

## 2. SOLUTIONS

### 2.1 Introduction

You are familiar with mixtures. The mixture is a combination of two or more substances. Air is a mixture of gases, rock is a mixture of two or more minerals and so forth.

Recall that the mixtures are (a) homogeneous in which mixing of components is uniform or (b) heterogeneous which have nonuniform mixing of components.

We studied in standard XI, that homogeneous mixtures are classified according to the size of their constituent particles as colloids or as true solutions. In this chapter we deal with the properties of homogeneous mixtures especially of true solutions.

#### Can you recall ?

The size of particles of colloids and those of true solutions.



The solutions are commonly found in all life processes. The body fluids are solutions. The solutions are also important for industrial processes, and many other areas.

#### Can you recall ?

The terms solute and solvent.



The solution is a homogeneous mixture of two or more pure substances. A true solution consists of a solvent and one or more solutes. We explore the properties of binary true solutions containing only one solute.

### 2.2 Types of solutions

We generally think that a solution is a either solid dissolved in liquid or a mixture of two liquids. There are other types of solutions as well. The solute and the solvent may be in any of three states namely, solid, liquid or gas. The solutions thus may involve any

combination of these three states of their components. This gives rise to nine types of solutions depending on the states of solute and solvent. These are summarised in table 2.1.

**Table 2.1 : Types of solutions**

| No. | State of solute | State of solvent | Some examples                                                |
|-----|-----------------|------------------|--------------------------------------------------------------|
| 1   | Solid           | Liquid           | Sea water, benzoic acid in benzene, sugar in water           |
| 2   | Solid           | Solid            | Metal alloys such as brass, bronze.                          |
| 3   | Solid           | Gas              | Iodine in air                                                |
| 4   | Liquid          | Liquid           | Gasoline, ethanol in water.                                  |
| 5   | Liquid          | Solid            | Amalgams of mercury with metals as mercury in silver         |
| 6   | Liquid          | Gas              | Chloroform in nitrogen                                       |
| 7   | Gas             | Liquid           | Carbonated water ( $\text{CO}_2$ in water), oxygen in water. |
| 8   | Gas             | Solid            | $\text{H}_2$ in palladium                                    |
| 9   | Gas             | Gas              | Air ( $\text{O}_2$ , $\text{N}_2$ , Ar and other gases)      |

Our focus, in this chapter, will be on the solution of solid in liquid with some attention to a solution of gas in liquid. The solvent in most of the cases will be water.

#### Can you recall ?

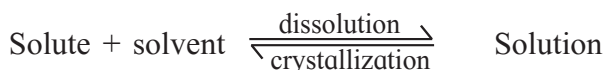
The different units used to express the concentrations of solutions.



### 2.3 Capacity of solution to dissolve solute

Chemists need to know the capacity of solutions to dissolve a solute. Suppose that a solute is added to a solvent. It dissolves readily at first. The dissolution then slows down as more solute is added. If we continue the

addition of solute, the dissolution stops. The solution at this point is said to be saturated. A dynamic equilibrium can be reached where the number of solute molecules leaving the crystal to pass into solution is equal to the number returning from the solution to the crystal. Thus,



A saturated solution contains maximum amount of solute dissolved in a given amount of solvent at a given temperature. A solution containing greater than the equilibrium amount of solute is said to be supersaturated solution. Such solutions are unstable. The precipitation occurs by the addition of a tiny crystal of solute and the supersaturated solution changes to saturated solution.

**2.4 Solubility :** The solubility of a solute is its amount per unit volume of saturated solution at a specific temperature. The solubility of a solute is its maximum concentration and expressed in the concentration units  $\text{mol L}^{-1}$ .

**2.4.1 Factors affecting solubility :** The extent to which a substance dissolves in a solvent varies greatly with different substances. It depends on the nature of solute and solvent, temperature and pressure.

**i. Nature of solute and solvent :** Generally the compounds with similar chemical character are more readily soluble in each other than those with entirely different chemical characters. The saying that ‘like dissolves like’ guides to predict the solubility of a solute in a given solvent.

Thus, substances having similar intermolecular forces are likely to be soluble in each other. Generally polar solutes dissolve in polar solvents. This is because in these, solute-solute, solute-solvent and solvent-solvent interactions are all of similar magnitude. For example, NaCl dissolves in water. The strong ion-dipole interactions of  $\text{Na}^+$  and  $\text{Cl}^-$  ions with water molecules, hydrogen bonding between water molecules

and ion-ion attractions between  $\text{Na}^+$  and  $\text{Cl}^-$  ions are comparable.

#### Can you recall ?

The types of force between molecules.



Nonpolar organic compounds like cholesterol dissolves in nonpolar solvent such as benzene.

#### Can you tell ?

Why naphthalene dissolves in benzene but not in water?



Sugar dissolves in water! The dissolution of sugar in water is due to intermolecular hydrogen bonding between sugar and water.

#### ii. Effect of temperature on solubility :

How solubility of substance changes with temperature depends on enthalpy of solution. Many solids, for example KCl, dissolve in water by endothermic process, that is, with the absorption of heat. When temperature is increased by adding heat to the system, the solubility of substance increases according to the Le-Chatelier principle. Addition of heat causes a stress on the saturated solution. This stress favours endothermic process.

#### Can you recall ?

Le-Chatelier principle, exothermic and endothermic processes.



On the other hand, when the substance dissolves in water by an exothermic process its solubility decreases with an increase of temperature. The substances such as  $\text{CaCl}_2$  and  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  dissolve in water releasing heat.

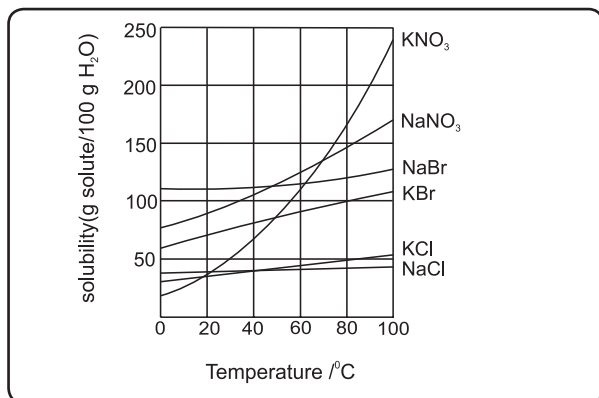
#### Can you tell ?

Anhydrous sodium sulphate dissolves in water with the evolution of heat. What is the effect of temperature on its solubility ?



It is important to understand that there is no direct correlation between solubility and exothermicity or endothermicity. For example, dissolution of  $\text{CaCl}_2$  in water is exothermic and that of  $\text{NH}_4\text{NO}_3$  is endothermic. The solubility of these increases with the temperature.

Figure 2.1 shows the result of experimental determination of solubilities of some ionic solids in water at various temperatures. Following are some experimental observations from Fig 2.1



**Fig. 2.1 : Variation of solubilities of some ionic solids with temperature**

- Solubilities of NaBr, NaCl and KCl change slightly with temperature.
- Solubilities of  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and KBr increase appreciably with increasing temperature.
- Solubility of  $\text{Na}_2\text{SO}_4$  decreases with increase of temperature.

The solubility of gases in water usually decreases with increase of temperature. When gases are dissolved in water, the gas molecules in liquid phase are condensed. The condensation is an exothermic process. The solubility of gases in water must decrease as temperature is raised.

In united states about 1000000 billion gallons of water from rivers and lakes are used for industrial cooling. The cooling process heats water. The hot water then returns to rivers and lakes. The solubility of oxygen decreases in hot water thereby affecting the life of cold blooded animals like fish.

### iii. Effect of pressure on solubility

Pressure has no effect on the solubilities of solids and liquids as they are incompressible. However pressure greatly affects solubility of gases in liquids. The solubility of gases increases with increasing pressure. The quantitative relationship between gas solubility in a liquid and pressure is given by Henry's law.

**Henry's law:** It states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution. Thus,

$$S \propto P \text{ or } S = K_H P \quad \dots\dots\dots (2.1)$$

where,  $S$  is the solubility of the gas in  $\text{mol L}^{-1}$ ,  $P$  is the pressure of the gas in bar over the solution.  $K_H$ , the proportionality constant is called Henry's law constant.

$$\text{Units of } K_H : K_H = \frac{S}{P} = \frac{\text{mol L}^{-1}}{\text{bar}} = \text{mol L}^{-1} \text{ bar}^{-1}$$

When  $P = 1 \text{ bar}$ ,  $K_H = S$ . Thus,  $K_H$  is the solubility of the gas in a liquid when its pressure over the solution is 1 bar.

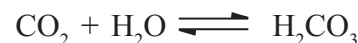
#### Demonstration of Henry's law.

Before sealing the bottle of soft drink, it is pressurised with a mixture of air,  $\text{CO}_2$  saturated with water vapour. Because of high partial pressure of  $\text{CO}_2$ , its amount dissolved in soft drink is higher than the solubility of  $\text{CO}_2$  under normal conditions.

When the bottle of soft drink is opened, excess dissolved  $\text{CO}_2$  comes out with effervescence.

#### Exceptions to Henry's law

Gases like  $\text{NH}_3$  and  $\text{CO}_2$  do not obey Henry's law. The reason is that these gases react with water.



Because of these reactions,  $\text{NH}_3$  and  $\text{CO}_2$  gases have higher solubilities than expected by Henry's law.

### Do you know ?



O<sub>2</sub> gas has very low solubility in water. However, its solubility in blood is exceedingly high. This is because of binding of O<sub>2</sub> molecule to haemoglobin present in blood.



**Problem 2.1 :** The solubility of N<sub>2</sub> gas in water at 25 °C and 1 bar is  $6.85 \times 10^{-4}$  mol L<sup>-1</sup>. Calculate (a) Henry's law constant (b) molarity of N<sub>2</sub> gas dissolved in water under atmospheric conditions when partial pressure of N<sub>2</sub> in atmosphere is 0.75 bar.

#### Solution :

$$\begin{aligned} \text{a. } K_H &= \frac{S}{P} = \frac{6.85 \times 10^{-4} \text{ mol dm}^{-3}}{1 \text{ bar}} \\ &= 6.85 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1} \end{aligned}$$

$$\begin{aligned} \text{b. } S &= K_H P = 6.85 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1} \\ &\quad \times 0.75 \text{ bar} \\ &= 5.138 \times 10^{-4} \text{ mol L}^{-1} \end{aligned}$$

**Problem 2.2 :** The Henry's law constant of methyl bromide (CH<sub>3</sub>Br), is 0.159 mol L<sup>-1</sup> bar<sup>-1</sup> at 25°C. What is the solubility of methyl bromide in water at 25°C and at pressure of 130 mmHg?

#### Solution :

According to Henry's law

$$S = K_H P$$

$$1. K_H = 0.159 \text{ mol L}^{-1} \text{ bar}^{-1}$$

$$\begin{aligned} 2. P &= 130 \text{ mm Hg} \times \frac{1}{760 \text{ mm Hg/atm}} \\ &= 0.171 \text{ atm} \times 1.013 \text{ bar/atm} \\ &= 0.173 \text{ bar} \end{aligned}$$

$$\begin{aligned} \text{Hence, } S &= 0.159 \text{ mol L}^{-1} \text{ bar}^{-1} \times 0.173 \text{ bar} \\ &= 0.271 \text{ M} \end{aligned}$$

## 2.5 Vapour pressure of solutions of liquids

**in liquids :** Consider a binary solution of two volatile liquids A<sub>1</sub> and A<sub>2</sub>. When the solution is placed in a closed container, both the liquids vaporize. Eventually an equilibrium is established between vapor and liquid phases. Both the components are present in the vapour phase. The partial pressure of the components are related to their mole fractions in the solution. This relationship is given by Raoult's law.

**2.5.1 Raoult's law :** It states that the partial vapour pressure of any volatile component of a solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.

Suppose that for a binary solution of two volatile liquids A<sub>1</sub> and A<sub>2</sub>,  $P_1$  and  $P_2$  are their partial vapour pressures and  $x_1$  and  $x_2$  are their mole fractions in solution. Then according to Raoult's law,

$$\text{we write } P_1 = x_1 P_1^0 \text{ and } P_2 = x_2 P_2^0 \dots\dots\dots (2.2)$$

where  $P_1^0$  and  $P_2^0$  are vapour pressures of pure liquids A<sub>1</sub> and A<sub>2</sub>, respectively.

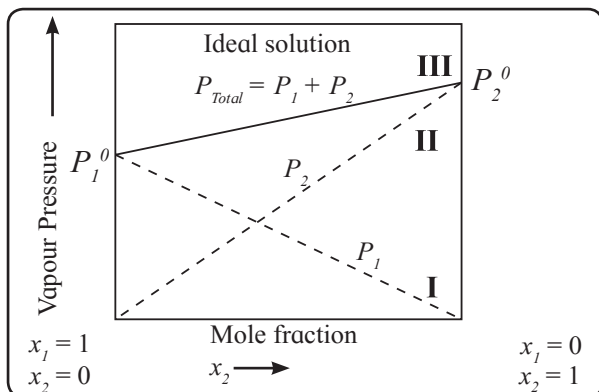
According to Dalton's law of partial pressures, the total pressure  $P$  above the solution is,

$$\begin{aligned} P &= P_1 + P_2 \\ &= P_1^0 x_1 + P_2^0 x_2 \dots\dots\dots (2.3) \end{aligned}$$

Since  $x_1 = 1 - x_2$ , the Eq. (2.2) can also be written as

$$\begin{aligned} P &= P_1^0 (1 - x_2) + P_2^0 x_2 \\ &= P_1^0 - P_1^0 x_2 + P_2^0 x_2 \\ &= (P_2^0 - P_1^0) x_2 + P_1^0 \dots\dots\dots (2.4) \end{aligned}$$

Because  $P_1^0$  and  $P_2^0$  are constants, a plot of  $P$  versus  $x_2$  is a straight line as shown in the Fig 2.2. The figure also shows the plots of  $P_1$  versus  $x_1$  and  $P_2$  versus  $x_2$  according to the equations 2.2. These are straight lines passing through origin.



**Fig. 2.2 : Variation of vapour pressure with mole fraction of solute**

i. For  $P$  versus  $x_2$  straight line,

$$P = P_1^0 \text{ at } x_2 = 0 \text{ and } P = P_2^0 \text{ at } x_2 = 1$$

ii. For  $P_1$  versus  $x_1$  straight line,

$$P_1 = 0 \text{ at } x_1 = 0 \text{ and } P_1 = P_1^0, \text{ at } x_1 = 1$$

iii. For  $P_2$  versus  $x_2$  straight line,

$$P_2 = 0 \text{ at } x_2 = 0 \text{ and } P_2 = P_2^0 \text{ at } x_2 = 1$$

#### Composition of vapour phase :

The composition of vapour in equilibrium with the solution can be determined by Dalton's law of partial pressures.

If we take  $y_1$  and  $y_2$  as the mole fractions of two components in the vapour, then  $P_1 = y_1 P$  and  $P_2 = y_2 P$

where  $P_1$  and  $P_2$  are the partial pressures of two components in the vapour and  $P$  is the total vapour pressure.

**Problem 2.3 :** The vapour pressures of pure liquids A and B are 450 mm Hg and 700 mm Hg, respectively at 350 K. Find the composition of liquid and vapour if total vapour pressure is 600 mm.

**Solution :** i. Compositions of A and B in the solution are  $x_1$  and  $x_2$

$$P = (P_2^0 - P_1^0) x_2 + P_1^0$$

$$P_1^0 = 450 \text{ mmHg}, P_2^0 = 700 \text{ mmHg},$$

$$P = 600 \text{ mmHg}$$

$$\text{Hence, } 600 \text{ mm Hg} = (700 \text{ mm Hg} -$$

$$450 \text{ mm Hg})x_2 + 450 \text{ mm Hg} \\ = 250x_2 + 450$$

$$600 - 450 = 150 = 250x_2 \text{ or } x_2 = \frac{150}{250} = 0.6$$

$$x_1 = 1 - x_2 = 1 - 0.6 = 0.4$$

ii. Compositions of A and B in vapour are  $y_1$  and  $y_2$  respectively.

$$P_1 = y_1 P \text{ and } P_2 = y_2 P, P_1 = P_1^0 x_1 \text{ and}$$

$$P_2 = P_2^0 x_2$$

$$y_1 = \frac{P_1}{P} = \frac{P_1^0 x_1}{P} = \frac{450 \text{ mm Hg} \times 0.4}{600 \text{ mmHg}} \\ = 0.3$$

$$y_2 = 1 - y_1 = 1 - 0.3 = 0.7$$

## 2.5.2 Ideal and nonideal solutions

### 1. Ideal solutions

i. Ideal solutions obey Raoult's law over entire range of concentrations.

ii. No heat is evolved or absorbed when two components forming an ideal solution are mixed. Thus, the enthalpy of mixing is zero.  $\Delta_{\text{mix}} H = 0$

iii. There is no volume change when two components forming an ideal solution are mixed. Thus volume of an ideal solution is equal to the sum of volumes of two components taken for mixing.

$$\Delta_{\text{mix}} V = 0$$

iv. In an ideal solution solvent-solute, solute-solute and solvent-solvent molecular interactions are comparable.

v. The vapour pressure of ideal solution always lies between vapour pressures of pure components, as shown in Fig. 2.2.

It is important to understand that perfectly ideal solutions are uncommon and solutions such as benzene + toluene behave nearly ideal.

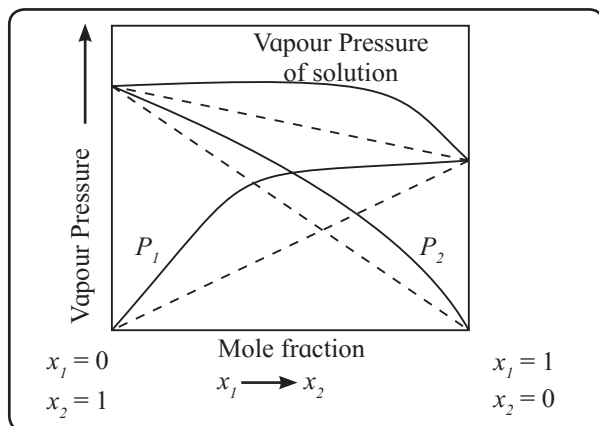
### 2. Nonideal solutions

i. These solutions do not obey Raoult's law over the entire range of concentrations.

ii. The vapour pressures of these solutions can be higher or lower than those of pure components.

- iii. Deviation from the Raoult's law : These solutions show two types of deviation from the Raoult's law.

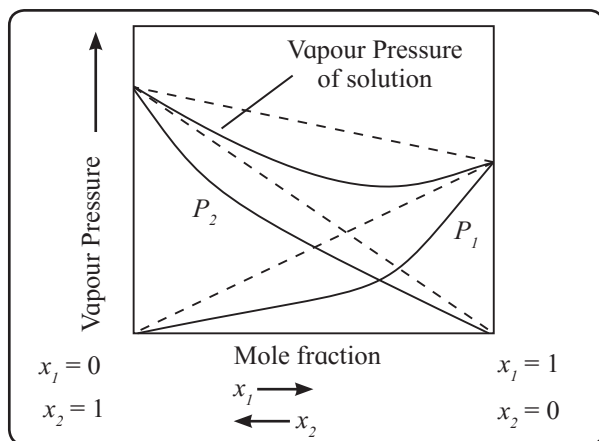
#### A. Positive deviations from Raoult's law -



**Fig. 2.3 : Positive deviations from Raoult's law**

The solutions in which solute-solvent intermolecular attractions are weaker than those between solute-solute molecules and solvent-solvent molecules, exhibit positive deviations. The vapour pressures of such solutions are higher than those of pure components as shown in Fig. 2.3. The solutions of ethanol and acetone, carbon disulphide and acetone show positive deviations from the Raoult's law.

#### B. Negative deviations from Raoult's law



**Fig. 2.4 : Negative deviations from Raoult's law**

The solutions in which the interactions between solvents and solute molecules are stronger than solute-solute or solvent-solvent interactions, exhibit negative deviations. The

vapour pressures of such solutions are lower than those of pure components as shown in Fig. 2.4. The solutions of phenol and aniline, chloroform and acetone exhibit negative deviations from the Raoult's law.

#### 2.6 Colligative properties of nonelectrolyte solutions :

The physical properties of solutions that depend on the number of solute particles in solutions and not on their nature are called colligative properties. These are

1. vapour pressure lowering
2. boiling point elevation
3. freezing point depression
4. osmotic pressure

While dealing with colligative properties of nonelectrolyte solutions, the relatively dilute solutions with concentrations 0.2 M or less are considered.

**2.7 Vapour pressure lowering :** When a liquid in a closed container is in equilibrium with its vapours, the pressure exerted by the vapour on the liquid is its vapour pressure.

#### Can you recall ?

Vapour pressure of a liquid



- Experiments have shown that when a nonvolatile, nonionizable solid is dissolved in a liquid solvent, the vapour pressure of the solution is lower than that of pure solvent. In other words the vapour pressure of a solvent is lowered by dissolving a nonvolatile solute into it. When the solute is nonvolatile it does not contribute to the vapour pressure above the solution. Therefore, the vapour pressure of solution is equal to the vapour pressure of solvent above the solution.
- If  $P_1^0$  is the vapour pressure of pure solvent and  $P_1$  is the vapour pressure of solvent above the solution, then

$$P_1 < P_1^0$$

The vapour pressure lowering is

$$\Delta P = P_1^0 - P_1 \quad \dots\dots\dots (2.5)$$

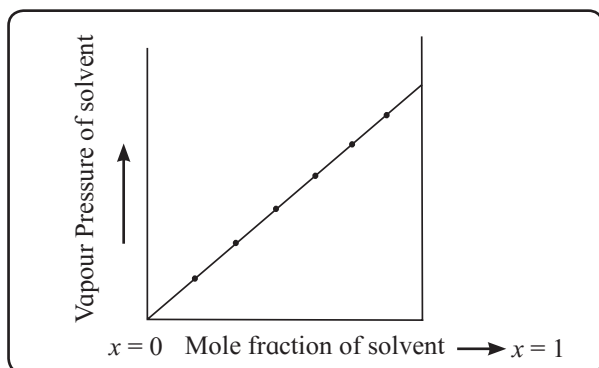
iii. Why the vapour pressure of solution containing nonvolatile solute is lower than that of pure solvent? Vapour pressure of a liquid depends on the ease with which the molecules escape from the surface of liquid. When nonvolatile solute is dissolved in a solvent, some of the surface molecules of solvent are replaced by nonvolatile solute molecules. These solute molecules do not contribute to vapour above the solution. Thus, the number of solvent molecules available for vaporization per unit surface area of solution is less than the number at the surface of pure solvent. As a result the solvent molecules at the surface of solution vaporize at a slower rate than pure solvent. This results in lowering of vapour pressure.

**2.7.1 Raoult's law for solutions of nonvolatile solutes :** We saw in section 2.5.1 that Raoult's law expresses the quantitative relationship between vapour pressure of solution and vapour pressure of solvent.

In solutions of nonvolatile solutes, the law is applicable only to the volatile solvent. The law states that the vapour pressure of solvent over the solution is equal to the vapour pressure of pure solvent multiplied by its mole fraction in the solution. Thus

$$P_1 = P_1^0 x_1$$

A plot of  $P_1$  versus  $x_1$  is a straight line as shown in Fig. 2.5



**Fig. 2.5 : Variation of vapour pressure of solution with mole fraction of solvent**

For a binary solution containing one solute,

$$x_1 = 1 - x_2$$

It therefore, follows that

$$\begin{aligned} P_1 &= P_1^0 x_1 \\ &= P_1^0 (1 - x_2) \\ &= P_1^0 - P_1^0 x_2 \end{aligned}$$

$$\text{or} \quad P_1^0 - P_1 = P_1^0 x_2$$

The Eq. (2.5) defines  $P_1^0 - P_1$  as  $\Delta P$ , the lowering of vapour pressure. Hence

$$\Delta P = P_1^0 x_2 \quad \dots\dots\dots (2.6)$$

The Eq. (2.6) shows that  $\Delta P$  depends on  $x_2$  that is on number of solute particles. Thus,  $\Delta P$ , the lowering of vapour pressure is a colligative property.

### 2.7.2 Relative lowering of vapour pressure

The ratio of vapour pressure lowering of solvent divided by the vapour pressure of pure solvent is called relative lowering of vapour pressure. Thus

Relative vapour pressure lowering

$$= \frac{\Delta P}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} \quad \dots\dots\dots (2.7)$$

The Eq. (2.6) shows that

$$\frac{\Delta P}{P_1^0} = x_2 = \frac{P_1^0 - P_1}{P_1^0} \quad \dots\dots\dots (2.8)$$

Thus, relative lowering of vapour pressure is equal to the mole fraction of solute in the solution. Therefore, relative vapour pressure lowering is a colligative property.

### 2.7.3 Molar mass of solute from vapour pressure lowering :

We studied that the relative lowering of vapour pressure is equal to the mole fraction  $x_2$  of solute in the solution.

From Eq. 2.6, it follows that :

$$\frac{\Delta P}{P_1^0} = x_2 \quad \dots\dots\dots (2.8)$$

Recall (Chapter 10, sec 10.5.6) that the mole fraction of a component of solution is equal to its moles divided by the total moles in the solution. Thus,

$$x_2 = \frac{n_2}{n_1 + n_2}$$

where  $n_1$  and  $n_2$  are the moles of solvent and solute respectively, in the solution.

We are concerned only with dilute solutions hence  $n_1 \gg n_2$  and  $n_1 + n_2 \approx n_1$ . The mole fraction  $x_2$  is then given by

$$x_2 = \frac{n_2}{n_1} \quad \text{and} \quad \frac{\Delta P}{P_1^0} = \frac{n_2}{n_1} \quad \dots\dots\dots (2.9)$$

Suppose that we prepare a solution by dissolving  $W_2$  g of a solute in  $W_1$  g of solvent. The moles of solute and solvent in the solution are then,

$$n_2 = \frac{W_2}{M_2} \quad \text{and} \quad n_1 = \frac{W_1}{M_1} \quad \dots\dots\dots (2.10)$$

where  $M_1$  and  $M_2$  are molar masses of solvent and solute, respectively. Substitution of Eq. (2.10) into Eq. (2.9) yields

$$x_2 = \frac{\Delta P}{P_1^0} = \frac{W_2/M_2}{W_1/M_1} \quad \frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1} \quad \dots\dots\dots (2.11)$$

Knowing all other quantities, molar mass of solute  $M_2$  can be calculated.

**Problem 2.4 :** A solution is prepared by dissolving 394 g of a nonvolatile solute in 622 g of water. The vapour pressure of solution is found to be 30.74 mm Hg at 30 °C. If vapour pressure of water at 30 °C is 31.8 mm Hg, what is the molar mass of solute?

**Solution :**

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1}$$

$$W_2 = 394 \text{ g}, W_1 = 622 \text{ g}, M_1 = 18 \text{ g mol}^{-1},$$

$$P_1 = 30.74 \text{ mm Hg}, P_1^0 = 31.8 \text{ mm Hg}$$

Substitution of these quantities into the equation gives

$$\frac{31.8 \text{ mm Hg} - 30.74 \text{ mm Hg}}{31.8 \text{ mm Hg}} = \frac{394 \text{ g} \times 18 \text{ g mol}^{-1}}{M_2 \times 622 \text{ g}}$$

$$0.0333 = \frac{11.4 \text{ g mol}^{-1}}{M_2}$$

$$M_2 = \frac{11.4 \text{ g mol}^{-1}}{0.0333} = 342 \text{ g mol}^{-1}$$

**Problem 2.5 :** The vapour pressure of pure benzene (molar mass 78 g/mol) at a certain temperature is 640 mm Hg. A nonvolatile solute of mass 2.315 g is added to 49 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of solute?

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

$$P_1^0 = 640 \text{ mm Hg}, P_1 = 600 \text{ mm Hg}, \\ W_1 = 49 \text{ g}, W_2 = 2.315 \text{ g}$$

$$\text{Hence, } \frac{640 \text{ mm Hg} - 600 \text{ mm Hg}}{640 \text{ mm Hg}} = \frac{2.315 \text{ g} \times 78 \text{ g/mol}}{40 \text{ g} \times M_2}$$

$$\frac{40 \text{ mm Hg}}{640 \text{ mm Hg}} = \frac{2.315 \text{ g} \times 78 \text{ g/mol}}{40 \text{ g} \times M_2}$$

$$M_2 = \frac{2.315 \text{ g} \times 78 \text{ g/mol} \times 640 \text{ mm Hg}}{40 \text{ mm Hg} \times 40 \text{ g}} \\ = 72.23 \text{ g mol}^{-1}$$

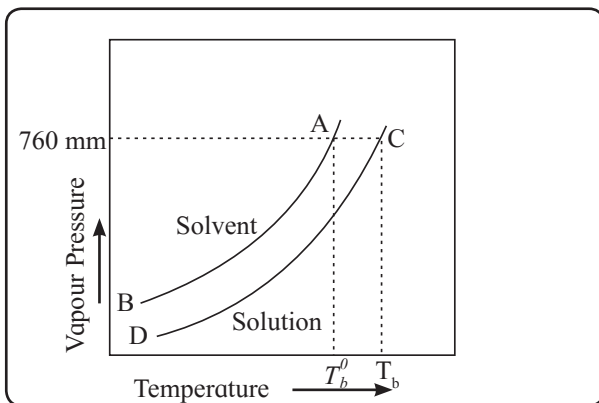
**2.8 Boiling point elevation :** Recall that the boiling point of liquid is the temperature at which its vapour pressure equals the applied pressure. For liquids in open containers the applied pressure is atmospheric pressure.

It has been found that the boiling point of a solvent is elevated by dissolving a nonvolatile solute into it. Thus, the solutions containing nonvolatile solutes boil at temperatures higher than the boiling point of a pure solvent.

If  $T_b^0$  is the boiling point of a pure solvent and  $T_b$  that of a solution,  $T_b > T_b^0$ . The difference between the boiling point of solution and that of pure solvent at any given constant pressure is called the boiling point elevation.

$$\Delta T_b = T_b - T_b^0 \quad \dots\dots\dots (2.12)$$

**2.8.1 Boiling point elevation as a consequence of vapour pressure lowering :** To understand the elevation of boiling point, let us compare the vapour pressures of solution and those of pure solvent. The vapour pressures of solution and of pure solvent are plotted as a function of temperature as shown in Fig. 2.6.



**Fig. 2.6 : Vapour pressure-temperature of pure solvent and solution**

As stated in section 2.7 that at any temperature the vapour pressure of solution is lower than that of pure solvent. Hence, the vapour pressure-temperature curve of solution (CD) lies below that of solvent (AB). The difference between the two vapour pressures increases as temperature and vapour pressure increase as predicted by the equation

$$\Delta P = x_2 P_1^0$$

The intersection of the curve CD with the line corresponding to 760 mm is the boiling point of solution. The similar intersection of the curve AB is the boiling point of pure solvent. It is clear from the figure that the boiling point ( $T_b$ ) of the solution is higher than that of pure solvent ( $T_b^0$ )

At the boiling point of a liquid, its vapour pressure is equal to 1 atm. In order to reach boiling point, the solution and solvent must be heated to a temperature at which their respective vapour pressures attain 1 atm. At any given temperature the vapour pressure of solution is lower than that of pure solvent. Hence, the vapour pressure of solution needs higher temperature to reach 1 atm than that needed for vapour pressure of solvent. In other words the solution must be heated to

higher temperature to cause it to boil than the pure solvent.

**2.8.2 Boiling point elevation and concentration of solute :** The boiling point elevation is directly proportional to the molality of the solution. Thus,

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = K_b m \quad \dots\dots\dots (2.13)$$

where  $m$  is the molality of solution. The proportionality constant  $K_b$  is called boiling point elevation constant or molal elevation constant or ebullioscopic constant.

$$\text{If } m = 1, \quad \Delta T_b = K_b$$

Thus, ebullioscopic constant is the boiling point elevation produced by 1 molal solution.

$$\text{Units of } K_b : K_b = \frac{\Delta T_b}{m} = \frac{K}{\text{mol kg}^{-1}} = K \text{ kg mol}^{-1}$$

#### Remember...

$K_b$  and  $\Delta T_b$  are the differences between two temperatures. Hence, their values will be the same in K or in  $^{\circ}\text{C}$ .



We are dealing with the systems whose temperature is not constant. Therefore, we cannot express the concentration of solution in molarity which changes with temperature whereas molality is temperature independent.

Therefore the concentration of solute is expressed in mol/kg (molality) rather than mol/L (molarity).

#### 2.8.3 Molar mass of solute from boiling point elevation

$$\text{The Eq. (2.13) is } \Delta T_b = K_b m$$

Suppose we prepare a solution by dissolving  $W_2$  g of solute in  $W_1$  g of solvent.

$$\text{Moles of solute in } W_1 \text{ g of solvent} = \frac{W_2}{M_2}$$

where  $M_2$  is the molar mass of solute.

$$\text{Mass of solvent} = W_1 \text{ g} = \frac{W_1 \text{ g}}{1000 \text{ g/kg}} = \frac{W_1}{1000} \text{ kg}$$

Recall the expression of molality,  $m$ .

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}} = \frac{W_2/M_2 \text{ mol}}{W_1/1000 \text{ kg}} = \frac{1000 W_2}{M_2 W_1} \text{ mol kg}^{-1} \quad \dots\dots\dots (2.14)$$

Substitution of this value of  $m$  in Eq. (2.13) gives

$$\Delta T_b = K_b \frac{1000 W_2}{M_2 W_1}$$

Hence,

$$M_2 = \frac{1000 K_b W_2}{\Delta T_b W_1} \dots\dots\dots (2.15)$$

**Problem 2.6 :** The normal boiling point of ethyl acetate is  $77.06^\circ\text{C}$ . A solution of 50 g of a nonvolatile solute in 150 g of ethyl acetate boils at  $84.27^\circ\text{C}$ . Evaluate the molar mass of solute if  $K_b$  for ethyl acetate is  $2.77^\circ\text{C kg mol}^{-1}$ .

**Solution :**

$$M_2 = \frac{1000 K_b W_2}{\Delta T_b W_1}$$

$$W_2 = 50 \text{ g}, W_1 = 150 \text{ g},$$

$$\begin{aligned} \Delta T_b &= T_b - T_b^0 = 84.27^\circ\text{C} - 77.06^\circ\text{C} \\ &= 7.21^\circ\text{C} = 7.21 \text{ K} \end{aligned}$$

$$K_b = 2.77^\circ\text{C kg mol}^{-1} = 2.77 \text{ K kg mol}^{-1}$$

Substitution of these in above equation

$$\begin{aligned} M_2 &= \frac{1000 \text{ g Kg}^{-1} \times 2.77 \text{ K kg mol}^{-1} \times 50 \text{ g}}{7.21 \text{ K} \times 150 \text{ g}} \\ &= 128 \text{ g mol}^{-1} \end{aligned}$$

**Problem 2.7 :** 3.795 g of sulphur is dissolved in 100 g of carbon disulfide. This solution boils at 319.81 K. What is the molecular formula of sulphur in solution? The boiling point of the solvent is 319.45 K.

(Given that  $K_b$  for  $\text{CS}_2 = 2.42 \text{ K kg mol}^{-1}$  and atomic mass of S = 32 u)

$$M_2 = \frac{1000 K_b W_2}{\Delta T_b W_1}$$

$$W_1 = 100 \text{ g}, W_2 = 3.795 \text{ g}$$

$$\Delta T_b = (319.81 - 319.45) \text{ K} = 0.36 \text{ K}$$

$$\begin{aligned} M_2 &= \frac{1000 \text{ g kg}^{-1} \times 2.42 \text{ K kg mol}^{-1} \times 3.795 \text{ g}}{0.36 \text{ K} \times 100 \text{ g}} \\ &= 255.10 \text{ g mol}^{-1} \end{aligned}$$

Atomic mass of S = 32 u

Therefore number of atoms in a molecule of sulphur

$$\begin{aligned} &= \frac{\text{molar mass of S}}{\text{atomic mass of S}} = \frac{255.1}{32} \\ &= 7.92 \approx 8 \end{aligned}$$

The molecular formula would be  $\text{S}_8$  in  $\text{CS}_2$

## 2.9 Depression in freezing point

Recall that freezing point of a liquid is the temperature at which liquid and solid are in equilibrium and the two phases have the same vapour pressure.

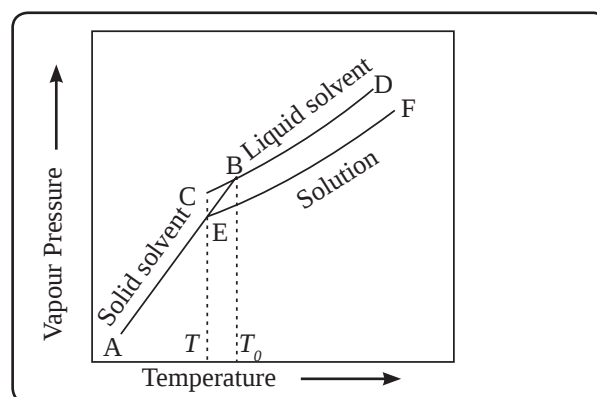
The general experimental observation is that the freezing point of a solvent is lowered by dissolving a nonvolatile solute into it. Thus, freezing point of solution containing a nonvolatile solute is lower than that of pure solvent.

If  $T_f^0$  is the freezing point of pure solvent and  $T_f$  that of a solution in which nonvolatile solute is dissolved,  $T_f^0 > T_f$ . The difference between the freezing point of pure solvent and that of the solution is depression in freezing point.

$$\text{Thus } \Delta T_f = T_f^0 - T_f \dots\dots\dots (2.16)$$

### 2.9.1 Freezing point depression as a consequence of vapour pressure lowering

The effect of dissolution of a nonvolatile solute into a solvent on freezing point of solvent can be understood in terms of the vapour pressure lowering.



**Fig. 2.7 : Variation of vapour pressure with temperature of pure solvent, solid solvent and solution**

Consider the vapour pressure-temperature diagram as shown in Fig. 2.7. The diagram consists of three curves. AB is the vapour pressure curve of solid solvent while CD is the vapour pressure curve of pure liquid solvent. EF is the vapour pressure curve of solution that always lies below the pure solvent.

It is important to note that solute does not dissolve in solid solvent.

The curves AB and CD intersect at point B where solid and liquid phases of pure solvent are in equilibrium. The two phases have the same vapour pressure at B. The temperature corresponding to B is the freezing point of solvent ( $T_f^0$ ).

Similarly at E, the point of intersection of EF and AB, the solid solvent and solution are in equilibrium. They have the same vapour pressure at E. The temperature corresponding to E is the freezing point of solution,  $T_f$ .

It is clear from the figure that freezing point of solution  $T_f$  is lower than that of pure solvent  $T_f^0$ . It is obvious because the vapour pressure curve of solution lies below that of solvent.

Why freezing point of solvent is lowered by dissolving a nonvolatile solute into it? At the freezing point of a pure liquid the attractive forces among molecules are large enough to cause the change of phase from liquid to solid.

In a solution, the solvent molecules are separated from each other because of solute molecules. Thus, the separation of solvent molecules in solution is more than that in pure solvent. This results in decreasing the attractive forces between solvent molecules. Consequently, the temperature of the solution is lowered below the freezing point of solvent to cause the phase change.

**2.9.2 Freezing point depression and concentration of solute :** As varied experimentally for a dilute solution the freezing point depression ( $\Delta T_f$ ) is directly proportional to the molality of solution. Thus,

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m \dots\dots\dots (2.17)$$

The proportionality constant  $K_f$  is called freezing point depression constant or cryoscopic constant.

If  $m = 1$ ,  $\Delta T_f = K_f$ . The cryoscopic constant thus is the depression in freezing point produced by 1 molal solution of a nonvolatile solute.

$$\begin{aligned} \text{Unit of } K_f : \frac{\Delta T_f}{m} &= \frac{\text{K or } ^\circ\text{C}}{\text{mol kg}^{-1}} \\ &= \text{K kg mol}^{-1} \text{ or } ^\circ\text{C kg mol}^{-1} \end{aligned}$$

### 2.9.3 Molar mass of solute from freezing point depression

Refer to Eq. (2.17),  $\Delta T_f = K_f m$

The molality  $m$  of the solution is given by Eq. (2.14) as

$$m = \frac{1000W_2}{M_2W_1}$$

Substitution of Eq. (2.14) into Eq. (2.17) gives

$$\Delta T_f = K_f \frac{1000W_2}{M_2W_1}$$

$$\text{Hence, } M_2 = \frac{1000K_fW_2}{\Delta T_fW_1} \dots\dots\dots (2.18)$$

**Problem 2.8 :** 1.02 g of urea when dissolved in 98.5 g of certain solvent decreases its freezing point by 0.211K. 1.609 g of unknown compound when dissolved in 86 g of the same solvent depresses the freezing point by 0.34 K. Calculate the molar mass of the unknown compound.

(Molar mass of urea = 60 g mol<sup>-1</sup>)

**Solution :**

| Urea                           | Unknown compound               |
|--------------------------------|--------------------------------|
| $W_2 = 1.02 \text{ g}$         | $W_2' = 1.609 \text{ g}$       |
| $W_1 = 98.5 \text{ g}$         | $W_1' = 86 \text{ g}$          |
| $\Delta T_f = 0.211 \text{ K}$ | $\Delta T_f' = 0.34 \text{ K}$ |
| $M_2 = 60 \text{ gmol}^{-1}$   | $M_2' = ?$                     |

$$1000K_f = \frac{M_2 \times \Delta T_f \times W_1}{W_2}$$

$$\begin{aligned}
 1000K_f &= \frac{M_2' \times \Delta T_f' \times W_1'}{W_2'} \\
 &= \frac{60 \text{ g mol}^{-1} \times 0.211 \text{ K} \times 98.5 \text{ g}}{1.02 \text{ g}} \\
 &= \frac{M_2' \times 0.34 \text{ K} \times 86 \text{ g}}{1.609 \text{ g}} \\
 \frac{1247.01 \text{ g K mol}^{-1}}{1.02} &= \frac{M_2' \times 29.24 \text{ K}}{1.609} \\
 1222.55 \text{ g K mol}^{-1} &= M_2' \times 18.173 \\
 M_2' &= \frac{1222.55 \text{ g K mol}^{-1}}{18.175 \text{ K}} = 67.3 \text{ g mol}^{-1}
 \end{aligned}$$

**2.10 Osmotic pressure :** Besides the boiling point elevation and freezing point depression, the osmotic pressure is associated with vapour pressure lowering and can be used to determine molar masses of dissolved solutes.

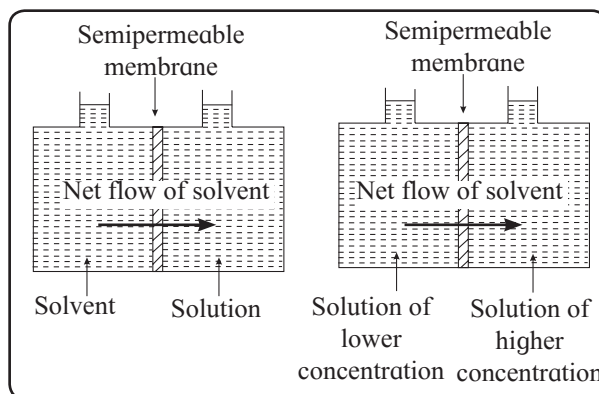
**Semipermeable membrane :** The osmotic pressure phenomenon involves the use of semipermeable membrane.

It is a film such as cellophane which has pores large enough to allow the solvent molecules to pass through them. These pores are small enough not to allow the passage of large solute molecules or ions of high molecular mass through them. The semipermeable membrane selectively allows passage of solvent molecules.

**2.10.1 Osmosis :** When a solution and pure solvent or two solutions of different concentrations are separated by a semipermeable membrane, the solvent molecules pass through the membrane.

What is the direction of flow of solvent molecules? It is important to understand that the passage of solvent molecules through the semipermeable membrane takes place in both directions, since solvent is on both sides of the membrane. However, the rate of passage of solvent molecules into the solution or from more dilute solution to more concentrated solution is found to be greater than the rate in the reverse direction. This is favourable since

the vapour pressure of solvent is greater than that of solution. The net spontaneous flow of solvent molecules into the solution or from more dilute solution to more concentrated solution through a semipermeable membrane is called osmosis. See Fig. 2.8.

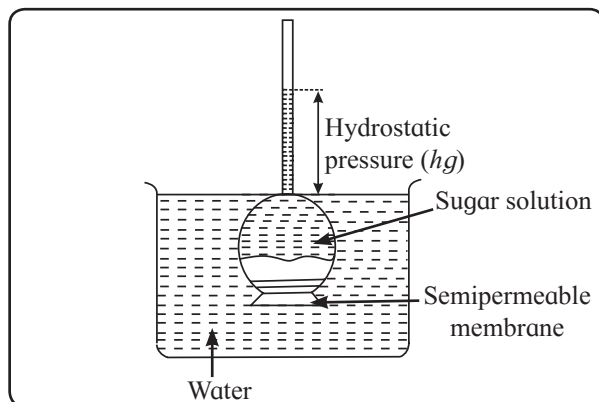


**Fig. 2.8 : Osmosis**

As a result of osmosis, the amount of liquid on the pure solvent side or more dilute solution side decreases. Consequently, the amount of liquid on the other side increases. This results in decrease of the concentration of solution.

**2.10.2 Osmotic pressure :** Osmosis can be demonstrated with experimental set up shown in Fig. 2.9

Semipermeable membrane is firmly fastened across the mouth of thistle tube. The solution of interest is placed inside an inverted thistle tube. This part of the tube and the membrane are then immersed in a container of pure water.



**Fig. 2.9 : Osmosis and osmotic pressure**

As a result, some of the solvent passes through the membrane into the solution. It causes the liquid level in the tube to rise. The liquid column in the tube creates hydrostatic pressure that pushes the solvent back through the membrane into the container. The column of liquid in the tube continues to rise and eventually stops rising. At this stage hydrostatic pressure developed is sufficient to force solvent molecules back through the membrane into the container at the same rate they enter the solution.

An equilibrium is thus established where rates of forward and reverse passages are equal. The height of liquid column in the tube remains constant. This implies that the hydrostatic pressure has stopped osmosis.

### Remember...

It is important to note that osmotic pressure is not the pressure produced by a solution. It exists only when the solution is separated from the solvent by a suitable kind of semipermeable membrane.



The hydrostatic pressure that stops osmosis is an osmotic pressure ( $\pi$ ) of the solution. The hydrostatic pressure is equal to  $h\rho g$  where  $h$  is the height of liquid column in the tube,  $\rho$  is density of solution and  $g$  is acceleration due to gravity.

### 2.10.3 Isotonic, hypertonic and hypotonic solutions

**i. Isotonic solutions :** Two or more solutions having the same osmotic pressure are said to be **isotonic solutions**.

For example, 0.1 M urea solution and 0.1 M sucrose solution are isotonic because their osmotic pressures are equal. Such solutions have the same molar concentrations but different concentrations in g/L. If these solutions are separated by a semipermeable membrane, there is no flow of solvent in either direction.

### ii. Hypertonic and hypotonic solutions :

If two solutions have unequal osmotic pressures, the more concentrated solution with higher osmotic pressure is said to be **hypertonic solution**.

The more dilute solution exhibiting lower osmotic pressure is said to be **hypotonic solution**.

For example, if osmotic pressure of sucrose solution is higher than that of urea solution, the sucrose solution is hypertonic to urea solution, and the urea solution is hypotonic to sucrose solution.

### 2.10.4 Osmotic pressure and concentration of solution

For very dilute solutions, the osmotic pressure follows the equation,

$$\pi = \frac{n_2 RT}{V} \quad \dots\dots\dots (2.19)$$

where  $V$  is the volume of a solution in  $\text{dm}^3$  containing  $n_2$  moles of nonvolatile solute.  $R$  is the gas constant equal to  $0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$  and  $\pi$  is osmotic pressure in atm.

The term  $n_2/V$  is concentration in molarity ( $M$ ). Eq. (2.19) thus can be written as

$$\pi = MRT \quad \dots\dots\dots (2.20)$$

Note that the solute concentration is expressed in molarity while calculating osmotic pressure rather than molality. The reason is that osmotic pressure measurements are made at a specific constant temperature. It is not necessary to express concentration in a temperature independent unit like molality.

### 2.10.5 Molar mass of solute from osmotic pressure

Consider Eq. (2.19)  $\pi = \frac{n_2 RT}{V}$

If the mass of solute in  $V$  litres of solution is  $W_2$  and its molar mass is  $M_2$  then  $n_2 = W_2/M_2$ . With this value of  $n_2$ , Eq. (2.19) becomes

$$\pi = \frac{W_2 RT}{M_2 V} \text{ or } M_2 = \frac{W_2 RT}{\pi V} \quad \dots\dots\dots (2.21)$$

### Remember...

Osmotic pressure is much larger and therefore more precisely measurable property than other colligative properties. It is therefore, useful to determine molar masses of very expensive substances and of the substances that can be prepared in small quantities.



**2.10.6 Reverse osmosis :** As mentioned earlier osmosis is a flow of solvent through a semipermeable membrane into the solution.

The direction of osmosis can be reversed by applying a pressure larger than the osmotic pressure.

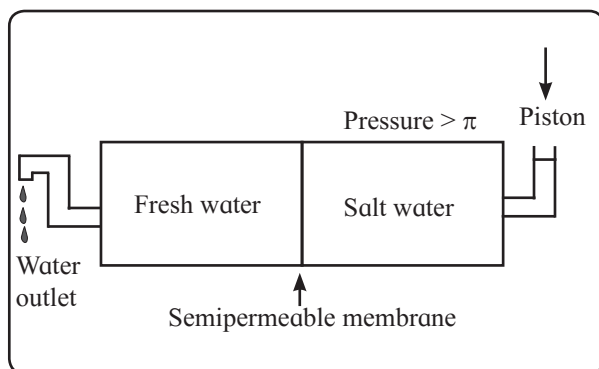


Fig. 2.10 : Reverse osmosis

The pure solvent then flows from solution into pure solvent through semipermeable membrane. This phenomenon is called reverse osmosis. Fig. 2.10 shows the schematic set up for reverse osmosis. Fresh water and salty water are separated by a semipermeable membrane. When the pressure larger than the osmotic pressure of solution is applied to solution, pure water from salty water passes into fresh pure water through the membrane.

**Problem 2.9 :** What is the molar mass of a solute if a solution prepared by dissolving 0.822 g of it in 300 m<sup>3</sup> dm<sup>3</sup> of water has an osmotic pressure of 149 mm Hg at 298 K?

**Solution :**

$$M_2 = \frac{W_2 RT}{\pi V}$$

$$W_2 = 0.822 \text{ g}$$

$$R = 0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\pi = 149 \text{ (mmHg)} = \frac{149 \text{ (mmHg)}}{760 \text{ (mmHg/atm)}} \\ = 0.196 \text{ atm}$$

$$V = 300 \text{ mL} = 0.3 \text{ dm}^3$$

$$M_2 = \frac{0.822 \text{ g} \times 0.08205 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.196 \text{ atm} \times 0.3 \text{ dm}^3} \\ = 342 \text{ g mol}^{-1}$$

### 2.11 Colligative properties of electrolytes

#### Can you recall ?

Electrolytes and nonelectrolytes.



Solutions of nonelectrolytes in water exhibit colligative properties as described in the preceding sections. These solutions also give, for the dissolved substances, the molar masses expected from their chemical formulae.

The study of colligative properties of electrolytes, however, require a different approach than used for colligative properties of nonelectrolytes. Following are the experimental observations for the colligative behavior of electrolytes.

- The solutions of electrolytes also exhibit colligative properties which do not obey the relations of nonelectrolytes.
- The colligative properties of the solutions of electrolytes are greater than those to be expected for solutions of nonelectrolytes of the same concentration.
- The molar masses of electrolytes in aqueous solutions determined by colligative properties are found to be considerably lower than the formula masses.

Why the colligative properties of electrolyte solutions are greater than those for nonelectrolyte solutions of the same concentration? Recall that electrolytes dissociate into two or more ions when

dissolved in water whereas nonelectrolytes do not. Stated differently, one formula unit of electrolyte dissolved in water produces two or more ions. Consequently number of particles in solution increases.

The colligative properties of electrolyte solutions are thus higher than the nonelectrolyte solutions.

If 1.25 m sucrose solution has  $\Delta T_f$  of  $2.32^\circ\text{C}$ , what will be the expected value of  $\Delta T_f$  for 1.25m  $\text{CaCl}_2$  solution?

For example, when  $\text{NaCl}$  is dissolved in water, it produces two ions,  $\text{Na}^+$  and  $\text{Cl}^-$ , whereas sucrose does not dissociate. It is expected then that the colligative property of 0.1 m  $\text{NaCl}$  is twice that of 0.1 m sucrose solution.

### 2.11.1 van't Hoff factor(i)

To obtain the colligative properties of electrolyte solutions by using relations for nonelectrolytes, van't Hoff suggested a factor  $i$ . It is defined as the ratio of colligative property of a solution of electrolyte to the colligative property of nonelectrolyte solution of the same concentration. Thus

$$i = \frac{\text{colligative property of electrolyte solution}}{\text{colligative property of nonelectrolyte solution of the same concentration}}$$

$$= \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{(\Delta T_b)}{(\Delta T_b)_0} = \frac{(\Delta P)}{(\Delta P)_0} = \frac{(\pi)}{(\pi)_0} \quad \dots\dots\dots (2.22)$$

where quantities without subscript refer to electrolytes and those with subscript to nonelectrolytes.

The van't Hoff factor  $i$  is also defined in an alternative but exactly in equivalent manner as

$$i = \frac{\text{actual moles of particles in solution after dissociation}}{\text{moles of formula units dissolved in solution}} \quad \dots\dots\dots (2.23)$$

$$= \frac{\text{formula mass of substance}}{\text{observed molar mass of substance}}$$

$$= \frac{M_{\text{theoretical}}}{M_{\text{observed}}} \quad \dots\dots\dots (2.24)$$

Thus,  $i$  is equal to 1 for nonelectrolyte, 2 for  $\text{KNO}_3$  and  $\text{NaCl}$ , 3 for  $\text{Na}_2\text{SO}_4$  and  $\text{CaCl}_2$  and so forth. The colligative properties of these electrolytes are, therefore, twice and thrice respectively as those of nonelectrolytes of the same concentration.

The foregoing arguments are valid only for infinitely dilute solutions where the dissociation of electrolytes is complete.

In reality especially at high concentrations, the colligative properties of strong electrolytes and their  $i$  values are usually smaller than expected. The reason is that the electrostatic forces between oppositely charged ions bring about the formation of ion pairs. Each ion pair consists of one or more cations and one or more anions held together by electrostatic attractive forces. This results in decrease in the number of particles in solution causing reduction in the expected  $i$  value and colligative properties.

### 2.11.2 Modification of expressions of colligative properties :

The expressions of colligative properties mentioned earlier for nonelectrolytes are to be modified so as to make them applicable for electrolyte solutions. The modified equations are

$$\text{i. } \Delta P = i P_1^0 x_2 = i \frac{W_2 M_1}{M_2 W_1} \times P_1^0$$

$$\text{ii. } \Delta T_b = i K_b m = i \frac{1000 K_b W_2}{M_2 W_1}$$

$$\text{iii. } \Delta T_f = i K_f m = i \frac{1000 K_f W_2}{M_2 W_1}$$

$$\text{iv. } \pi = i \text{ MRT} = i \frac{W_2 RT}{M_2 V}$$

### 2.11.3 van't Hoff factor and degree of dissociation :

A discussion of colligative properties of electrolytes in the preceding sections is based on the fact that the electrolytes are completely dissociated in their aqueous solutions. This is approximately true

for solutions of strong electrolytes and not for weak electrolytes that dissociate to a small extent. The weak electrolytes involve the concept of degree of dissociation ( $\alpha$ ), that changes the van't Hoff factor.

### Relation between van't Hoff factor and degree of dissociation

Consider an electrolyte  $A_xB_y$  that dissociates in aqueous solution as



Initially : 1 mol            0            0

At equilibrium :

(1- $\alpha$ ) mol    (x  $\alpha$  mol) (y  $\alpha$ ) mol

If  $\alpha$  is the degree of dissociation of electrolyte, then the moles of cations are  $\alpha x$  and those of anions are  $\alpha y$  at equilibrium. We have dissolved just 1 mol of electrolyte initially.  $\alpha$  mol of electrolyte dissociates and (1- $\alpha$ ) mol remains undissociated at equilibrium.

Total moles after dissociation

$$\begin{aligned} &= (1-\alpha) + (x\alpha) + (y\alpha) \\ &= 1+\alpha(x+y-1) \\ &= 1+\alpha(n-1) \dots\dots\dots (2.26) \end{aligned}$$

where,  $n = x+y$  = moles of ions obtained from dissociation of 1 mole of electrolyte.

The van't Hoff factor given by Eq. (2.23) is

$i =$

$$\frac{\text{actual moles of particles in solution after dissociation}}{\text{moles of formula units dissolved in solution}}$$

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

$$\text{Hence } i = 1 + \alpha(n-1) \text{ or } \alpha = \frac{i-1}{n-1} \dots\dots\dots(2.27)$$

**Problem 2.10 :** 0.2 *m* aqueous solution of KCl freezes at -0.680 °C. Calculate van't Hoff factor and osmotic pressure of solution at 0 °C. ( $K_f = 1.86 \text{ K kg mol}^{-1}$ )

**Solution :**

$$\Delta T_f = K_f m$$

$$\Delta T_f = 0.680 \text{ K}, m = 0.2 \text{ mol kg}^{-1}$$

$$\begin{aligned} (\Delta T_f)_0 &= 1.86 \text{ K kg mol}^{-1} \times 0.2 \text{ mol kg}^{-1} \\ &= 0.372 \text{ K} \end{aligned}$$

$$i = \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{0.680 \text{ K}}{0.372 \text{ K}} = 1.83$$

$$(\pi)_0 = MRT$$

$$= \frac{n_2}{V} RT$$

$$= \frac{0.2 \text{ mol} \times 0.08205 \text{ L atm.mol}^{-1}\text{K}^{-1} \times 273\text{K}}{1\text{L}}$$

$$= 4.48 \text{ atm}$$

$$i = 1.83 = \frac{\pi}{\pi_0}$$

$$\pi = 1.83 \times 4.48 \text{ atm}$$

$$\pi = 8.2 \text{ atm}$$

**Problem 2.11 :** 0.01*m* aqueous formic acid solution freezes at -0.021 °C. Calculate its degree of dissociation.  $K_f = 1.86 \text{ K kg mol}^{-1}$

$$\Delta T_f = i K_f m$$

$$\Delta T_f = 0^\circ\text{C} - (-0.021^\circ\text{C}) = 0.021^\circ\text{C}$$

$$m = 0.01 \text{ mol kg}^{-1}$$

$$0.021 = i \times 1.86 \text{ K kg mol}^{-1} \times 0.01 \text{ mol kg}^{-1}$$

$$i = \frac{0.021}{1.86 \times 0.01} = 1.13$$

$$\alpha = \frac{i-1}{n-1} = i-1 \text{ because } n = 2$$

$$\text{Hence, } \alpha = 1.13 - 1 = 0.13 = 13\%$$

**Problem 2.12 :** 3.4 g of  $\text{CaCl}_2$  is dissolved in 2.5 L of water at 300 K. What is the osmotic pressure of the solution? van't Hoff factor for  $\text{CaCl}_2$  is 2.47.

**Solution :**

$$\pi = iMRT = i \frac{W_2 RT}{M_2 V}$$

$$i = 2.47, W_2 = 3.4 \text{ g}, R = 0.08206 \text{ dm}^3\text{atm K}^{-1} \text{ mol}^{-1}, T = 300 \text{ K}, M_2 = 40+71 = 111 \text{ g mol}^{-1}, V = 2.5 \text{ dm}^3$$

$$\pi = 2.47 \times$$

$$\frac{3.4 \text{ g} \times 0.08206 \text{ dm}^3\text{atm K}^{-1}\text{mol}^{-1} \times 300 \text{ K}}{111 \text{ g mol}^{-1} \times 2.5 \text{ dm}^3}$$

$$= 0.745 \text{ atm}$$

**Problem 2.13 :** Which of following solutions will have maximum boiling point elevation and which have minimum freezing point depression assuming the complete dissociation? (a) 0.1 m KCl (b) 0.05 m NaCl (c) 1m  $\text{AlPO}_4$  (d) 0.1 m  $\text{MgSO}_4$

**Solution :** Boiling point elevation and freezing point depression are colligative properties that depend on number of particles in solution. The solution having more number of particles will have large boiling point elevation and that having less number of particles would show minimum freezing point depression.

- (a)  $\text{KCl} \rightarrow \text{K}^{\oplus} + \text{Cl}^{\ominus}$  Total particles in  
0.1m 0.1m 0.1m solution = 0.2 mol
- (b)  $\text{NaCl} \rightarrow \text{Na}^{\oplus} + \text{Cl}^{\ominus}$  Total particles in  
0.05m 0.05m 0.05m solution = 0.1 mol
- (c)  $\text{AlPO}_4 \rightarrow \text{Al}^{3\oplus} + \text{PO}_4^{3\ominus}$  Total particles in  
1m 1m 1m solution = 2.0mol
- (d)  $\text{MgSO}_4 \rightarrow \text{Mg}^{2\oplus} + \text{SO}_4^{2\ominus}$  Total particles in  
0.1m 0.1m 0.1m solution = 0.2mole

$\text{AlPO}_4$  solution contains highest moles and hence highest number particles and in turn, the maximum  $\Delta T_b$ . NaCl solution has minimum moles and particles. It has minimum  $\Delta T_f$ .

Arrange the following solutions in order of increasing osmotic pressure. Assume complete ionization. a) 0.5m  $\text{Li}_2\text{SO}_4$  b) 0.5m KCl c) 0.5m  $\text{Al}_2(\text{SO}_4)_3$  d) 0.1m  $\text{BaCl}_2$ .

**Problem 2.14 :** Assuming complete dissociation, calculate the molality of an aqueous solution of KBr whose freezing point is  $-2.95^\circ\text{C}$ .  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$

**Solution :**



i =

$$\frac{\text{moles of particles after dissociation}}{\text{moles of particles dissolved}} = \frac{2}{1} = 2$$

$$\Delta T_f = iK_fm$$

$$\Delta T_f = 0^\circ\text{C} - (-2.95^\circ\text{C}) = 2.95^\circ\text{C}$$

$$m = \frac{\Delta T_f}{iK_f} = \frac{2.95 \text{ K}}{2 \times 1.86 \text{ K kg mol}^{-1}} = 0.793 \text{ mol kg}^{-1}$$



## Exercises



### 1. Choose the most correct option.

- The vapour pressure of a solution containing 2 moles of a solute in 2 moles of water (vapour pressure of pure water = 24 mm Hg) is
  - 24 mm Hg
  - 32 mm Hg
  - 48 mm Hg
  - 12 mm Hg
- The colligative property of a solution is
  - vapour pressure
  - boiling point
  - osmotic pressure
  - freezing point
- In calculating osmotic pressure the concentration of solute is expressed in
  - molarity
  - molality
  - mole fraction
  - mass percent
- Ebullioscopic constant is the boiling point elevation when the concentration of solution is
  - 1m
  - 1M
  - 1 mass%
  - 1 mole fraction of solute.
- Cryoscopic constant depends on
  - nature of solvent
  - nature of solute
  - nature of solution
  - number of solvent molecules

- vi. Identify the correct statement
- vapour pressure of solution is higher than that of pure solvent.
  - boiling point of solvent is lower than that of solution
  - osmotic pressure of solution is lower than that of solvent
  - osmosis is a colligative property.
- vii. A living cell contains a solution which is isotonic with 0.3 M sugar solution. What osmotic pressure develops when the cell is placed in 0.1 M KCl solution at body temperature?
- 5.08 atm
  - 2.54 atm
  - 4.92 atm
  - 2.46 atm
- viii. The osmotic pressure of blood is 7.65 atm at 310 K. An aqueous solution of glucose isotonic with blood has the percentage (by volume)
- 5.41 %
  - 3.54 %
  - 4.53 %
  - 53.4 %
- ix. Vapour pressure of a solution is
- directly proportional to the mole fraction of the solute
  - inversely proportional to the mole fraction of the solute
  - inversely proportional to the mole fraction of the solvent
  - directly proportional to the mole fraction of the solvent
- x. Pressure cooker reduces cooking time for food because
- boiling point of water involved in cooking is increased
  - heat is more evenly distributed in the cooking space
  - the higher pressure inside the cooker crushes the food material
  - cooking involves chemical changes helped by a rise in temperature.
- xi. Henry's law constant for a gas  $\text{CH}_3\text{Br}$  is  $0.159 \text{ mol dm}^{-3} \text{ atm}$  at  $25^\circ\text{C}$ . What is the solubility of  $\text{CH}_3\text{Br}$  in water at  $25^\circ\text{C}$  and a partial pressure of  $0.164 \text{ atm}$ ?
- $0.0159 \text{ mol L}^{-1}$
  - $0.164 \text{ mol L}^{-1}$
  - $0.026 \text{ M}$
  - $0.042 \text{ M}$
- xii. Which of the following statement is NOT correct for 0.1 M urea solution and 0.05 M sucrose solution?
- osmotic pressure exhibited by urea solution is higher than that exhibited by sucrose solution
  - urea solution is hypertonic to sucrose solution
  - they are isotonic solutions
  - sucrose solution is hypotonic to urea solution

## 2. Answer the following in one or two sentences

- What is osmotic pressure?
- A solution concentration is expressed in molarity and not in molality while considering osmotic pressure. Why?
- Write the equation relating boiling point elevation to the concentration of solution.
- A 0.1 m solution of  $\text{K}_2\text{SO}_4$  in water has freezing point of  $-4.3^\circ\text{C}$ . What is the value of van't Hoff factor if  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ ?
- What is van't Hoff factor?
- How is van't Hoff factor related to degree of ionization?
- Which of the following solutions will have higher freezing point depression and why ?  
a.  $0.1 \text{ m NaCl}$  b.  $0.05 \text{ m Al}_2(\text{SO}_4)_3$
- State Raoult's law for a solution containing a nonvolatile solute
- What is the effect on the boiling point of water if 1 mole of methyl alcohol is added to  $1 \text{ dm}^3$  of water? Why?
- Which of the four colligative properties is most often used for molecular mass determination? Why?

## 3. Answer the following.

- How vapour pressure lowering is related to a rise in boiling point of solution?
- What are isotonic and hypertonic solutions?

- iii. A solvent and its solution containing a nonvolatile solute are separated by a semipermeable membrane. Does the flow of solvent occur in both directions? Comment giving reason.
  - iv. The osmotic pressure of  $\text{CaCl}_2$  and urea solutions of the same concentration at the same temperature are respectively 0.605 atm and 0.245 atm. Calculate van't Hoff factor for  $\text{CaCl}_2$ .
  - v. Explain reverse osmosis.
  - vi. How molar mass of a solute is determined by osmotic pressure measurement?
  - vii. Why vapour pressure of a solvent is lowered by dissolving a nonvolatile solute into it?
  - viii. Using Raoult's law, how will you show that  $\Delta P = P_1^0 x_2$ ? Where  $x_2$  is the mole fraction of solute in the solution and  $P_1^0$  vapour pressure of pure solvent.
  - ix. While considering boiling point elevation and freezing point depression a solution concentration is expressed in molality and not in molarity. Why?
4. Derive the relationship between degree of dissociation of an electrolyte and van't Hoff factor.
  5. What is effect of temperature on solubility of solids in water? Give examples.
  6. Obtain the relationship between freezing point depression of a solution containing nonvolatile nonelectrolyte and its molar mass.
  7. Explain with diagram the boiling point elevation in terms of vapour pressure lowering.
  8. Fish generally needs  $\text{O}_2$  concentration in water at least 3.8 mg/L for survival. What partial pressure of  $\text{O}_2$  above the water is needed for the survival of fish? Given the solubility of  $\text{O}_2$  in water at  $0^\circ\text{C}$  and 1 atm partial pressure is  $2.2 \times 10^{-3}$  mol/L (0.054 atm)
  9. The vapour pressure of water at  $20^\circ\text{C}$  is 17 mm Hg. What is the vapour pressure of solution containing 2.8 g urea in 50 g of water? (16.17 mm Hg)
  10. A 5% aqueous solution (by mass) of cane sugar (molar mass 342 g/mol) has freezing point of 271K. Calculate the freezing point of 5% aqueous glucose solution. (269.06 K)
  11. A solution of citric acid  $\text{C}_6\text{H}_8\text{O}_7$  in 50 g of acetic acid has a boiling point elevation of 1.76 K. If  $K_b$  for acetic acid is  $3.07^\circ\text{C kg mol}^{-1}$ , what is the molality of solution? (0.573 m)
  12. An aqueous solution of a certain organic compound has a density of  $1.063 \text{ g mL}^{-1}$ , an osmotic pressure of 12.16 atm at  $25^\circ\text{C}$  and a freezing point of  $-1.03^\circ\text{C}$ . What is the molar mass of the compound? (334 g/mol)
  13. A mixture of benzene and toluene contains 30% by mass of toluene. At  $30^\circ\text{C}$ , vapour pressure of pure toluene is 36.7 mm Hg and that of pure benzene is 118.2 mm Hg. Assuming that the two liquids form ideal solutions, calculate the total pressure and partial pressure of each constituent above the solution at  $30^\circ\text{C}$ . (86.7 mm,  $P = 96.5$  mm)
  14. At  $25^\circ\text{C}$  a 0.1 molal solution of  $\text{CH}_3\text{COOH}$  is 1.35 % dissociated in an aqueous solution. Calculate freezing point and osmotic pressure of the solution assuming molality and molarity to be identical. ( $-0.189^\circ\text{C}$ , 2.48 atm)
  15. A 0.15 m aqueous solution of KCl freezes at  $-0.510^\circ\text{C}$ . Calculate  $i$  and osmotic pressure at  $0^\circ\text{C}$ . Assume volume of solution equal to that of water (1.83, 6.15 atm)
- Activity :**

Boil about 100 mL of water in a beaker. Add about 10 to 15 g of salt ( $\text{NaCl}$ ) to the boiling water. Write your observations and conclusions.

