CHAPTER 02

Solutions

1. A **solution** is a homogeneous mixture of two or more substances whose composition can be varied within certain limits.
2. **Expression of concentration** Composition of a solution can be described by expressing its concentration.

   Several ways to describe the concentration of the solution quantitatively are as follows :

   - Percentage by mass (w/w)
   $$= \frac{\text{Mass of component in the solution}}{\text{Total mass of the solution}} \times 100$$
   - Percentage by volume (V/V)
   $$= \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100$$
   - Parts per million (ppm)
   $$= \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$
   - **Mole fraction** (χ) is the ratio of number of moles of one component to the total number of moles of all the components present in the solution.
     Mole fraction of solute,
   $$\chi_{(\text{solute})} = \frac{n_{(\text{solute})}}{n_{(\text{solute})} + n_{(\text{solvent})}}$$
     It is independent of temperature.

   For a given solution, sum of mole fractions of all the components of a solution is unity, i.e.
   $$\boxed{\chi_1 + \chi_2 + \ldots + \chi_i = 1}$$
   - **Molarity** (M) is defined as the number of moles of solute dissolved in one litre or one cubic decimetre of the solution.
   $$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}}$$
   - **Normality** (N)
   $$= \frac{\text{Number of gram-equivalent of solute}}{\text{Volume of solution (in L)}}$$
   where,
   $$\text{g-equivalents} = \frac{\text{mass of solute } (W)}{\text{equivalent weight of solute } (E)}$$
   $$\text{Normality} \times \text{equivalent weight} = \text{Molarity} \times \text{molecular weight}$$
   - **Molality** (m) is defined as the number of moles of the solute per kilogram of the solvent.
   $$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

   (Molality, mole fraction, mass fraction, etc. are preferred over molarity, normality, etc. because they are temperature independent).
3. **Solubility** of a substance is its maximum amount that can be dissolved (in a specified amount of solvent) at a specified temperature. It depends upon the nature of solute and solvent at a specified temperature and pressure.
4. **Henry's law** states that, the partial pressure of the gas (p) is proportional to the mole fraction of the gas (χ) in the solution.

   Mathematically, it is expressed as
   $$p \propto \chi \quad \text{or} \quad p = K_H \chi$$
   where, K_H is called Henry's law constant.

   Higher the value of K_H at a particular temperature, lower is the solubility of the gas in the liquid.

   Solubility of gas decreases with increase in temperature. This is the reason that aquatic species are more comfortable in cold water rather than in warm water.
5. The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called **vapour pressure**.
6. **Raoult's law** states that at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution, i.e. $p_1 \propto \chi_1$ and $p_1 = p_1^\circ \chi_1$.

   For a solution of two miscible components, 1 and 2,
   $$p_{\text{total}} = p_1 + p_2 = p_1^\circ \chi_1 + p_2^\circ \chi_2$$
   As we know, $\chi_1 + \chi_2 = 1$ or $\chi_1 = 1 - \chi_2$,
   $$p_{\text{total}} = p_1^\circ + (p_2^\circ - p_1^\circ)\,\chi_2$$

7. Solutions obeying Raoult's law over a entire range of concentration are called **ideal solutions** and those do not obey this law are called **non-ideal solutions**.

For positive deviation,

$A—B$ interaction $<$ $A—A$ or $B—B$ interactions

e.g. CS_2 + acetone, acetone + benzene.

For negative deviation,

$A—B$ interaction $>$ $A—A$ or $B—B$ interactions

e.g. chloroform + acetone, chloroform + benzene.

8. Azeotropes are binary mixtures having same composition in liquid and vapour phase and boil at constant temperature. There are two types of azeotropes which are:

- **Minimum boiling azeotropes** These solutions show positive deviation from Raoult's law, e.g. ethanol-water mixture.
- **Maximum boiling azeotropes** These solutions show large negative deviation from Raoult's law, e.g. nitric acid-water mixture.

9. The properties of solutions which depend only on the number of solute particles, not on the nature of the solute particles are known as **colligative properties**.

These properties are as follows:

- **Relative lowering of vapour pressure** in an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temperature.

$$\boxed{\chi_2 = \frac{\Delta p_1}{p_1^\circ} = \frac{p_1^\circ - p_1}{p_1^\circ}} \quad \text{or} \quad \boxed{\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{W_2 M_1}{W_1 M_2}}$$

Here, component number (1) is solvent and component number (2) is solute, W_1 and W_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute, respectively.

- **Elevation of boiling point** (ΔT_b) (Ebullioscopy) is the difference in the boiling points of the solution (T_b) and pure solvent (T_b°). It depends on the number of solute particles rather than on their nature.

$$\Delta T_b = T_b - T_b^\circ$$

Experimentally, $\Delta T_b \propto m$ or $\Delta T_b = K_b \cdot m$

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

K_b = molal boiling point elevation constant or ebullioscopic constant (in K kg mol^{-1}).

- **Depression in freezing point** (ΔT_f) (Cryoscopy) is the decrease in the freezing point of solution when non-volatile solute is dissolve in it.

Thus, $\Delta T_f = T_f^\circ - T_f$

or $\Delta T_f = K_f \times m = K_f \times \dfrac{W_2 \times 1000}{M_2 \times W_1}$

where, m = molality and K_f = freezing point depression constant or cryoscopic constant (K kg mol^{-1}).

- **Osmosis** is a process which involves the flow of solvent molecules through a semipermeable membrane from pure solvent to the solution and **osmotic pressure** of the solution (π) is the pressure that just stops the flow of solvent.

$$\pi = CRT \quad \Rightarrow \quad \pi = \frac{W_2 RT}{VM_2} \quad (C = \text{Molarity})$$

10. **Isotonic solutions** are the solutions having same osmotic pressure at a given temperature. In case of two solutions of different osmotic pressures, the solution with higher osmotic pressure is called **hypertonic solution** and that with lower osmotic pressure is called **hypotonic solution.**

11. **Phenomena on the basis of osmosis** People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. This resulting puffiness or swelling is called **edema**.

12. In **reverse osmosis,** the solvent flows from solution side towards pure solvent, if external pressure is higher than osmotic pressure applied on solution side. It is used for desalination of sea water. Solvent moves from solution to pure solvent side.

13. Molar masses that are either lower or higher than the calculated (expected) or normal value are called **abnormal molar masses**.

14. **van't Hoff factor** (i) is defined as the ratio of the experimental or observed value of the colligative property to the calculated value of the colligative property.

$$\text{or} \quad i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

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

In case of association/dissociation, i is also introduced in the formula of colligative properties. *These are as follows :*

i.e. $\Delta T_b = iK_b \cdot m;\ \Delta T_f = iK_f \cdot m$

$$\pi = iCRT \quad \text{and} \quad \frac{p_1^\circ - p_1}{p_1^\circ} = i\,\chi_{\text{solute}}$$

15. **Degree of Dissociation/Association** (α) **and van't Hoff Factor** (i)

α = degree of dissociation/association

- Degree of dissociation $\alpha = \dfrac{i-1}{n-1}$

  n = number of particles per molecules.

- Degree of association $\alpha = \dfrac{i-1}{\left(\dfrac{1}{n}-1\right)}$

  $i = 1$, for non electrolytes; $i > 1$, for dissociation; $i < 1$, for association.

16. **Some Important Facts**

- Intramolecular H-bonding lowers boiling point.
- Benzoic acid and acetic acid dimerises in benzene.
- When egg is kept in saturated salt solution after removing the hard shell using dil. HCl, egg will shrink due to osmosis.

- $CaCl_2$ acts as a non-volatile solute and results depression in freezing point. Thus, snow is reduced (as it melts) and prevents blocking of roads in cold region.
- Ethylene glycol is mixed with radiator water to decrease the freezing point of water in cold region.
- Camphor is used for molecular mass determination due to its volatile nature.
- To increase the solubility of CO_2 in soft drinks, the bottle is sealed under high pressure.
- Helium-oxygen mixture is used by deep sea divers because of its low solubility in blood.

Practice Questions

1. If two bottles *A* and *B* contain 1 M and 1 m aqueous solution of sulphuric acid respectively,

(a) *A* is more concentrated than *B*
(b) *B* is more concentrated than *A*
(c) concentration of *A* is equal to concentration of *B*
(d) it is not possible to compare the concentration

2. What is the percentage of solute in the resultant solution, if it is obtained by mixing 300g of 30% and 200g of 20% solution by weight?

(a) 50% *(b)* 26%
(c) 62% *(d)* 32%

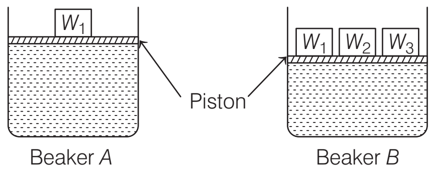
3. What is the molarity of K^+ in aqueous solution that contains 17.4 ppm of K_2SO_4 (Molar mass $=174 \text{ g mol}^{-1}$) ?

(a) 2×10^{-2} M *(b)* 2×10^{-3} M
(c) 4×10^{-4}M *(d)* 2×10^{-4}M

4. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH is supplied. What is the mole fraction of methyl alcohol in the solution?

(a) 1.100 *(b)* 0.090
(c) 0.086 *(d)* 0.050

5. For a solution of gases in a solvent, consider a system as shown below :



Which of the following beaker will have the greater solubility of a gas?

(a) Beaker *B*
(b) Beaker *A*
(c) Both will have same solubility
(d) Solubility remains unaffected by change in weights.

6. Calculate the concentration of nitrogen present in the water. Assuming that, the temperature is 25°C, total pressure is 1 atm and mole fraction of nitrogen is 0.78. [K_H for nitrogen $= 8.42\times10^{-7}$ M/mm Hg]

(a) 4.99 M *(b)* 4.99×10^{-2} M
(c) 4.99×10^{-4} M *(d)* None of these

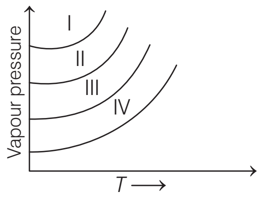
7. The solubility of N_2 in water at 300 K and 500 torr partial pressure is 0.01g L^{-1}. The solubility in (g L^{-1}) at 750 torr partial pressure is

(a) 0.02 *(b)* 0.015 *(c)* 0.0075 *(d)* 0.005

8. When a binary solution of two volatile liquids is taken in a closed vessel, then

(a) Both the components would evaporate and an equilibrium would be established between vapour phase and liquid phase
(b) Both the components would evaporate but equilibrium would not be established between vapour phase and liquid phase
(c) None of components would evaporate and no equilibrium would be established between vapour phase and liquid phase
(d) None of the above

9. The following diagram shows the vapour pressure curves for CH_3F, CH_3OH, CH_3COOH and HCHO



Curves I, II, III and IV respectively are

(a) CH_3F; HCHO; CH_3OH; CH_3COOH
(b) CH_3COOH; CH_3OH; CH_3F; HCHO
(c) HCHO; CH_3F; CH_3OH; CH_3COOH
(d) CH_3OH; CH_3COOH; HCHO; CH_3F

10. Raoult's law becomes a special case of Henry's law, when

(a) $K_H = p_i^\circ$ *(b)* $K_H > p_i^\circ$
(c) $K_H < p_i^\circ$ *(d)* $K_H \geq p_i^\circ$

11. At 300 K two pure liquids A and B have 150 mm Hg and 100 mm Hg vapour pressures, respectively. In an equimolar liquid mixture of A and B, the mole fraction of B in the vapour mixture at this temperature is

(a) 0.6　　*(b)* 0.5
(c) 0.8　　*(d)* 0.4

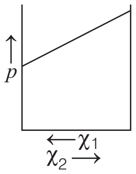
12. The vapour pressure of pure $CHCl_3$ and CH_2Cl_2 are 200 and 41.5 atm respectively. The weight of $CHCl_3$ and CH_2Cl_2 are respectively 11.9 g and 17 g. The vapour pressure of solution will be

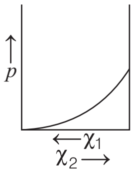
(a) 80.5 atm *(b)* 79.5 atm *(c)* 94.3 atm *(d)* 105.5 atm

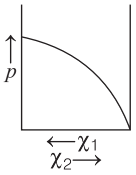
13. For an ideal solution, the correct option is

(a) $\Delta_{mix} V \neq 0$ at constant T and p
(b) $\Delta_{mix} H = 0$ at constant T and p
(c) $\Delta_{mix} G = 0$ at constant T and p
(d) $\Delta_{mix} S = 0$ at constant T and p

14. For a binary ideal liquid solution, the variation in total vapour pressure *versus* composition of solution is given by which of the curves?

(a) 

(b) 

(c) 

(d) Both (a) and (b)

15. The solution which show large positive deviation from Raoult's law form

(a) maximum boiling azeotrope at a specific composition.
(b) maximum freezing azeotrope at a specific composition.
(c) minimum boiling azeotrope at a specific composition.
(d) minimum freezing azeotrope at a specific composition.

16. The examples of minimum boiling azeotropes are

(a) aniline + acetone　　*(b)* acetic acid + pyridine
(c) HCl + water　　*(d)* cyclohexane + ethanol

17. The solution that forms maximum boiling azeotrope is

(a) carbon disulphide – acetone
(b) benzene – toluene
(c) acetone – chloroform
(d) *n*-hexane – *n*-heptane

18. Relative lowering of vapour pressure is a colligative property because

(a) it depends on the concentration of a non-electrolyte solute in solution and does not depend on the nature of the solute molecules
(b) it depends on number of particles of electrolytic solute in solution as well as on the nature of the solute particles
(c) it depends on the concentration of a non-electrolyte solute in solution as well as on the nature of the solute molecules
(d) it depends on the concentration of an electrolyte or non-electrolyte solute in solution as well as on the nature of solute molecules

19. At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mm Hg, lowering of vapour pressure will be (Molar mass of urea = 60 g mol^{-1})

(a) 0.027 mm Hg　　*(b)* 0.031 mm Hg
(c) 0.017 mm Hg　　*(d)* 0.028 mm Hg

20. Vapour pressure of pure benzene is 119 torr and that of toluene is 37.0 torr at the same temperature. Mole fraction of toluene in vapour phase which is in equilibrium with solution of benzene and toluene having a mole fraction of toluene 0.50, will be

(a) 0.137　　*(b)* 0.237
(c) 0.435　　*(d)* 0.205

21. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at $-6°$ C will be (K_f for water = 1.86 K kg mol^{-1} and molar mass of ethylene glycol = 62 g mol^{-1})

(a) 804.32 g　　*(b)* 204.30 g
(c) 400.00 g　　*(d)* 304.60 g

22. Osmotic pressure method is used to determine molar mass of protein, macromolecules like polymers, biomolecules etc., because

(a) osmotic pressure is measured at room temperature
(b) osmotic pressure depends upon molality
(c) these are not stable at higher temperature and have poor solubility
(d) All of the above

23. The van't Hoff factor (i) for a compound which undergoes dissociation in one solvent and association in other solvent is respectively

(a) greater than one and greater than one
(b) less than one and greater than one
(c) less than one and less than one
(d) greater than one and less than one

24. If boiling point of water is 100°C. How much gram of NaCl is added in 500 g of water to increase its boiling point by approx 1°C? $[(K_b)_{H_2O} = 0.52 \text{ K kg mol}^{-1}]$

(a) 2.812 g　　*(b)* 28.12 g
(c) 14.06 g　　*(d)* 7.03 g

25. The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M $BaCl_2$ in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L^{-1}) in solution is

(a) 4×10^{-2}
(b) 16×10^{-4}
(c) 4×10^{-4}
(d) 6×10^{-2}

ANSWERS

1. (b)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (a)	**9.** (a)	**10.** (a)
11. (d)	**12.** (c)	**13.** (b)	**14.** (d)	**15.** (c)	**16.** (d)	**17.** (c)	**18.** (a)	**19.** (c)	**20.** (b)
21. (a)	**22.** (c)	**23.** (d)	**24.** (b)	**25.** (d)					

Hints & Solutions

1. (*b*) 1 M H_2SO_4 means 1 mole of H_2SO_4 dissolved in 1000 cc of solution, whereas 1 m H_2SO_4 means 1 mole of H_2SO_4 dissolved in 1000 g of water.

Total volume of 1 m solution will be greater than 1000 cc due to extra mole of H_2SO_4. Hence, number of moles per 1000 cc will be less than 1 mole.

Thus, bottle *B* containing 1 m aqueous solution is more concentrated than bottle *A* containing 1 M aqueous solution.

2. (*b*) Solute in 300 g of 30% solution = 90 g

Solute in 200 g of 20% solution = 40 g

Total grams of solute = 130 g

Total grams of solution = 300 + 200 = 500 g

$$\% \text{ of solute in the final solution} = \frac{130}{500} \times 100 = 26\%$$

3. (*d*) K_2SO_4 is 17.4 ppm, i.e. 10^6 mL has 17.4 g K_2SO_4

$$1 \text{ L } (10^3 \text{ mL}) \text{ has } K_2SO_4 = \frac{17.4 \times 10^3}{10^6} = 0.0174 \text{ g/L}$$

$$= \frac{0.0174}{174} \text{ mol/L}$$

$$\therefore \quad [K_2SO_4] = 1 \times 10^{-4} \text{M}$$

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$$

$$\therefore \quad [K^+] = 2 \times 10^{-4} \text{ M}$$

4. (*c*) Given, molality = 5.2 m

$$\therefore \text{ Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent (in kg)}}$$

$\therefore$ Number of moles of methyl alcohol

$$= 5.2 \text{ m} \times 1 \text{ kg} \qquad [\because 1\text{kg} = 1000 \text{ g}]$$

$$n_1(CH_3OH) = 5.2,$$

$$n_2(H_2O) = \frac{1000}{18} = 55.56$$

$$\therefore \quad n_1 + n_2 = 5.20 + 55.56 = 60.76 \text{ mol}$$

$$\therefore \quad \chi_{CH_3OH} = \frac{n_1}{n_1 + n_2} = \frac{5.2}{60.76} = 0.086$$

5. (*a*) Beaker *B* will have greater solubility of a gas in liquid than Beaker *A*. This is because, solubility of a gas in liquid directly proportional to the pressure of a gas.

On increasing the weight over the piston, the pressure over the solution phase increases.

6. (*c*) $p_{N_2} = \chi_{N_2} \times p_{\text{total}}$ $\qquad [\because 1 \text{ atm} = 760 \text{ mmHg}]$

$$p_{N_2} = 0.78 \times 1 \text{ atm}$$
$$= 0.78 \times 760 \text{ mm} = 592.8 \text{ mm}$$

Concentration in solution

$$= K_H \times p_{N_2}$$
$$= 8.42 \times 10^{-7} \text{M (mm)}^{-1} \times 592.8 \text{ mm}$$
$$= 4.99 \times 10^{-4} \text{M}$$

7. (*b*) According to Henry's law, $\frac{p_1}{p_2} = \frac{S_1}{S_2}$

[p_1 and p_2 are partial pressures and S_1 and S_2 are solubilities]

$$\Rightarrow \quad \frac{500}{750} = \frac{0.01}{S_2}$$

$$\Rightarrow \quad S_2 = \frac{750 \times 0.01}{500} = 0.015 \text{g L}^{-1}$$

8. (*a*) When a binary solution of two volatile liquids is taken in a closed vessel, then both the components get evaporated and finally a state of equilibrium is established between the vapour and liquid phase.

The total pressure in this case is the sum of the partial pressure of each component.

9. (*a*) The vapour pressure increases with decrease in intermolecular interactions. Moreover, lesser the intermolecular forces, more is the volatility and, hence higher vapour pressure at a given temperature. Therefore, CH_3F has highest vapour pressure, while CH_3COOH has lowest vapour pressure. Thus, option (a) is correct.

10. (*a*) According to Raoult's law, the vapour pressure of a volatile component in a given solution is

$$p_i = p_i^\circ \chi_i$$

If in the solution of a gas in liquid, the volatile component exists as a gas, then according to Henry's law,

$$p = K_H \chi$$

Therefore, Raoult's law becomes a special case of Henry's law when K_H becomes equal to p_i°.

11. (*d*) In equimolar liquid mixture,

$$\chi_A = 0.5, \quad \chi_B = 0.5$$

$$\because \quad p = p_A^\circ \chi_A + p_B^\circ \chi_B$$

So, $\quad p = 0.5 \times 150 + 0.5 \times 100 = 125$

Now, let Y_B be the mole fraction of vapour B then

$$Y_B = \frac{\chi_B p_B^\circ}{p} = \frac{0.5 \times 100}{125} = 0.4$$

12. (*c*) Given,

Vapour pressure of pure $CHCl_3[p_1]$ and $CH_2Cl_2[p_2] = 200$ atm and 41.5 atm respectively. Weight (w_1) of $CHCl_3$ and $CH_2Cl_2(w_2) = 11.9$ g and 17g respectively. Molar mass of $CHCl_3(M_1)$ and $CH_2Cl_2(M_2) = 119$ g mol^{-1} and 85 g mol^{-1} respectively. Thus, number of moles (n) of $CHCl_3 = \frac{11.9}{119} = 0.1$ mol

Number of moles of $CH_2Cl_2 = \frac{17}{85} = 0.2$ mol

$$\therefore \quad p_{\text{total}} = p_1\chi_1 + p_2\chi_2$$

$$\chi_1 = \frac{n_1}{n_T} = \frac{0.1}{0.3} = 0.33$$

$$\chi_2 = \frac{n_2}{n_T} = \frac{0.2}{0.3} = 0.66$$

$$p_{\text{Total}} = 200 \times 0.33 + 41.5 \times 0.66$$

$$= 94.33 \text{ atm}$$

13. (*b*) Ideal solutions are those which obey Raoult's law over all concentration ranges at a given temperature,
e.g. benzene-toluene, *n*-hexane-*n*-heptane, etc.

For an ideal solution,

$$\Delta V_{\text{mix}} = 0, \Delta H_{\text{mix}} = 0,$$

$$\Delta G_{\text{mix}} < 0, \Delta S_{\text{mix}} > 0.$$

14. (*d*) Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1. Thus, the variation in total vapour pressure *versus* composition of solution is given by then curves given in option (a) and (b).

15. (*c*) The solution which shows large positive deviation from Raoult's law forms minimum boiling azeotrope at a specific composition.

e.g. ether-acetone, ethanol-water etc.

16. (*d*) In cyclohexane and ethanol, the intermolecular interactions are weaker than those between cyclohexane-cyclohexane and ethanol-ethanol. Therefore, shows positive deviation from Raoult's law and hence forms minimum boiling azeotropes.

17. (*c*) Solution which show negative deviation from Raoult's law are called maximum boiling azeotrope. Hence, acetone and chloroform forms maximum boiling azeotrope.

18. (*a*) Relative lowering of vapour pressure is a colligative property because

(i) it does not depend upon nature of solute.
(ii) it depends upon number of solute particles.
(iii) it depends upon concentration of non-electrolyte solution.

19. (*c*) Given,

p° = vapour pressure of pure water of 25°C
= 35 mm Hg

χ_B = mole fraction of solute (urea)

$$= \frac{n_B}{n_A + n_B} = \frac{\frac{0.60}{60}}{\frac{360}{18} + \frac{0.60}{60}}$$

$$= \frac{0.01}{20 + 0.01}$$

$$= \frac{0.01}{20.01} = 0.0005$$

i = van't Hoff factor = 1 (for urea)

Now, according to Raoult's law

$$\Delta p = \chi_B \times i \times p^\circ$$

On substituting the above given values, we get

$$\Delta p = 0.0005 \times 1 \times 35 = 0.0175 \text{ mm Hg}$$

20. (*b*) Given : $p_B^\circ = 119$ torr

$$p_T^\circ = 37 \text{ torr}$$

$$\chi_T = 0.50$$

From Raoult's law, for ideal solution

$$p = p^\circ{}_B \chi_B + p^\circ{}_T \chi_T \quad [B = \text{benzene}, T = \text{toluene}]$$

$$= 119 \times 0.5 + 37 \times 0.5 \qquad [\because \chi_B = 1 - \chi_T]$$

$$= 59.5 + 18.5$$

$$= 78 \text{ torr}$$

$\therefore$ Mole fraction of toluene in vapour phase

$$(y_T)_V = \frac{p^\circ{}_T \chi_T}{p} = \frac{18.5}{78} = 0.237$$

21. (*a*) Given, $w_2 = 4 \text{ kg} = 4000$ g

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

$$M_2 = 62 \text{ g/mol}$$

$$\Delta T_f = 0^\circ - (-6^\circ\text{C}) = 6^\circ\text{C}$$

As we know that,

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

$$6 = \frac{1000 \times 1.86 \times w_1}{62 \times 4000}$$

$$w_1 = \frac{6 \times 62 \times 4000}{1000 \times 1.86}$$

$$\Rightarrow \quad w_1 = 800 \text{ g} \approx 804.32 \text{ g}$$

23. (*d*) In case of dissociation, van't Hoff factor $i > 1$ and in case of association, van't Hoff factor $i < 1$.

24. (*b*) Given, $\Delta T_b = 1° \text{ C}$ and M (NaCl) $= 58.5$ g/mol

$K_b(H_2O) = 0.52 \text{ K kg mol}^{-1}$

For NaCl, $n = 2$ and $w_{\text{solvent}} = 500$ g

Thus, $$\Delta T_b = i \times K_b \times \frac{w_{\text{(solute)}}}{M_{\text{(solute)}}} \times \frac{1000}{w_{\text{(solvent)}}}$$

$$1 = 2 \times 0.52 \times \frac{w}{58.5} \times \frac{1000}{500}$$

$$w = \frac{58.5 \times 500}{2 \times 0.52 \times 1000} = 28.125 \text{ g}$$

25. (*d*) Concentration of $BaCl_2 = 0.01$ M (Given)

$$\pi_{XY} = 4\pi_{BaCl_2} \qquad \text{(Given)}$$

$$i \times CRT = 4 \times i \times CRT$$

For the calculation of i,

$$XY \longrightarrow X^+ + Y^- \qquad \text{(Here, } i = 2)$$

$$BaCl_2 \longrightarrow Ba^{2+} + 2Cl^- \qquad \text{(Here, } i = 3)$$

Putting the values of i in (i)

$$2 \times [XY] = 4 \times 3 \times [BaCl_2]$$

$$2 \times [XY] = 12 \times 0.01$$

$$[XY] = \frac{12 \times 0.01}{2}$$

So, the concentration of $XY = 0.06 \text{ mol L}^{-1}$

$$= 6 \times 10^{-2} \text{ mol L}^{-1}$$