

(vii) *Molality*: Molality (m) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \quad (2.9)$$

For example, 1.00 mol kg^{-1} (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water.

Each method of expressing concentration of the solutions has its own merits and demerits. Mass %, ppm, mole fraction and molality are independent of temperature, whereas molarity is a function of temperature. This is because volume depends on temperature and the mass does not.

Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene. *Example 2.3*

Molar mass of $\text{C}_2\text{H}_4\text{O}_2$: $12 \times 2 + 1 \times 4 + 16 \times 2 = 60 \text{ g mol}^{-1}$

$$\text{Moles of } \text{C}_2\text{H}_4\text{O}_2 = \frac{2.5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0417 \text{ mol}$$

Mass of benzene in kg = $75 \text{ g} / 1000 \text{ g kg}^{-1} = 75 \times 10^{-3} \text{ kg}$

$$\begin{aligned} \text{Molality of } \text{C}_2\text{H}_4\text{O}_2 &= \frac{\text{Moles of } \text{C}_2\text{H}_4\text{O}_2}{\text{kg of benzene}} = \frac{0.0417 \text{ mol} \times 1000 \text{ g kg}^{-1}}{75 \text{ g}} \\ &= 0.556 \text{ mol kg}^{-1} \end{aligned}$$

Solution

Intext Questions

- 2.1** Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.
- 2.2** Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.
- 2.3** Calculate the molarity of each of the following solutions: (a) 30 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 4.3 L of solution (b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL .
- 2.4** Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.
- 2.5** Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1} .

2.3 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 solution of a solid or a gas in a liquid.

2.3.1 Solubility of a Solid in a Liquid

Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, 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.



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.

Effect of temperature

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by equation 2.10. This, being dynamic equilibrium, must follow **Le Chateliers Principle**. In general, if in a *nearly saturated solution*, the dissolution process is endothermic ($\Delta_{\text{sol}} H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{\text{sol}} H < 0$) the solubility should decrease. These trends are also observed experimentally.

Effect of pressure

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.

2.3.2 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 increase with increase of pressure. For solution of gases in a solvent, consider a system as shown in Fig. 2.1 (a). The lower part is 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 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. 2.1 (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.

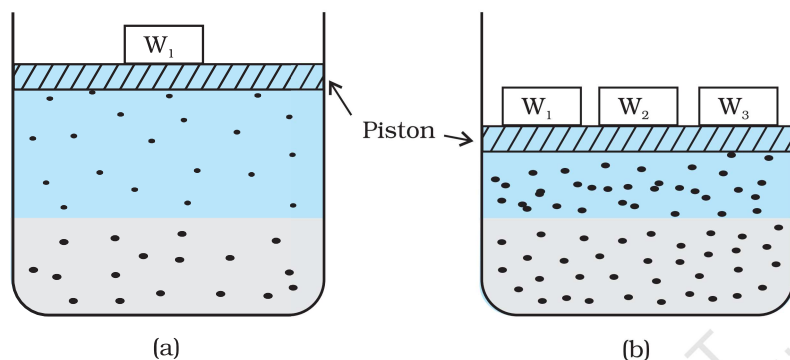


Fig. 2.1: Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.

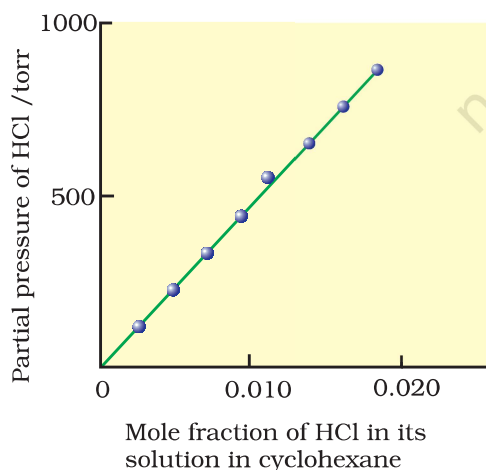


Fig. 2.2: Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant, K_H .

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 partial pressure of the gas present above the surface of liquid or solution**. 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**. 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:

$$p = K_H x \quad (2.11)$$

Here K_H is the Henry's law constant. If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 2.2.

Different gases have different K_H values at the same temperature (Table 2.2). This suggests that K_H is a function of the nature of the gas.

It is obvious from equation (2.11) 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 2.2 that K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases

Table 2.2: 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			

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.

Example 2.4 If N₂ gas is bubbled through water at 293 K, how many millimoles of N₂ gas would dissolve in 1 litre of water? Assume that N₂ exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N₂ 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:

$$x(\text{Nitrogen}) = \frac{p(\text{nitrogen})}{K_H} = \frac{0.987 \text{ bar}}{76.480 \text{ bar}} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if n represents number of moles of N₂ in solution,

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

(n in denominator is neglected as it is $\ll 55.5$)

$$\text{Thus } n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol}$$

$$= \frac{7.16 \times 10^{-4} \text{ mol} \times 1000 \text{ mmol}}{1 \text{ mol}} = 0.716 \text{ mmol}$$

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

- To increase the solubility of CO₂ in soft drinks and soda water, the bottle is sealed under high pressure.
- 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 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).

- 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

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 dissolution process involves dynamic equilibrium and thus must follow **Le Chatelier's Principle**. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

Intext Questions

- 2.6** H_2S , a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.
- 2.7** Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

2.4 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. Solutions of gases in liquids have already been discussed in Section 2.3.2. In this Section, 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.

2.4.1 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 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 the **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

$$p_1 \propto x_1$$

$$\text{and } p_1 = p_1^0 x_1 \quad (2.12)$$

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

Similarly, for component 2

$$p_2 = p_2^0 x_2 \quad (2.13)$$

where p_2^0 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:

$$p_{\text{total}} = p_1 + p_2 \quad (2.14)$$

Substituting the values of p_1 and p_2 , we get

$$\begin{aligned} p_{\text{total}} &= x_1 p_1^0 + x_2 p_2^0 \\ &= (1 - x_2) p_1^0 + x_2 p_2^0 \end{aligned} \quad (2.15)$$

$$= p_1^0 + (p_2^0 - p_1^0) x_2 \quad (2.16)$$

Following conclusions can be drawn from equation (2.16).

- (i) Total vapour pressure over the solution can be related to the mole fraction of any one component.
- (ii) Total vapour pressure over the solution varies linearly with the mole fraction of component 2.

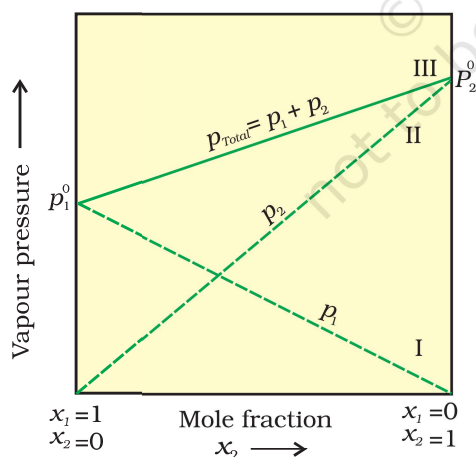


Fig. 2.3: The plot of vapour pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2 , respectively). The total vapour pressure is given by line marked III in the figure.

- (iii) 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. 2.3. These lines (I and II) pass through the points for which x_1 and x_2 are equal to unity. Similarly the plot (line III) of p_{total} versus x_2 is also linear (Fig. 2.3). The minimum value of p_{total} is p_1^0 and the maximum value is p_2^0 , assuming that component 1 is less volatile than component 2, i.e., $p_1^0 < p_2^0$.

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:

$$p_1 = y_1 p_{\text{total}} \quad (2.17)$$

$$p_2 = y_2 p_{\text{total}} \quad (2.18)$$

In general

$$p_i = y_i p_{\text{total}} \quad (2.19)$$

Vapour pressure of chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg 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 vapour phase.

Example 2.5

Solution

(i) Molar mass of $\text{CH}_2\text{Cl}_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85 \text{ g mol}^{-1}$

Molar mass of $\text{CHCl}_3 = 12 \times 1 + 1 \times 1 + 35.5 \times 3 = 119.5 \text{ g mol}^{-1}$

Moles of $\text{CH}_2\text{Cl}_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}$

Moles of $\text{CHCl}_3 = \frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$

Total number of moles = $0.47 + 0.213 = 0.683 \text{ mol}$

$x_{\text{CH}_2\text{Cl}_2} = \frac{0.47 \text{ mol}}{0.683 \text{ mol}} = 0.688$

$x_{\text{CHCl}_3} = 1.00 - 0.688 = 0.312$

Using equation (2.16),

$$\begin{aligned} p_{\text{total}} &= p_1^0 + (p_2^0 - p_1^0) x_2 = 200 + (415 - 200) \times 0.688 \\ &= 200 + 147.9 = 347.9 \text{ mm Hg} \end{aligned}$$

(ii) Using the relation (2.19), $y_i = p_i/p_{\text{total}}$, we can calculate the mole fraction of the components in gas phase (y_i).

$$p_{\text{CH}_2\text{Cl}_2} = 0.688 \times 415 \text{ mm Hg} = 285.5 \text{ mm Hg}$$

$$p_{\text{CHCl}_3} = 0.312 \times 200 \text{ mm Hg} = 62.4 \text{ mm Hg}$$

$$y_{\text{CH}_2\text{Cl}_2} = 285.5 \text{ mm Hg} / 347.9 \text{ mm Hg} = 0.82$$

$$y_{\text{CHCl}_3} = 62.4 \text{ mm Hg} / 347.9 \text{ mm Hg} = 0.18$$

Note: Since, CH_2Cl_2 is a more volatile component than CHCl_3 , [$p_{\text{CH}_2\text{Cl}_2}^0 = 415 \text{ mm Hg}$ and $p_{\text{CHCl}_3}^0 = 200 \text{ mm Hg}$] and the vapour phase is also richer in CH_2Cl_2 [$y_{\text{CH}_2\text{Cl}_2} = 0.82$ and $y_{\text{CHCl}_3} = 0.18$], it may thus be concluded that **at equilibrium, vapour phase will be always rich in the component which is more volatile.**

2.4.2 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 $p_i = x_i p_i^0$. 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_i^0 . Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_i^0 .

2.4.3 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 have learnt in Unit 5, Class XI, that liquids at a given temperature vapourise and under

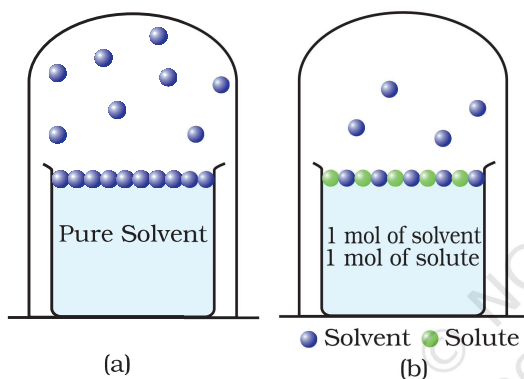


Fig. 2.4: Decrease in the vapour pressure of the solvent on account of the presence of solute in the solvent (a) evaporation of the molecules of the solvent from its surface is denoted by ●, (b) in a solution, solute particles have been denoted by ● and they also occupy part of the surface area.

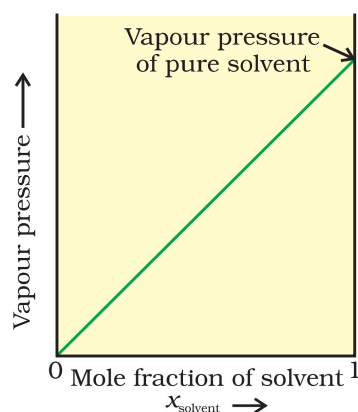
equilibrium conditions the pressure exerted by the vapours of the liquid over the liquid phase is called vapour pressure [Fig. 2.4 (a)]. In a pure liquid the entire surface is occupied by the molecules of the liquid. If a non-volatile solute is added to a solvent to give a solution [Fig. 2.4.(b)], the 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.**

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 vapour phase and contribute to vapour pressure. Let p_1 be

Fig. 2.5
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.



the vapour pressure of the solvent, x_1 be its mole fraction, p_1^0 be its vapour pressure in the pure state. Then according to Raoult's law

$$p_1 \propto x_1$$

$$\text{and } p_1 = x_1 p_1^0 \quad (2.20)$$

The proportionality constant is equal to the vapour pressure of pure solvent, p_1^0 . A plot between the vapour pressure and the mole fraction of the solvent is linear (Fig. 2.5).

2.5 Ideal and Non-ideal Solutions

Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

2.5.1 Ideal Solutions

The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solutions*. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$\Delta_{\text{mix}}H = 0, \quad \Delta_{\text{mix}}V = 0 \quad (2.21)$$

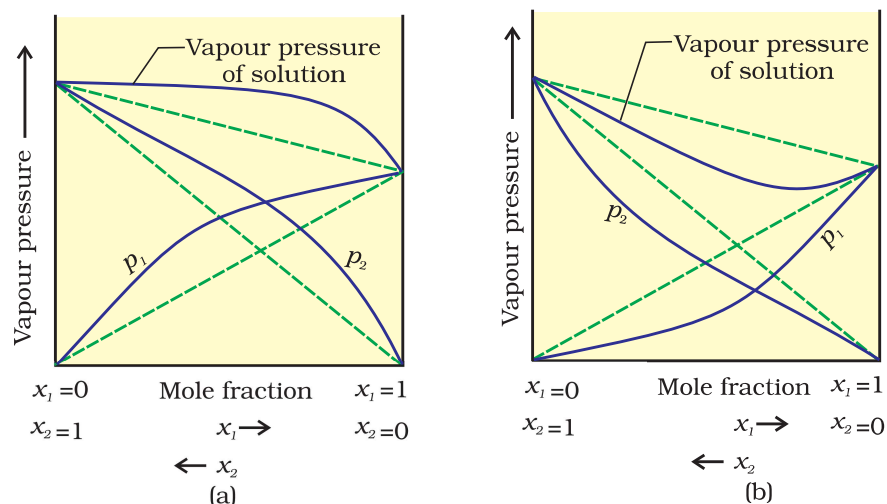
It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behaviour of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

2.5.2 Non-ideal Solutions

When a solution does not obey Raoult's law over the entire range of concentration, then it is called *non-ideal solution*. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law (equation 2.16). If it is higher, the solution exhibits **positive deviation** and if it is lower, it exhibits **negative deviation** from Raoult's law. The plots of vapour pressure as a function of mole fractions for such solutions are shown in Fig. 2.6.

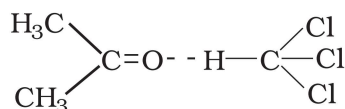
The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour

Fig.2.6
The vapour pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.



pressure and result in positive deviation. Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law [Fig. 2.6 (a)]. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.

In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapour pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.



This decreases the escaping tendency of molecules for each component and consequently the vapour pressure decreases resulting in negative deviation from Raoult's law [Fig. 2.6. (b)].

Some liquids on mixing, form **azeotropes** which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called **minimum boiling azeotrope** and **maximum boiling azeotrope**. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

Intext Question

2.8 The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

2.6 Colligative Properties and Determination of Molar Mass

We have learnt in Section 2.4.3 that the vapour pressure of solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapour pressure. These are: (1) relative lowering of vapour pressure of the solvent (2) depression of freezing point of the solvent (3) elevation of boiling point of the solvent and (4) osmotic pressure of the solution. **All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called colligative properties** (colligative: from Latin: co means together, ligare means to bind). In the following Sections we will discuss these properties one by one.

2.6.1 Relative Lowering of Vapour Pressure

We have learnt in Section 2.4.3 that the vapour pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The equation (2.20) given in Section 2.4.3 establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent, i.e.,

$$p_1 = x_1 p_1^0 \quad (2.22)$$

The reduction in the vapour pressure of solvent (Δp_1) is given as:

$$\begin{aligned} \Delta p_1 &= p_1^0 - p_1 = p_1^0 - p_1^0 x_1 \\ &= p_1^0 (1 - x_1) \end{aligned} \quad (2.23)$$

Knowing that $x_2 = 1 - x_1$, equation (2.23) reduces to

$$\Delta p_1 = x_2 p_1^0 \quad (2.24)$$

In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes.

Equation (2.24) can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 \quad (2.25)$$