Landsberger method; b) Beckmann thermometer.

Beckmann thermometer contains a mercury reservoir at the top. The amount of mercury in the bulb can be varied. The thermometer can be used to measure temperatures from 234 K to 523 K. This thermometer does not give actual temperature. For measuring rise of boiling point, or depression in freezing point, only difference in temperature is required. This can be used with an accuracy of 0.001.

The flask is connected to a graduated tube B which also contains the solvent. Solvent in flask A is boiled so that the vapours pass into the solvent in B, where these vapours emerge in small bubbles through a number of holes at the end of the tube. The temperature of the solvent rises and when it becomes constant, it is noted. Any excess vapours pass from the right hand top portion (H) of the graduated tube (B) into the condenser (C). A known mass of the non-volatile solute is then added to the solvent in

B. The solution is then again heated by passing the vapours of the solvent through it. When the temperature reaches a constant value, it is noted. The passage of vapours is stopped and the volume of the solution is noted as shown on the graduated tube. A thermometer, which is graduated in tenths of a degree and is capable of reading upto 0.01°, is generally used. One such thermometer is the Beckmann thermometer (Fig. 12.4b. Knowing the density of the solvent, the mass of the solvent in the solution can be calculated. The volume of the solute is supposed to be negligible. The difference between the two boiling points gives the elevation in boiling point.

2) Cottrell's Method

The apparatus is as shown in Fig. 12.5. It consists of a graduated tube A which contains the liquid-solvent or the solution. An inverted funnel is placed in the tube A through which the bubbles rise. When the liquid starts boiling, a steam of liquid and the vapours is poured over the bulb of a Beckmann thermometer so that the bulb of the thermometer is covered with a thin layer of the boiling liquid. After determining the boiling point of the pure solvent, a known mass of the solute is added and the boiling point of the solution is again determined. The difference between the two readings gives the elevation in boiling point.

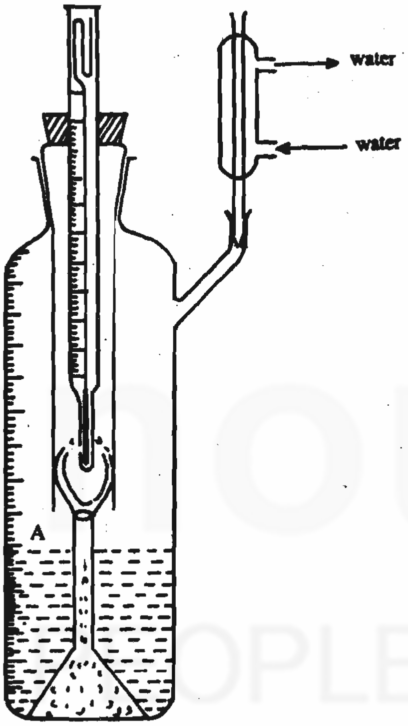

Fig. 12.5: Apparatus for Cottrell's method.

Example 2

The boiling point of chloroform was raised by 0.320 K when 5.15×10^{-4} kg of an organic compound was dissolved in 3.50×10^{-2} kg of chloroform. Calculate the molar mass of the organic compound. Molal elevation constant for chloroform is 3.90 K kg mol^{-1}

Solution

$$\Delta T_b = 0.320\text{ K};\ w_2 = 5.15 \times 10^{-4}\text{ kg}$$
$$w_1 = 3.50 \times 10^{-2}\text{ kg};\ K_b = 3.90\text{ K kg mol}^{-1}$$

Using Eq. 12.25, we have

$$M_2 = \frac{3.90\text{ K kg mol}^{-1} \times 5.15 \times 10^{-4}\text{ kg}}{0.320\text{ K} \times 3.50 \times 10^{-2}\text{ kg}}$$

$$= 0.179\text{ kg mol}^{-1}$$

In the next section, we shall study the effect of addition of a non-volatile solute on the freezing point of a solvent.

SAQ 2

Explain why the boiling point of a solution is higher than that of a pure solvent.

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12.4 DEPRESSION OF FREEZING POINT

Freezing point of a liquid is the temperature at which the liquid and the corresponding solid form have the same vapour pressure. Since, the addition of a non-volatile solute decreases the vapour pressure of the solvent, the vapour pressure-temperature curve of a solution (II) lies below that of pure solvent (I) as shown in Fig. 12.6. When the solution reaches the freezing point, the solid phase separating out is the pure solvent. Assuming that vapours obey ideal gas laws and that the volumes of the solid and the liquid are negligible in comparison with the volume of vapours, the equilibrium between solid solvent (ice) and vapour at constant external pressure is given by Clausius-Clapeyron equation,

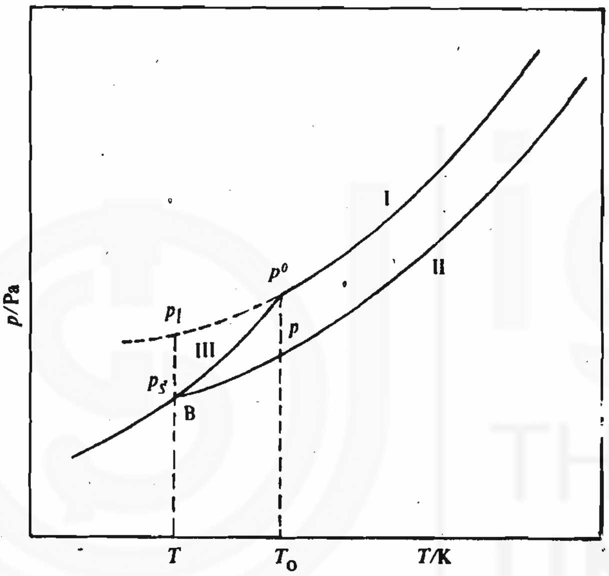

Fig. 12.6 : Depression of freezing point: I) solvent curve; II) solution curve; III) curve for ice.

$$\frac{\mathrm{d}\ln p_s}{\mathrm{d}T} = \frac{\Delta H_{\text{sub}}}{RT^2} \qquad \ldots (12.26)$$

where ΔH_{sub} is the molar enthalpy of sublimation. Similarly, for the equilibrium between liquid and vapour, the Clausius-Clapeyron equation gives,

$$\frac{\mathrm{d}\ln p_l}{\mathrm{d}T} = \frac{\Delta H_{\text{vap}}}{RT^2} \qquad \ldots (12.27)$$

where ΔH_{vap} is the molar enthalpy of evaporation of the liquid. If this equation is to hold good for the supercooled liquid, then Eqs. 12.26 and 12.27 will be applicable at the same temperature, i.e., T in Fig. 12.6.

Subtracting Eq. 12.27 from Eq. 12.26, we have,

$$\frac{\mathrm{d}\ln p_s}{\mathrm{d}T} - \frac{\mathrm{d}\ln p_l}{\mathrm{d}T} = \frac{\Delta H_{\text{sub}}}{RT^2} - \frac{\Delta H_{\text{vap}}}{RT^2} \qquad \ldots (12.28)$$

or $$\frac{\mathrm{d}\ln (p_s/p_l)}{\mathrm{d}T} = \frac{\Delta H_{\text{sub}} - \Delta H_{\text{vap}}}{RT^2} \qquad \ldots (12.29)$$

$$\text{or}\quad \frac{d\ln(p_s/p_l)}{dT} = \frac{\Delta H_{fus}}{RT^2} \qquad \ldots (12.30)$$

where ΔH_{fus} is the molar enthalpy of fusion and is equal to $(\Delta H_{sub} - \Delta H_{vap})$. At the freezing point of the solution, the vapour pressure of the solid (ice) must be equal to that of the solution (p_1) with which it is in equilibrium, i.e., at the point B in Fig. 12.6, $p_s = p_1$. Hence at the freezing point of the solution,

$$\frac{d\ln(p_1/p_l)}{dT} = \frac{\Delta H_{fus}}{RT^2} \qquad \ldots (12.31)$$

where p_1 is the vapour pressure of the solution and p_l that of the supercooled solvent at the same temperature. According to Raoult's law (Eq. 12.1),

$$\frac{p_1}{p_l} = x_1 \qquad \ldots (12.32)$$

Using this in Eq. 12.31,

$$\frac{d\ln x_1}{dT} = \frac{\Delta H_{fus}}{RT^2} \qquad \ldots (12.33)$$

For the pure solvent $(x_1 = 1)$, the freezing point is T_0 and for the solution $(x_1 = x_1)$, the freezing point is T. On integration of Eq. 12.33 between T_0 and T as also between 1 and x_1, we get

$$\int_1^{x_1} d\ln x_1 = \frac{\Delta H_{fus}}{R}\int_{T_0}^{T}\frac{dT}{T^2}$$

$$\ln x_1 = -\frac{\Delta H_{fus}}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$

$$\text{or}\quad \ln x_1 = -\frac{\Delta H_{fus}}{R}\left[\frac{T_0 - T}{TT_0}\right] \qquad \ldots (12.34)$$

If the solution is very dilute, T and T_0 are not much different and $TT_0 \simeq T_0^2$.

Also $T_0 - T = \Delta T_f$ = Depression in freezing point.

Eq. 12.34 thus reduces to

$$\ln x_1 = -\frac{\Delta H_{fus}}{R}\cdot\frac{\Delta T_f}{T_0^2} \qquad \ldots (12.35)$$

Since $x_1 + x_2 = 1$

$$\ln x_1 = \ln(1 - x_2)$$

and since x_2 is very small, $\ln(1 - x_2) = -x_2$

Eq. 12.35 thus reduces to

$$-x_2 = -\frac{\Delta H_{fus}}{R}\cdot\frac{\Delta T_f}{T_0^2}$$

$$\text{or}\quad \Delta T_f = \frac{RT_0^2}{\Delta H_{fus}}x_2 \qquad \ldots (12.36)$$

But $x_2 = \frac{w_2 M_1}{w_1 M_2}$ in the case of a dilute solution as per Eq. 12.17.

Hence Eq. 12.36 can be writen as

$$\Delta T_f = \frac{RT_0^2 M_1}{\Delta H_{fus}}\cdot\frac{w_2}{w_1 M_2} = \frac{K_f w_2}{w_1 M_2} \qquad \ldots (12.37)$$

$$\text{where } K_f = \frac{RT_0^2 M_1}{\Delta H_{fus}} \qquad \ldots (12.38)$$

K_f is the molal depression constant.

Eq. 12.37 can also we written as

$$\Delta T_f = \frac{K_f w_2 / M_2}{w_1} = K_f \frac{n_2}{w_1}$$

i.e., $\Delta T_f = K_f m$ . . . (12.39)
where m is the molality of the solution.

The molal depression constants (K_f) for a few solvents are given in Table 12.2.

Table 12.2: Molal Depression Constants

Solvent	K_f K kg mol^{-1}	Solvent	K_f K kg mol^{-1}
Water	1.85	Cyclohexane	20.20
Benzene	5.12	Camphor	40.00
Nitrobenzene	6.90	Acetic acid	3.90

Determination of Relative Molecular Mass

Eq. 12.37 is used for determining the relative molecular mass of a non-volatile soulte. Note that the solution should be dilute and, on cooling, the solid solvent alone must separate. The following methods are used for measuring the depression of freezing points.

1) The Beckmann Method

The type of apparatus used is shown in Fig. 12.7.

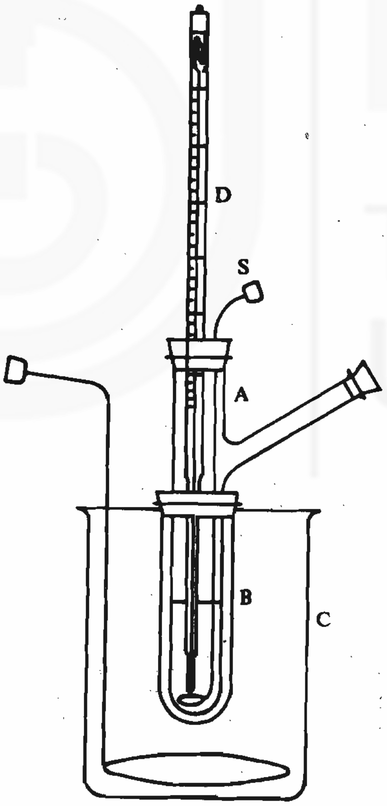

Fig. 12.7 : Determination of freezing point—Beckmann method.

A known mass (w_1) of the pure solvent is taken in the tube A fitted with a Beckmann thermometer D and a stirrer(S). The tube A is fitted inside another tube B leaving an air space between the outer wall of the tube A and the inner wall of the tube B. The whole arrangement described above is immersed in a freezing mixture contained in the vessel C. The temperature of the freezing mixture should be about 5° below the freezing point of the pure solvent. The temperature of the solvent in the tube A is allowed to fall until it is 0.5° below its normal freezing point, i.e., the liquid is allowed to be supercooled without the solid being separated. The liquid is then stirred.

vigorously. It causes the crystallization to commence and the temperature of the solvent rises to its freezing point which is recorded. The tube A is then removed, the solvent is allowed to melt and a weighed amount of the solute (w_2) is dissolved. The freezing point of the solution is determined by the same method as for the solvent. The difference between the two readings gives the depression of the freezing point.

2) Rast Method

This method can be used for determining the relative molecular masses of those non-volatile solutes which are soluble in molten camphor. It can be seen from Table 12.2 that the molal depression constant of camphor is very high, i.e., 40.00 K kg mol^{-1}. It means that when one mole of a solute is dissolved in one kilogram of camphor, the depression in freezing point is 40°, which can be read using ordinary thermometers.

For a substance, the melting point of the solid phase and the freezing point of the liquid phase are the same.

A small amount of camphor is thoroughly powdered and then introduced into a capillary tube. Its melting point is then determined. A known mass of the solute is then mixed with 10 to 15 times its mass of camphor and, the whole mixture is melted. After cooling, the solid mixture is thoroughly powdered and, its melting point determined as described for camphor. The difference between the two readings gives the depression of freezing point.

Example 3

An aqueous solution containing 5.00×10^{-4} kg of a solute in 4.00×10^{-2} kg of water was found to freeze at 272.72 K. Calculate the molar mass of the solute. Molar enthalpy of fusion of ice at its melting point (273.15 K) is 6021 J mol^{-1}.

Solution

Using Eq. 12.38, we have

$$K_f = \frac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (273.15\ \text{K})^2 \times (0.018\ \text{kg mol}^{-1})}{6021\ \text{J mol}^{-1}}$$

$$= 1.85\ \text{K kg mol}^{-1}$$

$\Delta T_f = (273.15 - 272.72)\ \text{K} = 0.43\ \text{K}$

(Since 273.15 K is the freezing point of water)

Using Eq. 12.37.

$$M_2 = \frac{K_f\, w_2}{\Delta T_f\, w_1} = \frac{1.85\text{K kg mol}^{-1}}{0.43\ \text{K}} \times \frac{5.00 \times 10^{-4}\ \text{kg}}{4.00 \times 10^{-2}\ \text{kg}}$$

$$= 0.0538\ \text{kg mol}^{-1}$$

Molar mass of the solute = 0.0538 kg mol^{-1}

SAQ 3

When a non-volatile solute is added to a solvent, the depression in freezing point is more than the elevation of boiling point. Explain.

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12.5 OSMOTIC PRESSURE

When a solution is separated from the pure solvent by a semipermeable membrane, it is observed that the solvent tends to pass through the membrane into the solution and dilutes it. This phenomenon, called **osmosis,** was first reported by Noket in 1748 for low molecular mass solutes in water. The best semipermeable membrane known is a film of copper ferrocyanide, $Cu_2[Fe(CN)_6]$. For high molecular mass solutes in organic solvents, the membranes used are thin films of either cellulose acetate or cellulose nitrate.

Let us now understand the term, osmotic pressure (π). Consider Fig. 12.8 in which A is a chamber open at one end and, fitted with a movable piston B, at the other. The chamber is divided by means of a semipermeable membrane C into two sections; one is filled with a pure solvent and the other with the solution of a non-volatile solute in the same solvent. Because of osmosis, the solvent will tend to pass through the membrane into the solution and displace the piston upward. The motion of the piston and, osmosis of the solvent, can be prevented by the application of a pressure over the piston. The mechanical pressure which must be applied on a solution to prevent osmosis of the solvent into the solution through a semipermeable membrane is called the **osmotic pressure** of the solution. This pressure for a given solution depends on many factors but not on the nature of the membrane.

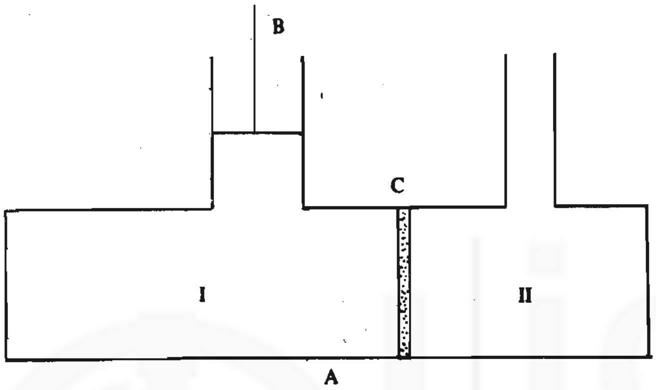

Fig. 12.8 : Osmotic pressure measurement; I-section containing the solution: II-section containing the solvent.

A semipermeable membrane allows the passage of only the solvent particles through it. It does not allow the passage of solute particles through it. Various substances which may serve as semipermeable membranes are plant cells, cells in animal body, etc. These membranes are, however, very weak and are not perfectly semipermeable. In the laboratory, a semipermeable membrane of copper ferrocyanide is generally used. To withstand high pressure, copper ferrocyanide is deposited on the walls of a porous pot electrolytically.

An alternative definition for osmotic pressure can be given as follows:

The chemical potential of a solvent is smaller in a solution than in pure state. Osmotic pressure is also defined as the pressure applied to the solution so that the chemical potential of the solvent in the solution becomes equal to that of pure solvent.

Isotonic solutions are those solutions which have the same osmotic pressure.

Osmosis takes place in living cells also. If a cell is immersed in a solution having a higher osmotic pressure than the cell sap, water will pass out of the cell through the selectively permeable membrane. The cytoplasm will then shrink and detach from the cell wall. This phenomenon is called **'Plasmolysis'.** By taking a number of solutions of a given substance at different concentrations and observing the change in the cell, it is possible to find out the solution which just fails to bring about plasmolysis. So this solution will have the same osmotic pressure as that of the cell sap and is said to be **isotonic** with it. It has been observed that red blood corpuscles are isotonic with a 0.91 per cent solution of sodium chloride.

Measurement of Osmotic Pressure

The most commonly used method for measuring osmotic pressure of solutions is that discovered by Berkeley and Hartley.

Berkeley and Hartley's Method

The apparatus is as shown in Fig. 12.9. It consists of a porous tube A with a semipermeable membrane of copper ferrocyanide deposited on its walls. The porous tube is fitted with a solvent reservoir on one side and a capillary indicator (B) on the other side. The porous tube containing the semipermeable membrane is filled with the pure solvent and is surrounded by another tube (C) made of gun metal, containing the solution whose osmotic pressure is to be measured. Due to osmosis, the solvent from the porous tube passes through the semipermeable membrane into the solution. This movement of solvent particles is indicated by a fall in level in the capillary indicator.

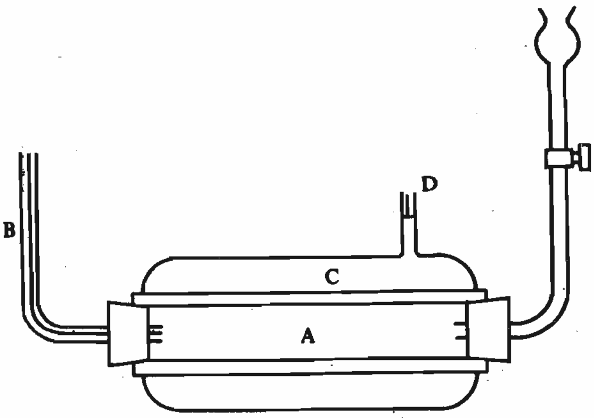

Fig. 12.9: Berkeley and Hartley's apparatus.

A hydrostatic pressure is applied to the solution through the tube D. The pressure at which the movement of the solvent is reversed is the osmotic pressure of the solution.

The osmotic pressure values of aqueous solutions of sucrose at 287 K are given in Table 12.3.

Table 12.3: Osmotic Pressure Values of Aqueous Solutions of Sucrose at 287 K.

c/mol dm^{-3}	$10^{-5} \times \pi$/Pa	
	Observed	Calculated
5.88×10^{-2}	1.34	1.39
8.09×10^{-2}	2.00	1.91
1.19×10^{-1}	2.75	2.80
1.80×10^{-1}	4.04	4.23

The experimental values of osmotic pressure of solutions as shown in Table 12.3 indicate that in dilute solutions, the osmotic pressure is proportional to the concentration of the solution at constant temperature. Based on such observations, van't Hoff deduced the laws of osmotic pressure and an equation (Eq. 12.48) relating concentration of a solution to its osmotic pressure. Using Eq. 12.48, it is possible to calculate osmotic pressure of a solution. Some calculated osmotic pressure values are entered in Table 12.3. Let us now study the laws of osmotic pressure and, deduce Eq. 12.48.

Laws of Osmotic Pressure

van't Hoff deduced the laws of osmotic pressure from the results oi various investigations on osmotic pressure. These are given below:

i) Osmotic pressure at constant temperature is directly proportional to the concentration of the solution. Mathematically.

$$\pi \propto c \qquad \ldots (12.40)$$

Since the concentration of a solution (in mol dm^{-3}) is inversely proportional to its volume (in dm^3 mol^{-1}), it follows that for a solution.

$$\pi \propto \frac{1}{V} \qquad \ldots (12.41)$$

or $\pi V =$ constant ... (12.42)

Eq. 12.42 is the analogue of Boyle's law for ideal gases.

ii) Osmotic pressure of a solution of given concentration is directly proportional to the temperature (in kelvin scale)

$$\pi \propto T \qquad \ldots (12.43)$$

iii) At constant temperature, equimolar solutions of different solutes have the same osmotic pressure. In other words, osmotic pressure of a solution is directly proportional to the number of moles of the solute.

$$\pi \propto n_2 \qquad \ldots (12.44)$$

From Eqs. 12.41, 12.43 and 12.44, we have,

$$\pi \propto \frac{n_2 T}{V} \qquad \ldots (12.45)$$

or $$\pi V = n_2 RT \qquad \ldots (12.46)$$

where R is a constant

or $$\pi = \frac{n_2}{V} RT \qquad \ldots (12.47)$$

But $\frac{n_2}{V}$ = concentration of the solution = c

i.e., $\pi = cRT$ $\qquad \ldots (12.48)$

Eq. 12.47 can also be written as,

$$\pi = \frac{w_2 RT}{M_2 V} \qquad \ldots (12.49)$$

By comparing the osmotic pressure of a cane sugar solution with the pressure exerted by hydrogen gas at the same temperature and concentration, van't Hoff showed that the value of R is the same as the gas constant. Thus, R may be taken to be equal to gas constant.

Using Eq. 12.49, we can calculate the osmotic pressure of a solution, if we know the mass and molar mass of the solute as well as the temperature and volume of the solution.

Example 4

Calculate the osmotic pressure of an aqueous solution containing 50.0 kg of sucrose ($C_{12}H_{22}O_{11}$) in 1.00 m^3 of a solution at 300 K.

Solution

Mass of solute = 50.0 kg

Molar mass of solute = 0.342 kg mol^{-1}

Volume of solution = 1.00 m^3

Temperature = 300 K

Using Eq. 12.49,

$$\pi = \frac{50.0\ \text{kg}}{0.342\ \text{kg mol}^{-1}} \times \frac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K})}{1.00\ \text{m}^3}$$

$$= 3.65 \times 10^5\ \text{Pa}$$

12.6 VAN'T HOFF FACTOR

The colligative properties depend on the number of particles of the solute. In cases where the solute associates or dissociates in solution, abnormal results are obtained.

In case of association, the number of effective molecules decreases and consequently, the observed values of the colligative properties are less in magnitude than those calculated for unassociated molecules. Also due to association, each molecular cluster will have more than one molecule, and hence, the experimentally obtained relative molecular masses will be higher than the actual relative molecular masses.

In case of dissociation, the number of effective particles will increase and hence, the colligative properties will be higher in magnitude than those calculated for undissociated molecules. The experimentally observed relative molecular mass value will be less than that of the actual value.

Theoretical value refers to the value calculated assuming no association or dissociation. Apparent or observed value refers to the value calculated based on experimental results.

vant't Hoff introduced a factor *i*, now known as van't Hoff factor, to indicate such deviations from normal behaviour.

$$i = \frac{\text{Observed value of the colligative property}}{\text{Theoretical value of the colligative property}} \quad \text{... (12.50)}$$

Since these properties vary inversely to the relative molecular masses of the solutes, we can write Eq. 12.50 as,

$$i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} \quad \text{... (12.51)}$$

We will now explain how this van't Hoff factor is used in calculating the degree of association or dissociation.

Calculation of Degree of Association

Degree of association is defined as the fraction of the total number of molecules which combine to form bigger molecules. Consider one mole of A dissolved in a given volume of a solvent. We can write for association of *n* molecules,

$$nA \rightleftharpoons A_n \quad \text{... (12.52)}$$

If x is the degree of association, then the number of moles of unassociated A = $(1-x)$ and the number of moles of $A_n = \frac{x}{n}$

Hence, the total number of effective moles of A

$$= (1-x) + \frac{x}{n}$$

Since the observed colligative property is proportional to number of effective moles of A, observed colligative property is proportional to $(1-x+\frac{x}{n})$. But if we were to get the theoretical value for the colligative property, the number of mole of A must be one only.

Then from Eq. 12.51, we have,

$$i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}$$

$$i = \frac{(1-x+x/n)}{1} = (1-x+x/n) \quad \text{... (12.53)}$$

Thus, knowing n and i, x can be calculated.

Example 5

1.65×10^{-3} kg of acetic acid, when dissolved in 0.100 kg of benzene, increased the boiling point by 0.36 K. Calculate the van't Hoff factor and the degree of association of acetic acid in benzene assuming that acetic acid exists as a dimer in benzene. K_b for benzene is 2.53 K kg mol^{-1}.

Solution

Theoretical molar mass of acetic acid = 0.060 kg mol^{-1}

Using Eq. 12.25, observed molar mass of acetic acid

$$= \frac{(2.53 \text{ K kg mol}^{-1})}{0.36 \text{ K}} \times \frac{1.65 \times 10^{-3} \text{ kg}}{0.100 \text{ kg}} = 0.116 \text{ kg mol}^{-1}$$

Using Eq. 12.51, van't Hoff factor,

$$i = \frac{0.060 \text{ kg mol}^{-1}}{0.116 \text{ kg mol}^{-1}} = 0.517$$

Since acetic acid exists as a dimer in benzene, we can write the following expression:

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Let x be the degree of association and the number of moles of CH_3COOH before association be 1.

Hence, number of moles of unassociated $CH_3COOH = 1-x$ and number of moles of associated $CH_3COOH = \frac{x}{2}$

Total no. of effective moles $= 1-x+\frac{x}{2} = 1-\frac{x}{2}$

Using Eq. 12.53,

$$0.517 = \frac{1-\frac{x}{2}}{1}$$

or $x = 0.966$

Thus, acetic acid is 96.6% associated.

Calculation of Degree of Dissociation

The degree of dissociation denotes the fraction of the total number of molecules which dissociates to give smaller species. Let us consider the dissociation of MA to give M^+ and A^- ions. Let x be the degree of dissociation.

$$\underset{1-x}{MA} \rightleftharpoons \underset{x}{M^+} + \underset{x}{A^-}$$

Total number of moles after dissociation $= 1-x+x+x = 1+x$. Then,

$$i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} = \frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}$$

$$\text{Hence } i = \frac{1+x}{1} \qquad \text{...(12.54)}$$

Hence, x can be calculated, if i is known.

Example 6

4.60×10^{-3} kg of sodium chloride was dissolved in 0.130 kg of water at 280 K. The osmotic pressure of the solution was found to be 2.66×10^{6} Pa. Calculate the van't Hoff factor and the degree of dissociation. Density of the solution is 1.02×10^{3} kg m^{-3}

Solution

$$\text{Volume of the solution} = \frac{\text{Mass of the solution}}{\text{Density of the solution}}$$

$$= \frac{(4.60 \times 10^{-3} \text{ kg} + 0.130 \text{ kg})}{1.02 \times 10^{3} \text{ kg m}^{-3}}$$

$$= 1.32 \times 10^{-4} \text{ m}^3$$

Using Eq. 12.49, the theoretical value of the osmotic pressure can be calculated as follows:

$$\pi = \frac{4.60 \times 10^{-3} \text{ kg} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 280 \text{ K}}{5.85 \times 10^{-2} \text{ kg mol}^{-1} \times 1.32 \times 10^{-4} \text{ m}^3}$$

$$= 1.39 \times 10^{6} \text{ Pa}$$

Using Eq. 12.50,

$$i = \frac{2.66 \times 10^6 \text{ Pa}}{1.39 \times 10^6 \text{ Pa}} = 1.91$$

Using Eq. 12.54,

$$1.91 = \frac{1 + x}{1} = 1 + x$$

$$x = 0.91$$

SAQ 4

State whether the following statements are true or false:

i) Two solutions having same concentration and at the same temperature are isotonic.

ii) van't Hoff factor, $i = \frac{\pi_{\text{observed}}}{\pi_{\text{calculated}}}$

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SAQ 5

Which of the following solutions will exert greater osmotic pressure:

0.1 M sodium chloride or 0.1 M sucrose? What is the reason?

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12.7 SUMMARY

The colligative properties of a solution depend upon the number of particles of a solute present in the solution. These properties are independent of the nature of the solute. The colligative properties are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. According to Raoult's law, relative lowering of vapour pressure is equal to the mole fraction of the solute. Since the addition of a non-volatile solute to a solvent decreases the vapour pressure of the solvent, the boiling point of the solution containing a non-volatile solute is higher than that of the pure solvent. On the other hand, the freezing point of a solvent is lowered by the addition of a non-volatile solute to it.

When two solutions of different concentrations are separated by means of a semipermeable membrane, the flow of solvent occurs from a solution of lower solute concentration to that of higher concentration. This is called osmosis. van't Hoff showed that the osmotic pressure bears the same relationship to the concentration and temperature of the solution as the pressure of a gas to its concentration and temperature. When two solutions have the same osmotic pressure, they are called isotonic solutions. When a solute associates or dissociates in the solution, abnormal results are obtained. To account for all abnormal cases, van't Hoff introduced a factor *i*, now called van't Hoff factor.

12.8 TERMINAL QUESTIONS

1) Define colligative property. Name four of them.

2) How is molal elevation constant related to the enthalpy of vaporization? What are its units?

3) Derive the formula, $\Delta T_f = K_f m$.

4) The molal depression constant for water is 3.6 times its value for molal elevation constant. If the boiling point of an aqueous solution of urea is 373.25 K, what will be its freezing point? Assume that water boils at 373 K and freezes at 273 K.

5) Calculate the molal depression constant of water at 273 K. The enthalpy of fusion of ice at 273 K is 6.03 kJ mol^{-1}

6) A current of dry air was passed through a solution containing 5.0×10^{-3} kg of a non-volatile solute in 0.10 kg of water and then through pure water. The loss in mass of the solution was found to be 8.00×10^{-4} kg and the loss in mass of pure water 2.00×10^{-5} kg. Find the molar mass of the solute.

7) The molar enthalpy of vaporization of water at 373 K is 40.6 kJ mol^{-1} At what temperature will a solution containing 5.60×10^{-3} kg of glucose in 1.00 kg of water boil? Assume the boiling point of water to be 373 K.

8) A solution containing 4.0×10^{-3} kg of a non-volatile organic solute in 1.00×10^{-3} m^3 of the solution exerts an osmotic pressure of 6.66×10^4 Pa at 300 K. Calculate the molar mass of the solute.

9) An aqueous solution prepared by dissolving 0.5 kg of potassium chloride in 100 kg of water was found to freeze at 272.76 K. Calculate the van't Hoff factor and degree of dissociation of solute at this concentration. K_f for H_2O is 1.85 K kg mol^{-1} and the freezing point of water is 273 K.

12.9 ANSWERS

Self Assessment Questions

1) i) True ii) False iii) False.

2) See Sec. 12.3.

3) We know that $\Delta T_f = K_f m$ and $\Delta T_b = K_b m$. It is clear from the above expressions that since the molal depression constant for a solvent is more than the molal elevation constant, $\Delta T_f > \Delta T_b$.

4) i) True ii) True.

5) 0.1 M NaCl solution will exert greater osmotic pressure due to dissociation.

Terminal Questions

1) Colligative properties of solutions are those properties which depend only upon the number of particles of solute present in the solution and are independent of the nature of the solute. These are relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure.

2) $$K_b = \frac{R T_0^2 M_1}{\Delta H_{vap}}.$$

The units of K_b are K kg mol^{-1}.

3) See Sec. 12.4.

4) If molal elevation constant is K_b, then molal depression constant is 3.6 K_b.

Boiling point of water = 373 K.

Elevation in boiling point = $\Delta T_b = (373.25\ \text{K} - 373\ \text{K}) = 0.25\ \text{K}$
Using Eq. 12.24,

$$\Delta T_b = 0.25\ \text{K} = K_b m \qquad (1)$$

and using Eq. 12.39,

$$\Delta T_f = K_f m = 3.6\ K_b m \qquad (2)$$

Dividing Eq. (2) by (1) we get

$$\frac{\Delta T_f}{0.25\ \text{K}} = \frac{3.6\ K_b m}{K_b m} = 3.6$$

$$\Delta T_f = 3.6 \times 0.25\ \text{K} = 0.9\ \text{K}$$

Freezing point of solution = 273 K − 0.9 K
= 272.1 K.

5) Using Eq. 12.38,

$$K_f = \frac{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times (273\ \text{K})^2 \times 1.8 \times 10^{-2}\ \text{kg mol}^{-1}}{6.03 \times 10^3\ \text{J mol}^{-1}}$$

$$= 1.85\ \text{K kg mol}^{-1}.$$

6) Mass of solute (w_2) = 5.0×10^{-3} kg

Mass of solvent (w_1) = 0.10 kg

Molar mass of solvent (M_1) = 1.80×10^{-2} kg mol^{-1}

Loss in mass of solution (w_A) = 8.00×10^{-4} kg

Loss in mass of water (w_B) = 2.00×10^{-5} kg

Using Eqs. 12.7 and 12.11,

$$\frac{w_2 M_1}{w_1 M_2} = \frac{w_B}{w_A + w_B}$$

$$M_2 = \frac{w_2 M_1}{w_1} \cdot \frac{w_A + w_B}{w_B} = \frac{5.0 \times 10^{-3}\ \text{kg} \times 1.8 \times 10^{-2}\ \text{kg mol}^{-1} \times 8.20 \times 10^{-4}\ \text{kg}}{0.10\ \text{kg} \times 2.00 \times 10^{-5}\ \text{kg}}$$

$$M_2 = 0.0370\ \text{kg mol}^{-1}$$

7) Molar enthalpy of vaporisation of water at 373 K
= 40.6 kJ mol^{-1}
= 4.06×10^4 J mol^{-1}
Using Eq. 12.21,

$$K_b = \frac{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times (373\ \text{K})^2 \times 1.8 \times 10^{-2}\ \text{kg mol}^{-1}}{4.06 \times 10^4\ \text{J mol}^{-1}}$$

$$= 0.513\ \text{K kg mol}^{-1}$$

$$\text{No. of moles of Glucose} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{5.60 \times 10^{-3}\ \text{kg}}{1.80 \times 10^{-1}\ \text{kg mol}^{-1}}$$

$$= 3.11 \times 10^{-2}\ \text{mol}$$

$$\text{Molality of the solution } (m) = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (kg)}}$$

$$= \frac{3.11 \times 10^{-2}\ \text{mol}}{1.00\ \text{kg}} = 3.11 \times 10^{-2}\ \text{mol kg}^{-1}$$

Using Eq. 12.24,
$\Delta T_b = K_b m = 0.513\ \text{K kg mol}^{-1} \times 3.11 \times 10^{-2}\ \text{mol kg}^{-1}$
$= 0.016$ K
Boiling point of solution = 373 K + 0.016 K = 373.016 K

8) Using Eq. 12.49, we have

$$6.66 \times 10^4 \text{ Pa} \times 1.00 \times 10^{-3} \text{ m}^3 = \frac{4.0 \times 10^{-3} \text{ kg}}{M_2} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}$$

$$\text{or } M_2 = \frac{(4.0 \times 10^{-3} \text{ kg})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{6.66 \times 10^4 \text{ Pa} \times 1.00 \times 10^{-3} \text{ m}^3}$$

$$= 0.150 \text{ kg mol}^{-1}$$

9) Normal molar mass of KCl $= 7.45 \times 10^{-2}$ kg mol^{-1}
Using Eq. 12.37, observed molar mass of KCl

$$= \frac{(1.85 \text{ K kg mol}^{-1}) \times (0.5 \text{ kg})}{(100 \text{ kg})(0.24 \text{ K})}$$

$$= 3.85 \times 10^{-2} \text{ kg mol}^{-1}$$

Using Eq. 12.51, van't Hoff factor,

$$i = \frac{\text{Theoretical molar mass of KCl}}{\text{Observed molar mass of KCl}}$$

$$i = \frac{7.45 \times 10^{-2} \text{ kg mol}^{-1}}{3.85 \times 10^{-2} \text{ kg mol}^{-1}} = 1.94 \qquad \text{... (1)}$$

Let x be the degree of dissociation of KCl. Then

$$\begin{array}{ccccc} \text{KCl} & \rightleftharpoons & \text{K}^+ & + & \text{Cl}^- \\ 1-x & & x & & x \end{array}$$

Total number of moles at equilibrium after dissociation
$= 1 - x + x + x = 1 + x$

$$\text{van't Hoff factor, } i = \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}} = \frac{1 + x}{1} \qquad \text{... (2)}$$

From (1) and (2) we have $1 + x = 1.94$

Hence, degree of dissociation, $x = 0.94$.

UNIT 13 PHASE EQUILIBRIA

Structure

13.1 INTRODUCTION

The study of the effect of various parameters such as pressure, temperature or composition on the physical state of chemical substances is the subject matter of phase equilibria. In Unit 9, you have studied the criteria for equilibrium. In unit 14, we shall consider the various aspects of chemical equilibria. In this unit, we shall discuss physical equilibria. This means :

- focussing our attention on the equilibria regarding physical state and
- relating physical equilibria to various parameters such as pressure, temperature and composition using phase rule.

We shall define the terms such as phase, component, degrees of freedom and phase transition. We will deduce phase rule. One component system will be studied in the light of phase rule. Among the two component systems, only solid-liquid and solid-gas systems will be discussed. We have discussed liquid-liquid systems in Units 10 and 11 of this block. Applications of phase equilibria study will also be included in our discussion.

Objectives

After studying this unit, you should be able to:

- define the terms, phase, component and degrees of freedom,
- calculate the number of phases, components and degrees of freedom in a system,
- state and deduce the phase rule,
- comment on the stability of the phases of subliming and non-subliming substances,
- explain the two types of phase transitions, and
- apply the phase rule to the study of one component and two component systems.

13.2 DEFINITION OF THE TERMS

In 1876, Gibbs deduced a simple relationship among the number of phases in equilibrium, the number of components and the number of intensive variables known as degrees of freedom. Let us first define the terms phase, component and degrees of freedom.

Phase

Phase (*P*) is defined as a physically distinct and homogeneous part of the system that is mechanically separable from other parts of the system. The definition as suggested by Gibbs is that a phase is a state of matter that is uniform throughout, not only in chemical composition but also in physical state.

Let us discuss some examples for counting the number of phases in a system.

- A gas or a gaseous mixture is a single phase since there cannot be an interface between one gas and another. Air, for example, is one phase system, although it is a mixture of many gases.
- A system of totally miscible liquids will exist in one phase only as far as the liquid phase is concerned. But since each liquid has its vapour above, the total number of phases in a system of miscible liquids is two, one for the liquid and the other for vapour. These two phases are separated by the surface of the solution in the liquid phase.
- A system of two immiscible liquids has a total of three phases, two for the substances in the liquid state and another for the vapour phase containing vapours of both the liquids.
- A crystal is a single phase. Different solids having different crystal structures constitute different phases, irrespective of the fact whether they have same chemical composition or not. A mixture of graphite and diamond constitutes two phases although both are only allotropic modifications of carbon.

Next we take up the definition of the word, component.

Components

The number of components (*C*) in a system is the smallest number of substances in terms of which the composition of all the phases in the system can be described separately. The number of components may be smaller than the number of chemical substances that are present in the system.

The definition is easy to apply when the species do not react, for then we simply count their number. For example, phase equilibria containing ice, water and its vapour is a one component system since the composition of each phase can be expressed in terms of the component, H_2O, only. A mixture of ethanol and water is a two component system.

If the species react chemically and are at equilibrium, we have to take into account the significance of the phrase' all the phases' in the above definition. Dissociation of calcium carbonate in a closed vessel is a two component system although at first it may appear to be a three component system, namely, $CaCO_3$, CaO and CO_2.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

You can see that the composition of any one species is related to the other two and the dissociation of calcium carbonate is, therefore, a two component system.

In the case of solid ammonium chloride being heated in a closed vessel, there is an equilibrium between the solid ammonium chloride and its vapour (which consists of ammonia and hydrogen chloride molecules). Since both the phases have the formal composition 'NH_4Cl', it is a one component system. However, if ammonia or hydrogen chloride is added to the system, the system has two components because now the relative amounts of hydrogen chloride and ammonia are not the same.

If there are 'S' substances (may be chemical compounds or ionic species) and 'R' relations (which include equations representing chemical equilibria or charge neutrality) among them, then the number of components (C) can be calculated using the equation,

$$C = S - R \qquad \ldots (13.1)$$

To illustrate this, we can consider two examples. If you consider a solution of glucose in water, there are two substances and hence $S = 2$. But there is no relation between them and so $R = 0$; therefore, $C = 2$ and this is a two component system.

Let us reexamine the equilibrium of solid ammonium chloride with its vapour. Here $S = 3$ since there are three substances, NH_4Cl, NH_3 and HCl. But $R = 2$ since these are two relations as shown below :

(1) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
(2) Concentration of NH_3 = Concentration of HCl (and both of them are in gaseous phase).

Therefore $C = S - R = 3 - 2 = 1$. This is a one component system. If extra HCl (g) is added, then the second relation given above no more holds. That is, $R = 1$ although $S = 3$. This is therefore a two component system, as $C = S - R = 3 - 1 = 2$.

Degrees of Freedom

The number of degrees of freedom (F) or variance of a system is the smallest number of intensive variables such as pressure, temperature and composition which are to be specified to describe the state of the system completely.

- If $F = 0$, the system is invariant and this means none of the intensive variables can be changed.
- In case $F = 1$, the system is univariant and one of the intensive variables can be changed.
- For a bivariant system, F is equal to 2, and two of the intensive variables can be changed.

The phase rule relates the degrees of freedom to the number of phases and the components. Before studying phase rule, let us recapitulate the criteria for equilibrium.

SAQ 1

Calculate the number of phases in the following cases :

a) A closed beaker partially filled with toluene and water;

b) A closed beaker partially filled with acetone and water.

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SAQ 2

Calculate the number of components in the following cases :

a) Dissociation of ammonia in a closed vessel;

b) Dissociation of ammonia in a closed vessel containing nitrogen.

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13.3 CRITERIA FOR EQUILIBRIUM

In unit 9, we have discussed the conditions for equilibrium; the changes in Helmholtz free energy function (at constant volume and temperature) and Gibbs free energy function (at constant pressure and temperature) are zero for a system under equilibrium.

That is, $dA = 0$ and $dG = 0$ ... (13.2)

Apart from this, the chemical potential of a component must be the same in all the phases at equilibrium. If there are three phases α, β and γ for the component i, then we can write

$$\mu_{i\alpha} = \mu_{i\beta} = \mu_{i\gamma} \qquad \ldots (13.3)$$

The conclusion given in Eq. 13.3 comes from the fact that a substance will tend to pass spontaneously from the phase where it has higher chemical potential to the phase of lower chemical potential. The phase change of a substance would continue till the chemical potentials become equal in all the phases (in which case the resulting system is said to have attained equilibrium). For example, if at any temperature and pressure, ice, water and its vapour are in equilibrium then,

$$\mu_{\text{ice}} = \mu_{\text{water}} = \mu_{\text{vapour}}$$

Normally, a system can attain equilibrium conditions from either direction. For example, the equilibrium between ice and water at 273.15 K and 1.013×10^5 Pa (1 atm) pressure can be attained either by partial melting of ice or partial freezing of water. This is a stable equilibrium. But yet another variety, called metastable equilibrium, also exists which certainly does not represent a condition of stability. To illustrate this, you can consider the case of cooling water slowly and carefully to a temperature of 272 K (or even lower) without the appearance of ice. But starting from ice at a lower temperature, and heating it, it is not possible to have water at 272 K. Thus a metastable equilibrium can be attained from one way only and not by both the ways. A system under metastable equilibrium reverts to stable equilibrium if disturbed even slightly by stirring or by the addition of a phase which is stable under the experimental conditions. Thus water at 272 K on slight stirring or on the addition of a small quantity of ice, begins to solidify and, as temperature rises to 273 K, the conditions of stable equilibrium are established.

13.4 PHASE RULE

In a heterogeneous equilibrium, not influenced by gravitational or electrical or magnetic forces, the number of degrees of freedom (F) of the system is defined by the number of components (C) and the number of phases (P) according to the equation,

$$F = C - P + 2 \qquad \ldots (13.4)$$

Once the values of C and P are known, F can be calculated.

Let us take up some examples to understand Eq. 13.4. In the vaporization equilibrium of water ($C = 1$), there are two phases (liquid and vapour) and hence, $F = C - P + 2 = 1 - 2 + 2 = 1$. That is, specifying pressure or temperature fixes the other. This is all the more understandable from the general statement that at a particular temperature, vapour pressure of a liquid is constant. If all the three phases, ice, water and its vapour, are to be in equilibrium, then $F = 1 - 3 + 2 = 0$; that is, the system is invariant. This means all the three phases of water are in equilibrium only at a fixed temperature and pressure. Any effort to change pressure or temperature results in the disappearance of one of the phases.

Deduction of Phase Rule

Having stated the phase rule, we shall now deduce the same. Consider a system of C components existing in P phases. We want to calculate the number of independent variables or degrees of freedom 'F' in order to define the state of the system completely. The value of F can be given by the following equation also:

$$F = \text{(Total number of variables)} - \text{(number of relations)} \quad \ldots (13.5)$$

First let us calculate the total number of variables. To define the composition of **each phase,** it is necessary to define the concentration of $(C-1)$ constituents of that phase. For P phases, the total number of concentration variables is $P(C-1)$ and these, along with two variables, pressure and temperature, constitute the total number of variables.

$$\text{Total number of variables} = P(C-1) + 2 \quad \ldots (13.6)$$

Regarding the number of relations, we know that for one component existing in three phases α, β and γ, there are two relations,

$$\mu_\alpha = \mu_\beta \text{ and } \mu_\beta = \mu_\gamma$$

The relation $\mu_\alpha = \mu_\gamma$ need not be specified but is understood. As two relations are required for three phases of a component, $(P-1)$ relations are there for P phases of **a component.** Hence, a total number of $C(P-1)$ relations exist for P phases of C components.

$$\text{Number of relations} = C(P-1) \quad \ldots (13.7)$$

Using Eqs. 13.6 and 13.7 in Eq. 13.5,

$$F = P(C-1) + 2 - C(P-1)$$

$$= PC - P + 2 - PC + C$$

i.e., $F = C - P + 2$ ... (13.8)

Having derived phase rule, we will apply it to various systems. Its application can be seen in the study of phase diagrams. A phase diagram speaks about the stability of various phases at various temperatures, pressures and compositions.

SAQ 3

The four phases of sulphur are rhombic, monoclinic, liquid and vapour. Can all these four phases exist in equilibrium at a particular temperature and pressure?

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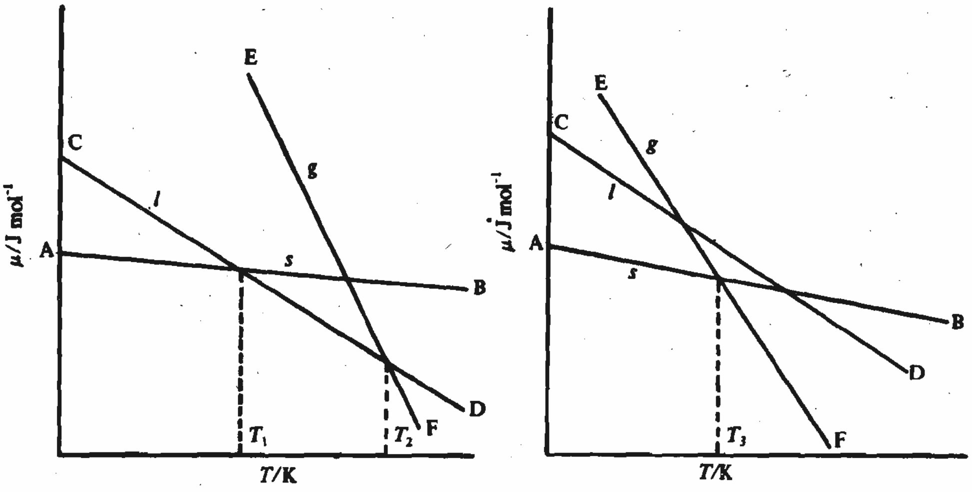
13.5 STABILITY OF THE PHASES OF A PURE SUBSTANCE

The golden rule with reference to phase study is that the phase with the lowest chemical potential is the stable phase. This rule can be used in making inferences from the curves obtained by plotting chemical potential of a pure substance against temperature for each phase. For most of the substances, μ against T plots for solid, liquid and vapour phases are of the type shown in Fig. 13.1 (a).

At the melting point (T_1), the solid curve (AB) and the liquid curve (CD) meet. Similarly, at the boiling point (T_2), the liquid curve (CD) and the vapour curve (EF) meet.

Applying the golden rule given at the beginning of this section, we can infer that for substances exhibiting behaviour of the type represented in Fig. 13.1 (a), solid phase is the stable phase below the melting point. Between melting and boiling points, liquid phase is stable and above boiling point, vapour phase is stable. Evidently this is applicable for non-subliming substances.



(a) (b)

Fig.13.1: μ against T plots at constant pressure: (a) for non-subliming substances; (b) for subliming substances; in both the plots, g, l and s refer to vapour, liquid and solid phase curves.

In the case of subliming substances, μ against T curves are of the type shown in Fig. 13.1 (b). The sublimation temperature (T_3), is the point of intersection between the solid (AB) and the vapour (EF) curves. Hence, below T_3, solid phase is stable and above T_3, the vapour phase is stable.

As per Clapeyron equation studied earlier, we are aware that a decrease in pressure affects melting and boiling points to different extent. If the pressure is reduced sufficiently, the boiling point of a liquid may even fall below the melting point of a solid whereby the substance is said to sublime. Hence the type of μ Vs T curves and the type of stable phases would be decided by the experimental conditions of pressure as well. This explains the fact that above 5.2×10^5 Pa pressure, solid carbon dioxide melts to give a liquid and, below 5.2×10^5 Pa pressure, solid carbon dioxide sublimes.

Clapeyron equation (Eq. 9.49 of Unit 9) gives a quantitative account of the variation of equilibrium temperature with pressure,

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \qquad \dots (9.49)$$

This equation could be used for any phase equilibria.

SAQ 4

Fig. 13.1a or b gives μ against T plot of a pure substance at constant pressure. For a substance in a closed system,

$$d\mu = \overline{V}dp - \overline{S}dT.$$

What thermodynamic property of a substance is given by the slope of Fig. 13.1a or b?

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13.6 PHASE TRANSITIONS AND HEAT CAPACITY ANOMALIES

The transition from one phase to another on the change of temperature or pressure or both is generally referred to as phase transition. The phase transitions are of two types. Those phase transitions requiring latent heat for the transition are called first order phase transitions. Typical examples of this category are the conversion of ice to water or water to steam or rhombic sulphur to monoclinic sulphur. During each of these transitions, heat is absorbed but without any observable temperature change. This means that in a first order phase transition, heat capacity, which is the ratio of heat absorbed to temperature change, is infinitely large.

The other variety, second order phase transition, does not require any latent heat. As a result, during the transition, heat capacity also changes through a finite amount only. Typical examples for second order phase transitions are in the conducting — superconducting transformations. During this transition, material loses electrical resistance. Lead, indium and titanium etc undergo transition of this type. In the following sections, we discuss the application of the phase rule to one and two component systems which are instances of first order phase transition.

13.7 APPLICATION OF PHASE RULE TO ONE COMPONENT SYSTEMS

Application of phase rule (Eq. 13.8) to one component system leads to the general expression,

$$F = 1 - P + 2 = 3 - P \qquad \ldots (13.9)$$

Hence, a maximum of three phases can be present at a point in this case. It is called a triple point and the system is invariant ($F = 0$).

For one component system, p against T plot is quite convenient. Then, $\mathrm{d}p/\mathrm{d}T$ gives the slope of the plot. For each equilibrium, this is defined by Clapeyron equation (Eq. 9.49). If $\mathrm{d}p/\mathrm{d}T$ is negative, you can expect that as temperature increases ($\mathrm{d}T$ = positive), pressure would decrease ($\mathrm{d}p$ = negative) and the curve is of the type shown in Fig. 13.2(a). But if $\frac{\mathrm{d}p}{\mathrm{d}T}$ is positive, then an increase in temperature ($\mathrm{d}T$ = positive) causes an increase in pressure also ($\mathrm{d}p$ = positive), as shown in Fig. 13.2(b).

Fig. 13.2: Types of p against T plots: (a) $\frac{\mathrm{d}p}{\mathrm{d}T}$ is negative; b) $\frac{\mathrm{d}p}{\mathrm{d}T}$ is positive.

You can calculate $\mathrm{d}p/\mathrm{d}T$ using Clapeyron equation once ΔH and ΔV are known. Normally to calculate the change in molar volume of a substance between two phases α, and β, densities of the phases (d_α and d_β) and the molar mass (M) of the substance are used.

$$\Delta V = V_\beta - V_\alpha = \left(\frac{M}{d_\beta} - \frac{M}{d_\alpha}\right) = M\left(\frac{1}{d_\beta} - \frac{1}{d_a}\right) \qquad \ldots (13.10)$$

The p against T plots for various phases are made by measuring the equilibrium temperatures corresponding to various pressures. Let us now study the phase diagram of water.

Phase Diagram of Water

The phase diagram for water is given in Fig. 13.3. It would be interesting to apply Clapeyron equation (Eq. 9.49) and phase rule (Eq. 13.8) to this phase equilibria.

Let us first apply Clapeyron equation to the following three equilibria:

i) Fusion (ice ⟶ water)

ii) Vaporization (water ⟶ vapour)

iii) Sublimation (ice ⟶ vapour)

For all the above transitions, ΔH is positive. Ice floats on water and this means, density of water is more than that of ice and the molar volume of ice is more than that of water. Again, when a small quantity of water is heated, steam comes out in large volume. Thus the molar volume of steam is more than that of liquid water. Similarly, molar volume of steam is larger than that of ice. We use V to represent the molar volume of a particular phase.

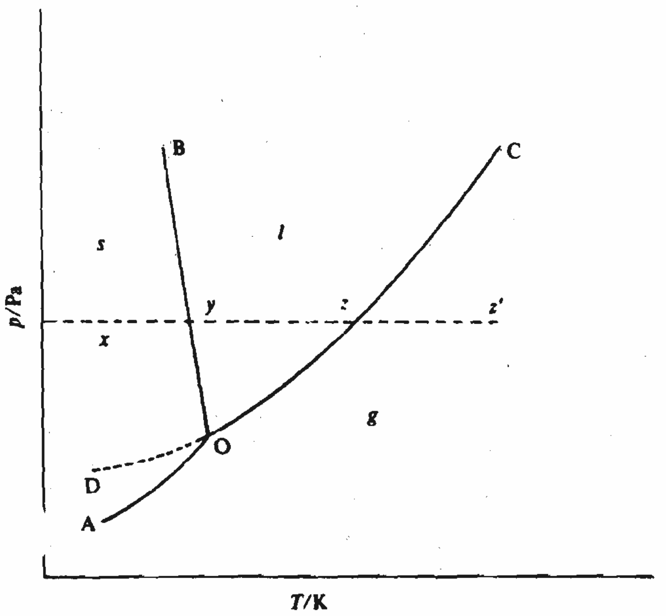

Fig. 13.3: Phase diagram of water; s, l and g stand for solid, liquid and vapour phases.

Using the above ideas, $\frac{dp}{dT}$ values for the three equilibria can be calculated. Note that the temperatures are all positive.

$$\text{Fusion: } \frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{(+ve)}{(+ve)\,(-ve)} = (-ve) \qquad \ldots (13.11)$$

$$\text{Vaporization: } \frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{(+ve)}{(+ve)\,(+ve)} = (+ve) \qquad \ldots (13.12)$$

$$\text{Sublimation: } \frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{(+ve)}{(+ve)\,(+ve)} = (+ve) \qquad \ldots (13.13)$$

$\Delta V_{\text{fusion}} = V_{\text{water}} - V_{\text{ice}}$ = negative

$\Delta V_{\text{vaporization}} = V_{\text{vapour}} - V_{\text{water}}$ = positi

$\Delta V_{\text{sublimation}} = V_{\text{vapour}} - V_{\text{ice}}$ = positive

The decrease of melting point of ice with increase of pressure has an interesting application in winter sports. In ice-skating, for example, there is a bladelike metal frame attached to the shoes of the skater. This arrangement ensures minimum area of contact between the skater and ice surface. Because of this, there is a high pressure exerted on the ice surface on which the skater stands and moves. At this increased pressure, the melting point of ice is much low. Hence ice melts and provides a lubricating layer of water which speeds up the skater's movement.

Eq. 13.11 shows a negative slope for the p against T plot for fusion, and the curve OB, the fusion curve of ice, illustrates this. Eqs. 13.12 and 13.13 indicate positive slopes. The vaporization curve of water (OC) and the sublimation curve of ice (AO) bear testimony to this. In short, the increase of pressure depresses the melting point of ice, whereas the boiling point of water and sublimation temperature of ice are increased. Also the sublimation curve (AO) has a steeper slope than the vaporization curve (OC) since near the point O,

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{vaporization}} + \Delta H_{\text{fusion}}.$$

Although ice exists in various crystalline modifications at high pressures, they have not been shown in Fig. 13.3 for simplicity.

Application of Phase Rule to Curves

Let us now apply phase rule, $F = 3 - P$ to these three curves. Since along each curve, there are two phases in equilibrium, $P = 2$ and $F = 3 - 2 = 1$. That is, the mention of temperature or pressure automatically fixes the value of the other parameter when two phases are in equilibrium. The curve OD is the vapour pressure curve of metastable water. You may be interested to know that water, if cooled very carefully, may exist in the liquid state even below freezing temperature. Water is then said to be supercooled. It is in a metastable equilibrium with its vapour under these conditions. The p against T relationship of this metastable equilibrium is given by the dotted curve OD. The curve OD is above OA signifying that the metastable system has a higher vapour pressure than the stable one at the same temperature. Slight stirring or addition of ice to water in metastable equilibrium results in the commencement of solidification of water and return to stable equilibrium. The curve OC terminates at C, the critical temperature, above which a substance exists only as a gas.

Application of Phase Rule to Areas in the Diagram

Inside the area AOB, ice is the stable phase, whereas in the regions BOC and AOC, the stable phases are water and vapour, respectively. Application of phase rule requires ($F = 3 - 1 = 2$) two degrees of freedom, namely, precise specification of both temperature and pressure to specify a point.

Triple Point

The point O is called the triple point and all the three phases coexist at this pressure and temperature (273.16 K and 610 Pa). This is an invariant point, since $F = 3 - 3 = 0$ and the change of temperature or pressure causes the disappearance of one of the phases.

Let us utilise the phase diagram in understanding the changes taking place when ice at atmospheric pressure (approximately 10^5 Pa) and below 273.15 K, as represented by the point x, is heated. At 273.15 K, ice begins to melt and this is indicated by the point y. The temperature remains constant till fusion is complete. Again the temperature increases and at a point z (373.15 K), there is equilibrium between water and vapour. Once again temperature remains constant till vaporization is complete. After this, again the temperature increases, and at a point z', it is in the form of steam completely. So far, we studied the phase diagram of water. Let us now study the phase diagram of sulphur.

The Phase Diagram of Sulphur

The phase diagram of sulphur (Fig. 13.4) is interesting due to the phase transition curves of the two allotropic modifications, and the presence of a metastable triple point.

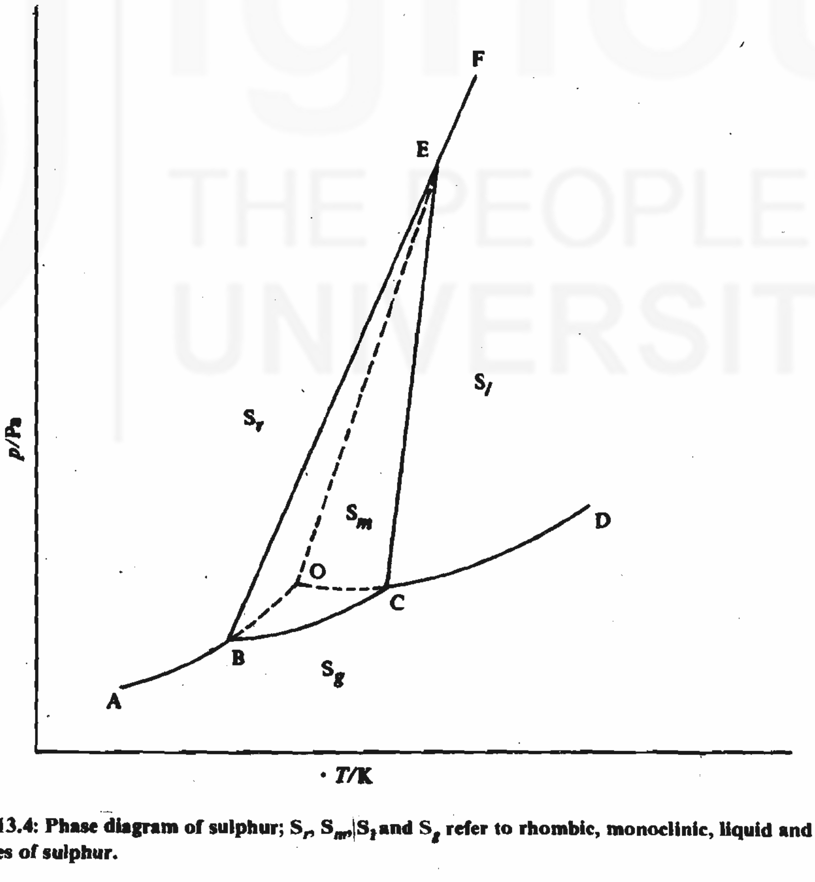

Fig. 13.4: Phase diagram of sulphur; S_r, S_m|S_l and S_g refer to rhombic, monoclinic, liquid and vapour phases of sulphur.

The stable form of sulphur at ordinary temperatures and under one atmosphere pressure is rhombic sulphur. If rhombic sulphur is heated, it slowly transforms to solid monoclinic sulphur at 368.6 K. Above 368.6 K, monoclinic sulphur is stable and it melts at 392.2 K to give liquid sulphur which is stable upto its boiling point (717.8 K). The transformation of one crystalline modification to another is often very slow and, if rhombic sulphur is heated quickly to 387.2 K, it melts. The curve BO represents the metastable equilibrium, between rhombic sulphur and sulphur vapour. Likewise, if liquid sulphur is allowed to cool quickly, monoclinic sulphur may not separate out at C, and CO represents metastable equilibrium between liquid and vapour forms of sulphur. The curve OE is the fusion curve of rhombic sulphur and it again represents metastable equilibrium.

The curves AB and BC are the sublimation curves of rhombic and monoclinic forms. BE represents the transition from rhombic to monoclinic form. CE and EF are the fusion curves of monoclinic and rhombic forms. CD is the vapour pressure curve of liquid sulphur.

Application of Clapeyron equation to various equilibria mentioned above indicates that for all these changes (from left to right in every case in Fig. 13.4), the change in enthalpy and molar volume are positive although the magnitudes are different. Hence the slopes $\frac{dp}{dT}$ (as given by $\frac{\Delta H}{T\Delta V}$) are positive for all the curves. This indicates that for all the transitions (from left to right in Fig. 13.4), the equilibrium temperatures increase with pressure. Application of phase rule to these curves gives $F = 3 - P = 3 - 2 = 1$, which means that specification of temperature or pressure is sufficient to define the equilibrium along each of the curves.

In the regions ABE, BEC, ECD and below ABCD, only one phase is stable and hence $F = 3 - 1 = 2$. That is, within the above regions, both pressure and temperature are to be specified to define any point.

There are four triple points corresponding to three stable equilibria and one metastable equilibria. The phases under equilibrium in each of these triple points is given in Table 13.1. In this table, B, C, E and O stand for the points specified in Fig. 13.4. Also S_r, S_m, S_l and S_g stand for rhombic, monoclinic, liquid and vapour forms of sulphur.

Table 13.1: Triple points in the Phase Diagram of Sulphur

At	Phases under equilibrium
B	S_r, S_m and S_g
C	S_m, S_l and S_g
E	S_r, S_m and S_l
O	S_r, S_l and S_g (metastable)

The application of phase rule to these triple points indicates that the system is invariant ($P = 3$ and $F = 3 - 3 = 0$). In this section, we applied the phase rule to one component systems. In the next section, we shall take up the study of two component systems.

SAQ 5

The phase diagram of carbon dioxide is given in Fig. 13.5.

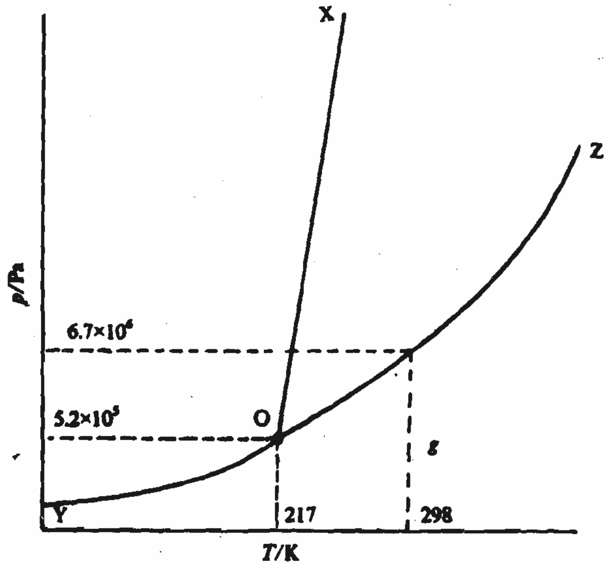

Fig. 13.5: Phase diagram of carbon dioxide; s, *l* and *g* stand for solid, liquid and vapour phases.

Using this phase diagram, answer the following:

a) suggest a name for the curve YO.

b) identify the triple point.

c) carbon dioxide gas cylinders are filled at 6.7×10^6 Pa and 298 K. What are the phases in equilibrium inside the cylinder?

....

....

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13.8 APPLICATION OF PHASE RULE TO TWO COMPONENT SYSTEMS

Two component systems are also known as binary systems. When a single phase is present in a two component system, phase rule states that $F = 2 - 1 + 2 = 3$. This requires three variables in order to specify a system. We must have a phase diagram in three coordinate axes to understand such a system. Since it is quite difficult to understand such a diagram, it is simplified as a two dimensional plot, keeping one of the three variables constant. In this case, each type of equilibria is studied separately. Thus the usual practice is to study liquid-gas, liquid-liquid, solid-liquid and solid-gas equilibria individually. We concentrate our attention on the solid-liquid equilibria in this section. The solid-gas equilibria will be studied in Section 13.9.

Phase Rule for the Condensed Systems

Solid-liquid equilibria are characterised generally by the absence of gas phase and are not much affected by small changes in pressure. Systems in which the gas phase is absent are called condensed systems. Measurements on solid-liquid equilibria in condensed systems are usually carried out at atmospheric pressure. Because of the relative insensitivity of such systems to small variations in pressure, the pressure may be considered constant. For such a system, the phase rule takes the form,

$$F = C - P + 1 \qquad \ldots (13.14)$$

Eq. 13.14 is known as phase rule for condensed systems. For two component systems, Eq. 13.14 becomes.

$$F = 3 - P \qquad \ldots (13.15)$$

The solid-liquid equilibria are best represented using temperature-composition diagram. Let us now discuss a method suitable for studying solid-liquid equilibria.

Thermal Analysis

Thermal analysis is a convenient method to study solid-liquid equilibria. In this method, solids of different compositions are separately heated above their melting points. The resulting liquids are cooled slowly and the cooling curves are constructed by plotting temperature against time. A break in the cooling curve indicates the crystallisation of a solid. But a horizontal portion ('halt') in the curve represents the separation of a second solid and, the temperature remains constant indicating the presence of three phases—two solids and a liquid. At this point, $F = 0$. Once solidification is complete, temperature falls gradually giving a smooth curve again. A typical cooling curve for two component systems is shown in Fig. 13.6. The portion *ab* represents the gradual cooling of a liquid. The portion *bc*, with a different slope and a break at *b* shows the crystallisation of a solid phase. The horizontal portion *cd* represents the separation of a second solid phase of certain composition and, the temperature halt continues till *d* when the last drop of the liquid is solidified. The portion *de* represents the cooling of the solid mixture.

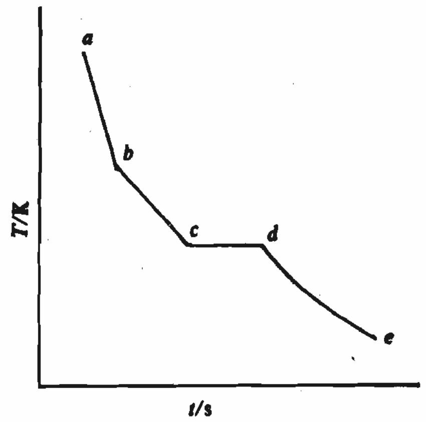

Fig. 13.6 : Cooling curve for two component systems: *b* denotes the break and *cd* the halt, *T* and *t* stand for temperature and time, respectively.

Using the temperature corresponding to the breaks and the halts in the cooling curves, the solid-liquid phase diagrams are constructed. We first take up the study of simple eutectic systems.

Simple Eutectic Systems

Binary systems illustrating this type are completely miscible in the liquid phase but are immiscible in the solid phase. Such systems have a phase diagram as represented in Fig. 13.7. Bismuth-cadmium system illustrates this type.

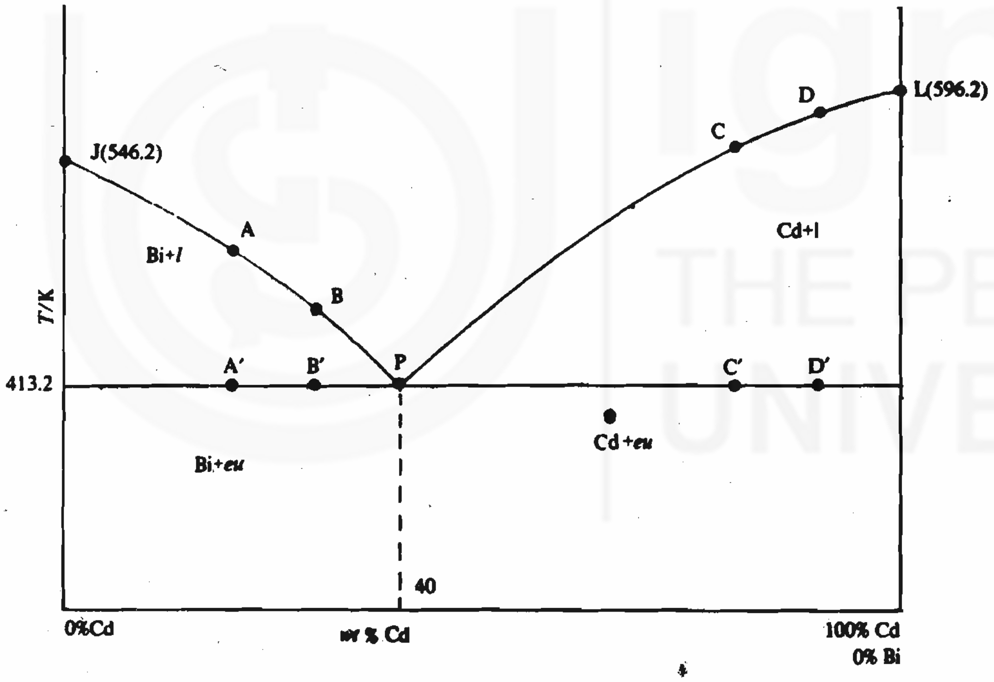

Fig.13.7: Bi—Cd eutectic system: *l* stands for melt and *eu* stands for eutectic mixture; *T* and wt % refer to temperature and weight percentage, respectively.

The melting points and Bi and Cd are represented by the points J and L. The curve JP represents the concentrations of solutions saturated with Bi and the curve LP, the concentrations of solutions saturated with Cd at different temperatures. Alternatively, the curve JP represents the freezing points of solutions which yield solid Bi on cooling, whereas, the curve LP, gives the freezing points of solutions yielding solid Cd. Above JPL, there is only liquid phase, called melt, which is a solution of both the metals. Hence, representing any point in this region where only one phase exists, both composition and temperature are to be specified. Along JP and LP, two phases (Bi and melt or Cd and melt) exist and hence $F = 3-2 = 1$. To define any point along the curves JP and LP, either temperature or composition need be mentioned.

At P (413.2 K and 40% Cd), both the curves meet and three phases—solid Bi, solid Cd and their liquid solution—exist. Hence P is an invariant ($F = 3-3 = 0$) point. Such a point is known as eutectic point. It is the lowest melting point for any solid

From Bi—Cd phase equilibria study, we understand that for binary systems of this type, addition of one component to another brings down the melting point. This has a practical application in the metallurgy of aluminium, which is obtained by the electrolysis of fused bauxite. Bauxite has a high melting point and the addition of cryolite (Na_3AlF_6) brings down the melting point of bauxite. The recognition of this aspect of phase equilibria is one of the important factors which have contributed to the large scale production of aluminium and its resultant price decrease by about 10,000 times during the last hundred years.

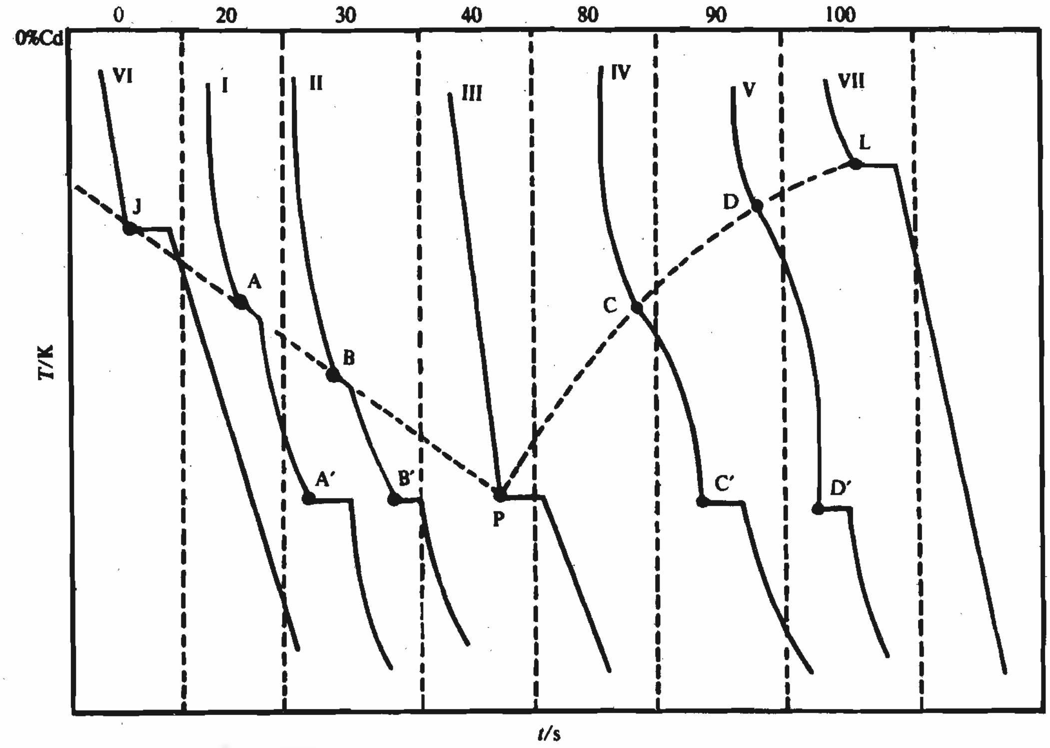

Fig. 13.8: Cooling curves for Bi—Cd system.

mixture of Bi and Cd. The word 'eutectic' in Greek means easily melted. At temperatures below 413.2 K, the system is completely a solid. Although eutectic mixture contains both metals in a definite ratio, it is not a compound, as under a microscope, the presence of two different crystals can be seen.

The significance of the phase digaram can be understood by considering the cooling curve pattern of several mixtures of Bi and Cd (Fig. 13.8). On cooling a 20% solution of Cd (curve I) in Bi, the temperature drops gradually and on reaching the point A. solid Bi begins to separate. During crystallisation, heat equivalent to the enthalpy of fusion of bismuth, is released. Because of this, there is a break in the curve at the point A. Along AA′, more and more solid Bi separates and the remaining liquid melt becomes richer in Cd. At A′, the eutectic mixture separates, and due to the presence of three phases, temperature remains constant. This corresponds to the horizontal portion of the curve. Once the liquid is completely solidified into the eutectic mixture, cooling proceeds smoothly again. The curve II represents a cooling of 30% Cd melt. The only difference between I and II is that solid Bi appears at a still lower temperature B. Again, at B′, there is a halt signifying the separation of the eutectic mixture. If a melt containing 40% Cd is cooled (curve III), there is no break in the curve; but a halt is seen at 413.2 K indicating the crystallisation of the eutectic mixture. Curve IV represents cooling of 80% Cd solution and the cooling curve experiences a break at C representing the separation of solid Cd, while the remaining melt approaches the eutectic composition. At C′, the eutectic mixture solidifies which is again marked by a halt in the cooling curve. Curve V is a cooling curve for 90% Cd solution, having a break at D and a halt at D′. The curves VI and VII represent the cooling curves of pure bismuth and cadmium liquids, respectively. Both the curves VI and VII correspond to one component systems and hence there is a halt in these curves where solid bismuth (at J) or solid cadmium (at L) begins to separate. From the cooling curves I to VII, the temperatures at J, A, B, P, L, D and C, corresponding to the different compositions of bismuth and cadmium, are noted and used in the plot of temperature against composition given in Fig. 13.7.

Apart from Bi—Cd system, there are many other examples such as Al—Sn, Sn—Pb, Ag—Pb, etc., which form eutectic mixtures. Eutectic systems have many practical applications.

- Solder which is used for joining electrical components is an eutectic mixture consisting of 67% by weight tin and 33% by weight lead.
- Pattinson's process of extracting silver from a lead—silver alloy containing even a

low percentage of silver also makes use of the eutectic formation principle. A solid lead—silver alloy containing a low percentage (say, 1%) of silver is heated above its melting point and slowly cooled. When the temperature reaches 600 K lead separates out as solid which can be removed from the melt. The melt continuously becomes richer in silver. At 576 K, eutectic mixture containing 2.6% silver solidifies from which silver can be extracted.

The eutectics formed by salt—water system are used as freezing mixtures. We shall shortly study this in detail.

It is worth pointing out that the formation of compounds and of solid solutions are also known in the solid—liquid equilibria of two component systems. But the studies are quite similar to eutectic systems, although individual phase diagrams differ considerably.

Salt—Water System

Salt-water system can belong to one of the following types:
i) Eutectic type (Example: $KI—H_2O$)
ii) Compound formation (Example: $Na_2SO_4—H_2O$)
As an illustration of salt—water system, we discuss $KI—H_2O$ system for which the phase diagram is given in Fig. 13.9. The curve AB is the fusion curve of ice. The addition of KI to ice depresses the melting point of ice. BC is the solubility curve of KI. You can see that the curve BC does not extend upto the melting point of pure KI. since it is quite above the critical temperature of water. Both the curves meet at B, the eutectic point (250.2 K) of this system. It is the lowest temperature that can be attained by the addition of KI to ice.

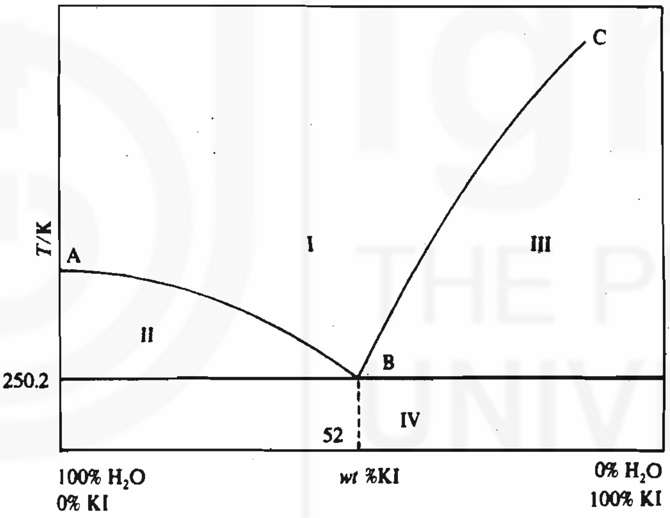

Fig. 13.9 : $KI—H_2O$ system:
I) Solution;
II) Solution + ice;
III) Solution + KI;
IV) KI + ice.

One of the applications of salt-water system is in the preparation of freezing mixtures. When salt is added to ice under adiabatic conditions (i.e., to ice in vacuum flask), ice melts. In doing so, it absorbs heat from the rest of the mixture. The temperature falls and, if enough salt is added, cooling continues down to the eutectic temperature.

In Table 13.2, eutectic temperature and eutectic composition of various ice—salt systems are given.

Table 13.2: Eutectic temperature of Freezing Mixtures

Name of the system	% Salt in the eutectic	(Eutectic temperature)/K
NH_4NO_3—ice	43.0	255.2
NH_4Cl—ice	19.7	257.8
$NaNO_3$—ice	33.3	255.1
KI—ice	52.0	250.2
$NaCl.2H_2O$—ice	23.0	252.1

Another application of salt-ice equilibrium is in the clearance of ice blocked roads in the cold countries. If for example, the temperature in that region is above 252 K, the spreading of a large quantity of common salt (more than corresponding to eutectic composition) on the road covered with ice helps melting the ice. The heat for melting the ice is readily available from the surrounding atmosphere of the ice-covered road. Hence, melting takes place without a decrease in temperature.

SAQ 6

Silver and lead form an eutectic with 2.6% by weight silver. The eutectic temperature is 576 K. The melting points of lead and silver are 600 K and 1243 K. Draw the phase diagram of Pb—Ag system on a rough scale and mark the stable phases in various regions. Explain the changes that would occur if melt containing 60% silver is cooled.

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13.9 APPLICATION OF PHASE RULE TO SOLID-GAS EQUILIBRIA

A simple example of gas-solid equilibrium which involves compound formation is the reaction between solid calcium oxide and gaseous carbon dioxide yielding calcium carbonate.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

The application of phase rule to this equilibrium gives $F = 2 - 3 + 2 = 1$; this means, fixation of temperature fixes equilibrium pressure of carbon dioxide. In Unit 14 of Block IV of this course, we will arrive at the conclusion that at constant temperature, the equilibrium pressure of carbon dioxide, also known as dissociation pressure, is constant for the above system.

It is interesting to study using Fig. 13.10 as to what happens when carbon dioxide is steadily admitted into a closed space containing calcium oxide at constant temperature. No reaction will occur until the pressure of the gas has risen to the dissociation pressure value at that temperature. At this pressure, the combination takes place and the pressure remains constant until all the calcium oxide has been converted to calcium carbonate. After this, pressure will rise again.

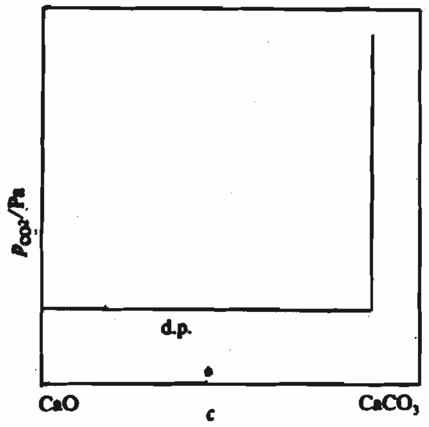

Fig. 13.10: $CaCO_3$—CaO—CO_2 system; d.p. stands for dissociation pressure; p_{CO_2} stands for the pressure of CO_2 and c the composition.

Similarly, starting from calcium carbonate kept in presence of carbon dioxide at a high pressure, let us decrease the pressure gradually. No dissociation takes place till the pressure reaches its dissociation pressure value at the temperature. Once this value is reached, the dissociation of calcium carbonate starts and the pressure remains constant. After complete dissociation of calcium carbonate to calcium oxide, pressure of carbon dioxide can be decreased again.

13.10 SUMMARY

In this unit, we have explained the terms phase, component and degree of freedom and derived the phase rule. The phase rule has then been applied to phase equilibria of one and two component systems. This unit helps us in understanding the influence of parameters like pressure, temperature and composition on the phase equilibria of substances. Some of the practical applications of such studies have also been explained.

13.11 TERMINAL QUESTIONS

1) Examine the following statements and write 'true' for the correct ones and 'false' for the wrong ones :
   a) The number of phases of a mixture of three gases enclosed in a container is 3.
   b) The number of phases of a mixture of ethyl alcohol and water is 2.
   c) The equilibrium point among ice, water and vapour is called eutectic point.
   d) The number of phases present in a vessel half filled with water is 1.
   e) The melting point of ice decreases with increasing pressure.

2) Fill in the blanks :
   a) The equilibrium between liquid water and vapour below 273 K is an example for a ..
   ....
   b) In a one component system, maximum number of phases that can coexist in a true equilibrium is ....
   c) Boiling point of water .... with increase in pressure.
   d) A phase transition requiring latent heat is called .... phase transition.
   e) A melt of eutectic composition when cooled shows only a .... in the cooling curve.

3) Suggest some applications of eutectic system studies.

4) Rice, dal and vegetables are cooked faster inside a pressure cooker than in an open vessel. Explain the reason.

5) If solid ammonium chloride is allowed to dissociate in a vessel already containing some ammonia, calculate the value of F.

6) Using Fig. 13.9, identify the solids that will come out in sequence if, the following solutions are cooled from 298 K to 250.2 K :
   a) 20% KI solution
   b) 60% KI solution
   c) 52% KI solution.

7) Calculate the slope $\frac{dp}{dT}$ of the fusion curve of ice near its melting point, if the enthalpy of fusion ice is 6.003×10^3 J mol^{-1}, the densities of water and ice are 999.8 and 916.8 kg m^{-3} and the normal melting point of ice is 273.15 K.

8) Calculate the number of components in the following system :
   a) Sugar in water
   b) Potassium chloride in water.

13.12 ANSWERS

Self-Assessment Questions

1) a) 3 (two due to toluene and water liquids which are immiscible and, one due to their vapours).

   b) 2 (since acetone and water are miscible).

2) a) $C = 1$ as per Eq. 13.1, since $S = 3$ and $R = 2$.
   b) $C = 2$, since $S = 3$ and $R = 1$.

3) The four phases of sulphur cannot coexist since then $F = -1$.

4) $\left(\frac{\partial \mu}{\partial T}\right)_p = -\bar{S}$ for a closed system, hence the slope of Fig. 13.1a or b gives the partial molar entropy of a substance with the sign inverted.

5) a) Sublimation curve
   b) The point O corresponding to pressure 5.2×10^5 Pa and temperature 217 K.
   c) Liquid and vapour.

6)

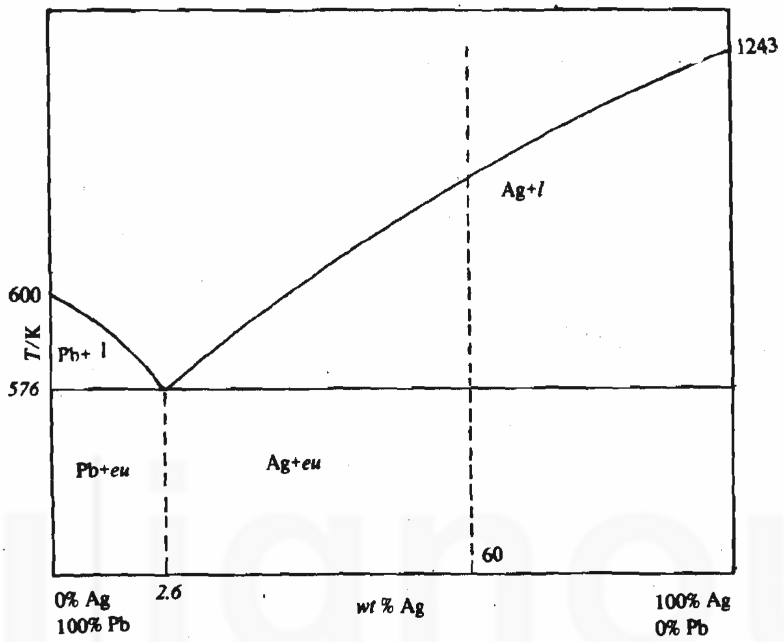

Fig. 13.11 : Ag-Pb System; *l* stands for melt and *eu* stands for eutectic.

When a melt containing 60% Ag is cooled, first the temperature decreases gradually. Then solid Ag starts forming and there is a break in the cooling rate. Once the remaining melt reaches 2.6% Ag composition, the whole mass begins to solidify and the temperature is constant till the solidification is complete. After that, the temperature decreases again.

Terminal Questions

1) a) False   b) True
   c) False   d) False
   e) True.

2) a) metastable equilibrium
   b) 3
   c) increases
   d) first order
   e) halt.

3) See Sec. 13.8.

4) Increase of pressure inside the closed cooker causes an increase in the boiling point of water. Due to higher temperature thus obtained, the cooking is faster inside the pressure cooker. In an open vessel, the boiling point of water is 373 K and the temperature is not enough for fast cooking.

5) $C=2$, $P=2$ and $F=2$.

6) a) First ice separates and finally a mixture of ice and KI solidifies
   b) First KI separates and finally a mixture of ice and KI solidifies
   c) A mixture of KI and ice separates together at 250.2 K.

7) Using Eq. 13.10 and Eq. 9.49 we get.

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{TM\left(\frac{1}{d_{\text{water}}} - \frac{1}{d_{\text{ice}}}\right)}$$

Where $\Delta H = 6.003 \times 10^3$ J mol^{-1}
$T = 273.15$ K
$M = 0.018$ kg mol^{-1}
$d_{water} = 999.8$ kg m^{-3}
$d_{ice} = 916.8$ kg m^{-3}
Slope $dp/dT = -1.34 \times 10^7$ Pa K^{-1}

8) a) Using Eq. 13.1, $C = 2$, since $S = 2$ and $R = 0$
b) The solution contains three species, water molecules, K^+ ions and Cl^- ions.
Hence $S = 3$. But $[K^+] = [Cl^-]$.
$R = 1$ and $C = 3 - 1 = 2$.