Solutions - Part 2

Objectives

After going through this lesson, the learners will be able to understand the following:

- Describe the solubility of a solid, liquid or a gases solute in a liquid.
- Describe Henry's law and Roult's law and their various applications in our everyday life.

Contents Outline

- Introduction
- Solubility
    - Solubility of a Solid in a Liquid
    - Solubility of a Gas in a Liquid
- Vapour Pressure of Liquid Solutions
    - Vapour Pressure of Liquid-Liquid Solutions
    - Raoult's Law as a special case of Henry's Law
    - Vapour Pressure of Solutions of Solids in Liquids

Introduction

In the previous module, we have studied different types of solutions and calculation of concentration of liquid solutions. A solution is formed when a solute is dissolved in a suitable amount of solvent. In this Module, we shall study the important concept of solubility of a solute (gases, liquid or solid) in a liquid solvent. We shall also study various factors on which the solubility of a solute depends i.e. nature of solvent, temperature and pressure, etc. We shall also describe and discuss important laws such as Henry's law and Roult's law. Henry's law describes the quantitative relationship between solubility and pressure of a gases solute. The Roult's law relates the vapour pressure and the composition of the solution. We shall see that these concepts are very important to understand a large number of observations that we make in our everyday life.

Solubility

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in the solution of a solid or a gas in a liquid.

Solubility of a Solid in a Liquid

Every solid does not dissolve in a given liquid. Sodium chloride and sugar dissolve readily in water, whereas naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say **like dissolves like**.

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation. A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

Solute + Solvent $\rightleftharpoons$ Solution   (1)

At this stage, the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a **saturated solution.** An unsaturated solution is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its solubility.

Earlier we have observed that solubility of one substance into another depends on the nature of the substances. In addition to these variables, two other parameters, i.e., temperature and pressure also control this phenomenon.

Example 1

If the solubility product of CuS is 6×10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

Solution:

Solubility of CuS = S mole per litre

$K_{sp} = [Cu^{2+}][S^{2-}] = S^2$

$S = \sqrt{6x10^{-16}} = 2.5 \times 10^{-8}$ moles/litre = 2.5×10^{-8} M

Effect of Temperature on Solubility of a Solid in a Liquid

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by equation (1). This, being dynamic equilibrium, must follow Le Chatelier's Principle. In general, if in a nearly saturated solution, the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{sol}H < 0$) the solubility should decrease. These trends are also observed experimentally.

Effect of Pressure on Solubility of a Solid in a Liquid

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

Solubility of a Gas in a Liquid

Many gases dissolve in water. Oxygen dissolves only to a small extent in water. It is this dissolved oxygen which sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. Solubility of gases in liquids is greatly affected by pressure and temperature. The solubility of gases increases with increase of pressure. For solution of gases in a solvent, consider a system as shown in Fig. 1 (a). The lower part is the solution and the upper part is gaseous system at pressure p and temperature T. Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions the rate of gaseous particles entering and leaving the solution phase is the same. Now increase the pressure over the solution phase by compressing the gas to a smaller volume [Fig. 1 (b)]. This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as Henry's law. The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas. Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of partial pressure of the gas. If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.
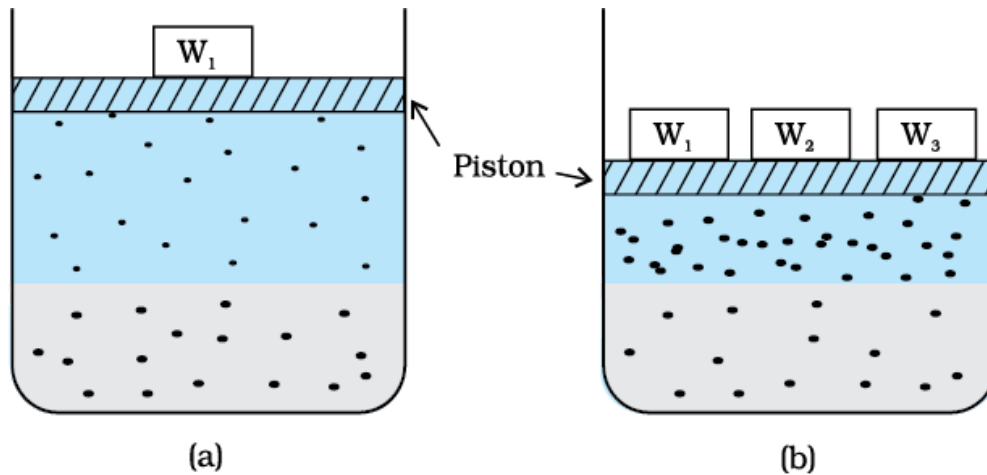

Fig.1: Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.

The most commonly used form of Henry's law states that "**the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution**" and is expressed as:

$$p \ = \ K_H x \tag{2}$$

Here K_H is the Henry's law constant. If we draw a graph between partial pressure of the gas versus the mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 2.
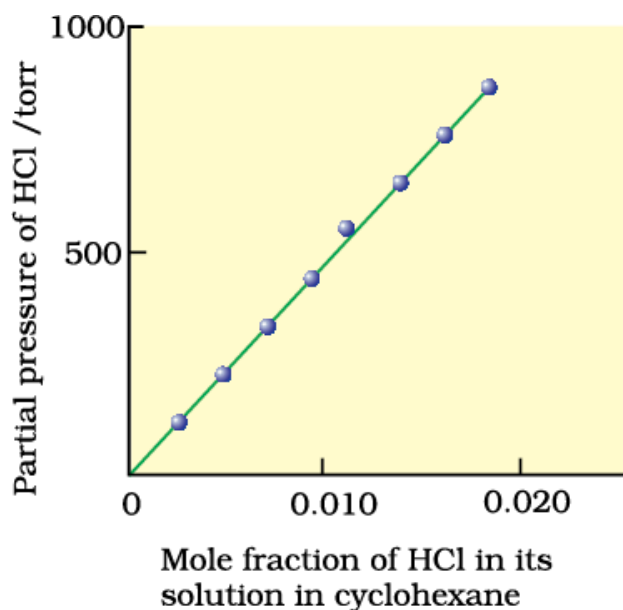
Fig. 2: Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant, K_H.

Different gases have different K_H values at the same temperature (Table 1). This suggests that K_H is a function of the nature of the gas.

It is obvious from equation (2) that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. It can be seen from Table 1 that K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

Table 1: Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	K_H/kbar	Gas	Temperature/K	K_H/kbar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	1.83×10^{-5}
N_2	303	88.84	Methane	298	0.413
O_2	293	34.86	Vinyl chloride	298	0.611
O_2	303	46.82			

Example 2

If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

Solution

The solubility of gas is related to the mole fraction in aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus: p (nitrogen)

$$x(Nitrogen) = \frac{p\,(Nitrogen)}{K_H} = \frac{0.987\ bar}{76,480\ bar} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if n represents number of moles of N_2 in solution,

$$x(Nitrogen) = \frac{n\ mol}{n\ mol + 55.5\ mol} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

(n in denominator is neglected as it is $<<$ 55.5)

Thus n $= 1.29 \times 10^{-5} \times 55.5$ mol $= 0.716$ m mol

Applications of Henry's Law

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

   a. To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

   b. Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards the surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

   c. At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

Effect of Temperature on Solubility of a Gas in a Liquid

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt in the last Section that the dissolution process involves dynamic equilibrium and thus must follow the Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

Vapour Pressure of Liquid Solutions

Liquid solutions are formed when solvent is a liquid. The solute can be a gas, a liquid or a solid. In this module, we shall discuss the solutions of liquids and solids in a liquid. Such solutions may contain one or more volatile components. Generally, the liquid solvent is volatile. The solute may or may not be volatile. We shall discuss the properties of only binary solutions, that is, the solutions containing two components, namely, the solutions of (i) liquids in liquids and (ii) solids in liquids.

Vapour Pressure of Liquid-Liquid Solutions

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between the vapour phase and the liquid phase. Let the total vapour pressure at this stage be p_{total} and p_1 and p_2 be the partial vapour pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as Raoult's law which states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

Thus, for component 1

$p_1 \propto x_1$

and $\quad p_1 = p_1^o x_1$ (3)

where p_1^0 is the vapour pressure of pure component 1 at the same temperature.

Similarly, for component 2

$$p_2 = p_2^o x_2 \qquad (4)$$

where p_2^o represents the vapour pressure of the pure component 2.

According to Dalton's law of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

$$p_{total} = p_1 + p_2 \qquad (5)$$

Substituting the values of p_1 and p_2, we get

$$p_{total} = x_1 p_1^o + x_2 p_2^o$$

$$p_{total} = (1 - x_2) p_1^o + x_2 p_2^o \qquad (6)$$

$$= p_1^o + (p_2^o - p_1^o) x_2 \qquad (7)$$

Following conclusions can be drawn from equation (7).

    a. Total vapour pressure over the solution can be related to the mole fraction of any one component.

    b. Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

    c. Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

A plot of p_1 or p_2 versus the mole fractions x_1 and x_2 for a solution gives a linear plot as shown in Fig. 3. These lines (I and II) pass through the points and respectively when x_1 and x_2 equal unity. Similarly the plot (line III) of ptotal versus x_2 is also linear (Fig. 3). The minimum value of p_{total} is p_1^o and the maximum value is p_2^o, assuming that component 1 is less volatile than component 2, i.e., $p_1^o < p_2^o$
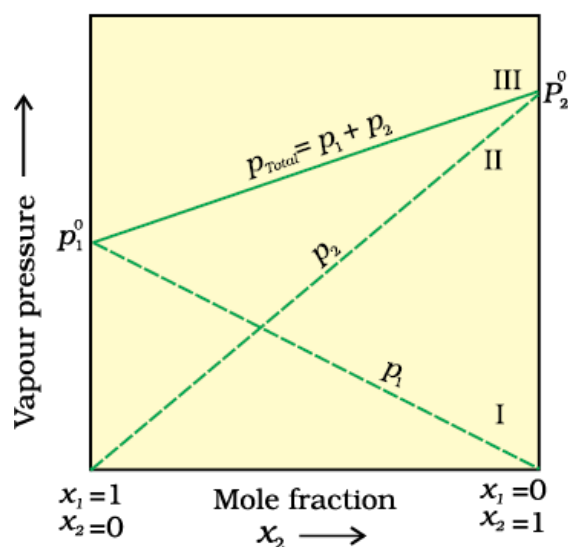
Fig. 3:The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2, respectively). The total vapour pressure is given by line marked III in the figure.

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

$$p_1 = y_1\, p_{total} \tag{8}$$

$$p_2 = y_2\, p_{total} \tag{9}$$

In general

$$p_i = y_i\, p_{total} \tag{10}$$

Example 3

Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mmHg and 415 mmHg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 298 K and, (ii) mole fractions of each component in the vapour phase.

Solution

(i) Molar mass of CH_2Cl_2 = 12 g mol^{-1} × 1 + 1 g mol^{-1} × 2 + 35.5 g mol^{-1} × 2 = 85 g mol^{-1}

Molar mass of $CHCl_3$ = 12 g mol^{-1} × 1 + 1 g mol^{-1} × 1 + 35.5 g mol^{-1} × 3 = 119.5 g mol^{-1}

Moles of $CH_2Cl_2 = \dfrac{40g}{85\ g\ mol^{-1}} = 0.47\ mol$

Moles of $CHCl_3 = \dfrac{25.5 g}{119.5\ g\ mol^{-1}} = 0.213\ mol$

Total moles = 0.47 + 0.213 = 0.683 mol

$x_{CH_2Cl_2} = \dfrac{0.47\ mol}{0.683\ mol} = 0.688$

$x_{CHCl_3} = 1 - 0.688 = 0.312$

Using eq (7), we have

$p_{\text{total}} = p_1^o + (p_2^o - p_1^o)\ x_2 = 200$ mmHg + (415 mmHg – 200 mmHg) × 0.688

$p_{\text{total}} = 200$ mmHg + 147.9 mmHg = 347.9 mmHg

(ii) Using the relation (10), $y_i = p_i/p_{\text{total}}$, we can calculate the mole fraction of the components in gas phase (y_i).

$p_{CH_2Cl_2} = 0.688 \times 415$ mmHg = 285.5 mmHg

$p_{CHCl_3} = 0.312 \times 200$ mmHg = 62.4 mmHg

$y_{CH_2Cl_2} = \dfrac{285.5\ mmHg}{347.9\ mmHg} = 0.82$

$y_{CHCl_3} = \dfrac{62.4\ mmHg}{347.9\ mmHg} = 0.18$

Note: Since, CH_2Cl_2 is a more volatile component than $CHCl_3$ [$p_{CH_2Cl_2}^o = 415$ mmHg and

$p_{CHCl_3}^o = 200$ mmHg] and the vapour phase is also richer in CH_2Cl_2

[$y_{CH_2Cl_2} = 0.82$ & $y_{CHCl_3} = 0.18$], it may thus be concluded that **at equilibrium, vapour phase will always be rich in the component which is more volatile.**

Raoult's Law as a Special case of Henry's Law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $p_i = x_i p_i^o$. In the solution of a gas in a liquid, one of the components is so volatile that it exists as a gas and we have already seen that its solubility is given by Henry's law which states that

$p = K_H\ x.$

If we compare the equations for Raoult's law and Henry's law, it can be seen that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in

solution. Only the proportionality constant K_H differs from p_1^o. Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_1^o.

Vapour Pressure of Solutions of Solids in Liquids

Another important class of solutions consists of solids dissolved in liquid, for example, sodium chloride, glucose, urea and cane sugar in water and iodine and sulphur dissolved in carbon disulphide. Some physical properties of these solutions are quite different from those of pure solvents. For example, vapour pressure. We know that liquids at a given temperature vapourise and under equilibrium conditions the pressure exerted by the vapours of the liquid over the liquid phase is called vapour pressure [Fig. 4 (a)]. In a pure liquid the entire surface is occupied by the molecules of the liquid. If a non-volatile solute is added to a solvent to give a solution [Fig. 4 (b)], the vapour pressure of the solution is solely from the solvent alone. This vapour pressure of the solution at a given temperature is found to be lower than the vapour pressure of the pure solvent at the same temperature. In the solution, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced.

The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature. For example, decrease in the vapour pressure of water by adding 1.0 mol of sucrose to one kg of water is nearly similar to that produced by adding 1.0 mol of urea to the same quantity of water at the same temperature.

Raoult's law in its general form can be stated as, for any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.
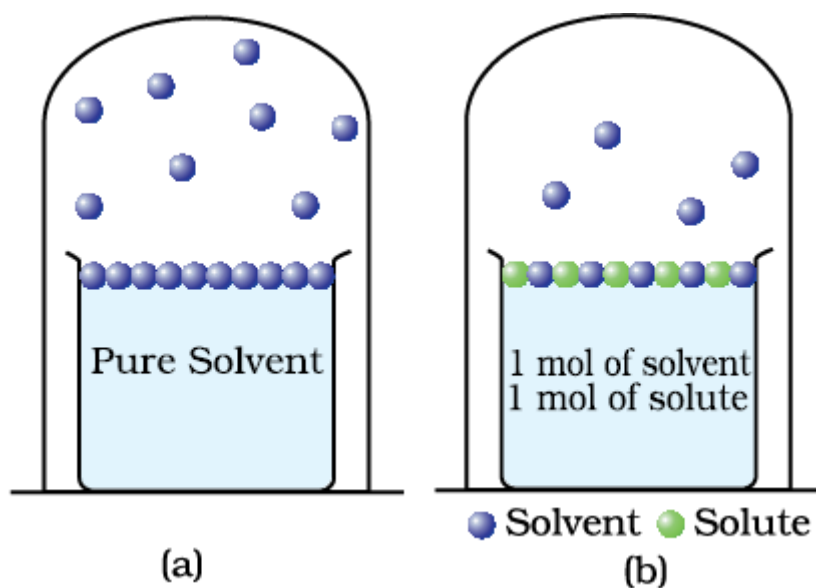
Fig. 4: Decrease in the vapour pressure of the solvent on account of the presence of solute in the solvent (a) evaporation of the molecules of the solvent from its surface is denoted by ●, (b) in a solution, solute particles have been denoted by ● and they also occupy part of the surface area.
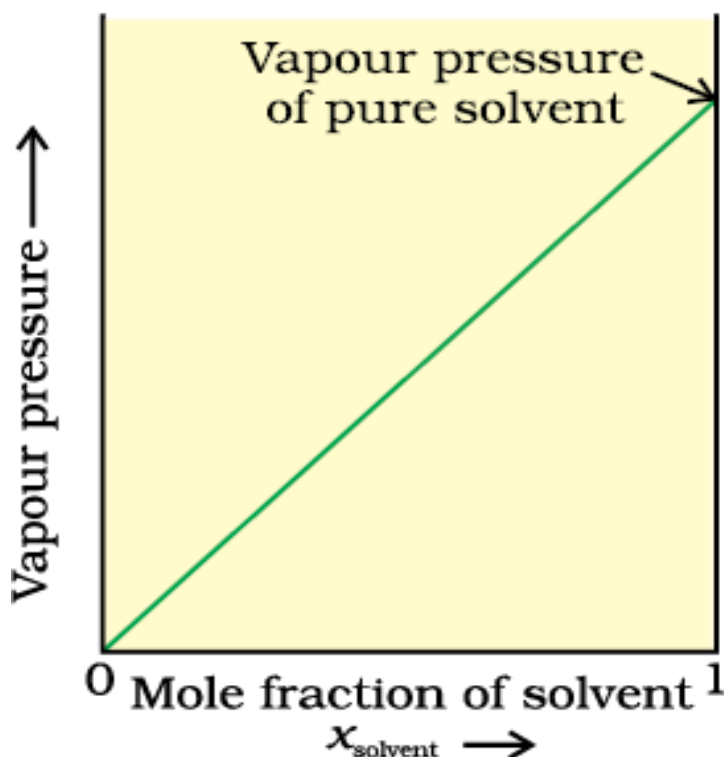

Fig. 5: If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent.

In a binary solution, let us denote the solvent by 1 and solute by 2. When the solute is non-volatile, only the solvent molecules are present in the vapour phase and contribute to vapour pressure. Let p_1 be the vapour pressure of the solvent, x_1 be its mole fraction, p_1^o be its vapour pressure in the pure state. Then according to Raoult's law

$p_1 \propto x_1$

and $p_1 = p_1^o x_1$ (11)

The proportionality constant is equal to the vapour pressure of pure solvent, p_1^o. A plot between the vapour pressure and the mole fraction of the solvent is linear (Fig. 5).

Example 4

The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

Solution

Moles of solute in 1 molal solution = 1 mol

Mass of water as solvent in 1 molal solution = 1 kg = 1000 g

Moles of solvent water $= \frac{Mass\ of\ water}{Molar\ mass\ of\ water} = \frac{1000\ g}{18\ g\ mol^{-1}} = 55.55 \text{mol}$

Total moles of solute and solvent in the solution = 1 mol + 55.55 mol = 56.55 mol

Mole fraction of solvent water; x_1 in solution $= \frac{Moles\ of\ solvent\ (water)}{Total\ moles\ of\ solute\ \&\ solvent\ (water)}$

$= \frac{55.55\ mol}{56.55\ mol} = 0.982$

The vapour pressure of pure solvent $= p^o$ = 12.3 kPa

The vapour pressure of the solution $(p) = x_{solvent} \times p^o = (12.3 \text{ kPa} \times 0.982)$ kPa = 12.08 kPa