

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 ( $\Delta p_1$ ) 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

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

The expression on the left hand side of the equation as mentioned earlier is called **relative lowering of vapour pressure and is equal to the mole fraction of the solute**. The above equation can be written as:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \left( \text{since } x_2 = \frac{n_2}{n_1 + n_2} \right) \quad (2.26)$$

Here  $n_1$  and  $n_2$  are the number of moles of solvent and solute respectively present in the solution. For dilute solutions  $n_2 \ll n_1$ , hence neglecting  $n_2$  in the denominator we have

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \quad (2.27)$$

$$\text{or } \frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \quad (2.28)$$

Here  $w_1$  and  $w_2$  are the masses and  $M_1$  and  $M_2$  are the molar masses of the solvent and solute respectively.

From this equation (2.28), knowing all other quantities, the molar mass of solute ( $M_2$ ) can be calculated.

### Example 2.6

The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol<sup>-1</sup>). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

### Solution

The various quantities known to us are as follows:

$$p_1^0 = 0.850 \text{ bar}; \quad p = 0.845 \text{ bar}; \quad M_1 = 78 \text{ g mol}^{-1}; \quad w_2 = 0.5 \text{ g}; \quad w_1 = 39 \text{ g}$$

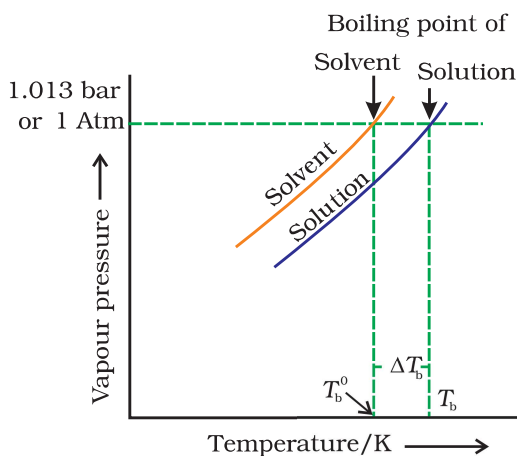
Substituting these values in equation (2.28), we get

$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_2 \times 39 \text{ g}}$$

$$\text{Therefore, } M_2 = 170 \text{ g mol}^{-1}$$

### 2.6.2 Elevation of Boiling Point

We have learnt in Unit 5, Class XI, that the vapour pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapour pressure is equal to the atmospheric pressure. For example, water boils at 373.15 K (100° C) because at this temperature the vapour pressure of water is 1.013 bar (1 atmosphere). We have also learnt in the last section that vapour pressure of the solvent decreases in the presence of non-volatile solute. Fig. 2.7 depicts the variation of vapour pressure of the pure solvent and solution as a function of temperature. For example, the vapour pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapour pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling



**Fig. 2.7:** The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that  $\Delta T_b$  denotes the elevation of boiling point of a solvent in solution.

point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 2.7. Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure.

Let  $T_b^0$  be the boiling point of pure solvent and  $T_b$  be the boiling point of solution. The increase in the boiling point  $\Delta T_b = T_b - T_b^0$  is known as **elevation of boiling point**.

Experiments have shown that for **dilute solutions** the elevation of boiling point ( $\Delta T_b$ ) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m \quad (2.29)$$

$$\text{or } \Delta T_b = K_b m \quad (2.30)$$

Here  $m$  (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality,  $K_b$  is called **Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant)**. The unit of  $K_b$  is  $\text{K kg mol}^{-1}$ . Values of  $K_b$  for some common solvents are given in Table 2.3. If  $w_2$  gram of solute of molar mass  $M_2$  is dissolved in  $w_1$  gram of solvent, then molality,  $m$  of the solution is given by the expression:

$$m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1} \quad (2.31)$$

Substituting the value of molality in equation (2.30) we get

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \quad (2.32)$$

$$M_2 = \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \quad (2.33)$$

Thus, in order to determine  $M_2$ , molar mass of the solute, known mass of solute in a known mass of the solvent is taken and  $\Delta T_b$  is determined experimentally for a known solvent whose  $K_b$  value is known.

18 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar?  $K_b$  for water is  $0.52 \text{ K kg mol}^{-1}$ .

### Example 2.7

Moles of glucose =  $18 \text{ g} / 180 \text{ g mol}^{-1} = 0.1 \text{ mol}$   
 Number of kilograms of solvent = 1 kg  
 Thus molality of glucose solution =  $0.1 \text{ mol kg}^{-1}$   
 For water, change in boiling point

### Solution

$$\Delta T_b = K_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1} = 0.052 \text{ K}$$

Since water boils at 373.15 K at 1.013 bar pressure, therefore, the boiling point of solution will be  $373.15 + 0.052 = 373.202 \text{ K}$ .

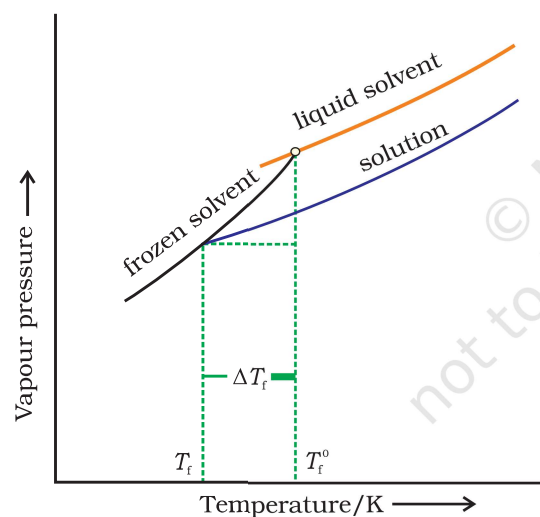
**Example 2.8** The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute.  $K_b$  for benzene is  $2.53 \text{ K kg mol}^{-1}$

**Solution** The elevation ( $\Delta T_b$ ) in the boiling point =  $354.11 \text{ K} - 353.23 \text{ K} = 0.88 \text{ K}$   
Substituting these values in expression (2.33) we get

$$M_2 = \frac{2.53 \text{ K kg mol}^{-1} \times 1.8 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.88 \text{ K} \times 90 \text{ g}} = 58 \text{ g mol}^{-1}$$

Therefore, molar mass of the solute,  $M_2 = 58 \text{ g mol}^{-1}$

**2.6.3 Depression of Freezing Point** The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig. 2.8). We know that at the freezing point of a substance, the solid phase is in



**Fig. 2.8:** Diagram showing  $\Delta T_f$  depression of the freezing point of a solvent in a solution.

dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase. A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent as is clear from Fig. 2.8. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.

Let  $T_f^0$  be the freezing point of pure solvent and  $T_f$  be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.

$\Delta T_f = T_f^0 - T_f$  is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point ( $\Delta T_f$ ) for **dilute solution** (ideal solution) is directly proportional to molality,  $m$  of the solution. Thus,

$$\Delta T_f \propto m$$

or  $\Delta T_f = K_f m$  (2.34)

The proportionality constant,  $K_f$ , which depends on the nature of the solvent is known as **Freezing Point Depression Constant or Molal**

**Depression Constant or Cryoscopic Constant.** The unit of  $K_f$  is  $\text{K kg mol}^{-1}$ . Values of  $K_f$  for some common solvents are listed in Table 2.3.

If  $w_2$  gram of the solute having molar mass as  $M_2$ , present in  $w_1$  gram of solvent, produces the depression in freezing point  $\Delta T_f$  of the solvent then molality of the solute is given by the equation (2.31).

$$m = \frac{w_2 / M_2}{w_1 / 1000} \quad (2.31)$$

Substituting this value of molality in equation (2.34) we get:

$$\Delta T_f = \frac{K_f \times w_2 / M_2}{w_1 / 1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1} \quad (2.35)$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} \quad (2.36)$$

Thus for determining the molar mass of the solute we should know the quantities  $w_1$ ,  $w_2$ ,  $\Delta T_f$ , along with the molal freezing point depression constant.

The values of  $K_f$  and  $K_b$ , which depend upon the nature of the solvent, can be ascertained from the following relations.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{\text{fus}}H} \quad (2.37)$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{\text{vap}}H} \quad (2.38)$$

Here the symbols  $R$  and  $M_1$  stand for the gas constant and molar mass of the solvent, respectively and  $T_f$  and  $T_b$  denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further,  $\Delta_{\text{fus}}H$  and  $\Delta_{\text{vap}}H$  represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

**Table 2.3: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents**

Solvent	b. p./K	$K_b/\text{K kg mol}^{-1}$	f. p./K	$K_f/\text{K kg mol}^{-1}$
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.79
Carbon tetrachloride	350.0	5.03	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

**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,

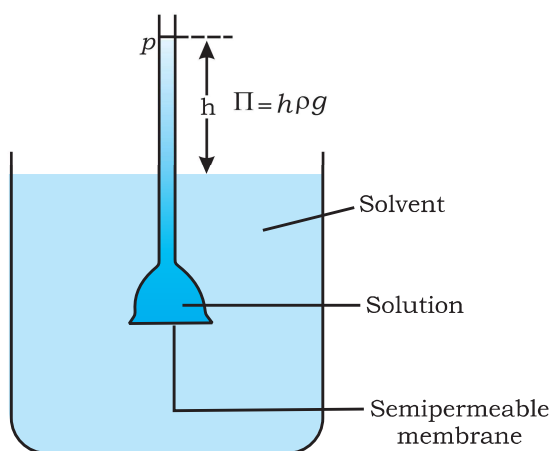
$$M_2 = \frac{5.12 \text{ K kg mol}^{-1} \times 1.00 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.40 \times 50 \text{ g}} = 256 \text{ g mol}^{-1}$$

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.