Physical Chemistry

CHM 111

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PHYSICAL CHEMISTRY

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Module 3

Solutions and Phase Rule

Unit 1:   Solutions

Unit 2:   Colligative Properties

Unit 3:   Phase Equilibria

Unit 1

Solid State Thermochemistry

Content

1.0 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.

2.0 Learning Outcomes

After studying this unit, you should be able to:

i.   define a solution
ii.   list various types of solutions
iii. express concentration of solutions in different ways
iv.   define solubility and explain the solubility curves, and
v.   state Raoult's law

3.0 Learning Outcome

3.1 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 1.

Table 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 adsorted 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.

Self-Assessment Exercise 1

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

i) Steel
ii) Sodium amalgam
iii) Soda water

3.2   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:

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 aqlution, we say that the solution is 0.1 molar (0.1 M).

Molarity (M)   =   Number of moles of the solute …………………………………..... (1)
                              Volume of the solution

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).

Molality(m) = Number of moles of the solute ……………………………………………(2)
                          Mass of the solvent in kg

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.

Normality (N) =   Strength in g dm^3
                              Equivalent weight ………………………………………………….(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* mole of a

solute is dissolved in n mole of a solvent, the mole fraction of the solvent and the solute are given by the following expressions:

Mole fraction of the solvent (X_1) = $\dfrac{n_1}{n_1 + n_2}$ ....(4)

Mole fraction of the solute (X_2) = $\dfrac{n_2}{n_1 + n_2}$ ....(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 l00g of solution   = 10% (V/W)

10 g NaCl present in 100 g of solution   = 10% (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.

One ppm = $\dfrac{Mass\ of\ Solute\ (g)}{Total\ Mass\ of\ Solution\ (g)}$ x 10^6 ....(6)

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

Example

Concentrated sulphuric acid contains 98% acid by weight:' its density is 1.85 x 10^3

kgm^{-3}.Calculate its molarity.

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

$= \dfrac{\text{Mass of sulphuric acid in m}^3}{\text{Molar mass x } 10^3 \text{ dm}^3}$

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

= 18.5 M

Self-Assessment Exercise 2

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

3.3 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. 1.
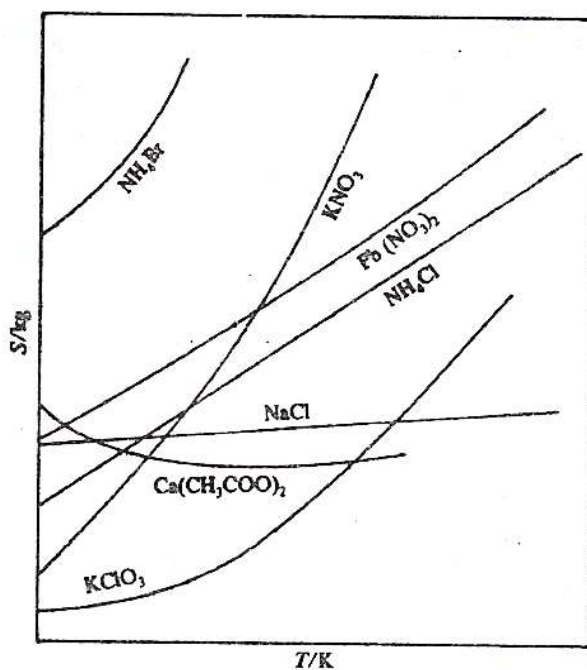

Fig. 1: Solubility curves of different solutes: S stands for solubility and T for temperature.

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.

3.4 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 o .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 2.

Table 2: Absorption Coefficients at 29.3 K

Solvent	Carbondioxide	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

3.4.1 Factors Affecting Solubility of Gases

The solubility of a gas in a liquid depends upon:

(i)   temperature

(ii)   pressure, and

(iii)   nature of the: gas, and the solvent.

Let us consider each of them.

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.

[According to Le Chatelier's principle, if a system under equilibrium is subjected to a change of concentration; pressure or temperature, the system shifts in such a way that tends to undo the effect of that change]

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:

$$p = Kx \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(7)$$

where p is the partial pressure of the gas over the solution and x is the solubility of the as in terms of its mole fraction in the solution; X 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. 7, the Henry's law constant is given as

$$K = p/x \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(8)$$

K has the dimensions of pressure. K is not constant as expected from Eq. 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. 2.
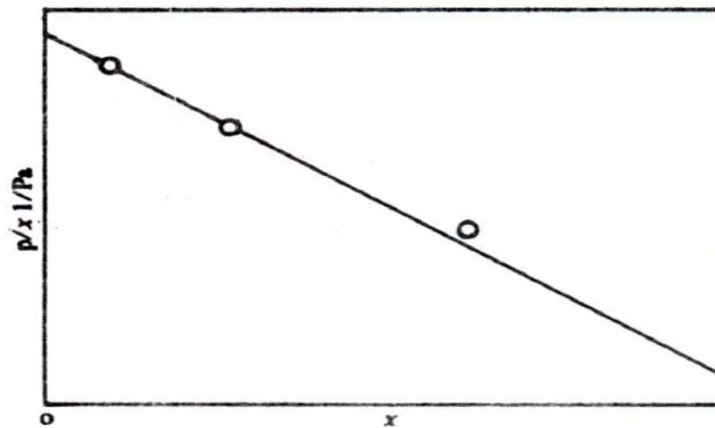

Fig. 2: Evaluation of Henry's law constant.

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Table 3: Henry's Law Constants at 198 K for some gases

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_2	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.

$H_2O + HCl \leftrightarrow H_3O^+ + Cl^-$

$H_2O + NH_3 \leftrightarrow NH_4OH \leftrightarrow NH_4^+ + OH^-$
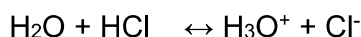
3. Nature of the gas and the solvent

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 ~ore soluble in common solvents.

Example 1

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

Solution

K = 4.40 x 10^9 Pa

p= 1.00 x 10^5 Pa

Mole fraction of oxygen,

$$xO_2 = \frac{nO_2}{nO_2 + nH_2O} = \frac{nO_2}{nO_2 + \left(\frac{1.00}{0.018}\right)mol} = \frac{nO_2}{56.6mol}$$

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. 8, we get

$$4.40 \times 10^9 Pa = \frac{1.00 \times 10^5 Pa}{nO_2/55.6mol} = \frac{1.00 \times 10^5 Pa}{nO_2} \times 55.6mol$$

$nO_2 = \dfrac{1.00 \times 10^5 Pa}{4.40 \times 10^9} \times 55.6\,mol = 1.26 \times 10^{-3}$

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

Self-Assessment Exercise 3

1. Why cannot fish live in warm water?

3.5   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).

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**.

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,

$p_A = p^o_A x_A$ ……………………………………………………………………….(9)

and $p_B = p^o_B x_B$ …………………………………………………………………..(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

$p = p_A + p_B = p^o_A x_A + p^o_B x_B$ …………………………………………………(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, Band B, and A and B are all alike

Thermodynamically,ideal solutions are those in which there is no volume change (ΔV_{mixing} = 0) and enthalpy change (ΔH_{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) ΔH_{mixing} = 0

iii) ΔV_{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

$p_A \neq p^o_A x_A$ ....(12)

and $p_B \neq p^o_B x_B$ ....(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 4.

Table 4: Liquid pain showing deviation from Raoult's law

Positive Deviation	Negative Deviation
H_2O + C_2H_2OH	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 x 10^5 Pa. When one more mole of B is added to the solution, the vapour pressure of the solution is 2.1 x 10^5 Pa. Calculate the vapour pressures of A and B in the pure state.

Solution

According to Eq. 11, total vapour pressure of the solution is given by,

p = $p^o{}_A x_A$ + $p^o{}_B x_B$

Substituting the values, we get

1.0 x 10^5 Pa = $p^o{}_A$ $(\frac{1.0}{1.0+2.0})$ + $p^o{}_B$ $(\frac{2.0}{1.0+2.0})$

or   2.0 x 10^5 Pa = $p^o{}_A$ /3.0 + 2.0 $p^o{}_B$ /3.0

or $p^o{}_A$ + 2.0 $p^o{}_B$ = 6.0 x 10^5 Pa…………………………………………………..(i)

Also 2.1 x 10^5 Pa = $p^o{}_A$ $(\frac{1.0}{1.0+3.0})$ + $p^o{}_B$ $(\frac{3.0}{1.0+3.0})$

 or $p^o{}_A$ + 3.0 $p^o{}_B$ = 8.4 x 10^5 Pa …………………………………………………..(ii)

From (i) and (ii)

$p^o{}_B$ = 2.4 x 10^5 Pa   and

$p^o{}_A$ = 1.2 x 10^5 Pa

Self-Assessment Exercise 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 x 10^4 Pa. The vapour pressures of pure acetone and pure chloroform at 308 K are 4.60 x 10^4 Pa and 3.92 x 10^4 Pa, respectively. Verify whether this solution is ideal or not.

3.6 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. 9 and 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. 3. - 13
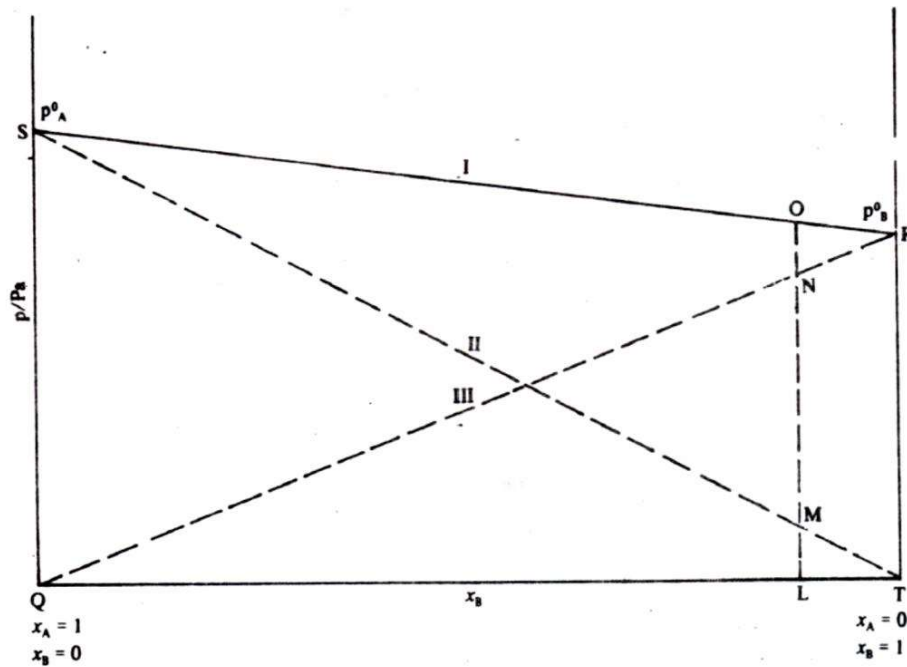
Curve I : Total vapour pressure of solution;

Curve II : Partial vapour pressure of A, $p_A = p^o_A x_A$

Curve III : Partial vapour pressure of B, $p_B = p^o_B x_B$

Fig. 3: Vapour pressure curves for ideal solution:

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 0 partial vapour pressure of B with its mole fraction in liquid solution and curve ST (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^o_A and p^o_B) 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. 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).

3.6.1 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,

$p_A > p°_A x_A$ ....(14)

$p_B > p°_B x_B$ ....(15)

and $p > p°_A x_A + p°_B x_B$ ....(16)

In Fig. 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. 4 are obtained. In ethanol, there is a strong intermolecular hydrogenbonding.

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. \
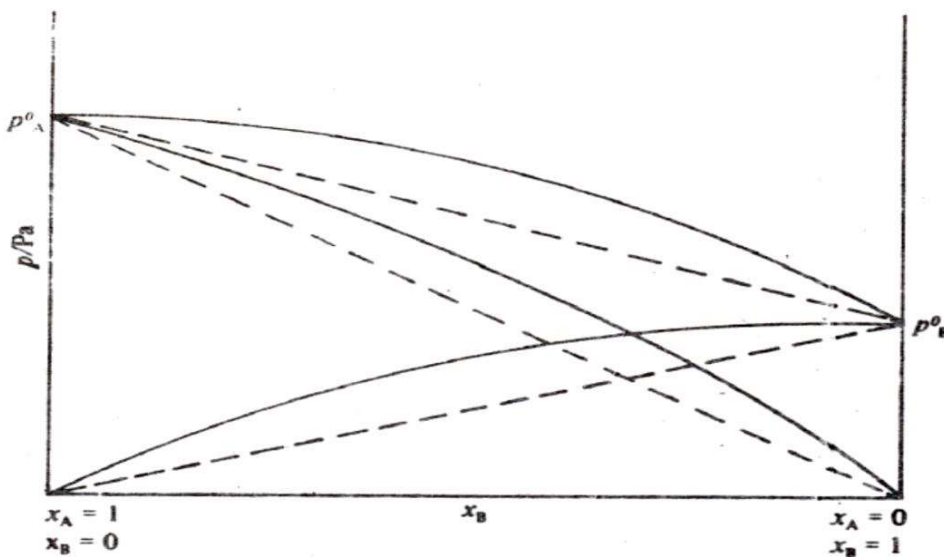

Fig. 4 : Curves showing positive deviation CromRaoult's law.

3.6.2 Vapour Pressure Curves of Solutions Showing Negative Deviation

If the intermolecular forces between A and Bare st.ronger 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. 5.
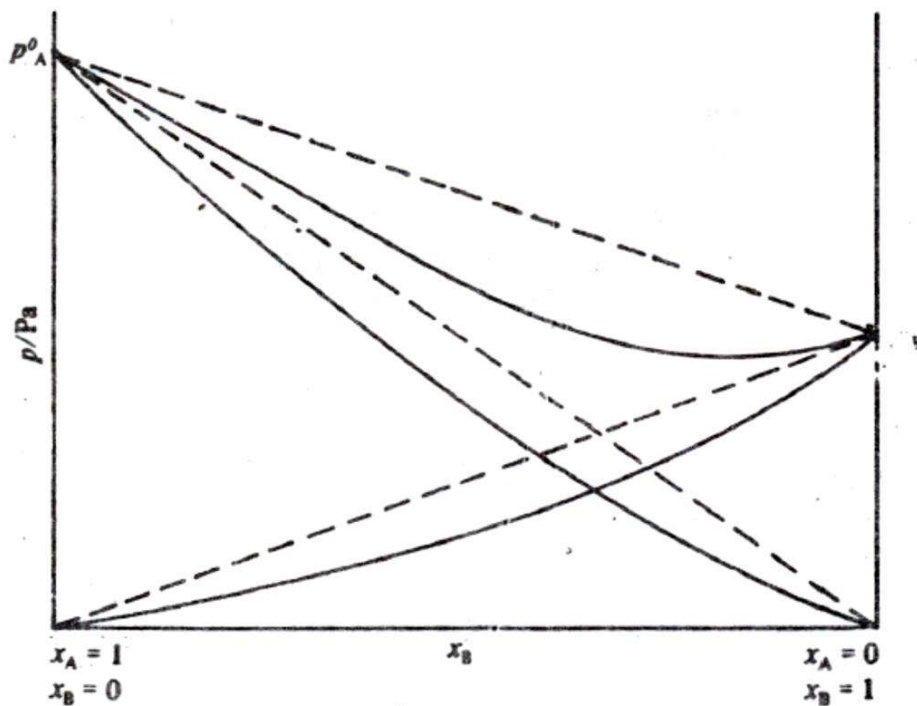
Fig. 5: Curves showing negative deviation from Raoult's law.

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.

4.0 Conclusion

You have learnt in this unit that a solution is a homogeneous mixture of two or more substances, the composition of which may vary. Also that 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. A solution may also be classified based on the number of constituents and also on the state of the solute and the solvent. 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. You have also learnt that liquid solutions obeying Raoult's law are called ideal solutions while those which do not obey the law are called non-ideal solutions.

5.0 Summary

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.

6.0 Tutor-Marked Assignment

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 'x' .

   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^{-1} kg of the solute, then calculate the molalityof 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 300K. 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 law 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.

7.0 References/ Further Reading

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Unit 2

Colligative Properties

Content

1.0 Introduction

In Unit 1, we discussed the completely miscible liquid systems. We also 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:

(i) relative lowering of vapour pressure,

(ii) elevation of boiling point,

(iii) depression of freezing point, and

(ivi) osmotic pressure.

We shall study these properties in this unit.

2.0 Learning Outcomes

After studying this unit, you should be able to :

i.   explain what is meant by colligative propetty,
ii.   state Raoult's law of relative lowering. of vapour pressure
iii. derive an expression relating the elevation of boiling point of a solution to its molality
iv.   define molal elevation constant
v.   derive an expression relating the depression of freezing point of a solution to its molality
vi.   define molal depression constant, define osmotic pressure
vii. 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
viii. explain van't Hoff factor.

3.0 Learning Content

3.1 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^o_1). If a non-volatile solute is added to this liquid,

the equilibrium vapour pressure liquid (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

$$p_1 = p^o_1 x_1 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

where x_1 is the mole fraction of the solvent in the solution and p^o 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. 1 that p_1 will also be less than p^o_1. The lowering of vapour pressure when a non-volatile solute is added to a solvent is given by ($p^o_1 - p_1$).

Substituting for p_1 from Eq. 1, we get

$$p^o_1 - p_1 = p^o_1 - p^o_1 x_1 = p^o_1(1 - x_1) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(2)$$

Since $x_1 + x_2 = 1$

$$p^o_1 - p_1 = p^o_1 x_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..(3)$$

where x_2 is the mole fraction of the solute.

According to Eq. 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. 3 can be written as

$$\frac{p^o_1 - p_1}{p^o_1} = x_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(4)$$

The expression on the left-hand side of Eq. 4 is called the relative lowering of vapour pressure. Eq, 4 also may be stated as:

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.

3.1.1 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. 4, we have

$$\frac{p^o_1 - p_1}{p^o_1} = x_2 = \frac{n_2}{n_1 + n_2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(5)$$

or $\quad \dfrac{p^o_1 - p_1}{p^o_1} \quad = \quad \dfrac{w_2/M_2}{w_1/M_1 + w_2/M_2}$ ………………………………………………………….(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. 6 reduces to

$\quad \dfrac{p^o_1 - p_1}{p^o_1} \quad = \quad \dfrac{w_2/M_2}{w_1/M_1} \quad = \dfrac{w_2 M_1}{w_1 M_2}$ …………………………………………….(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. 7.

3.1.2 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. 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 ß-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.
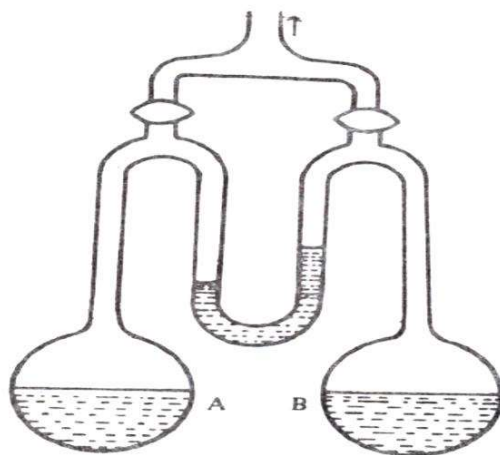
Fig. 1: Static method for determining the lowering of vapour pressure.

ii) Dynamic Method

This method is due to Ostwald and Walker. In this method (Fig. 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
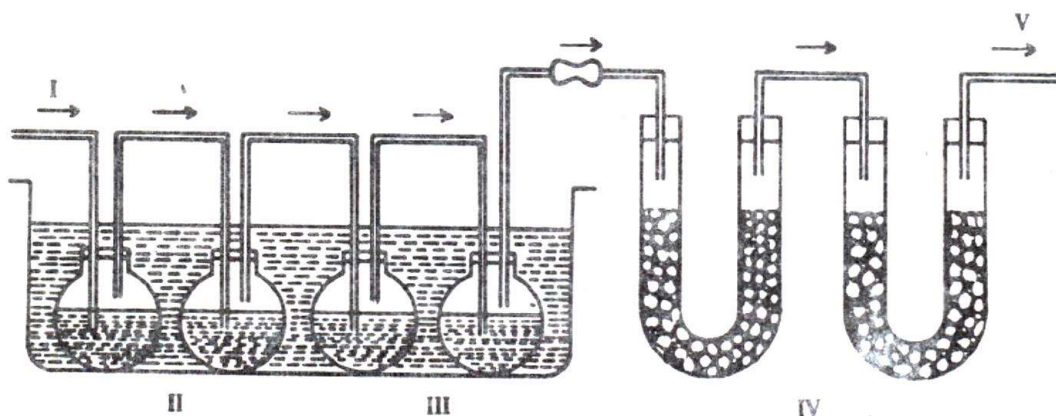

Fig. 2: Ostwald and Walker's apparatus for measuring the vapour pressure lowering:

i) air;

ii) solution bulbs;

iii) solvent bulbs;

iv) weighed $CaCl_2$ tubes;

v) dry air solution.

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^o_1 is the vapour pressure of the solvent, then we have

$W_B \alpha \ p^o_1 - p_2$…………………………………………………………………………..(8)

From Eqs. 7 and 8 we have

$(W_A + W_B) \alpha \ \ p_1 + p^o_1 - p_1$

or $(W_A + W_B) \alpha \ p^o_1$……………………………………………………………………(9)

From Eqs. 9 and 10 we have,

$$\frac{p^o_1 - p_1}{p_1} = \frac{W_B}{W_A + W_A}$$ …………………………………………………………………..(10)

Thus knowing WA and WB, the relative lowering of vapour pressure can be calculated using Eq. 11

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 x 10^3 Pa. Calculate the molar mass of the solute, if the vapour pressure of water at 300 K is 3.70 x 10^3 Pa.

Solution

W_1= 0.100 kg; W_2 = 0.012 kg

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

p^o_1 = 3.70 X 10^3 Pa; P_1 = 3.50 x 10^3 Pa

Using Eq. 7, we have

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

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

=0.040 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 nonvolatile solute is added to it.

Self-Assessment Exercise 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.

3.2   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. 3.
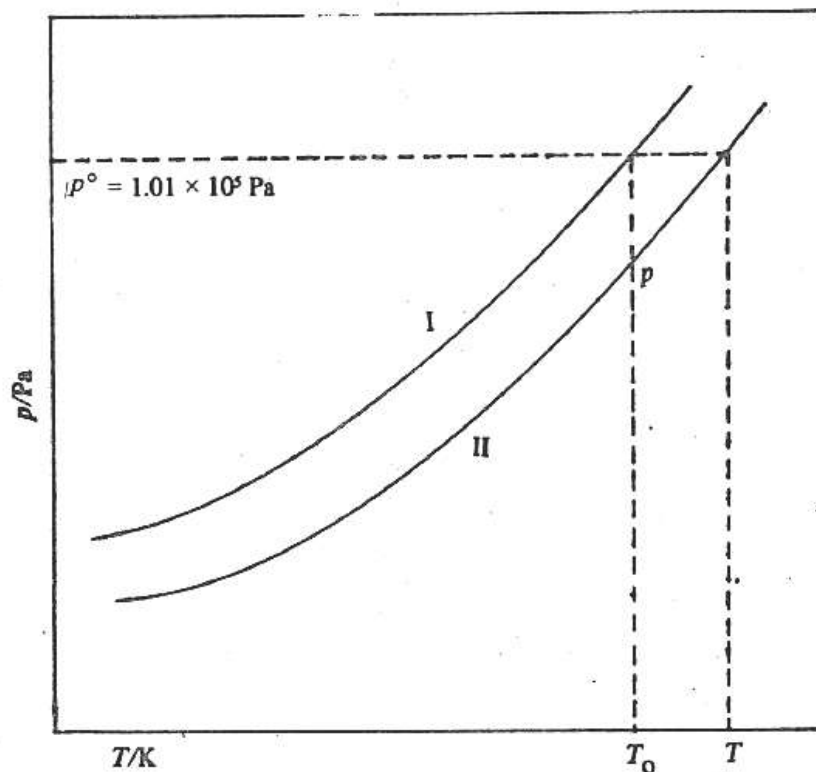

Fig. 3: Elevation of boiling point.

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_o and that of the solution is T so that the elevation in boiling point is $T - T_o = \Delta T_b)$ At temperature T_o, the lowering of vapour pressure of a solvent, when a non-volatile solute is added to it, is $p^o - p$. From the vapour pressure curve of the solution, it is clear that the vapour pressure of the solution is p at To and p^o at T. Applying the integrated form of the Clausius-Clapeyron equation, we have,

$$\ln \frac{p^o}{p} = \frac{\Delta H_{vap}}{R} \left[\frac{T - T_o}{T T_o} \right] \quad \text{..} (11)$$

where ΔH_{vap} represents the molar enthalpy of vaporization of the solvent at its normal boiling point To Since, the solution is dilute, To and T are not much different from each other. Eq. 11 may be written as

$$\ln \frac{p^o}{p} = \frac{\Delta H_{vap}}{R} \frac{\Delta T_b}{T^2_o} \quad \text{..} (12)$$

where, ΔT_b= Elevation in boiling point = T- To and T $\approx$ To so that TTo = T^2o. But

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$\ln \dfrac{p^o}{p} = -\ln \dfrac{p}{p^o} = -\ln\left(1 - \dfrac{p^o - p}{p^o}\right)$

$= -\ln(1 - x_2)$ (using Eq. 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, $\ln \dfrac{p^o}{P} = x_2$ ....(13)

From Eqs. 13 and 14, we have

$x_2 = \dfrac{\Delta H_{vap}}{R} \dfrac{\Delta T_b}{T^2 o}$ .... (14)

But

$x_2 = \dfrac{n_2}{n_1 + n_2}$ ....(15)

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. 15 may be written as

$x_2 = \dfrac{n_2}{n_1} = \dfrac{w_2/M_2}{w_1 M_1}$ ....(16)

From Eqs. 14 and 16, we have

$\dfrac{\Delta H_{vap}}{R} \dfrac{\Delta T_b}{T^2 o} = \dfrac{w_2/M_2}{w_1 M_1}$ ....(17)

or $\Delta T_b = \dfrac{RT2o\, w_2/M_2}{\Delta H_{vap}\, w_1/M_1} = \dfrac{RT^2 o M_1}{\Delta H_{vap}} x \dfrac{w_2}{w_1 M_2}$ ....(18)

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

Eq.18 reduces to

$\Delta T_b = \dfrac{RT^2 o M_1}{\Delta H_{vap}}$ ....(19)

The right hand side of Eq. 19 consists of constants R, To, 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.

$K_b = \dfrac{RT^2 o M_1}{\Delta H_{vap}}$ ....(20)

Using Eqs.18 and 20, we can write

$$\Delta T_b = K_b w_2/(w_1 M_2) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(21)$$

$$\text{or } \Delta T_b = K_b n_2/w_1 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(22)$$

$$\Delta T_b = K_b m \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(23)$$

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

3.2.1 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. 24 which is a rearranged form of Eq. 21.

$$M_2 = \frac{K_b}{\Delta T_b} \frac{w_2}{w_1} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(24)$$

The molal elevation constants (K_b) for some liquids are given in Table 1.

Table 1: Molal Elevation Constants

Solvent	$\dfrac{K_b}{\text{K kg mol}^{-1}}$	Solvent	$\dfrac{K_b}{\text{K kg mol}^{-1}}$
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

3.2.2 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:

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. 4a. It consists of flask A which contains the solvent.
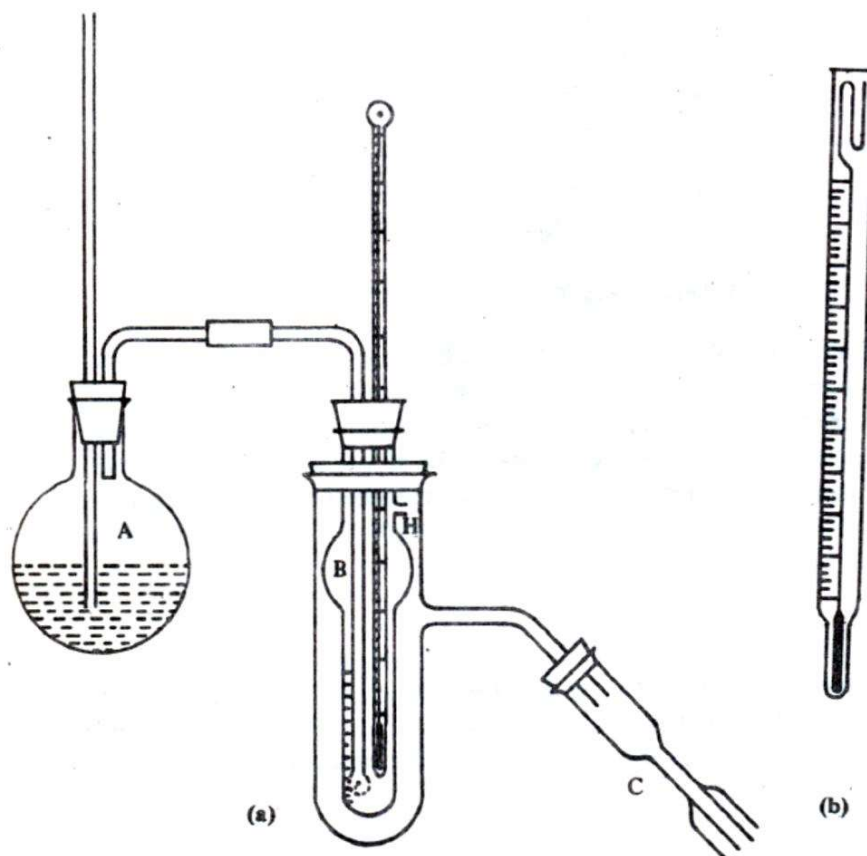
Fig. 4: a) Apparatus for Landsberger method; b) Beckmann thermometer

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 up to 0.01o is generally used. One such thermometer is the Beckmann thermometer (Fig. 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. 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.

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

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 x 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

ΔT_b = 0.320 K; W_2 = 5.15 X 10^{-4} kg

W_1= 3.50 x 10^{-2} kg; K_b = 3.90 K kg mol^{-1}

Using Eq. 25, we have

M_2 = 3.90 K kg mol^{-1} x 5.15 x 10^{-4} kg

      0.320 K x 3.50 x 10^{-2} kg

  = 0.179 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.

Self-Assessment Exercise 2

1. Explain why the boiling point of a solution is higher than that of a pure solvent.
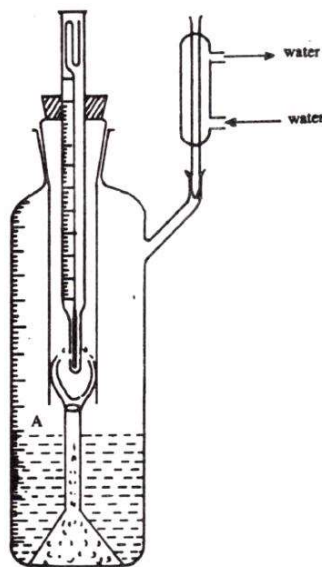
Fig. 5: Apparatus for Cottrell's metbod

3.3 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. 6. When the solution reaches the freezing point, the solid phase separating out is the pure solvent.

Fig. 6: Depression of freezing point: I) solvent curve; II) solution curve; III) curve for ice.

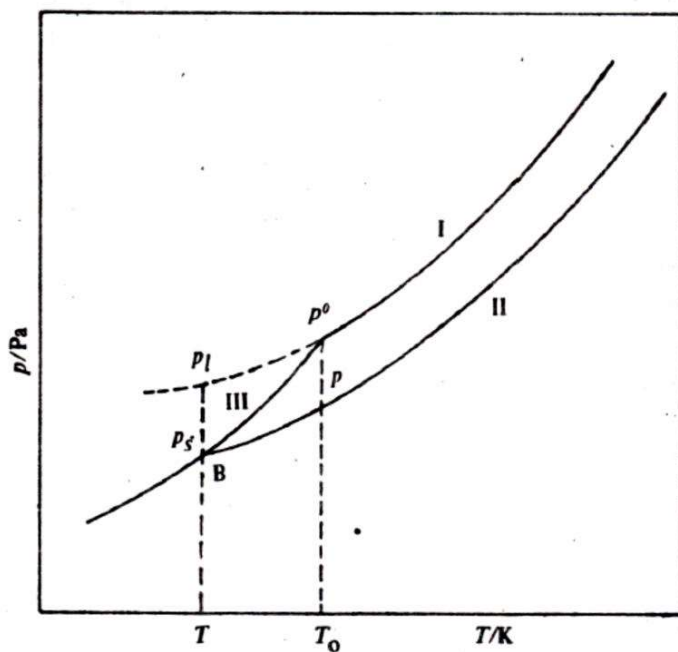Assuming that vapours obey ideal gas laws and that the volumes of the solid and the liquid are negligible in comparison with the volume of vapours, the equilibrium between solid solvent (ice) and vapour at constant external pressure is given by Clausius-Clapeyron equation,

$$\frac{d \ln p_s}{dT} = \frac{\Delta H_{sub}}{RT^2} \quad \text{.. (25)}$$

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

$$\frac{d \ln p_l}{dT} = \frac{\Delta H_{vap}}{RT^2} \quad \text{..(26)}$$

where AHvap is the molar enthalpy of evaporation of the liquid. If this equation is to hold good for the supercooled liquid, then Eqs. 25 and 26 will be applicable at the same temperature, i.e., T in Fig. 6.

Subtracting Eq. 27 from Eq. 26, we have,

$$\frac{d \ln p_s}{dT} - \frac{d \ln p_l}{dT} = \frac{\Delta H_{sub}}{RT^2} - \frac{\Delta H_{vap}}{RT^2} \quad \text{...(27)}$$

$$\frac{d \ln(p_s/p_l)}{dT} = \frac{\Delta H_{sub} - \Delta H_{vap}}{RT^2} \quad \text{..(28)}$$

$$\text{or} \quad \frac{d \ln(p_s/p_l)}{dT} = \frac{\Delta H_{fus}}{RT^2} \quad \text{..(29)}$$

where ΔH_{vap} is the molar enthalpy of fusion and is equal to (ΔH_{sub} - ΔH_{vap}). At the freezing point of the solution, the vapour pressure of the solid (ice) must be equal to that of the solution (PI) with which it is in equilibrium, i.e., at the point B in Fig. 6,

$P_s = P_l$ Hence at the freezing point of the solution,

$$\text{or} \quad \frac{d \ln(p_1/p_l)}{dT} = \frac{\Delta H_{fus}}{RT^2} \quad \text{..(30)}$$

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. 1),

$$p_1/p_l = x_1 \quad \text{..(31)}$$

Using this inEq. 31,

$$\frac{d \ln x_1}{dT} = \frac{\Delta H_{fus}}{RT^2} \quad \text{... (32)}$$

For the pure solvent (x_{1c}= 1), the freezing point is T_o and for the solution ($x_1 = x_l$), the freezing point is T. On integration of Eq, 33 between To and T as also between

1 and x1 we get

$$\int_1^{x1} d \ln x1 = \frac{\Delta H_{fus}}{R} \int_{T_o}^{T1} dT/T^2$$

$$\ln x_1 = -\frac{\Delta H_{fus}}{R}[1/T - 1/T_o]$$

or

$$\ln x_1 = -\frac{\Delta H_{fus}}{R}\left[\frac{T_o - T}{T\,T_o}\right] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(33)$$

If the solution is very dilute, T and To are not much different and $TT_o \approx T^2_o$.

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

Eq. 34 thus reduces to

$$\ln x_1 = -\frac{\Delta H_{fus}}{R}\,\frac{\Delta T_f}{T^2_o} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(34)$$

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. 35 thus reduces to

$$-x_2 = -\frac{\Delta H_{fus}}{R}\,\frac{\Delta T_f}{T^2_o}$$

or $$\Delta T_f = \frac{RT^2_o}{\Delta H_{fus}}\, x_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(35)$$

But $x_2 = w_2 M_1 / w_1 M_2$ in the case of a dilute solution as per Eq. 17.

Hence Eq. 36 can be writen as

$$\Delta T_f = \frac{RT^2_o M_1}{\Delta H_{fus}} \cdot \frac{w_2}{w_1 M_2} = \frac{K_f w_2}{w_1 M_2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(36)$$

where $$K_f = \frac{RT^2_o M_1}{\Delta H_{fus}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(37)$$

K_f is the molal depression constant.

Eq. 37 can also we written as

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

i.e. $$\Delta T_f = K_f\, m \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(38)$$

where m is the molality of the solution.

The molal depression constants (K_f) for a few solvents are given in Table 2.

Table 2: Molal Depression Constants

Solvent	$\dfrac{K_b}{\text{K kg mol}^{-1}}$	Solvent	$\dfrac{K_b}{\text{K kg mol}^{-1}}$
Water	1.81	Cyclohexane	20.20
Benzene	5.12	Camphor	40.00
Nitrobenzene	6.90	Acetic Acid	3.90

3.3.1 Determination of Relative Molecular Mass

Eq. 37 is used for determining the relative molecular mass of a non-volatile solute. 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. 7. 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.
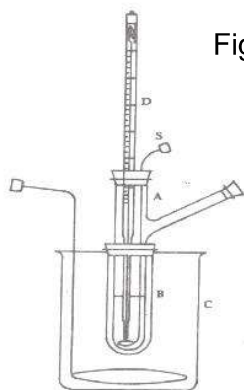

Fig. 7: Determination of freezing point-Beckmann method.

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

2) Rast Method

This method can be used for determining the relative molecular masses of those nonvolatile solutes which are soluble in molten camphor. It can be seen from Table 2 that the molal depression constant of camphor is very high, i.e., 40.00 K kg/mol. 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. 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.38, we have

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

$$= 1.85 \text{ K kg mol}''$$

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

(Since 273.15 K is the freezing point of water)

Using Eq. 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}

Self-Assessment Exercise 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.

3.4 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. 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;
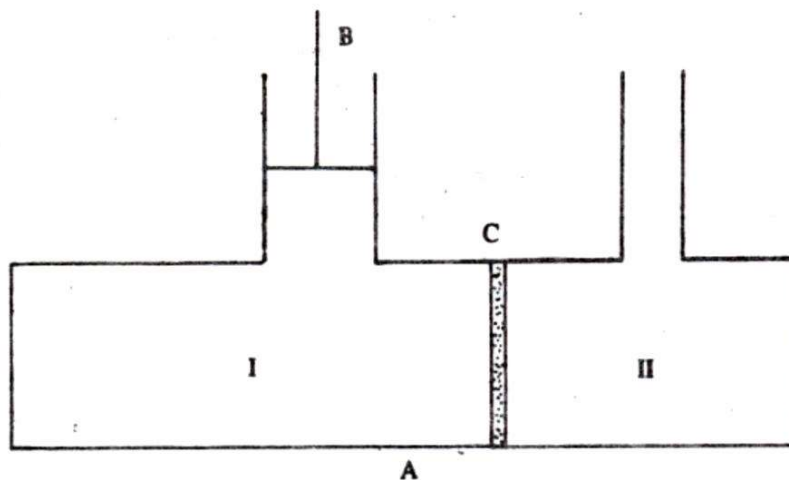

Fig. 8: Osmotic pressure measurement; I-section containing the solution: II-section containing the solvent.

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. 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.

3.4.1 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. 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.

[**NB**: 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].
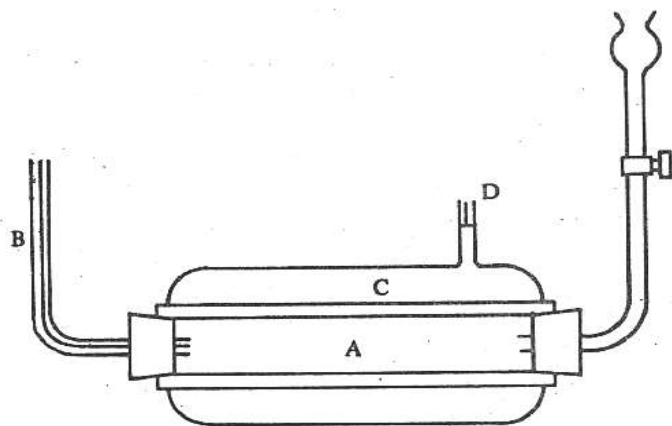

Fig. 9: Berkeley and Hartley's apparatus.

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 3.

Table 3: Osmotic Pressure Values of Aqueous Solutions of Sucrose at 287 K.

c/mol dm^{-3}	10^{-5} x π/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 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. 47) relating concentration of a solution to its osmotic pressure. Using Eq. 47, it is possible to calculate osmotic pressure of a solution. Some calculated osmotic pressure values are entered in Table 3. Let us now study the laws of osmotic pressure and, deduce Eq. 47.

3.4.2 Laws of Osmotic Pressure

van't Hoff deduced the laws of osmotic pressure from the results of 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.

π α C ....(39)

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.

π α 1/V ....(40)

or πV = constant ....(41)

Eq. 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)

π α T ....(42)

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.

π α n$_2$ .... (43)

From Eqs. 41, 43 and 44, we have,

$$\pi \ \alpha \ \frac{n_2 T}{V} \quad \text{..(44)}$$

Or $\Pi v = n_2 RT$ ....(45)

where R is a constant

or $\pi = \frac{n_2 RT}{V}$ ....(46)

or

But n_2/V = concentration of the solution = C

i.e., $\pi = CRT$ ....(47)

Eq. 47 can also be written as,

$$\pi = \frac{w_2 RT}{M_2 V} \quad \text{...(48)}$$

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. 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. 49,

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

$$= 3.65 \times 10^5 \text{ Pa} \times 1.00 \text{ m}^3$$

4.0 Conclusion

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.

5.0 Summary

In this unit you have learnt about the colligative properties of a solution and Raoult't law. 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.

You have also learnt that 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.

6.0 Tutor-Marked Assignments

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 morl

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? 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, for H_2O is 1.85 K kg/mol and the freezing point of water is 273K.

Unit 3

Phase Equilibria

Content

1.0 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 Module 4, Unit 1, we shall consider the various aspects of chemical equilibria. In this unit, we shall discuss physical equilibria. This means:

(i) focussing our attention on the equilibria regarding physical state and

(ii) 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.

2.0 Learning Outcomes

After studying this unit, you should be able to:

i.   define the terms, phase, component and degrees of freedom,

ii.   calculate the number of phases, components and degrees of freedom in a system,

iii.   state and deduce the phase rule,

iv.   comment on the stability of the phases of subliming and non-subliming substances,

v.   explain the two types of phase transitions.

3.0 Learning Outcomes

3.1 Definition of The Terms

Phase Equilibria

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.

(i)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. 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.

(ii) 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.

(iii) 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.

(iv) 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.

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 maybe smaller than the number of chemical substances that are present in the 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.

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

You can see that the composition of anyone 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$_4$Cl', 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, .

$C = S - R$ ....(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, NH4Cl, NH_3 and HCl. But R = 2 since these are two relations as shown below:

(1) $NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$

(2) Concentration of NH3 = 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 in- tensive variables such as pressure, temperature and composition which are to be specified to describe the state of the system completely.

(i)   If F = 0, the system is invariant and this means none of the intensive variables, can be changed.

(ii) In case F= 1, the system is univariant and one of the intensive variables can be changed.

(iii) For a bivariant system, F is equal to 2, and two of the intensive variables cart 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.

Self-Assessment Exercises 1

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

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

3.2 Criteria for Equilibrium

Phase Equllibria

In Module 2, 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 ………………………………………………………………. (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, ß and γ for the component i, then we can write

$$\mu_{i\alpha} = \mu_{i\beta} = \mu_{i\gamma} \text{ …………………………………………………(3)}$$

The conclusion given in' Eq. 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,

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

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.

3.3 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 ………………………………………………………………………... (4)

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

Let us take up some examples to understand Eq. 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

Havingstated 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= (Total number of variables) - (number of relations) …………………………….. (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.

Total number of variables = P(C-1) + 2 …………………………………………..…(6)

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

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

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.

Number of relations = C (P-1) …………………………………………………………(7)

Using Eqs. 6 and 7 in Eq. 5,

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

= PC- P + 2 - PC+ C

i.e., F = C- P+ 2 …………………………………………………………………………....(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.

Self-Assessment Exercise 2

1. 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?

3.4 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. 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. 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
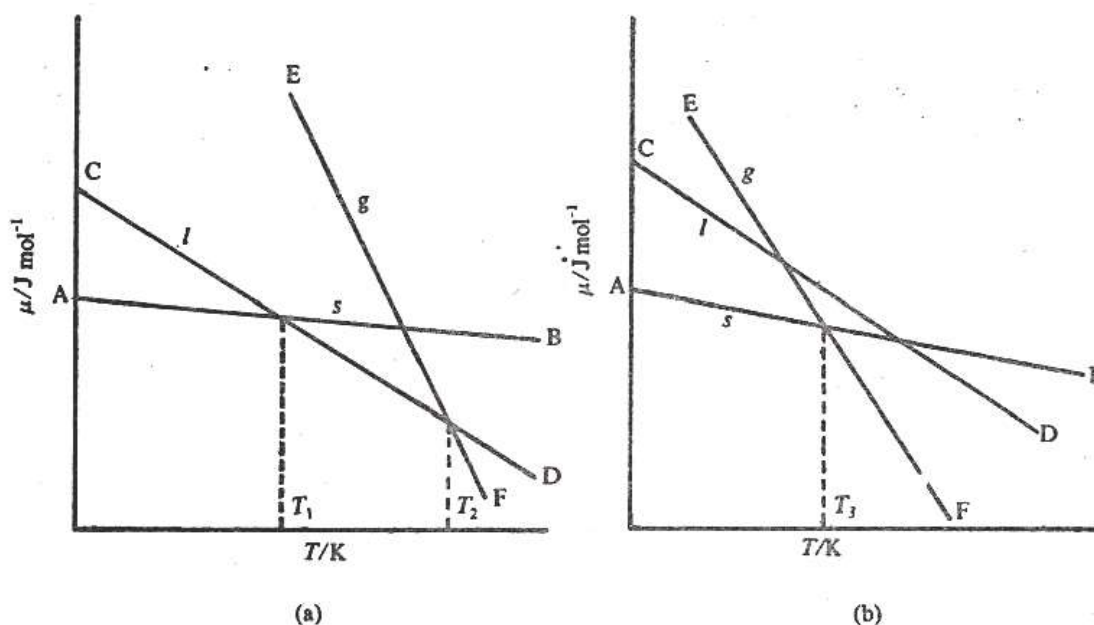

Fig.1: μ against T plots at constant pressure: (a) for non-subliming substances; (b) for subliming substances; in both the plots, g, I and s refer to vapour, liquid and solid phase curves.

In the case of subliming substances, μ against T curves are of the type shown in Fig. 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 x 10^5 Pa pressure, solid carbon dioxide melts to give a liquid and, below 5.2 x 10^5 Pa pressure, solid carbon dioxide sublimes.

Self-Assessment Exercise 3

Fig. 1a or b gives μ against *T* plot of a pure substance at constant pressure. For a substance in a closed system,

dμ = vdp - SdT

What thermodynamic property of a substance is given by the slope of Fig. 1a or b?

3.5   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.

4.0 Conclusion

Parameters such as pressure, temperature or composition affects the physical state of chemical substances. Physical equilibria can be related to various parameters such as pressure, temperature and composition using phase rule.

5.0 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.

6.0 Tutor-Marked Assignment

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.

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