

**Example 2.9** 45 g of ethylene glycol ( $C_2H_6O_2$ ) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.

**Solution** Depression in freezing point is related to the molality, therefore, the molality of the solution with respect to ethylene glycol =  $\frac{\text{moles of ethylene glycol}}{\text{mass of water in kilogram}}$

$$\text{Moles of ethylene glycol} = \frac{45 \text{ g}}{62 \text{ g mol}^{-1}} = 0.73 \text{ mol}$$

$$\text{Mass of water in kg} = \frac{600 \text{ g}}{1000 \text{ g kg}^{-1}} = 0.6 \text{ kg}$$

$$\text{Hence molality of ethylene glycol} = \frac{0.73 \text{ mol}}{0.60 \text{ kg}} = 1.2 \text{ mol kg}^{-1}$$

Therefore freezing point depression,

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} = 2.2 \text{ K}$$

$$\text{Freezing point of the aqueous solution} = 273.15 \text{ K} - 2.2 \text{ K} = 270.95 \text{ K}$$

**Example 2.10** 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is  $5.12 \text{ K kg mol}^{-1}$ . Find the molar mass of the solute.

**Solution** Substituting the values of various terms involved in equation (2.36) we get,

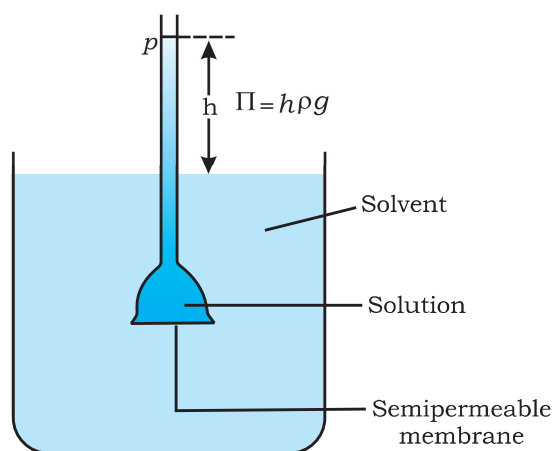
$$M_2 = \frac{5.12 \text{ K kg mol}^{-1} \times 1.00 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.40 \times 50 \text{ g}} = 256 \text{ g mol}^{-1}$$

Thus, molar mass of the solute =  $256 \text{ g mol}^{-1}$

#### 2.6.4 Osmosis and Osmotic Pressure

There are many phenomena which we observe in nature or at home. For example, raw mangoes shrivel when pickled in brine (salt water); wilted flowers revive when placed in fresh water, blood cells collapse when suspended in saline water, etc. If we look into these processes we

find one thing common in all, that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. Small solvent

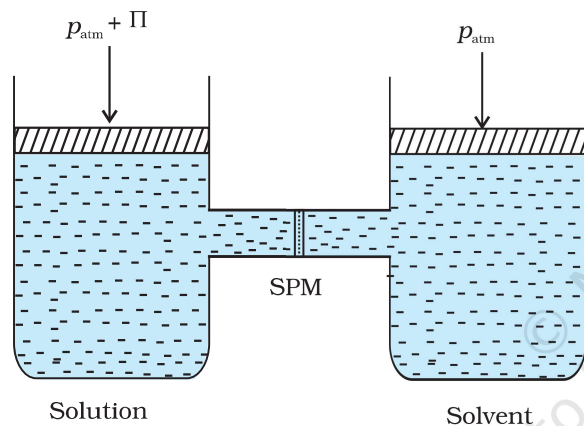


**Fig. 2.9**  
Level of solution rises in the thistle funnel due to osmosis of solvent.

molecules, like water, can pass through these holes but the passage of bigger molecules like solute is hindered. Membranes having this kind of properties are known as *semipermeable membranes* (SPM).

Assume that only solvent molecules can pass through these semipermeable membranes. If this membrane is placed between the solvent and solution as shown in Fig. 2.9, the solvent molecules will flow through the membrane from pure solvent to the solution. **This process of flow of the solvent is called osmosis.**

The flow will continue till the equilibrium is attained. The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. **This pressure that just stops the flow of solvent is called osmotic pressure of the solution.** The flow of solvent from dilute solution to the concentrated solution across a semipermeable membrane is due to osmosis. The important point to be kept in mind is that solvent molecules always flow from lower concentration to higher concentration of solution. The osmotic pressure has been found to depend on the concentration of the solution.



**Fig. 2.10:** The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution. This is illustrated in Fig. 2.10. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that **osmotic pressure is proportional to the molarity,  $C$  of the solution at a given temperature  $T$ .** Thus:

$$\Pi = C R T \quad (2.39)$$

Here  $\Pi$  is the osmotic pressure and  $R$  is the gas constant.

$$\Pi = (n_2 / V) R T \quad (2.40)$$

Here  $V$  is volume of a solution in litres containing  $n_2$  moles of solute. If  $w_2$  grams of solute, of molar mass,  $M_2$  is present in the solution, then  $n_2 = w_2 / M_2$  and we can write,

$$\Pi V = \frac{w_2 R T}{M_2} \quad (2.41)$$

$$\text{or} \quad M_2 = \frac{w_2 R T}{\Pi V} \quad (2.42)$$

Thus, knowing the quantities  $w_2$ ,  $T$ ,  $\Pi$  and  $V$  we can calculate the molar mass of the solute.

Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other

macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

**Two solutions having same osmotic pressure at a given temperature are called isotonic solutions.** When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

**Example 2.11**

200 cm<sup>3</sup> of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be  $2.57 \times 10^{-3}$  bar. Calculate the molar mass of the protein.

**Solution**

The various quantities known to us are as follows:  $\Pi = 2.57 \times 10^{-3}$  bar,

$$V = 200 \text{ cm}^3 = 0.200 \text{ litre}$$

$$T = 300 \text{ K}$$

$$R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

Substituting these values in equation (2.42) we get

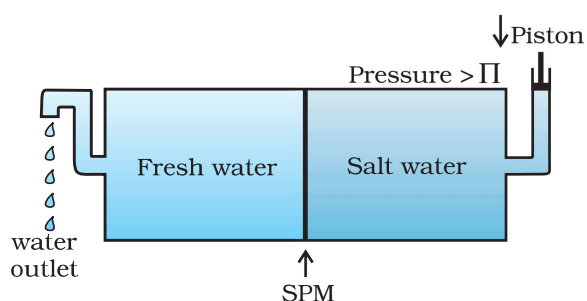
$$M_2 = \frac{1.26 \text{ g} \times 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{ bar} \times 0.200 \text{ L}} = 61,022 \text{ g mol}^{-1}$$

The phenomena mentioned in the beginning of this section can be explained on the basis of osmosis. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into its cells through osmosis. When placed in water containing less than 0.9% (mass/volume) salt, blood cells swell due to flow of water in them by osmosis. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting

puffiness or swelling is called **edema**. Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis. The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

### 2.6.5 Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called **reverse osmosis** and is of great practical utility. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Fig. 2.11.



**Fig. 2.11:** Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.

The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.

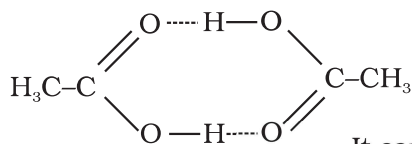
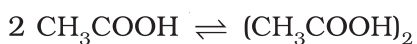
#### Intext Questions

- 2.9** Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea ( $\text{NH}_2\text{CONH}_2$ ) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.
- 2.10** Boiling point of water at 750 mm Hg is  $99.63^\circ\text{C}$ . How much sucrose is to be added to 500 g of water such that it boils at  $100^\circ\text{C}$ .
- 2.11** Calculate the mass of ascorbic acid (Vitamin C,  $\text{C}_6\text{H}_8\text{O}_6$ ) to be dissolved in 75 g of acetic acid to lower its melting point by  $1.5^\circ\text{C}$ .  $K_f = 3.9 \text{ K kg mol}^{-1}$ .
- 2.12** Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at  $37^\circ\text{C}$ .

## 2.7 Abnormal Molar Masses

We know that ionic compounds when dissolved in water dissociate into cations and anions. For example, if we dissolve one mole of KCl (74.5 g) in water, we expect one mole each of  $\text{K}^+$  and  $\text{Cl}^-$  ions to be released in the solution. If this happens, there would be two moles of particles in the solution. If we ignore interionic attractions, one mole of KCl in one kg of water would be expected to increase the boiling point by  $2 \times 0.52 \text{ K} = 1.04 \text{ K}$ . Now if we did not know about the degree of

dissociation, we could be led to conclude that the mass of 2 mol particles is 74.5 g and the mass of one mole of KCl would be 37.25 g. This brings into light the rule that, when there is dissociation of solute into ions, the experimentally determined molar mass is always lower than the true value.



Molecules of ethanoic acid (acetic acid) dimerise in benzene due to hydrogen bonding. This normally happens in solvents of low dielectric constant. In this case the number of particles is reduced due to dimerisation. Association of molecules is depicted as follows:

It can be undoubtedly stated here that if all the molecules of ethanoic acid associate in benzene, then  $\Delta T_b$  or  $\Delta T_f$  for ethanoic acid will be half of the normal value. The molar mass calculated on the basis of this  $\Delta T_b$  or  $\Delta T_f$  will, therefore, be twice the expected value. Such a molar mass that is either lower or higher than the expected or normal value is called as **abnormal molar mass**.

In 1880 van't Hoff introduced a factor  $i$ , known as the van't Hoff factor, to account for the extent of dissociation or association. This factor  $i$  is defined as:

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Here abnormal molar mass is the experimentally determined molar mass and calculated **colligative properties** are obtained by assuming that the non-volatile solute is neither associated nor dissociated. In case of association, value of  $i$  is less than unity while for dissociation it is greater than unity. For example, the value of  $i$  for aqueous KCl solution is close to 2, while the value for ethanoic acid in benzene is nearly 0.5.

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent,

$$\frac{p_1^0 - p_1}{p_1^0} = i \cdot \frac{n_2}{n_1}$$

Elevation of Boiling point,  $\Delta T_b = i K_b m$

Depression of Freezing point,  $\Delta T_f = i K_f m$

Osmotic pressure of solution,  $\Pi = i n_2 R T / V$

Table 2.4 depicts values of the factor,  $i$  for several strong electrolytes. For KCl, NaCl and MgSO<sub>4</sub>,  $i$  values approach 2 as the solution becomes very dilute. As expected, the value of  $i$  gets close to 3 for K<sub>2</sub>SO<sub>4</sub>.

**Table 2.4: Values of van't Hoff factor,  $i$ , at Various Concentrations for NaCl, KCl, MgSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>.**

Salt	*Values of $i$			van't Hoff Factor $i$ for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
MgSO <sub>4</sub>	1.21	1.53	1.82	2.00
K <sub>2</sub> SO <sub>4</sub>	2.32	2.70	2.84	3.00

\* represent  $i$  values for incomplete dissociation.

2 g of benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol<sup>-1</sup>. What is the percentage association of acid if it forms dimer in solution?

### Example 2.12

The given quantities are:  $w_2 = 2$  g;  $K_f = 4.9$  K kg mol<sup>-1</sup>;  $w_1 = 25$  g,

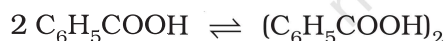
$$\Delta T_f = 1.62 \text{ K}$$

Substituting these values in equation (2.36) we get:

$$M_2 = \frac{4.9 \text{ K kg mol}^{-1} \times 2 \text{ g} \times 1000 \text{ g kg}^{-1}}{25 \text{ g} \times 1.62 \text{ K}} = 241.98 \text{ g mol}^{-1}$$

Thus, experimental molar mass of benzoic acid in benzene is  
= 241.98 g mol<sup>-1</sup>

Now consider the following equilibrium for the acid:



If  $x$  represents the degree of association of the solute then we would have  $(1 - x)$  mol of benzoic acid left in unassociated form and correspondingly  $\frac{x}{2}$  as associated moles of benzoic acid at equilibrium.

Therefore, total number of moles of particles at equilibrium is:

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

Thus, total number of moles of particles at equilibrium equals van't Hoff factor  $i$ .

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

### Solution

$$= \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}}$$

$$\text{or } \frac{x}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$$

$$\text{or } x = 2 \times 0.496 = 0.992$$

Therefore, degree of association of benzoic acid in benzene is 99.2 %.

### Example 2.13

0.6 mL of acetic acid ( $\text{CH}_3\text{COOH}$ ), having density  $1.06 \text{ g mL}^{-1}$ , is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was  $0.0205^\circ\text{C}$ . Calculate the van't Hoff factor and the dissociation constant of acid.

**Solution** Number of moles of acetic acid =  $\frac{0.6 \text{ mL} \times 1.06 \text{ g mL}^{-1}}{60 \text{ g mol}^{-1}}$   
 $= 0.0106 \text{ mol} = n$

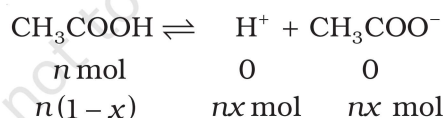
$$\text{Molality} = \frac{0.0106 \text{ mol}}{1000 \text{ mL} \times 1 \text{ g mL}^{-1}} = 0.0106 \text{ mol kg}^{-1}$$

Using equation (2.35)

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} = 0.0197 \text{ K}$$

$$\text{van't Hoff Factor } (i) = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} = 1.041$$

Acetic acid is a weak electrolyte and will dissociate into two ions: acetate and hydrogen ions per molecule of acetic acid. If  $x$  is the degree of dissociation of acetic acid, then we would have  $n(1-x)$  moles of undissociated acetic acid,  $nx$  moles of  $\text{CH}_3\text{COO}^-$  and  $nx$  moles of  $\text{H}^+$  ions,



Thus total moles of particles are:  $n(1-x+x+x) = n(1+x)$

$$i = \frac{n(1+x)}{n} = 1+x = 1.041$$

Thus degree of dissociation of acetic acid =  $x = 1.041 - 1.000 = 0.041$

Then  $[\text{CH}_3\text{COOH}] = n(1-x) = 0.0106(1-0.041)$ ,

$$[\text{CH}_3\text{COO}^-] = nx = 0.0106 \times 0.041, [\text{H}^+] = nx = 0.0106 \times 0.041.$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106(1.00 - 0.041)}$$

$$= 1.86 \times 10^{-5}$$

## Summary

A solution is a homogeneous mixture of two or more substances. Solutions are classified as solid, liquid and gaseous solutions. The concentration of a solution is expressed in terms of mole fraction, molarity, molality and in percentages. The dissolution of a gas in a liquid is governed by **Henry's law**, according to which, at a given temperature, the **solubility of a gas in a liquid is directly proportional to the partial pressure of the gas**. The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law, according to which the **relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non-volatile solute present in the solution**. However, in a binary liquid solution, if both the components of the solution are volatile then another form of Raoult's law is used. Mathematically, this form of the Raoult's law is stated as:  $p_{\text{total}} = p_1^0 x_1 + p_2^0 x_2$ . **Solutions which obey Raoult's law over the entire range of concentration are called ideal solutions**. Two types of deviations from Raoult's law, called positive and negative deviations are observed. Azeotropes arise due to very large deviations from Raoult's law.

The properties of solutions which depend on the number of solute particles and are independent of their chemical identity are called colligative properties. These are lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure. The process of osmosis can be reversed if a pressure higher than the osmotic pressure is applied to the solution. Colligative properties have been used to determine the molar mass of solutes. Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values.

Quantitatively, the extent to which a solute is dissociated or associated can be expressed by van't Hoff factor  $i$ . This factor has been defined as ratio of normal molar mass to experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

## Exercises

- 2.1 Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.
- 2.2 Give an example of a solid solution in which the solute is a gas.
- 2.3 Define the following terms:
  - (i) Mole fraction
  - (ii) Molality
  - (iii) Molarity
  - (iv) Mass percentage.
- 2.4 Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is  $1.504 \text{ g mL}^{-1}$ ?