B.Sc. (Honours & Sub.) Part-**I**
Paper-I

Topic: Dilute Solutions and Changes of State-I & Colligative Properties

UG
Subject-Chemistry

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So, to saturate 88 g of water, $CuSO_4$ required $= \frac{25}{100} \times 88$

$= 22\,g$

Thus, the mass of $CuSO_4$ to be added to 100 g of dilute solution to saturate it $= (22 - 12) = 10\,g$

5.9 COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behaviour as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as **colligative properties.** The colligative properties are:

(i) Lowering in the vapour pressure,
(ii) Elevation in the boiling point,
(iii) Depression in the freezing point and
(iv) Osmotic pressure.

Colligative properties are the properties of dilute solutions, that is why these are termed as *colligative properties of dilute solutions.* These properties are related to one another. Thus, if one is measured, the other can be calculated. The importance of these properties lies in the fact that they provide methods for the determination of molecular masses of dissolved solutes. The results are excellent if the following three conditions are satisfied:

(i) The solution should be very dilute.
(ii) The solute should be non-volatile.
(iii) The solute does not dissociate or associate in solution.

5.10 LOWERING IN THE VAPOUR PRESSURE

When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons:

(i) Percentage surface area occupied by the solvent decreases. Thus, the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the per cent surface area occupied by the solvent decreases.

(ii) According to Graham's law of evaporation,

$$\text{Rate of evaporation} \propto \frac{1}{\sqrt{\text{density}}}$$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus, both rate of evaporation and vapour pressure are lowered.

If p_0 is the vapour pressure of pure solvent and p_s is the vapour pressure of the solution, the difference $(p_0 - p_s)$ is termed **lowering in vapour pressure** and the ratio $\left[\frac{p_0 - p_s}{p_0}\right]$ is termed **relative lowering in vapour pressure.**

Raoult, in 1886, established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. The relationship is known as **Raoult's law.** It states that **the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution.**

If n moles of solute be dissolved in N moles of the solvent, the mole fraction of the solute will be $\frac{n}{n+N}$.

According to Raoult's law, $\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$

This is the mathematical expression for Raoult's law.

[**Modified form of Raoult's law:** The above relationship can be written as,

$$\frac{p_0}{p_0 - p_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

or $$\frac{p_0}{p_0 - p_s} - 1 = \frac{N}{n} \text{ or } \frac{p_s}{p_0 - p_s} = \frac{N}{n}$$

or $$\frac{p_0 - p_s}{p_s} = \frac{n}{N} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

This equation gives accurate results and is easy to apply.]

Derivation of Raoult's Law for a Dilute Solution

When a non-volatile solute is dissolved in a volatile solvent, a fraction of the surface of solvent is blocked by solute molecules where no evaporation occurs. Thus, under similar conditions, the vapour pressure is decreased. The vapour pressure of the solution, thus, depends upon the number of molecules of the solvent present on the surface of the solution. The number of such molecules is proportional to mole fraction of the solvent.

So, the vapour pressure of solution,

$$'p_s' \propto \frac{N}{n+N}$$

or $$p_s = k \cdot \frac{N}{n+N} \quad \text{... (i)}$$

(k is proportionality factor)

For pure solvent, $n = 0$

and hence, $$p_0 = k\frac{N}{0+N} = k \quad \text{... (ii)}$$

Putting the value of k in eq. (i)

$$p_s = p_0 \frac{N}{n+N}$$

Note : Isopiestic solutions : Two solutions having same vapour pressure at same temperature are known as **isopiestic** solutions.

or $$\frac{p_s}{p_0} = \frac{N}{n+N}$$

or $$1 - \frac{p_s}{p_0} = 1 - \frac{N}{n+N}$$

or $$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N} \qquad \text{... (iii)}$$

This is Raoult's equation.

If a solution is made by dissolving w_B g of solute (molecular mass m_B) in w_A g of the solvent (molecular mass m_A), the mole fraction of the solute will be

$$\frac{\dfrac{w_B}{m_B}}{\dfrac{w_A}{m_A} + \dfrac{w_B}{m_B}}$$

If the solution is very dilute, $\dfrac{w_B}{m_B}$ can be neglected in the denominator as compared to $\dfrac{w_A}{m_A}$. The eq. (iii), thus, becomes

$$\frac{p_0 - p_s}{p_0} = \frac{w_B \times m_A}{m_B \times w_A} \qquad \text{... (iv)}$$

This relationship is useful in the determination of the molecular mass of dissolved solute by measuring relative lowering of vapour pressure.

Measurement of Relative Lowering in Vapour Pressure (Ostwald and Walker Method)

The apparatus used is shown in Fig. 5.8. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent. Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like P_2O_5, conc. H_2SO_4 etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

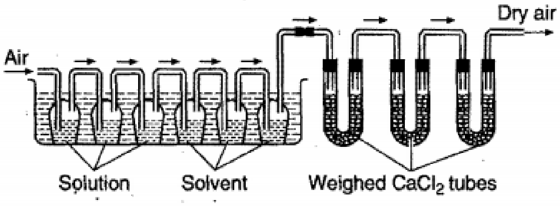

Fig. 5.8 Ostwald and Walker method

A current of pure dry air is bubbled through the series of bulbs as shown in Fig. 5.8. The air gets saturated with the vapours in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, *i.e.*, $p_0 - p_s$. The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto p_s$

Loss in mass in the solvent bulbs $\propto (p_0 - p_s)$

Total loss in both sets of bulbs $\propto [p_s + (p_0 - p_s)]$
$\propto p_0$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

$$\text{Thus, } \frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further, we know from Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w_B / m_B}{w_A / m_A + w_B / m_B}$$

$$\therefore \quad \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{w_B / m_B}{w_A / m_A + w_B / m_B}$$

The above relationship is used for calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied:

$$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{w_B \times m_A}{m_B \times w_A}$$

Vapour Pressure of Liquid and Temperature

$$\text{Liquid} \rightleftharpoons \text{Vapour} \qquad \Delta H_{\text{vap.}} > 0$$

Vapour pressure of liquid increases with temperature. Here, ΔH is enthalpy of vaporisation. A graphical representation of vapour pressure *versus* temperature is given below :

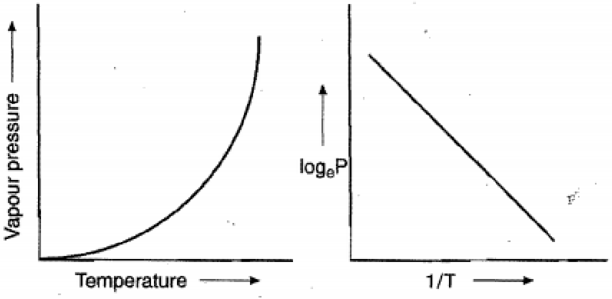

Fig. 5.9 Variation of vapour pressure with temperature

If vapour pressure of a liquid is known at a temperature; it can be calculated at another temperature using Clausius-Clapeyron equation :

$$\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap.}}}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Here, P_1 = Vapour pressure at temperature T_1
P_2 = Vapour pressure at temperature T_2

SOME SOLVED EXAMPLES

Example 25. *Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.*

Solution: According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$$

or

$$\Delta p = \frac{n}{n+N} \cdot p_0$$

Given: $n = \frac{50}{342} = 0.146$; $N = \frac{500}{18} = 27.78$ and $p_0 = 23.8$

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

Example 26. *The vapour pressure of pure benzene at a certain temperature is* 640 *mm Hg. A non-volatile solid weighing* 2.175 *g is added to* 39.0 *g of benzene. The vapour pressure of the solution is* 600 *mm Hg. What is the molecular mass of the solid substance?* **(IIT 1990; MLNR 1992)**

Solution: According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$$

Let m be the molecular mass of the solid substance.

$$n = \frac{2.175}{m}; N = \frac{39}{78} = 0.5$$

(molecular mass of benzene = 78)

$$p_0 = 640 \text{ mm}; \quad p_s = 600 \text{ mm}$$

Substituting the values in above equation,

$$\frac{640 - 600}{640} = \frac{\frac{2.175}{m}}{\frac{2.175}{m} + 0.5} = \frac{2.175}{2.175 + 0.5\,m}$$

$$m = \frac{2.175 \times 16 - 2.175}{0.5} = 65.25$$

Example 27. *A solution containing* 30 *g of a non-volatile solute in exactly* 90 *g of water has a vapour pressure of* 21.85 *mm of Hg at* 25°C. *Further,* 18 *g of water is then added to the solution; the new vapour pressure becomes* 22.15 *mm of Hg at* 25°C. *Calculate* (*a*) *molecular mass of the solute and* (*b*) *vapour pressure of water at* 25°C. **(MLNR 1990)**

Solution: Let the vapour pressure of water at 25°C be p_0 and molecular mass of the solute be m.

Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

For solution (I), $\frac{(p_0 - 21.85)}{21.85} = \frac{30 \times 18}{90 \times m}$ ... (i)

For solution (II), $\frac{(p_0 - 22.15)}{22.15} = \frac{30 \times 18}{108 \times m}$ ... (ii)

Dividing eq. (i) by eq. (ii),

$$\frac{(p_0 - 21.85)}{21.85} \times \frac{22.15}{(p_0 - 22.15)} = \frac{108}{90} = \frac{6}{5}$$

$$p_0 = 23.87 \text{ mm of Hg}$$

Substituting the value of p_0 in eq. (i)

$$m = 67.9$$

Example 28. *What mass of non-volatile solute (urea) needs to be dissolved in* 100 *g of water in order to decrease the vapour pressure of water by* 25%. *What will be the molality of solution?* **(IIT 1993)**

Solution: Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

If $p_0 = 100$ mm, then $p_s = 75$ mm

$$\frac{100 - 75}{75} = \frac{w \times 18}{100 \times 60}$$

$$w = 111.1$$

$$\text{Molality} = \frac{w \times 1000}{m \times W} = \frac{111.1 \times 1000}{60 \times 100} = 18.52\,m$$

Example 29. *A current of dry air was bubbled through a bulb containing* 26.66 *g of an organic compound in* 200 *g of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in bulb containing water was* 0.087 *g and gain in mass of the calcium chloride tube was* 2.036 *g. Calculate the molecular mass of the organic substance.*

Solution: $\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulb}}{\text{Gain in mass of CaCl}_2\text{ tube}}$

$$= \frac{0.087}{2.036}$$

Let the molecular mass of the organic substance be m. According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{m}}{\frac{26.66}{m} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18}m}$$

$$m = 53.75$$

Example 30. *The vapour pressure of a dilute aqueous solution of glucose is* 750 *mm Hg at* 373 *K. Calculate* (i) *molality,* (ii) *mole fraction of the solute.*

Solution: p_0 = Vapour pressure of water at 373 K = 760 mm Hg

Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

or

$$\frac{760 - 750}{750} = \frac{w}{Wm} \times 18$$

or

$$\frac{w}{W \times m} = \frac{10}{750 \times 18}$$

$$\text{Molality} = \frac{w}{W\times m}\times 1000 = \frac{10\times 1000}{750\times 18} = 0.74\,m$$

$$p_s = \text{Mole fraction of solvent} \times p_0;$$

$$\text{Mole fraction of solvent} = \frac{750}{760}$$

So, $$\text{Mole fraction of solute} = \left(1-\frac{750}{760}\right) = 0.0132$$

Example 31. *Calculate the vapour pressure of an aqueous solution which contains 5 mass per cent of urea. The vapour pressure of pure water is 23.5 mm Hg. Molar mass of urea is 60.*

Solution: Mass of urea = 5 g

Mass of water = (100 − 5) = 95 g

$$\text{No. of moles of urea} = \frac{5}{60} = 0.083$$

$$\text{No. of moles of water} = \frac{95}{18} = 5.278$$

$$\text{Total number of moles} = 5.278 + 0.083 = 5.361$$

$$\text{Mole fraction of solvent} = \frac{5.278}{5.361}$$

$$p_s = \text{Mole fraction of solvent} \times p_0 = \frac{5.278}{5.361}\times 23.5 = 23.14 \text{ mm}$$

Example 32. *10 g of glucose (molar mass 180) and 20 g of sucrose (molar mass 342) are dissolved in 100 g of water. What will be the vapour pressure of the resultant solution if the vapour pressure of water is 35 mm Hg?*

Solution: Mass of glucose = 10 g

No. of moles of glucose = 0.0556

Mass of sucrose = 20 g

No. of moles of sucrose = 0.0585

Mass of water = 100 g

No. of moles of water = 5.556

$$\text{Total number of moles} = 5.556 + 0.0585 + 0.0556 = 5.67$$

$$\text{Mole fraction of water} = \frac{5.556}{5.67}$$

$$\text{Vapour pressure of solution} = \text{Mole fraction of water} \times p_0 = \frac{5.556}{5.67}\times 35 = 34.3 \text{ mm Hg}$$

Example 33. *Calculate the vapour pressure of an aqueous solution of 1.0 molal glucose solution at 100°C.*

Solution: $$\text{Molality} = \frac{w}{m\times W}\times 1000$$

where, w = mass of solute in grams;
W = mass of solvent in grams

$$1.0 = \frac{w}{m\times W}\times 1000$$

or $$\frac{w}{m\times W} = \frac{1.0}{1000} = 0.001$$

Applying Raoult's law for dilute solution,

$$\frac{p_0 - p_s}{p_0} = \frac{w}{m\times W}\times M \qquad (M = 18)$$

$$\frac{760 - p_s}{760} = 0.001\times 18 \quad (p_0 = 760 \text{ mm at } 100°\text{C})$$

or $$p_s = 760 - 760\times 0.001\times 18 = 760 - 13.68 = 746.32 \text{ mm}$$

Example 34. *The vapour pressure of pure benzene at 50°C is 268 mm of Hg. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure 167 mm of Hg at 50°C?*

Solution: Applying Raoult's law in the following form:

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm} = \frac{w/m}{W/M}$$

= No. of moles of solute per mole of benzene

or $$\frac{n}{N} = \frac{(268-167)}{167} = 0.6047 \approx 0.605$$

Alternative method: We know that, p_s = Mole fraction of solvent × p_0

or 167 = Mole fraction of solvent × 268

So, $$\text{Mole fraction of solvent} = \frac{167}{268} = 0.623$$

Mole fraction of solute = 1 − 0.623 = 0.377

$$\frac{n}{N} = \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent}} = \frac{0.377}{0.623} = 0.605$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. The vapour pressure of water at 23°C is 19.8 mm. 0.1 mole glucose is dissolved in 178.2 g of water. What is the vapour pressure (in mm) of the resultant solution?

(a) 19 (b) 19.602 (c) 19.402 (d) 19.202

[Ans. (b)]

[Hint: $n_B = 0.1,\ n_A = \frac{178.2}{18} = 9.9$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{9.9}{9.9 + 0.1} = 0.99$$

$$p = p_0\,x_A = 19.8\times 0.99 = 19.602 \text{ mm}$$]

20. What is the vapour pressure of the solution containing 34.2 g of sucrose per 100 g of water at 25°C? The vapour pressure of water at 25°C is 23.75 mm.

(a) 20.3 mm (b) 23.10 mm
(c) unpredictable (d) 23.33 mm

[**Ans.** (d)]

[**Hint:** $n_A = \frac{w_A}{m_A} = \frac{100}{18} = 5.55$

$$n_B = \frac{34.2}{342} = 0.1$$

$$x_A = \frac{5.55}{5.55+0.1} = \frac{5.55}{5.65} = 0.982$$

$$p = p_0 x_A$$

$$= 23.75 \times 0.982 = 23.33 \text{ mm}]$$

21. Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is:

(a) 13.44 mm Hg (b) 14.12 mm Hg

(c) 31.2 mm Hg (d) 35.2 mm Hg

[**Ans.** (a)]

[**Hint:** $m = \frac{x_B \times 1000}{(1-x_B)m_A}$ x_B = mole fraction of solute

m_A = molar mass of solvent

$$1 = \frac{x_B \times 1000}{(1-x_B)\times 18}$$

$$x_B = 0.0176$$

$$x_A = 1 - 0.0176 = 0.9824$$

$$p = p_0 x_A$$

$$= 760 \times 0.9824 = 746.62$$

$$\Delta p = p_0 - p = 760 - 746.62$$

$$\approx 13.4]$$

22. The mass of a non-volatile solute (molecular mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% will be:

(a) 20 g (b) 30 g (c) 10 g (d) 40 g

[**Ans.** (c)]

[**Hint:** If $p_0 = 100$, then $p = 80$

$$p = p_0 x_A$$

$$80 = 100 \times x_A$$

$$x_A = 0.80$$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{114/114}{114/114 + w_B/40}$$

$$0.8 = \frac{1}{1 + w_B/40}$$

$$1 + \frac{w_B}{40} = \frac{1}{0.8}$$

$$w_B = 10 \text{ g}]$$

23. 3g urea is dissolved in 45g of water. The relative lowering of vapour pressure is : **[Comed (Karnataka) 2008]**

(a) 0.05 (b) 0.04 (c) 0.02 (d) 0.01

[**Ans.** (c)]

[**Hint:** $n_B = \frac{3}{60} = 0.05;$ $n_A = \frac{45}{18} = 2.5$

$$\frac{\Delta p}{p_0} = x_B = \frac{0.05}{2.5 + 0.05} = 0.0196 \approx 0.02]$$

24. When 25g of a non-volatile solute is dissolved in 100g of water, the vapour pressure is lowered by 0.225 mm. If the vapour pressure of water at 25°C is 17.5 mm, wl molecular mass of the solute ? **[EAMCET (En**

(a) 206 (b) 302 (c) 318 (d) 276

[**Ans.** (c)]

[**Hint :** $p = p_0 x_A$

$$(17.5 - 0.225) = 17.5 \times \frac{100/18}{100/18 + \frac{25}{m_B}}$$

$$\frac{17.275}{17.5}\left(\frac{100}{18} + \frac{25}{m_B}\right) = \frac{100}{18}$$

$$0.987\left(5.55 + \frac{25}{m_B}\right) = 5.55$$

$$5.55 + \frac{25}{m_B} = 5.628$$

$$m_B \approx 318 \text{ mm}]$$

5.11 ELEVATION OF BOILING POINT (Ebullioscopy)

The boiling point of a liquid is **the temperature at v vapour pressure is equal to the atmospheric press** vapour pressure of a liquid is lowered when a non-volat is added to it. Hence, the temperature of the solution vapour pressure will be equal to atmospheric pressur higher than the temperature of the pure solvent. In oth the boiling point of the solvent is elevated by the ad non-volatile solute. The difference in the boiling poi solution and the boiling point of the pure solvent i **elevation of boiling point.**

Elevation of boiling point,

(ΔT) = Boiling point of the solution − Boiling poin

This can be better understood by plotting a graph c pressure against temperature for a pure solvent and two of different concentrations. The curves of the solutions a below the curve of the pure solvent. The line P_0C repr atmospheric pressure. T_0, T_1 and T_2 represent the boili of pure solvent, solution I and solution II respecti vapour pressure of pure solvent, solution I and solu temperature T_0 are P_0, P_1 and P_2 respectively.

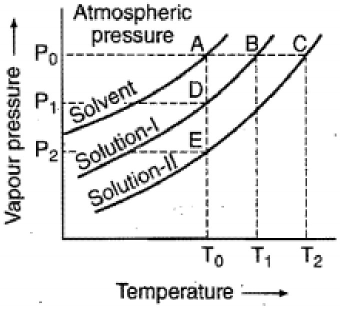

Fig. 5.10

Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus, ΔACE and ΔABD are similar.

Therefore,
$$\frac{AC}{AB} = \frac{AE}{AD}$$

or
$$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

or
$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or
$$\Delta T \propto \Delta P$$

From Raoult's law for dilute solution,

$$\frac{p_0 - p_s}{p_0} = \frac{w_B \times m_A}{m_B \times w_A}$$

(p_s = vapour pressure of solution)

or
$$p_0 - p_s = \frac{w_B \times m_A}{m_B \times w_A} \cdot p_0$$

For the pure solvent, p_0 (its vapour pressure at the boiling point) and m_A (its molecular mass) are constant. Therefore,

$$p_0 - p_s \propto \frac{w_B}{m_B \times w_A}$$

or
$$\Delta p \propto \Delta T \propto \frac{w_B}{m_B \times w_A}$$

or
$$\Delta T = K \cdot \frac{w_B}{m_B \times w_A} \qquad \text{... (i)}$$

where K is a constant, called as elevation constant.

When, $\frac{w_B}{m_B} = 1$, (one mole of solute) and $w_A = 1\,\text{g}$, then

$$\Delta T = K$$

Thus, boiling point constant is equal to the elevation in boiling point which would be theoretically produced when 1 mole of a non-volatile solute is dissolved in 1 g of the solvent.

If $\frac{w_B}{m_B} = 1$ and $w_A = 100\,\text{g}$,

Then,
$$\Delta T = \frac{K}{100} = K'$$

K' is called **molecular elevation constant.** It is defined as the **elevation in boiling point produced when 1 mole of the solute is dissolved in 100 g of the solvent.**

Thus,
$$K = 100K'$$

Putting this value in eq. (i),

$$\Delta T = 100\,K' \cdot \frac{w_B}{m_B\ w_A} \qquad \text{... (ii)}$$

If $\frac{w_B}{m_B} = 1$ and $w_A = 1000\,\text{g}$,

Then,
$$\Delta T = \frac{K}{1000} = K_b$$

K_b is called **molal elevation constant.** It is defined as the **elevation in boiling point produced when 1 mole of the solute is dissolved in 1000 g of the solvent.**

Thus,
$$K = 1000\,K_b$$

Putting this value in eq. (i),

$$\Delta T = \frac{1000 K_b\ w_A}{m_A\ w_B} \qquad \text{... (iii)}$$

or
$$\Delta T = \text{Molality} \times K_b$$

$$\left(\text{since } \frac{w_B}{m_B \times w_A} \times 1000 = \text{molality}\right)$$

The elevation in boiling point of a solution of non-electrolyte is proportional to its molality and equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation of boiling point.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^{\,2}}{1000\,L_v}$$

where, R is molar gas constant, T_b is the boiling point of the solvent on kelvin scale and L_v the latent heat of vaporisation of solvent in calories per gram.

For water
$$K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$$

The molal elevation constants for some common solvents are given in the following table:

Table 5.4 Molal Elevation Constants of Some Solvents

Solvent	B.pt. (°C)	Molal elevation constant (K kg mol^{-1})
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.67
Carbon tetrachloride	76.8	5.02
Benzene	80.0	2.70
Ethyl alcohol	78.4	1.15

If $K_b, w_A, \Delta T$ and w_B are known, molecular mass of a non-volatile solute can be determined. The most convenient method for the determination of ΔT in the laboratory is the **Landsberger method.**

---

* This relation may also be written as:
$$\Delta T = \frac{1000\,K_b \times w}{m \times W}$$
where, w and W are masses of solute and solvent respectively and m = molecular mass of solute.

5.12 DEPRESSION OF FREEZING POINT (Cryoscopy)

Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. Since, the addition of a non-volatile solute always lowers the vapour pressure of a solvent, therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of the pure solvent and its solution is called **depression of freezing point.**

Depression of freezing point

(ΔT) = Freezing point of the solvent

− Freezing point of the solution

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions, solution I and solution II. *CFB* is a curve for a solid solvent. The solvent, solution I and solution II vapour pressure curves meet *CFB* curve at points B, F and C respectively. Thus, T_0, T_1 and T_2 are the freezing points of pure solvent, solution I and solution II respectively. The vapour pressures at temperatures T_0, T_1 and T_2 for solvent, solution I and solution II are, thus, P_0, P_1 and P_2 respectively.

For very dilute solutions, the curves *FD* and *CE* are almost straight lines and *CB* is also nearly a straight line. The ΔBEC and ΔBDF are similar.

So,
$$\frac{EC}{DF} = \frac{BE}{BD}$$

or
$$\frac{T_0 - T_2}{T_0 - T_1} = \frac{P_0 - P_2}{P_0 - P_1}$$

or
$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or
$$\Delta T \propto \Delta P$$

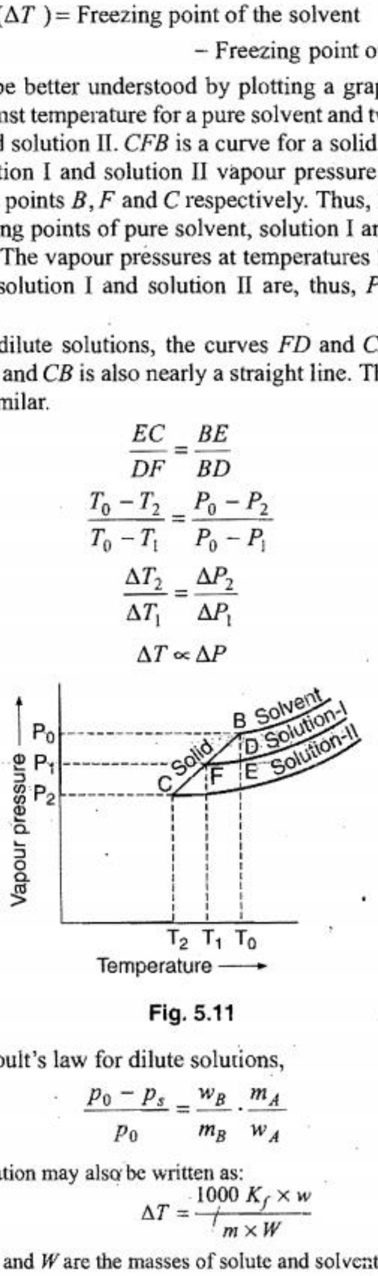

Fig. 5.11

From Raoult's law for dilute solutions,

$$\frac{p_0 - p_s}{p_0} = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A}$$

or
$$p_0 - p_s = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A} \cdot p_0$$

For the pure solvent, p_0 and m_B are constants. Therefore,

$$p_0 - p_s \propto \frac{w_B}{m_B\ w_A}$$

or
$$\Delta p \propto \frac{w_B}{m_B\ w_A}$$

or
$$\Delta p \propto \Delta T \propto \frac{w_B}{m_B\ w_A}$$

or
$$\Delta T = K \cdot \frac{w_B}{m_B\ w_A} \quad \text{... (i)}$$

where, K is a constant, called depression constant.

When, $\frac{w_B}{m_B} = 1$ (one mole of solute) and $w_A = 1\text{g}$

$$\Delta T = K$$

Thus, depression constant is equal to the depression of the freezing point which would be theoretically produced when one mole of a non-volatile solute is dissolved in 1 g of the solvent.

If $\frac{w_B}{m_B} = 1$ and $w_B = 100\text{g}$,

$$\Delta T = \frac{K}{100} = K'$$

K' is called molecular depression constant.

It is defined as the depression of freezing point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

Thus, $K = 100K'$

Putting this value in eq. (i),

$$\Delta T = \frac{100K' \times w_B}{m_B \times w_A} \quad \text{... (ii)}$$

If $\frac{w_B}{m_B} = 1$ and $w_A = 1000\text{g}$

$$\Delta T = \frac{K}{1000} = K_f$$

K_f is called molal depression constant.

It is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

Thus, $K = 1000K_f$

Putting this value in eq. (i),

$$\Delta T = 1000K_f \frac{w_B}{m_B\ w_A} \quad \text{... (iii)}$$

---

* This relation may also be written as:

$$\Delta T = \frac{1000\ K_f \times w}{m \times W}$$

where w and W are the masses of solute and solvent respectively and m = molecular mass of solute.

or $$\Delta T = \text{molality} \times K_f$$

K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_f = \frac{0.002\, T_f^2}{L_f}$$

where, T_f is the freezing point of solvent in absolute scale and L_f the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80}$$

$$= 1.86\,\text{K kg mol}^{-1}$$

The molal depression constants for some common solvents are given in the following table:

Table 5.5 Molal Depression Constants of Some Solvents

Solvent	**F.pt. (°C)**	**Molal elevation constant (K kg mol^{-1})**
Water	0.0	1.86
Ethyl alcohol	–114.6	1.99
Chloroform	–63.5	4.70
Carbon tetrachloride	–22.8	29.80
Benzene	5.5	5.12
Camphor	179.0	39.70

If $K_f, w_A, \Delta T$ and w_B are known, molecular mass of a non-volatile solute can be determined. ΔT is measured by Beckmann's method in the laboratory.

The molecular mass of non-volatile and non-ionisable solute can be calculated using following formula:

$$m_B = \frac{K_f}{\Delta T} \times \frac{w_B}{w_A} \times 1000$$

where, w_B and w_A are the masses of solute and solvent respectively.

Anti-freeze solutions : Water is used in radiators of cars and other automobiles. In cold countries where the atmospheric temperature becomes less than zero degree, the water in the radiators would freeze. Anti-freeze solutions are useful under these conditions when the vehicles are used in the regions of sub-zero temperature so that the water does not freeze in radiators. Such solutions are made by dissolving ethylene glycol in water. Freezing point can be lowered to the desired extent by varying the concentration of ethylene glycol. Glycerol can also be used as anti-freeze.

Freezing mixture : It is a mixture of ice and common salt (NaCl). It is used in the making of ice-cream and in the laboratories to create low temperatures. With the help of this mixture, a temperature as low as –33°C (240 K) can be achieved.

Note: Ebullioscopic and cryoscopic methods are effective when :

(i) Solutions are dilute. Solutions obey Raoult's law.
(ii) The solute is non-volatile.
(iii) There is no association or dissociation of solute molecules in the solution.
(iv) Solute does not form a solid solution with solvent in frozen state, *i.e.*, only solvent separates in solid state on freezing the solution.
(v) Equimolal quantities of different substances dissolved in the same quantity of solvent bring out the same depression in freezing point of the solvent under identical conditions.

SOME SOLVED EXAMPLES

Example 35. *On dissolving* 10.8 g *glucose* (*m.wt.* = 180) *in* 240 *g of water, its boiling point increases by* 0.13° *C. Calculate the molecular elevation constant of water.*

Solution: $$\Delta T = \frac{100K' \times w}{W \times m}$$

or $$K' = \frac{\Delta T \times W \times m}{100 \times w}$$

Given, $\Delta T = 0.13^\circ$ C, $W = 240$ g, $m = 180$ and $w = 10.8$ g

$$K' = \frac{0.13 \times 240 \times 180}{100 \times 10.8} = 5.2^\circ.$$

Example 36. *A solution of* 2.5 *g of a non-volatile solid in* 100 *g benzene is boiled at* 0.42°*C higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is* 2.67 *K kg mol*$^{-1}$.

Solution: $$m = \frac{1000K_b \times w}{W \times \Delta T}$$

Given, $K_b = 2.67,\ w = 2.5\,\text{g}, W = 100\,\text{g}, \Delta T = 0.42$

$$m = \frac{1000 \times 2.67 \times 2.5}{100 \times 0.42} = 158.9$$

The molecular mass of substance is 158.9.

Example 37. *The molal elevation constant for water is* 0.56 *K kg mol*$^{-1}$. *Calculate the boiling point of a solution made by dissolving* 6.0 *g of urea* (NH_2CONH_2) *in* 200 *g of water.*

Solution: $$\Delta T = \frac{1000K_b \times w}{m \times W}$$

Given, $K_b = 0.56\,\text{K kg mol}^{-1}, w = 6.0\,\text{g}, W = 200\,\text{g}, m = 60$

$$\Delta T = \frac{1000 \times 0.56 \times 6.0}{200 \times 60} = 0.28^\circ\,\text{C}$$

Thus, the boiling point of solution = b.pt. of water + ΔT

$$= (100^\circ\,\text{C} + 0.28^\circ\,\text{C}) = 100.28^\circ\,\text{C}$$

Example 38. *By dissolving* 13.6 *g of a substance in* 20 *g of water, the freezing point decreased by* 3.7°*C. Calculate the molecular mass of the substance. (Molal depression constant for water* = 1.863 *K kg mol*$^{-1}$)

Solution: $$m = \frac{1000K_f \times w}{W \times \Delta T}$$

Given, $K_f = 1.863\,\text{K kg mol}^{-1}$

$w = 13.6\,\text{g}, W = 20\,\text{g}, \Delta T = 3.7^\circ\,\text{C}$

$$m = \frac{1000 \times 1.863 \times 13.6}{20 \times 3.7} = 342.39$$

Example 39. *On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density $0.8\,g/mL$), its freezing point decreases by 0.40°C. Calculate the molecular mass of non-volatile substance ($K_f = 5.12\,K\ kg\ mol^{-1}$).*

Solution: Mass of benzene, W = volume × density

$$= 30 \times 0.8 = 24\text{ g}$$

Given, $K_f = 5.12\text{ K kg mol}^{-1}$, $w = 0.25\text{ g}$, $\Delta T = 0.40°\text{C}$.

We know that,

$$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 0.25}{24 \times 0.40} = 133.33$$

Example 40. *A solution of 1.25 g of a certain non-volatile substance in 20 g of water freezes at 271.94 K. Calculate the molecular mass of the solute ($K_f = 1.86\,K\ kg\ mol^{-1}$).*

Solution: Freezing point of solution = 271.94 K

Freezing point of water = 273.0 K

$$\Delta T = (273 - 271.94) = 1.06\text{ K}$$

We know that, $m = \dfrac{1000 K_f \times w}{W \times \Delta T}$

Given, $K_f = 1{,}86\text{ K kg mol}^{-1}$, $w = 1.25$ g, $W = 20$ g and $\Delta T = 1.06$ K.

$$m = \frac{1000 \times 1.86 \times 1.25}{20 \times 1.06} = 109.66$$

Example 41. *Two elements A and B form compounds having molecular formulae AB_2 and AB_4. When dissolved in 20.0 g of benzene, 1.0 g of AB_2 lowers the freezing point by 2.3°C, whereas 1.0 g of AB_4 lowers the freezing point by 1.3°C. The molal depression constant for benzene in 1000 g is 5.1. Calculate the atomic masses of A and B.*

Solution: We know that,

$$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

Molecular mass of AB_2 (from given data) $= \dfrac{1000 \times 5.1 \times 1}{20 \times 2.3}$

$$= 110.86$$

and Molecular mass of AB_4 (from given data) $= \dfrac{1000 \times 5.1 \times 1}{1.3 \times 20}$

$$= 196.15$$

Further, $AB_4 = A + 4B = 196.15$ ... (i)

$AB_2 = A + 2B = 110.86$ ... (ii)

Subtracting eq. (ii) from (i),

$$2B = 85.29$$

$$B = 42.645$$

Putting the value of B in eq. (ii),

$$A + 85.29 = 110.86$$

or $A = (110.86 - 85.29) = 25.57$

Thus, the atomic masses of A and B are 25.57 and 42.645 respectively.

Example 42. *1.355 g of a substance dissolved in 55 g of CH_3COOH produced a depression in the freezing point of 0.618°C. Calculate the molecular weight of the substance ($K_f = 3.85$).* **[CECE (Mains) Bihar 2005]**

Solution: $\Delta T = K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$

where, w_B = mass of solute, m_B = molar mass of solute, w_A = mass of solvent

$$0.618 = 3.85 \times \frac{1.355 \times 1000}{m_B \times 55}$$

$$m_B = 153.47$$

Example 43. *An aqueous solution of a non-volatile solute boils at 100.17°C. At what temperature will the solution freeze? (Given: $K_b = 0.512\,K\ kg\ mol^{-1}$ and $K_f = 1.86\,K\ kg\ mol^{-1}$)*

Solution: We know that,

$$\Delta T_b = \text{molality} \times K_b$$

$$0.17 = \text{molality} \times 0.512$$

Molality of the solution $= \dfrac{0.17}{0.512}\, m$

Let depression in freezing point be ΔT_f

$$\Delta T_f = \text{molality} \times K_f$$

$$= \frac{0.17}{0.512} \times 1.86 = 0.62°\text{ C}$$

Thus, the freezing point of the solution is

$$0.00 - 0.62 = -0.62°\text{C}$$

Example 44. *18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil (1.013 bar pressure)? K_b for water is $0.52\,K\ kg\ mol^{-1}$.*

Solution: $\Delta T = K_b \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$$\Delta T = 0.52 \times \frac{18 \times 1000}{180 \times 1000}$$

$$T - T_0 = 0.052$$

$$T - 373 = 0.052$$

$$T = 373.052\text{ K}$$

Example 45. *A solution of urea in water has boiling point of 100.15°C. Calculate the freezing point of the same solution if K_f and K_b for water are $1.87\,K\ kg\ mol^{-1}$ and $0.52\,K\ kg\ mol^{-1}$ respectively.*

Solution: $\Delta T_b = (100.15 - 100) = 0.15°\text{C}$

We know that, $\Delta T_b = \text{molality} \times K_b$

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.15}{0.52} = 0.2884$$

$$\Delta T_f = \text{molality} \times K_f$$

$$= 0.2884 \times 1.87 = 0.54^\circ \text{ C}$$

Thus, the freezing point of the solution = – 0.54 °C

Example 46. *In a cold climate, water gets frozen causing damage to radiator of a car. Ethylene glycol is used as antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at* $-6^\circ C$ *(*K_f *for water* $= 1.85\ K\ kg\ mol^{-1}$*).* **(IIT 1992)**

Solution: Given,

$$\Delta T = 6^\circ\text{C},\ W = 4\text{ kg} = 4000\text{ g},\ m = 62,\ K_f = 1.85$$

$$w = \frac{m \times W \times \Delta T}{1000 \times K_f}$$

$$= \frac{62 \times 4000 \times 6}{1000 \times 1.85} = 804.32\text{ g}$$

Example 47. *A solution containing* 0.2563 *g of naphthalene (molecular mass* = 128*) in* 50 *g of carbon tetrachloride yields a boiling point elevation of* 0.201°C *while a solution of* 0.6216 *g of an unknown solute in the same mass of the solvent gives a boiling point elevation of* 0.647°C*. Find the molecular mass of the unknown solute.*

Solution: We know that,

$$K_b = \frac{\Delta T_b \times W \times m}{1000 \times w}$$

For CCl_4,
$$K_b = \frac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$$

K_b is now used in the second part of the problem.

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

$$= \frac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44$$

Example 48. *Calculate the molal depression constant of a solvent which has freezing point* 16.6°C *and latent heat of fusion* $180.75\ J\ g^{-1}$.

Solution:
$$K_f = \frac{RT_f^2}{1000 \times L_f}$$

$$R = 8.314\text{ J K}^{-1}\text{ mol}^{-1},$$

$$T_f = 16.6^\circ\text{ C} = 273 + 16.6 = 289.6\text{ K},$$

$$L_f = 180.75\ \text{ J g}^{-1}.$$

Substituting the values in the above equation,

$$K_f = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

25. Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1}: **[JEE (Orissa) 2005]**

(a) 2.68 (b) 3.86 (c) 4.68 (d) 2.86

[**Ans.** (b)]

[**Hint:** $K_f = \dfrac{RT_0^{\ 2}}{1000L}$ $\qquad T_0 = 273 + 16.6 = 289.6\text{ K}$

$$= \frac{8.314 \times (289.6)^2}{1000 \times 180.75}$$

$$= 3.86]$$

26. The elevation in boiling point for 13.44 g of $CuCl_2$ dissolved in 1 kg of water as solvent will be ($K_b = 0.52\text{ K kg mol}^{-1}$; molar mass of $CuCl_2 = 134.4$ g/mol): **(IIT 2005)**

(a) 0.05 (b) 0.10 (c) 0.16 (d) 0.20

[**Ans.** (c)]

[**Hint:** $i = 3$, assuming complete ionization of $CuCl_2$

$$\Delta T = i \times K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$= 3 \times 0.52 \times \frac{13.44 \times 1000}{134.4 \times 1000} = 0.156 \approx 0.16]$$

27. A solution containing 7 g of a solute (molar mass 210 g mol^{-1}) in 350 g of acetone raised the boiling point of acetone from 56°C to 56.3°C. The value of ebullioscopic constant of acetone in K kg mol^{-1} is:

(a) 2.66 (b) 3.15 (c) 4.12 (d) 2.86

[**Ans.** (b)]

[**Hint:** $\Delta T = K_b \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$$0.3 = K_b \times \frac{7 \times 1000}{210 \times 350}$$

$$K_b = \frac{0.3 \times 210 \times 350}{7 \times 1000} = 3.15\text{ K kg mol}^{-1}]$$

28. The normal boiling point of toluene is 110.7°C and its boiling point elevation constant is $3.32\text{ K kg mol}^{-1}$. The enthalpy of vaporization of toluene is nearly:

(a) 17 kJ mol^{-1} (b) 21 kJ mol^{-1}

(c) 51 kJ mol^{-1} (d) 68 kJ mol^{-1}

[**Ans.** (b)]

[**Hint:** $K_b = \dfrac{RT_0^{\ 2}}{1000L}$; $3.32 = \dfrac{(8.314 \times 10^{-3}) \times (383.7)^2}{1000 \times L}$

$$L = 0.368\text{ kJ / g}$$

Latent heat per mol = 0.368 × molar mass of acetone

$$= 0.368 \times 58 = 21.344\text{ kJ mol}^{-1}]$$

29. An aqueous solution freezes at -0.186°C ($K_f = 1.86$ K kg mol^{-1}, $K_b = 0.512\text{ K kg mol}^{-1}$). The elevation of b. pt. of the solution is:

(a) 0.186 (b) 0.512 (c) $\frac{0.512}{1.86}$ (d) 0.0512

[**Ans.** (d)]

[**Hint:**

$$\Delta T = K_f \times m$$
$$0.186 = 1.86 \times m$$
$$m = 0.1$$
$$\Delta T = K_b \times m = 0.512 \times 0.1 = 0.0512]$$

30. The amount of urea to be dissolved in 500 cc of water ($K_f = 1.86$) to produce a depression of 0.186°C in the freezing point is: **[UGET (Manipal) 2006]**

(a) 9 g (b) 6 g (c) 3 g (d) 0.3 g

[**Ans.** (c)]

[**Hint:**

$$\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$$
$$0.186 = 1.86 \times \frac{w_B \times 1000}{60 \times 500}$$
$$w_B = 3\text{ g}]$$

31. What should be the freezing point of aqueous solution containing 17 g of C_2H_5OH in 1000 g of water (K_f for water $= 1.86\,\text{deg kg mol}^{-1}$)?

(a) – 0.69°C (b) 0.34°C

(c) 0.0°C (d) – 0.34°C

[**Ans.** (a)]

[**Hint:**

$$\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A} = 1.86 \times \frac{17 \times 1000}{46 \times 1000} = 0.69$$

$\therefore$ Freezing point of solution $= 0 - 0.69 = -0.69°\text{C}$]

5.13 OSMOSIS AND OSMOTIC PRESSURE

Osmosis: When a semipermeable membrane is placed between a solution and a solvent, it is observed that solvent molecules enter the solution and the volume of solution increases. It is also observed that if two solutions of unequal concentrations are separated by a semipermeable membrane, the solvent molecules from a solution of lower concentration move towards a solution of higher concentration. This phenomenon was first observed by **Abbe Nollet** (1748) and termed as **Osmosis** (Greek, *osmos* = to push). Osmosis is defined **as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.**

The phenomenon of osmosis can be demonstrated by the following experiment:

Two eggs of same size are taken and their outer hard shell is removed by dissolving in dilute hydrochloric acid. One of the eggs is placed in distilled water and the other in saturated salt solution.

After sufficient time, it is noticed that the egg placed in water swells up and that placed in salt solution shrinks. In the first case, water enters the concentrated egg fluid while in the second case, water comes out of the egg as salt solution is more concentrated than the egg fluid.

Difference between Osmosis and Diffusion

The two processes, diffusion and osmosis, can be distinguished in terms of the following aspects:

(i) In diffusion, solute as well as solvent molecules flow in opposite directions while in osmosis the flow of solvent molecules occurs in one direction only.

(ii) For osmosis, a semipermeable membrane* is required while for diffusion it is not required.

Semipermeable membrane

"*A membrane which allows the solvent molecules to pass through it but prevents the passage of solute molecules through it is called a semipermeable membrane.*"

Examples of semipermeable membranes are too many. Parchment paper, membranes covering the animal and plant cells and many gelatinous inorganic substances such as calcium phosphate and copper ferrocyanide, etc., act as semipermeable membranes. Animal and plant membranes are not all completely semipermeable. The best semipermeable membrane used is prepared by deposition of copper ferrocyanide, $Cu_2[Fe(CN)_6]$, in the pores of a porous pot.

Working of semipermeable membrane : Several theories have been put forward to explain the working of semipermeable membrane. These are :

(a) The sieve theory : The theory was suggested by Traube. According to this theory, a semipermeable membrane contains a large number of small pores which act like a sieve. The pores allow the smaller molecules of solvent to pass through it but does not allow the larger molecules of solute to do so. However, this theory fails in those cases of semipermeability where the solute molecules are smaller than the solvent molecules.

(b) The solution theory : According to this theory, a membrane is permeable to those substances which dissolve in it and is impermeable to those which are insoluble in it. Thus, a layer of phenol acts as a semipermeable membrane when placed between a solution of $Ca(NO_3)_2$. Phenol allows water to pass through it because water is soluble in phenol. It is impermeable to $Ca(NO_3)_2$ because $Ca(NO_3)_2$ is insoluble in phenol.

(c) Vapour pressure theory : According to this theory, a solvent can pass through a semipermeable membrane because the vapour pressure of the pure solvent is higher than the vapour pressure of the solution. This theory is widely accepted because it explains the phenomenon of osmosis.

Osmotic pressure: A porous pot is taken and a semipermeable membrane of copper ferrocyanide is deposited in its walls. It is fitted with a long glass tube with the help of a rubber stopper. It is filled with concentrated aqueous sugar solution and placed in distilled water. Osmosis occurs and the level of the solution in glass tube rises over a period of time. After a few days, the level becomes stationary. At this equilibrium state the hydrostatic pressure of the liquid column exactly balances the tendency which enables the water molecules to pass through semipermeable membrane.

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* Membranes which allow the passage of only solvent molecules through them are called semipermeable membranes. Egg membrane, goat's bladder and cell membranes can serve as semipermeable membranes but these are not perfect for laboratory measurements. Artificial membranes of gelatinous inorganic substances such as copper ferrocyanide are used these days as semipermeable membranes.

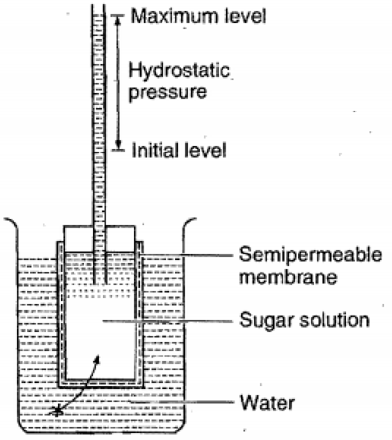

Fig. 5.12 Hydrostatic pressure determination

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution. Osmotic pressure is also defined **as the hydrostatic pressure built up on the solution which just stops the osmosis.**

$$\text{Osmotic pressure} = \text{hydrostatic pressure}$$

$$\pi = hdg$$

where, h = increase in level in the tube of unit cross section, d = density of solution and g = acceleration due to gravity.

Actually, this will not be an exact measure of osmotic pressure of the solution originally taken because sufficient dilution has taken place with time.

If osmosis takes place due to concentration gradient *i.e.*, when two solutions of different concentration are separated by semipermeable membrane then,

$$\pi = hdg = \Delta CRT$$

Alternative definition: An apparatus as shown in Fig. 5.13 consists of a water-tight chamber which is divided into two halves by a semipermeable membrane and fitted with a water-tight piston and a flow indicator in separate compartments. The compartment having a piston is filled with solution and the other compartment is filled with a pure solvent. Water (solvent) tries to flow into the solution side. To check this tendency, a certain pressure shall have to be applied by the piston. This external pressure is thus a measure of osmotic pressure of the solution. **The external pressure which must be applied on the solution in order to stop the flow of the solvent into the solution through semipermeable membrane is equal to osmotic pressure.**

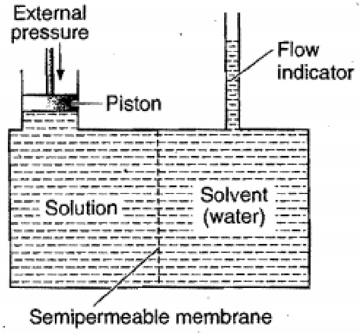

Fig. 5.13

Determination of Osmotic Pressure: Berkeley and Hartley's Method

Various methods are employed for the measurement of osmotic pressure but the best known method was suggested by Berkeley and Hartley. The apparatus used is shown in Fig. 5.14. A porcelain tube having copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. The porcelain tube is fitted with a reservoir of pure solvent at one end and a capillary tube at the other end. In a metallic jacket, there is an arrangement for applying external pressure which is measured with the help of pressure gauge.

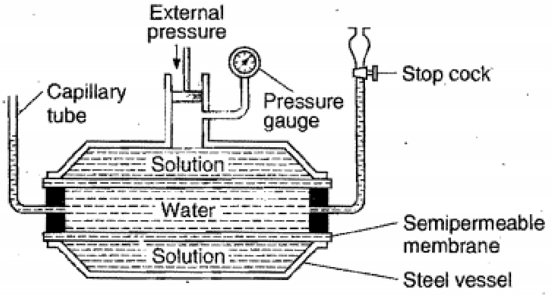

Fig. 5.14 Berkeley and Hartley's method

Procedure: The porcelain tube is filled with pure solvent and the metallic jacket with solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.

Advantages: (i) It is a quick and accurate method.

(ii) The concentration of the solution does not change because flow of solvent is not permitted into solution; so the results obtained by this method are reliable.

(iii) As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated. So, this method can be used to measure high osmotic pressures also.

Comparison of osmotic pressures: de-Vries developed an approximate method for comparing the relative osmotic pressures of aqueous solutions. A solution of low osmotic pressure is termed **hypotonic** and solution of high osmotic pressure is termed **hypertonic.** The protoplasmic layer, lining the cell walls of plant cells is easily penetrated by water but is almost impermeable to the substances dissolved in the cellular fluid. When a plant cell is placed in hypotonic solution, the water is drawn in and the cell swells. If the cell is placed in a hypertonic solution, water will diffuse out of the cell fluid and partial collapse of the cell will take place when hypotonic solution is separated from hypertonic solution using semipermeable membrane, then osmosis takes place from hypotonic to hypertonic because solvent concentration is greater in hypotonic solution. This phenomenon is known as **plasmolysis.** The change in cell can be observed under a microscope. When the plant cell is placed in the solution of same osmotic pressure as that of the cell fluid, no change in the structure of the cell is observed. Such solutions having same osmotic pressures are termed **isotonic.** By putting, therefore, cells of the same kind into solutions of different concentrations, it can be ascertained whether the solution is hypertonic or hypotonic or isotonic.

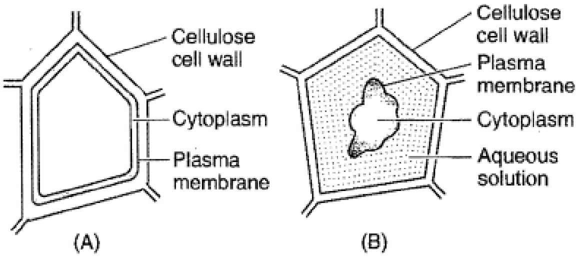

Fig. 5.15 Plasmolysis

Some biological explanation on the basis of osmosis are given below:

(i) In animals, circulation of water to all parts of body takes place due to osmosis.

(ii) Plant roots absorb water from soil due to osmosis. Concentration of cell sap inside the root hair cells is higher than that of water present in the soil. Water enters the root cells due to endosmosis.

(iii) Water absorbed by plant roots is circulated in the entire plant body and reaches to the top of a tall tree due to osmosis.

(iv) Osmosis helps in plant growth and germination of seeds.

(v) Red blood cells burst when placed in water; it is due to endosmosis.

(vi) Various functions of plants are controlled by osmosis, *e.g.*, stretching of leaves and flowers, opening and closing of flowers.

(vii) Use of salt and sugar in pickles and jams acts as preservatives. It prevents growth of bacteria and fungi by osmosis.

(viii) Dead bodies swell under water due to endosmosis.

(ix) When dried fruits and vegetables are placed in water, they slowly swell and return to the original form. It is again due to endosmosis of water into the fruits and vegetables.

Intravenous drip of saline water : Saline drip to the patients is also based on the principle of osmosis.

(i) A 0.91% solution of NaCl in water is isotonic to human blood. Hence, in this solution red blood cells neither swell nor shrink.

(ii) Aqueous solution of NaCl with concentration less than 0.91% is hypotonic to blood. On placing red blood cells in this solution, endosmosis results into bursting of RBCs.

(iii) Aqueous solution of NaCl with concentration more than 0.91% is **hypertonic** to blood. On placing red blood cells in it exosmosis or plasmolysis results into shrinking of cells.

5.14 VAN'T HOFF THEORY OF DILUTE SOLUTIONS

van't Hoff realised that an analogy exists between gases and solutions provided osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for dilute solutions of non-electrolytes the following laws hold good:

1. Boyle-van't Hoff law: The osmotic pressure (P or π) of a solution is directly proportional to its concentration (C) when the temperature is kept constant. The concentration of the solution containing one gram mole in V litre is equal to $\frac{1}{V}\left(C=\frac{1}{V}\right)$.

Thus, $$P \propto C \text{ (when temperature is constant)}$$

or $$P \propto \frac{1}{V}$$

or $$PV = \text{constant} \quad \text{or} \quad \pi V = \text{constant}$$

van't Hoff presumed that the osmotic pressure is due to the bombardment of solute molecules against the semipermeable membrane as the gas pressure is due to hits recorded by gas molecules against the walls of its container.

2. Pressure-Temperature law (Gay-Lussac-van't Hoff law): Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), *i.e.*,

$$P \propto T$$

or $$\frac{P}{T} = \text{constant} \quad \text{or} \quad \frac{\pi}{T} = \text{constant}$$

Combining the two laws, *i.e.*, when concentration and temperature both are changing, the osmotic pressure will be given by:

$$P \propto CT$$

or $$P = kCT$$

or $$P = k \cdot \frac{1}{V} \cdot T \qquad \left(\text{since, } C = \frac{1}{V}\right)$$

or $$PV = ST \text{ or } \pi V = ST$$

S is called molar solution constant.

Here, V is the volume of solution containing one gram mole of the solute. The value of S comes out to 0.082 litre atm K^{-1} mol^{-1} which is in agreement with the value of R, the molar gas constant. In case, the solution contains n gram moles in V litre, the general equation would become:

$$PV = nST \text{ or } \pi V = nST$$

3. Third law: Equimolecular solutions of different solutes exert equal osmotic pressure under identical conditions of temperature. Such solutions which have the same osmotic pressure are termed **isotonic or iso-osmotic.** When two isotonic solutions are separated by a semipermeable membrane, no flow of solvent molecules is observed on either side.

The law is similar to Avogadro's hypothesis. It can be stated as, **"Equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure, contain equal number of molecules".**

For solution I, $PV = n_1 ST$

For solution II, $PV = n_2 ST$

Thus, n_1 must be equal to n_2 when P, V and T are same.

The analogy of dilute solutions with gases is thus perfect. This led van't Hoff to suggest **that a solute in dissolved state (*i.e.,* in solution) behaves as a gas and the osmotic pressure of the solution is equal to the pressure which the solute would exert if it were a gas at the same temperature and occupying the same volume as that of the solution.** This statement is known as van't Hoff theory of dilute solutions.

5.15 DETERMINATION OF MOLECULAR MASSES

In the case of dilute solutions, it has been stated that the equation $PV = nST$ holds good. Instead of one gram mole of the solute present in V litre of solution, let w_B gram of solute (mol. mass m_B) be present in V' litre of solution; then

$$n = \frac{w_B}{m_B} \text{ and } V = V'$$

Thus, the equation $PV = nST$ becomes:

$$PV' = \frac{w_B}{m_B} \cdot ST$$

or

$$m_B = \frac{w_B \times S \times T}{PV'}$$

Knowing the value of P experimentally, the value of m_A, *i.e.*, molecular mass of the solute can be determined.

Consider two solutions I and II having n_1 and n_2 moles of the solute in V_1 and V_2 litres of solution respectively. Let P_1 and P_2 be their osmotic pressures at the same temperature (T).

From the equation $PV = nST$,

For solution I, $P_1 V_1 = n_1 ST$

or

$$P_1 = \frac{n_1}{V_1} ST$$

For solution II, $P_2 V_2 = n_2 ST$

or

$$P_2 = \frac{n_2}{V_2} ST$$

If both solutions are isotonic, *i.e.*, $P_1 = P_2$, obviously,

$$\frac{n_1}{V_1} ST = \frac{n_2}{V_2} ST$$

or

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

or

$$\frac{w_1 / m_1}{V_1} = \frac{w_2 / m_2}{V_2}$$

or

$$\frac{w_1}{m_1 \times V_1} = \frac{w_2}{m_2 \times V_2}$$

This is the condition for isotonic solutions.

If molecular mass of one solute is known, the molecular mass of the other can be determined without using osmotic pressure values.

Osmotic pressure of mixture of two solutions:

Case I: Let two solutions of same substance having different osmotic pressures π_1 and π_2 are mixed. Osmotic pressure of the resultant solution can be calculated as,

$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

where, V_1 and V_2 are the volumes of two solutions and π_R is the resultant osmotic pressure.

Case II: Let n_1 and n_2 are the number of moles of two different solutes present in V_1 and V_2 volumes respectively.

Osmotic pressure of the mixture can be calculated as,

$$\pi = \pi_1 + \pi_2 = \frac{n_1 i_1 RT}{(V_1 + V_2)} + \frac{n_2 i_2 RT}{(V_1 + V_2)}$$

$$\pi = \frac{(n_1 i_1 + n_2 i_2)}{(V_1 + V_2)} RT$$

Here, i_1 and i_2 are van't Hoff factor for the two solutes.

Some Solved Examples

Example 49. *200 cm^3 of an aqueous solution contains 1.26 g of a polymer. The osmotic pressure of such solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the polymer.*

Solution:

$$\pi V = \frac{w_B}{m_B} RT$$

$$m_B = \frac{w_B}{V} \times \frac{RT}{\pi}$$

$$= \frac{1.26}{0.2} \times \frac{0.083 \times 300}{2.57 \times 10^{-3}} = 61038 \text{ g mol}^{-1}$$

Example 50. *A solution is prepared by dissolving 1.08 g of human serum albumin, a protein obtained from blood plasma, in 50 cm^3 of aqueous solution. The solution has an osmotic pressure of 5.85 mm Hg at 298 K:*

(a) What is molar mass of albumin?

(b) What is height of water column placed in solution?

$$d(H_2O) = 1 \text{ g } cm^{-3}$$

Solution: (a) Molar mass of albumin can be calculated using following relation:

$$m_B = \frac{w_B \times RT}{\pi V} \quad \text{...(i)}$$

Given, $w_B = 1.08$ g; $R = 0.0821$ litre atm K^{-1} mol^{-1}

$$T = 298 \text{ K}, \pi = \frac{5.85}{760} \text{ atm}; V = \frac{50}{1000} = 0.05 \text{ litre}$$

Substituting these values in eq. (i)

$$m_B = \frac{1.08\times 0.0821\times 298}{(5.85/760)\times 0.05} = 68655 \text{ g/mol}$$

(b)
$$\pi = h\cdot d\cdot g$$
$$\frac{5.85}{760}\times 101325 = h\times 1\times 10^{-3}\times 9.8$$
$$\therefore \quad h = 7.958\times 10^{4}\text{ m} = 7.958\times 10^{6}\text{ cm}$$

Example 51. *Calculate osmotic pressure of 5% solution of cane sugar (sucrose) at 15°C.*

Solution: m = mol. mass of sucrose $(C_{12}H_{22}O_{11}) = 342$

$$w = 5\text{ g},\qquad V = 100\text{ mL} = 0.1\text{ litre}$$
$$S = 0.082,\qquad T = (15+273) = 288\text{ K}$$

Applying the equation $PV = \frac{w}{m}ST$,

$$P = \frac{5}{342}\times\frac{1}{0.1}\times 0.082\times 288$$
$$= 3.453\text{ atm}$$

Example 52. *The solution containing 10 g of an organic compound per litre showed an osmotic pressure of 1.18 atmosphere at 0°C. Calculate the molecular mass of the compound ($S = 0.0821$ litre atm per degree per mol).*

Solution: Applying the equation,

$$m = \frac{w}{PV}\cdot ST$$

Given, $w = 10$ g, $P = 1.18$ atm, $V = 1$ litre, $S = 0.0821$ and $T = 273$ K.

$$m = \frac{10}{1.18\times 1}\times 0.0821\times 273 = 189.94$$

Example 53. *The osmotic pressure of a solution containing 30 g of a substance in 1 litre solution at 20°C is 3.2 atmosphere. Calculate the value of S. The molecular mass of solute is 228.*

Solution: Applying the equation,

$$PV = \frac{w}{m}\cdot ST$$

or
$$S = \frac{m\times P\times V}{w\times T}$$

Given, $m = 228, P = 3.2$ atm, $V = 1$ litre, $w = 30$ g and

$$T = 20+273 = 293\text{ K}$$
$$S = \frac{228\times 3.2\times 1}{30\times 293}$$
$$= 0.083\text{ litre atm per degree per mol}$$

Example 54. *What is the volume of solution containing 1 g mole of sugar that will give rise to an osmotic pressure of 1 atmosphere at 0°C?*

Solution: Applying the equation $PV = n\cdot ST$,

$$V = \frac{n}{P}\times S\times T$$

Given, $n = 1, P = 1$ atm, $S = 0.0821$ and $T = 273$ K

$$V = \frac{1}{1}\times 0.0821\times 273 = 22.4\text{ litre}$$

Example 55. *Find the osmotic pressure of M/20 solution of urea at 27°C ($S = 0.0821$ lit atm K^{-1} mol^{-1}).*

Solution: Applying the equation $PV = n\cdot ST$,

$$P = \frac{n}{V}\cdot ST$$

or
$$P = \text{Molarity}\times S\times T$$

Given,

molarity $= \frac{1}{20} = 0.05, S = 0.0821$ and $T = 27+273 = 300$ K

Substituting values,

$$P = 0.05\times 0.0821\times 300 = 1.2315\text{ atm}$$

Example 56. *The osmotic pressure of a solution of an organic substance containing 18g in one litre of solution at 293 K is 2.414×10^{5} Nm^{-2}. Find the molecular mass of the substance if $S = 8.3\,JK^{-1}$ per mol.*

Solution: Applying the equation,

$$PV = \frac{w}{m}\cdot ST$$

or
$$m = \frac{w}{PV}\cdot ST$$

Given, $P = 2.414\times 10^{5}\text{ Nm}^{-2}, V = 1.0\text{ lit} = 1\times 10^{-3}\text{ m}^{3}$,

$S = 8.3\text{ JK}^{-1}$ per mol, $w = 18$ g and $T = 293$ K

$$m = \frac{18}{2.414\times 10^{5}\times 1\times 10^{-3}}\times 8{,}3\times 293 = 181.33$$

Example 57. *A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea if the molecular mass of cane sugar is 342.*

Solution: Let the molecular mass of urea be m_2.

$$\text{Molar concentration of sugar} = \frac{w_1}{m_1\times V_1} = \frac{5}{342\times 0.1}$$

and
$$\text{Molar concentration of urea} = \frac{w_2}{m_2\times V_2} = \frac{0.877}{m_2\times 0.1}$$

For isotonic solutions,

$$\frac{w_1}{m_1V_1} = \frac{w_2}{m_2V_2}$$
$$\frac{5}{342\times 0.1} = \frac{0.877}{m_2\times 0.1}$$
$$m_2 = \frac{0.877\times 342}{5} = 59.987$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

32. Find out the osmotic pressure of 0.25 *M* aqueous solution of urea at 27°C ($R = 0.082$ litre atm $K^{-1}mol^{-1}$, $R = 1.987$ cal $K^{-1}mol^{-1}$). **[CET (Gujarat) 2008]**
(a) 6.15 atm (b) 0.615 atm (c) 0.0615 atm (d) 61.5 atm
[Ans. (a)]

[Hint : $\pi = CRT$

$$= 0.25 \times 0.0821 \times 300$$
$$= 6.157 \text{ atm}]$$

33. Two solutions of glucose have osmotic pressures 1.5 and 2.5 atm. 1 litre of first solution is mixed with 2 litre of second solution. The osmotic pressure of the resultant solution will be:

(a) 1.62 atm (b) 6.12 atm (c) 1.26 atm (d) 2.16 atm

[Ans. (d)]

[Hint: $\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$

$$1.5 \times 1 + 2.5 \times 2 = \pi_R \times 3$$
$$\pi_R = \frac{6.5}{3} = 2.16 \text{ atm}]$$

34. 18 g glucose and 6 g urea are dissolved in 1 litre aqueous solution at 27°C. The osmotic pressure of the solution will be:

(a) 3.826 atm (b) 4.926 atm

(c) 2.92 atm (d) 9.42 atm

[Ans. (b)]

[Hint: $\pi V = (n_1 + n_2)RT$

$$\pi V = \left(\frac{w_1}{m_1} + \frac{w_2}{m_2}\right) RT$$
$$\pi \times 1 = \left(\frac{18}{180} + \frac{6}{60}\right) \times 0.0821 \times 300$$
$$\pi = 4.926 \text{ atm}]$$

35. A solution containing 10 g per dm^3 of urea (m.w. = 60) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is:

[CBSE (Medical) 2006]

(a) 250 g mol^{-1} (b) 300 g mol^{-1}

(c) 350 g mol^{-1} (d) 200 g mol^{-1}

[Ans. (b)]

[Hint: π_1 (urea) = π_2 (unknown solute)

$$C_1 \text{ (urea)} = C_2 \text{ (unknown solute)}$$
$$\left[\frac{w_B \times 1000}{m_B \times V}\right]_{\text{urea}} = \left[\frac{w_B \times 1000}{m_B \times V}\right]_{\text{unknown solute}}$$
$$\frac{10 \times 1000}{60 \times 1000} = \frac{5 \times 1000}{m_B \times 100}$$
$$m_B = 300 \text{ g mol}^{-1}]$$

36. The osmotic pressure of a solution at 0°C is 4 atm. What will be its osmotic pressure at 546 K under similar conditions?

(a) 4 atm (b) 2 atm (c) 8 atm (d) 1 atm

[Ans. (c)]

[Hint: $\frac{\pi_1}{\pi_2} = \frac{CRT_1}{CRT_2}$

$$\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$$
$$\frac{4}{\pi_2} = \frac{273}{546}$$
$$\pi_2 = 8 \text{ atm}]$$

37. The temperature at which 10% aqueous solution $\left(\frac{W}{V}\right)$ of glucose will exhibit the osmotic pressure of 16.4 atm, is :
($R = 0.082 \text{ dm}^3 \text{ atm K}^{-1}\text{mol}^{-1}$) **[PMT (Kerala) 2008]**

(a) 360°C (b) 180 K (c) 90 K (d) 300 K

(e) 360 K

[Ans. (e)]

[Hint : $\pi V = nRT$

$$\pi V = \frac{W}{m} RT$$
$$16.4 \times \left(\frac{100}{1000}\right) = \frac{10}{180} \times 0.082 \times T$$
$$\therefore \quad T = 360 \text{ K}]$$

5.16 REVERSE OSMOSIS

When a solution is separated from pure water by a semipermeable membrane, water moves towards the solution on account of osmosis. This process continues till osmotic pressure becomes equal to hydrostatic pressure or osmosis can be stopped by applying external pressure equal to osmotic pressure on solution. If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, *i.e.*, in reverse direction of the ordinary osmosis. This type of osmosis is termed **reverse osmosis.** Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

5.17 ABNORMAL COLLIGATIVE PROPERTIES

The colligative properties of solutions depend on the number of solute particles present in solution. Various relations derived for colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case, the total number of particles of the solute changes in solution, the colligative property shall also change accordingly. The number of particles in solution may change in two ways:

(i) By dissociation: When the substance is an electrolyte, *i.e.*, the substance undergoes ionisation and number of particles increases in solution, the ions act as particles. The number of particles, thus, increases on ionisation and the value of colligative property increases accordingly.

(ii) By association: When the substance undergoes association, *i.e.*, two or more molecules of the solute associate to form a single giant particle, the number of particles decreases and consequently the value of colligative property decreases. Thus,

Normal value of colligative property
∝ No. of particles of solute taken

Abnormal value of colligative property
∝ No. of particles of solute after ionisation or association

Thus, the ratio, $\frac{\text{Abnormal colligative property}}{\text{Normal colligative property}}$, may have the value either more than 1 or less than 1. The ratio is termed **van't Hoff factor** which is represented by '*i*'. Thus,

Table 5.6 Illustrations of van't Hoff Factor 'i' for Different Solutes

S. No.	Solute type	Example	Ionisation or association	No. of particles in the solution from 1 mole solute	van't Hoff factor 'i'	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose	—	1	1	m_{normal}
2.	Binary electrolyte AB type	NaCl, KCl CH_3COOH, etc.	$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A^+} + \underset{\alpha}{B^-}$	2	$1+\alpha$	$\frac{m_{\text{normal}}}{1+\alpha}$
3.	Ternary electrolyte AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$ H_2SO_4, $K_2[PtCl_6]$	$\underset{1-\alpha}{AB_2} \rightleftharpoons \underset{\alpha}{A^{2+}} + \underset{2\alpha}{2B^-}$	3	$1+2\alpha$	$\frac{m_{\text{normal}}}{1+2\alpha}$
			$\underset{1-\alpha}{A_2B} \rightleftharpoons \underset{2\alpha}{2A^+} + \underset{\alpha}{B^{2-}}$	3	$1+2\alpha$	$\frac{m_{\text{normal}}}{1+2\alpha}$
4.	Quaternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_3]$ $FeCl_3$, K_3PO_4	$\underset{1-\alpha}{AB_3} \rightleftharpoons \underset{\alpha}{A^{3+}} + \underset{3\alpha}{3B^-}$	4	$1+3\alpha$	$\frac{m_{\text{normal}}}{1+3\alpha}$
			$\underset{1-\alpha}{A_3B} \rightleftharpoons \underset{3\alpha}{3A^+} + \underset{\alpha}{B^{3-}}$	4	$1+3\alpha$	$\frac{m_{\text{normal}}}{1+3\alpha}$
5.	Association of solute	Benzoic acid forming dimer in benzene	$\underset{1-\alpha}{nA} \rightleftharpoons \underset{\frac{\alpha}{n}}{An}$	$\frac{1}{n}$	$\left[1-\left(1-\frac{1}{n}\right)\alpha\right]$	$\frac{m_{\text{normal}}}{\left[1-\left(1-\frac{1}{n}\right)\alpha\right]}$
6.	General electrolyte AB_{n-1}	One mole of solute giving n ions in the solution	$\underset{1-\alpha}{AB_{n-1}} \rightleftharpoons \underset{\alpha}{A^{+(n-1)}} + \underset{(n-1)\alpha}{(n-1)\,B^-}$	n	$[1+(n-1)\alpha]$	$\frac{m_{\text{normal}}}{[1+(n-1)\alpha]}$

$$i = \frac{P_{\text{obs.}}}{P_{\text{normal}}} = \frac{(\Delta p)_{\text{obs.}}}{(\Delta p)_{\text{normal}}}$$

$$= \frac{(\Delta T_b)_{\text{obs.}}}{(\Delta T_b)_{\text{normal}}} = \frac{(\Delta T_f)_{\text{obs.}}}{(\Delta T_f)_{\text{normal}}}$$

$$= \frac{\text{Actual no. of particles in solution}}{\text{No. of particles taken}}$$

(i) Suppose one molecule of an electrolyte gives 'n' ions on dissociation and 'α' is its degree of ionisation. Obviously,

$$\text{Number of ions produced} = n\alpha$$

and $$\text{Number of unionised molecules} = 1-\alpha$$

$$\text{Total number of particles in solution} = 1-\alpha+n\alpha$$

$$= 1+(n-1)\alpha$$

Thus,

$$\text{van't Hoff factor '}i\text{'} = \frac{1+(n-1)\alpha}{1} > 1 \text{ if } n \text{ is 2 or more}$$

and $$\alpha = \frac{i-1}{n-1}$$

(ii) Suppose 'n' molecules associate to form one giant molecule and 'α' is the degree of association; then .

$$\underset{(1-\alpha)}{nA} \rightleftharpoons \underset{\alpha/n}{(A)_n}$$

$$\text{Total number of particles in solution} = 1-\alpha+\alpha/n$$

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

Thus, $$\text{van't Hoff factor '}i\text{'} = \frac{1+\left(\frac{1}{n}-1\right)\alpha}{1} < 1 \text{ if } n \text{ is 2 or more}$$

$$\alpha = \frac{1-i}{1-1/n}$$

As, $$\text{Colligative property} \propto \frac{1}{\text{mol. mass}}$$

So, $$\frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

Thus, $$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

In case of dissociation,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1+(n-1)\alpha > 1$$

Observed mol. mass will always be less than normal mol. mass.

In case of association,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1+\left(\frac{1}{n}-1\right)\alpha < 1$$

Observed mol. mass will always be higher than normal mol. mass.

Relation between osmotic pressure and vapour pressure

Let an aqueous dilute solution filled in a capillary tube is closed at one end by a semipermeable membrane. The tube is placed in pure solvent (water). Entire apparatus is closed by a belljar. At osmotic equilibrium, the belljar is saturated with water vapour. At equilibrium osmotic pressure (π) becomes equal to hydrostatic pressure.

$$\pi = h \times d \qquad \text{... (i)}$$

where 'h' is height in the column, π is osmotic pressure.

Let, p_0 = Vapour pressure of pure solvent

p = Vapour pressure of solution

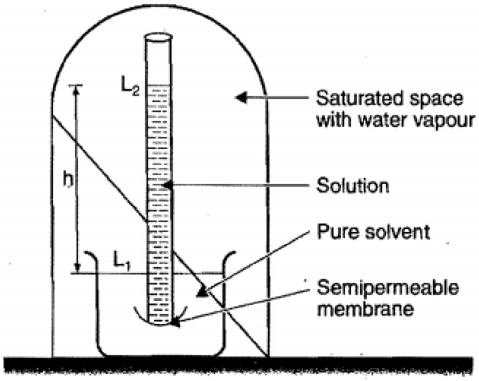

Fig. 5.16

Pressure at level $L_1 = p_0$; Pressure at level $L_2 = p$. Pressure at L_1 will be greater than pressure at L_2. Then

$$p_0 - p = hD \qquad \text{... (ii)}$$

where 'D' is density of solvent vapour at pressure p_0.

Dividing eq. (i) by eq. (ii), we have,

$$\frac{\pi}{p_0 - p} = \frac{hd}{hD} = \frac{d}{D}$$

at a fixed temperature d/D is constant.

$$\therefore \qquad \pi = \text{constant}\ (p_0 - p) \qquad \text{... (iii)}$$

$$i.e., \qquad \pi \propto (p_0 - p) \text{ or } \Delta p \qquad \text{... (iv)}$$

Thus, *osmotic pressure is directly proportional to the lowering of vapour pressure.*

We know that,

$$p_0 V = nRT$$

$$p_0 V = \frac{W}{M} RT$$

$$i.e., \qquad p_0 M = \frac{W}{V} RT = DRT$$

$$\therefore \qquad p_0 = \frac{RTD}{M} \qquad \text{... (v)}$$

Dividing eq. (iii) by eq. (v), we get

$$\frac{p_0 - p}{p_0} = \pi \times \frac{D}{d} \times \frac{M}{RTD}$$

$$\frac{\Delta p}{p_0} = \pi \frac{M}{dRT}$$

At a fixed temperature, π and $\frac{M}{dRT}$ is constant.

Thus, $\frac{\Delta p}{p_0} \propto \pi$, *i.e., osmotic pressure is proportional to relative lowering of vapour pressure.*

Partial pressure of immiscible liquids

Let 'A' and 'B' be the two volatile and immiscible liquids; p_A and p_B be the partial pressures of 'A' and 'B' respectively.

Then,
$$\frac{p_A}{p_B} = \frac{n_A}{n_B}$$

where, M_A and M_B are molar concentrations of 'A' and 'B' respectively.

$$\frac{p_A}{p_B} = \frac{W_A / m_A}{W_B / m_B}$$

where, W_A and W_B are weights of 'A' and 'B', m_A and m_B are molecular weights of 'A' and 'B' respectively.

Example 58. *Phenol associates in benzene to a certain extent for a dimer. A solution containing 20×10^{-3} kg of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. Calculate the fraction of the phenol that has dimerised (K_f of benzene is 5.12°K kg mol^{-1}).*

Solution: Observed mol. mass

$$= \frac{1000 \times K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 20 \times 10^{-3}}{1 \times 0.69} = 148.4$$

Normal mol. mass of phenol (C_6H_5OH) = 94

$$\text{So,} \qquad \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = \frac{94}{148.4}$$

$$= 1 + \left(\frac{1}{n} - 1\right)\alpha = 1 + \left(\frac{1}{2} - 1\right)\alpha$$

$$\frac{94}{148.4} = 1 - \frac{\alpha}{2}$$

$$\text{or} \qquad \alpha = 0.733 \quad \text{or} \quad 73.3\%$$

Example 59. *The freezing point depression of 0.001 m $K_x[Fe(CN)_6]$ is 7.10×10^{-3} K. Determine the value of x. Given, $K_f = 1.86$ K kg mol^{-1} for water.*

Solution:
$$\Delta x = i \times K_f \times m$$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

$$\alpha = \frac{i - 1}{n - 1}$$

$$1 = \frac{3.817 - 1}{(x + 1) - 1}$$

$$x = 2.817 \approx 3$$

$\therefore$ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

Example 60. *A $\frac{M}{10}$ solution of potassium ferrocyanide is 46% dissociated at 18°C. What will be its osmotic pressure?*

Solution: Normal osmotic pressure $= \frac{w}{m\times V}\times S\times T$

(when no dissociation has taken place)

$\frac{w}{m}=0.1, V=1\,\text{litre},\ S=0.0821, T=18+273=291\,\text{K}$

Normal osmotic pressure $=\frac{0.1}{1}\times 0.0821\times 291 = 2.389$ atm

Potassium ferrocyanide is an electrolyte. It dissociates as:

$$\underset{(1-\alpha)}{K_4Fe(CN)_6} \rightleftharpoons \underset{4\alpha}{4K^+} + \underset{\alpha}{[Fe(CN)_6]^{4-}}$$

Total number of particles $= 1-\alpha+4\alpha+\alpha = 1+4\alpha$

$\alpha = 0.46$; so, $1+4\alpha = 1+4\times 0.46 = 2.84$

$$\frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \frac{2.84}{1}$$

Observed osmotic pressure $= 2.84\times 2.389$

$= 6.785$ atm

Example 61. *A 0.5% aqueous solution of KCl was found to freeze at* $-0.24°$ *C. Calculate the van't Hoff factor and degree of dissociation of the solute at this concentration* (K_f *for water* $= 1.86\,K\,kg\,mol^{-1}$).

Solution: Observed mol. mass of KCl $=\frac{1000\times K_f\times w}{\Delta T\times W}$

Given, $K_f = 1.86\,\text{K kg mol}^{-1}, w = 0.5\,\text{g}, W = 100\,\text{g}, \Delta T = 0.24$

So, Observed mol. mass of KCl $=\frac{1000\times 1.86\times 0.5}{0.24\times 100} = 38.75$

Normal mol. mass of KCl $= 39+35.5 = 74.5$

$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

$$=\frac{74.5}{38.75} = 1.92$$

$$\underset{(1-\alpha)}{KCl} \rightleftharpoons \underset{\alpha}{K^+} + \underset{\alpha}{Cl^-}$$ (α is the degree of ionisation)

Total number of particles $= 1-\alpha+\alpha+\alpha = 1+\alpha$

$$i = 1+\alpha$$

$$1.92 = 1+\alpha$$

So, $\alpha = 1.92-1 = 0.92$

i.e., 92% dissociated.

Example 62. *The freezing point of a solution containing 0.2 g of acetic acid in 20 g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene* (K_f *for benzene is* $5.12\,K\,kg\,mol^{-1}$). **(IIT 1994)**

Solution: Let the observed molecular mass of acetic acid be m_{obs}.

$$m_{obs.} = \frac{1000\times K_f\times w}{W\times\Delta T}$$

$$=\frac{1000\times 5.12\times 0.2}{20\times 0.45} = 113.78$$

Normal molecular mass of acetic acid = 60

$$\begin{array}{lccc} & 2CH_3COOH & \rightleftharpoons & (CH_3COOH)_2 \\ \text{Before association} & 1 & & 0 \\ \text{After association} & (1-\alpha) & & \alpha/2 \end{array}$$

$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Obs. mol. mass}}$$

$$=\frac{1-\alpha+\alpha/2}{1}$$

$$\frac{60}{113.78} = 1-\frac{\alpha}{2}$$

or $\alpha = 0.945$

or 94.5% associated.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

38. 0.002 molar solution of NaCl having degree of dissociation of 90% at 27°C has osmotic pressure equal to:

(a) 0.94 bar
(b) 9.4 bar
(c) 0.094 bar
(d) 9.4×10^{-4} bar

[Ans. (c)]

[Hint: $\alpha = \frac{i-1}{n-1}$

$0.9 = \frac{i-1}{2-1}$; $i = 1.9$

$\pi = iCRT$

$= 1.9\times 0.002\times 0.082\times 300$

$= 0.094$ bar]

39. A 0.2 molal solution of KCl freezes at − 0.68°C. If K_f for H_2O is 1.86, the degree of dissociation of KCl is:

(a) 75%
(b) 83%
(c) 65%
(d) 92%

[Ans. (b)]

[Hint: $\Delta T = i\times K_f\times m$

$0.68 = i\times 1.86\times 0.2$

$i = 1.83$

$\alpha = \frac{i-1}{n-1}$

$= \frac{1.83-1}{2-1} = 0.83$

Ionization = 83%]

40. A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is:

(a) 122
(b) 31
(c) 244
(d) 62

[Ans. (d)]

[Hint: $\alpha = \frac{1-i}{1-\frac{1}{n}}$

$0.8 = \frac{1-i}{1-\frac{1}{4}}$; $i = 0.4$

$$\Delta T = iK_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$m_B = 62$]

41. van't Hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution):

(a) 1.6 (b) 2.6 (c) 3.6 (d) 4.6

[**Ans.** (b)]

[**Hint:** $Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$

$$n = 3$$

$$\alpha = \frac{i-1}{n-1}$$

$$0.8 = \frac{i-1}{3-1}$$

$i = 2.6$]

42. 0.1 *M* aqueous solution of $MgCl_2$ at 300 K is 4.92 atm. What will be the percentage ionization of the salt?

(a) 49% (b) 29% (c) 39% (d) 69%

[**Ans.** (a)]

[**Hint:** $\pi = iCRT$

$$4.92 = i \times 0.1 \times 0.0821 \times 300$$

$$i = 1.99$$

$$\alpha = \frac{i-1}{n-1}$$

$$= \frac{1.99-1}{3-1} = \frac{0.99}{2} = 0.49$$

Percentage ionization = 49%]

43. Which of the following solutions will exhibit highest boiling point? **(KCET 2006)**

(a) 0.01 *M* Na_2SO_4 (b) 0.01 *M* KNO_3

(c) 0.015 *M* urea (d) 0.015 *M* glucose

[**Ans.** (a)]

[**Hint:** $\Delta T = i \times k_b \times m$

$i \times m$ of Na_2SO_4 is highest, hence its boiling point will also be highest.

Na_2SO_4	$i \times m = 3 \times 0.01 = 0.03$
KNO_3	$i \times m = 2 \times 0.01 = 0.02$
Urea	$i \times m = 1 \times 0.015 = 0.015$
Glucose	$i \times m = 1 \times 0.015 = 0.015$]