2

Solutions

Facts that Matter

- **Solution:** A solution is a homogeneous mixture of two or more pure substances whose composition may be altered within certain limits.
- **Concentration of solution:** The concentration of a solution is expressed in terms of mole fraction, molarity, molality and in terms of weight and volume percentage.
- **Henry's law:** At a given temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas.
- **Lowering of vapour pressure:** The vapour pressure of the solvent is lowered by the presence of a non-volatile solute in the solution and this lowering of vapour pressure of the solvent is governed by Raoult's law.
- **Raoult's law:** Relative lowering of vapour pressure of the solvent over a solution is equal to the mole fraction of a non-volatile solute present in the solution.
- **Ideal solution:** Solution which obeys Raoult's law over the entire range of concentration is called ideal solution. Generally solutions exhibit two types of deviation from Raoult's law called *positive deviation* and *negative deviation*.
- **Azeotropes:** Liquid mixture which distill over without changes in the composition are called *constant boiling mixtures* or *Azeotropes* or *Azeotropic mixture*.
- **Colligative properties:** Properties of solution which depend on the number of solute particles and are independent of their chemical identity are called colligative properties. These are:
 - lowering of vapour pressure

- elevation of boiling point
- depression of freezing point
- Osmotic pressure
- Colligative properties have been used to determine the molar mass of solutes.
- **Abnormal molar mass:** Solutes which dissociate in solution exhibit molar mass lower than the actual molar mass and those which associate show higher molar mass than their actual values.
- **van't Hoff factor:** A factor appearing in the equations for colligative properties, equal to the ratio of the number of actual particles present to the number of undissociated particles, it was first suggested by Jacobus van't Hoff (1852-1911). It can be expressed by van't Hoff factor symbol bracket (*i*).

This factor has been defined as ratio of normal molar mass to the experimentally determined molar mass or as the ratio of observed colligative property to the calculated colligative property.

Types of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	A mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor mixed with nitrogen gas

Table : Types of Solutions

Liquid Solutions	Gas	Liquid	Oxygen gas dissolved in water			
	Liquid	Liquid	Aqueous solution of ethanol			
	Solid	Liquid	Aqueous solution of Glucose			
Solid Solutions	GasSolidLiquidSolidSolidSolid		Solution of hydrogen in palladium Sodium mercury amalgam Copper dissolved in molten gold			

Expressing Concentration of Solution

There are several ways by which we can describe the concentration of the solution quantitatively.

(i) Mass percentage (w/w): It is the amount of solute (in grams) dissolved per 100 g of solution, e.g. 10% solution of sodium chloride means 10 g of solid sodium chloride present in 100 g of solution.

Mass % of a component = $\frac{\text{Mass of the component in the solution} \times 100}{\text{Total mass of the solution}}$

(ii) Volume percentage (ν/ν) : It is defined as volume of a solute dissolved per 100 ml of solution.

Volume % of a solute = $\frac{\text{Volume of solute} \times 100}{\text{Total volume of solution}}$

- (iii) Mass by volume percentage: It is the mass of solute (in grams) dissolved in 100 mL of the solution.
- (iv) **Parts per million:** When a very small quantity of solute is present in a large quantity of a solution, the concentration of solute is expressed in terms of ppm. It is defined as the mass of the solute present in one million (10^6) parts by mass of the solution.

Thus, for a solute A, $ppm_A = \frac{Mass \text{ of } A}{Mass \text{ of solution}} \times 10^6$

The concentration of pollutants in water or atmosphere is often expressed in terms of ppm or $\mu g \text{ mL}^{-1}$.

(v) Mole fraction: It is the ratio of number of moles of a particular component to the total number of moles of all the components. e.g., mole fraction of component A.

$$x_{\rm A} = \frac{n_{\rm A}}{n_{\rm A} + n_{\rm B}}$$

where $n_{\rm A}$ is the number of moles of component 'A', and $n_{\rm B}$ is the number of moles of component B.

(vi) **Molarity (M):** It is expressed as the number of moles of solute per litre of solution.

$$M = \frac{n_{\rm B}}{\rm V} \times 1000$$

is the amount of solute and M_B is the molecular weight of solute.

or

40 Chemistry-XII –

 $M = \frac{W_{\rm B} \times 1000}{M_{\rm R} \times V}$ where $n_{\rm B}$ is the number of moles of solute. V is the volume of solution in ml. W_B

(vii) Molality (m): It is defined as number of moles of solute per 1000 g or 1kg of solvent.

$$m = \frac{n_{\rm B}}{W_{\rm A}} \times 1000$$
$$m = \frac{W_{\rm B}}{M_{\rm B} \times W_{\rm A}} \times 1000$$

or

where $n_{\rm B}$ is the number of moles of solute. $W_{\rm A}$ is weight of solvent in grams. $W_{\rm B}$ is amount of solute and 'M_B' is molecular weight of solute.

- **Dissolution:** When a solid solute is added continuously to a liquid solvent, the solute keeps on dissolving and the concentration of the solution keeps on increasing. This process is known as **dissolution**.
- Saturated solution: A solution in which no more solute can be further dissolved at the same temperature is called saturated solution.
- **Unsaturated solution:** It is a solution in which more amount of solute can be dissolved at the same temperature is called unsaturated solution.
- Effect of temperature: Mass %, mole fraction and molality do not change with temperature whereas molarity changes with temperature because volume of solution (liquid) changes with temperature.
- Solubility: Solubility of a substance is defined as the maximum amount of substance that can be dissolved in a specified amount of solvent at a given temperature.

Solubility of a solid in liquid:

Effect of temperature: The solubility of a solid in a liquid changes with temperature.

Solute + Solvent $\xrightarrow{\text{dissolution}}$ Solution

If the dissolution process is endothermic, the solubility should increase with rise in temperature and if it is exothermic, the solubility should decrease with rise in temperature.

Effect of pressure: Solubility of a solid in a liquid does not change with pressure as solids and liquids are highly incompressible.

Like dissolves like: Polar solutes dissolve in polar solvents and non-polar solutes dissolve in non-polar solvents. In general, a solute dissolves in a solvent if the intermolecular forces of attractions are similar in both.

Solubility of a gas in liquid:

(a)Increases with increase of pressure.

(b)Decreases with increase of temperature.

As dissolution of a gas in liquid is an exothermic process, the solubility should decrease with increase in temperature.

Henry's law: At constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of gas over the solution.

Or

The partial pressure of the gas in vapour phase (P) is directly proportional to the mole fraction of the gas(x) in the solution.

 $P = K_{\mu}x$

 K_{H} = Henry's law constant. It depends on the nature of gas.

Greater the K_H value, the lower will be the solubility of the gas and vice versa. K_H increases with increase in temperature, so solubility of a gas in a liquid decreases with increase of temperature.

Solutions **41**

Raoult's law:

Raoult's law in its general form can be stated as, "For any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction in the solution."

According to Raoult's law for a solution of two volatile liquids,

 $P_1 \propto x_1$, , $P_2 \propto x_2$ $P_1 = x_1 P_1^0$, $P_2 = x_2 P_2^0$ According to Raoult's law for a solution containing a volatile solvent and a non-volatile solute.

 $P_{solvent} = P_{solvent}^{o} x_{solvent}$ Since $P_{solution} = P_{solvent}$ $P_{solution} = P_{solvent}^{o} x_{solvent}$ When a non-volatile solute is dissolved in a pure solvent, the vapour pressure of the pure solvent decreases.

 $P_{solution} < P_{solvent}^{o}$ Because the non-volatile solute particles are present on the surface of solution, so the rate of evaporation of molecules of the volatile solvent from the surface of solution decreases.

Liquid-liquid volatile solutions are classified into two types on the basis of **Raoult's law as follows:**

(i) Ideal solution:

(a) The solution which obeys Raoult's law at all concentration and at all temperature *i.e.*, $P_{\star} = P_{\star}^{o} x_{\star}$

$$P_{p}^{A} = P_{p}^{A} x_{p}^{A}$$

- (b) If the intermolecular attractive forces between the solute-solvent particles (A-B interactions) are nearly equal to those between the solvent-solvent particles (A–A) and solute–solute particles (B–B), then it forms an ideal solution.

- (c) Enthalpy of mixing, $\Delta_{\text{mixing}} H = 0$. (d) Volume change on mixing, $\Delta_{\text{mixing}} V = 0$. (e) Examples: *n*-hexane and *n*-heptane, Bromoethane and chloroethane, o-Benzene and Toluene.

pressure /apour 0 Mole fraction x_A = $X_{\overline{A}}$ = 1 X_B = 0 X_B Total Vapour Pressure Curve for Ideal Solution

P°-

Vapour pressure

of solution

(ii) Non-Ideal solution:

(a) The solution which do not obey Raoult's law at all concentration and at all temperature *i.e.*,

$$P_A \neq P_A^o x_A$$
 and $P_B \neq P_B^o x_B$

- (b) If the intermolecular attractive forces between the solute-solvent particles (A-B interactions) are not equal (either stronger or weaker) to those between the solvent-solvent particles (A-A) and solute-solute particles (B-B), then it forms a non-ideal solution.
- (c) Enthalpy of mixing, Δ_{mixing} H is not equal to 0.
- (d) Volume change on mixing, Δ_{mixing} V is not equal to 0.
- (e) Examples: Ethanol and acetone, Ethanol and water, Chloroform and acetone, Nitric acid and water.



Types of Non-Ideal Solutions

- (a) Non-ideal solution showing positive deviations
 - (i) In this case, intermolecular attractive forces between the solute and solvent (A-B) particles are weaker than those between solvent-solvent (A-A) and solute-solute (B-B) particles *i.e.*,

$$P_{A} > P_{A}^{o} x_{A}$$
$$P_{B} > P_{B}^{o} x_{B}$$

(*ii*)
$$\Delta_{\text{mixing}} H = +ve$$

- (*iii*) $\Delta_{\text{mixing}} V = +ve$
- (*iv*) Dissolution is endothermic, so heating increases the solubility. Examples: Ethanol and acetone, Ethanol and water, CS_2 and acetone.

(b) Non-ideal Solution Showing Negative Deviations

(i) In this case, intermolecular attractive forces between the solute and solvent (A–B) particles are stronger than those between the solvent-sovlent (A–A) and the solute-solute (B–B) particles *i.e.*,

$$P_A < P_A^o x_A$$
 and $P_B < P_B^o x_B$

- $(iii) \Delta_{\text{mixing}} V = -ve$
- *(iv)* Dissolution is exothermic so heating decreases the solubility.

Examples: Chloroform and acetone, Nitric acid and water, Phenol and aniline.

• **Azeotropes:** These are the binary solutions (liquid mixtures) having the same composition in liquid and vapour phase and it is not possible to separate the components of an azeotrope by fractional distillation.

Types of Azeotropes:

(i) Minimum boiling azeotropes: The non-ideal solutions showing positive deviation form minimum boiling azeotrope at a specific composition.
 Example: 95% ethanol and 5% water (by volume).
 Ethanol = 251.2 K. Mater = 272 K. Ageotropa = 251.1 K.

Ethanol = 351.3 K, Water = 373 K, Azeotrope = 351.1 K.

- (*ii*) Maximum boiling azeotropes: The non-ideal solutions showing negative deviation form maximum boiling azeotrope at a specific composition.
 Example: 68% Nitric acid and 32% water (by mass).
 Nitric acid = 359 K, Water = 373 K, Azeotrope = 393.5 K
- Colligative Properties

٦

The properties of solution which depends on the no. of solute particles but irrespective of the nature of solute particles.

Example: Relative lowering of vapour pressure, Elevation of boiling point, Depression of freezing point, Osmotic pressure.

Application: By measuring a colligative property of a solution, molar mass of the non-volatile solute can be calculated.



Vapour pressure of solution





Conditions for getting accurate value of molar mass:

- (a) Solute must be non volatile
- (b) Solution must be dilute
- (c) Solute particles must not undergo any association or dissociation in the solution.
- (i) Relative lowering of vapour pressure: When a non volatile solute is added to a pure solvent its vapour pressure decreases.

P_{solution} < P^o_{solvent} According to Raoult's law $P_{solvent} = P_{solvent}^{o} x_{solvent}$ where, $P_{solution} = P_{solvent}$ (Since solute is non volatile) $P_{solution} = vapour pressure of solution.$ $P_{solvent}$ = vapour pressure of solvent in the solution. $P^{o}_{solvent}$ = vapour pressure of pure solvent. Therefore, $\begin{array}{l} {\rm P}_{\rm solution} \ = \ {\rm P}^{\rm o}_{\rm \ solvent} \ x_{\rm solvent} \\ {\rm P}_{\rm solution} \ = \ {\rm P}^{\rm o}_{\rm \ solvent} \ (1 - x_{\rm solute}) \end{array}$ (Since $x_{\text{solute}} + x_{\text{solvent}} = 1$) $(P^{o}_{solvent} - P_{solution}) = P^{o}_{solvent} x_{solute}$ (Lowering of vapour pressure) Therefore, relative lowering of vapour pressure = $(P^{o}_{solvent} - P_{solution})/P^{o}_{solvent} = x_{solute}$... (1) Since, it depends on the mole fraction of the solute (x_{solute}) , therefore it is a

colligative property.

To calculate molar mass:

 $x_{\text{solute}} = n_{\text{solute}} / n_{\text{solute}} + n_{\text{solvent}}$

Since the solution is dilute, n_{solute} can be neglected from the denominator.

$$x_{\text{solute}} = n_{\text{solute}} / n_{\text{solvent}} = \frac{W_{\text{solute}} / M_{\text{solute}}}{W_{\text{solvent}} / M_{\text{solvent}}}$$

(ii) Elevation of Boiling Point

ebullioscopic constant.

Boiling point: The temperature at which vapour pressure of liquid becomes equal to the atmospheric pressure.

The vapour pressure of the pure solvent decreases when non volatile solute is added to it and the boiling point is inversely proportional to the vapour pressure. Therefore, boiling point of the pure solvent increases when a non volatile solute is added.

i.e., $T>T_{b(solvent)}^{o}$ The difference in boiling point of solution and pure solvent is called elevation of boiling point (ΔT_b) .

 $\Delta T_{\rm b} = T_{\rm b}$ (solution) – $\Delta T_{\rm b}^{\rm o}$ (solvent)

For dilute solutions, the elevation of boiling point is directly proportional to molality (molal concentration) of the solution.

 $\Delta T_b = K_b$ molality ... (1) where $K_b =$ Boiling point elevation constant or molal elevation constant or

Molality
$$(m) = n_{\text{solute}} / W_{\text{solvent in kg}} = \frac{W_{\text{solute}} / M_{\text{solute}}}{W_{\text{solvent}} (\text{in kg})} \dots (2)$$

By substituting (2) in (1), the molar mass of the non volatile solute (M_{solute}) can be calculated.

44 Chemistry-XII -

(iii) Depression of freezing point

Freezing point: Temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in its solid phase.

Since the vapour pressure of the pure solvent decreases in the presence of non volatile solute and freezing point is directly proportional to the vapour pressure, the freezing point of pure solvent decreases when non volatile solute is added to it. T_f (solution) < T_f^o (solvent)

The difference in freezing point of pure solvent and solution is called depression of freezing point (ΔT_f)

$$\Delta T_f = T^o_{f(solvent)} - T_{f(solution)}$$

For dilute solutions, the depression of freezing point is directly proportional to molality (molal concentration) of solution.

$$T_f = K_f \text{ molality} \qquad \dots (1)$$

where K_f = freezing point depression constant or molal depression constant or cryoscopic constant.

Molality(m) =
$$\frac{W_{\text{solute}} / M_{\text{solute}}}{W_{\text{solvent}}(\text{in kg})}$$
 ... (2)

By substituting (2) in (1), the molar mass of the non-volatile solute can be calculated.

(*iv*) **Osmosis:** The process of flow of solvent molecules from pure solvent to the solution through semipermeable membrane.

Osmotic pressure (\Pi): Minimum pressure that must be applied to the solution to prevent the flow of solvent into the solution through a semipermeable membrane.

It is a colligative property as it is directly proportional to the molarity (molar concentration) of the solution at the given temperature.

 $\Pi = \text{Molarity} \times \mathbb{R} \times \mathbb{T} \text{ [since } \Pi = (n/\mathbb{V}) \times \mathbb{R} \times \mathbb{T} \text{]} \qquad \dots (1)$

Isotonic solutions: Two different solutions having the same osmotic pressure at the same temperature.

Hypertonic and hypotonic solutions: A solution which has more osmotic pressure than the other solution is hypertonic and similarly the solution having less osmotic pressure than the other solution is called hypotonic.

(v) Reverse osmosis: When a pressure greater than osmotic pressure is applied to the solution side, the pure solvent flows out of solution to the solvent side through semipermeable membrane, this process is called reverse osmosis.

Use: Reverse osmosis is used for desalination of sea water.

• Abnormal molar mass and van't Hoff factor (i)

When the non volatile solute particles undergo association (*e.g.*, acetic acid) or dissociation (*e.g.*, electrolytes like KCl, NaCl, etc.), the abnormal molar mass is observed. van't Hoff factor is defined as:

 $i = \frac{1}{\text{abnormal molar mass}}$

Formula to calculate *i*;

Total number of moles of particles after association or dissociation

Total number of moles of particles before association or dissociation

Solutions **45**

'*i*' value is always less than unity (i < 1) for association and '*i*' is greater than unity (i > 1) for dissociation. The modified equations for colligative properties when solute particles undergoing association or dissociation can now be written as:

1. $(P_{solvent}^{\circ} - P_{solution}^{\circ})/P_{solvent}^{\circ} = i \times x_{solute}$ 3. $\Delta T_{f}^{\circ} = i \times K_{f} \times molality$ 4. $\Pi = i \times C \times R \times T$

• Important Formulae

Molarity (M) =
$$\frac{W_B}{M_B V(L)}$$

Molality (m) = $\frac{W_B \times 1000}{M_B W_A(g)}$
 $\frac{\Delta p}{p^0} = \frac{p^0 - p}{p^0} = x_B$
 $\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B W_A}$
 $\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B W_A}$
 $\Pi = \frac{W_B RT}{M_B V}$

NCERT IN-TEXT QUESTIONS SOLVED

2.1. Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

Ans. Mass of solution = Mass of benzene
$$(C_6H_6)$$
 + Mass of CCl_4
= 22 g + 122 g = 144 g
Mass percentage of C_6H_6 = $\frac{Mass of benzene}{Mass of solution} \times 100 = \frac{22g}{144g} \times 100 = 15.28\%$
Mass percentage of CCl_4 = $\frac{122g}{144g} \times 100 = 84.72\%$

2.2. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Ans. 30% of benzene in carbon tetrachloride by mass means that Mass of benzene in the solution = 30 g Mass of solution = 100 g ∴ Mass of carbon tetrachloride = 100 - 30 g = 70 g Molar mass of benzene (C₆H₆) = 78 g mol⁻¹ Molar mass of CCl₄ = 12 + 4 × 35.5 = 154 g mol⁻¹ ∴ No. of moles of benzene = $\frac{Mass}{Molar mass} = \frac{30g}{78g mol^{-1}} = 0.385$ No. of moles of CCl₄ = $\frac{Mass}{Molar mass} = \frac{70g}{154g mol^{-1}} = 0.455$

46 ■ Chemistry-XII –

Mole fraction of benzene = $\frac{\text{Moles of benzene}}{\text{Total moles in the solution}}$ $= \frac{0.385}{0.385 + 0.455} = \frac{0.385}{0.84}$ = 0.458 Mole fraction of $CCl_4 = 1 - 0.458 = 0.542$ **2.3.** Calculate the molarity of each of the following solutions: (a) 30 g of $Co(NO_3)_2$. $6H_2O$ in 4.3 L of solution (b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL. **Ans.** (a) Molar mass of Co(NO₃)₂. $6H_2O = 58.7 + 2 (14 + 48) + 6 \times 18 \text{ g mol}^{-1}$ $= 58.7 + 124 + 108 \text{ g mol}^{-1} = 290.7 \text{ g mol}^{-1}$ No. of moles of $Co(NO_3)_2 \cdot 6H_2O$ $= \frac{Mass}{Molar mass} = \frac{30g}{290.7 g mol^{-1}} = 0.1031$ Volume of solution = 4.3 L:. Molarity of solution = $\frac{\text{No. of moles of solute}}{\text{Volume of solution in L}} = \frac{0.1031 \text{ mole}}{4.3} = 0.024 \text{ M}$ (b) 1000 mL of 0.5 M H_2SO_4 contains $H_2SO_4 = 0.5$ moles \therefore 30 mL of 0.5 M H₂SO₄ contains $H_2SO_4 = \frac{0.5}{1000} \times 30 \text{ mole} = 0.015 \text{ mole}$ Volume of solution = 500 mL = 0.500 L:. Molarity of solution = $\frac{\text{No. of moles of solute}}{\text{Volume of solution in L}} = \frac{0.015}{0.500} = 0.03 \text{ M}$ 2.4. Calculate the mass of urea (NH₂CONH₂) required in making 2.5 kg of 0.25 molal aqueous solution. Ans. 0.25 molal aqueous solution means that Moles of urea = 0.25 mole Mass of solvent (water) = 1 kg = 1000 gMolar mass of urea = $14 + 2 + 12 + 16 + 14 + 2 = 60 \text{ g mol}^{-1}$ \therefore 0.25 mole of urea = 60 × 0.25 mole = 15 g Total mass of the solution = 1000 + 15 g = 1015 g = 1.015 kgThus, 1.015 kg of solution contain urea = 15 g \therefore 2.5 kg of solution will require urea = $\frac{15}{1.015} \times 2.5$ kg = 37 g **2.5.** Calculate (a) molality, (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1} . Ans. 20% (mass/mass) aqueous KI solution means that Mass of KI = 20 gMass of solution in water = 100 gMass of solvent = 100 - 20 = 80 g = 0.080 kg (*a*) Calculation of molality: Molar mass of KI = $39 + 127 = 166 \text{ g mol}^{-1}$

Solutions **47**

Moles of KI =
$$\frac{20g}{166 \text{ g mol}^{-1}} = 0.120$$

Molality of solution = $\frac{\text{No. of moles of KI}}{\text{Mass of solvent (in kg)}} = \frac{0.120 \text{ mole}}{0.080 \text{ kg}} = 1.5 \text{ mol kg}^{-1}$

(b) Calculation of molarity:

Density of solution =
$$1.202 \text{ g mL}^{-1}$$

Volume of solution = $\frac{100 \text{ g}}{100 \text{ g}}$ = 83.2 mL = 0.0832 L

$$\frac{1.202 \text{ g mL}^{-1}}{\text{Moles of solute}} = \frac{0.120 \text{ mole}}{0.120 \text{ mole}}$$

~~

(c) Calculation of mole fraction of KI:

No. of moles of KI = 0.120

No. of moles of water =
$$\frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{80g}{18 \text{ g mol}^{-1}} = 4.44$$

Mole fraction of KI = $\frac{\text{No. of moles of KI}}{\text{Total no. of moles in solution}}$
= $\frac{0.120}{0.120 + 4.44} = \frac{0.120}{4.560} = 0.0263.$

2.6. H_2S , a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m. Calculate Henry's law constant.

Ans. Solubility of H_2S gas = 0.195 m =0.195 mole in 1 kg of the solvent (water)

1 kg of the solvent (water) = 1000 g = $\frac{1000 g}{18 g \text{ mol}^{-1}}$ = 55.55 moles

Mole fraction of H_2S gas in the solution(x) = $\frac{0.195}{0.195 + 55.55} = \frac{0.195}{55.745} = 0.0035$ Pressure at STP = 0.987 bar

Applying Henry's law

$$P_{H_2S} = K_H \times x_{H_2S}$$

$$K_H = \frac{P_{H_2S}}{x_{H_2S}} = \frac{0.987 \text{ bar}}{0.0035} = 282 \text{ bar}$$

2.7. Henry's law constant for CO_2 in water is 1.67×10^8 pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Ans.

$$K_{\rm H} = 1.67 \times 10^8 \text{ Pa}$$

$$P_{\rm CO_2} = 2.5 \text{ atm} = 2.5 \times 101325 \text{ Pa}$$
Applying Henry's law, $P_{\rm CO_2} = K_{\rm H} \times x_{\rm CO_2}$

$$x_{\rm CO_2} = \frac{P_{\rm CO_2}}{K_{\rm H}} = \frac{2.5 \times 101325 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}} = 1.517 \times 10^{-3}$$
i.e., $\frac{n_{\rm CO_2}}{n_{\rm H_2O} + n_{\rm CO_2}} = \frac{n_{\rm CO_2}}{n_{\rm H_2O}} = 1.517 \times 10^{-3}$

48 Chemistry-XII –

For 500 mL of soda water, water present = 500 mL

$$\therefore \qquad 500 \text{ g of } \text{H}_2\text{O} = \frac{500 \text{ g}}{18 \text{ g mol}^{-1}} = 27.78 \text{ moles}$$

$$\therefore \qquad \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}} = 1.517 \times 10^{-3}$$

$$\frac{n_{\text{CO}_2}}{27.78} = 1.517 \times 10^{-3}$$

$$n_{\text{CO}_2} = 1.517 \times 10^{-3} \times 27.78 = 42.14 \times 10^{-3} \text{ mole}$$

$$= 42.14 \text{ m mol} = 42.14 \times 10^{-3} \times 44 \text{ g} = 1.854$$
The upper program of multiplicities A and P are 450 and 700 mm Hz respective

2.8. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

$P_A^0 = 450 \text{ mm Hg}$ $P_B^0 = 700 \text{ mm Hg}$ Ans. Here

 $P_{Total} = 600 \text{ mm Hg}$

Applying Raoult's law,

 $P_{A} = x_{A} \times P_{A}^{0}$ $P_{B} = x_{B} \times P_{B}^{0} = (1 - x_{A})P_{B}^{0}$ $P_{Total} = P_{A} + P_{B} = x_{A} P_{A}^{0} + (1 - x_{A})P_{B}^{0} = P_{B}^{0} + (P_{A}^{0} - P_{B}^{0})x_{A}$ Substituting the given values, we get $600 = 700 + (450 - 700) x_A$ 250 $x_{\rm A} = 100$ or $x_{\rm A} = \frac{100}{250} = 0.40$ or Thus, composition of the liquid mixture will be

- $x_{\rm A}$ (mole fraction of A) = 0.40
- $x_{\rm B}^{\rm r}$ (mole fraction of B) = 1 0.40 = 0.60 $P_A = x_A \times P_A^0 = 0.40 \times 450 \text{ mm Hg} = 180 \text{ mm Hg}$ $P_B = x_B \times P_B^0 = 0.60 \times 700 \text{ mm Hg} = 420 \text{ mm Hg}$

Mole fraction of A in the vapour phase

Mole fraction of B in the vap

$$\frac{P_{A}}{P_{A} + P_{B}} = \frac{180}{180 + 420} = 0.30$$

our phase

$$1 - 0.30 = 0.70.$$

2.9. Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH₂CONH₂) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Ans. Here

$$P_{1}^{0} = 23.8 \text{mm}$$

$$W_{2} = 50 \text{ g}$$

$$M_{2}(\text{urea}) = 60 \text{ g mol}^{-1}$$

$$W_{1} = 850 \text{ g}$$

$$M_{1}(\text{Water}) = 18 \text{ g mol}^{-1}$$

Solutions **49**

g

Here we have to calculate P. On applying Raoult's law

$$\frac{P^{0} - P_{s}}{P^{0}} = \frac{n_{2}}{n_{1} + n_{2}} = \frac{W_{2} / M_{2}}{W_{1} / M_{1} + W_{2} / M_{2}}$$
$$= \frac{50 / 60}{850 / 18 + 50 / 60} = \frac{0.83}{48.05} = 0.017$$

Thus, relative lowering of vapour pressure = 0.017Substituting $P^0 = 23.8 \text{ mm Hg}$

We get,

$$\frac{23.8 - P_S}{P_S} = 0.017$$

$$23.8 - P_S = 0.017P_S$$

$$P_S = 23.4 \text{ mm Hg}$$

Thus, vapour pressure of water in the solution = 23.4 mm Hg

- **2.10.** Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C?
- **Ans.** Elevation in boiling point required $(\Delta T_{h}) = 100 99.63^{\circ} = 3.37^{\circ}$

Mass of solvent (water) $W_1 = 500 \text{ g}$ Mass of solute, $C_{12}H_{22}O_{11} = 342 \text{ g mol}^{-1}$ Molar mass of solvent $M_1 = 18 \text{ g mol}^{-1}$ Applying the formula,

$$M_{2} = \frac{1000 \text{ K}_{b} \text{ W}_{2}}{W_{1} \times \Delta \text{T}_{b}}$$

$$W_{2} = \frac{M_{2} \times \Delta \text{T}_{b} \times \text{W}_{1}}{1000 \times \text{K}_{b}}$$

$$= \frac{342 \text{ g mol}^{-1} \times 500 \text{ g} \times 3.37 \text{ K}}{1000 \times 0.52 \text{ kg mol}^{-1}} = 1108.2 \text{ g}$$

- **2.11.** Calculate the mass of ascorbic acid (vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. $K_f = 3.9 \text{ K kg mol}^{-1}$.
- **Ans.** Lowering in melting point $(\Delta T_b) = 1.5^{\circ}C$ Mass of solvent (CH₂COOH), $W_1 = 75$ g

Molar mass of solvent (CH₃COOH),
$$M_1 = 12 + 3 + 12 + 16 + 16 + 1$$

= 60 g mol⁻¹

ass of solute
$$(C_{c}H_{a}O_{c})$$

Molar mass of solute
$$(C_6H_8O_6)$$

 $M_2 = 72 + 8 + 96 = 17$

For acetic acid,

Applying formula,

$$M_{2} = 72 + 8 + 96 = 176 \text{ g mol}^{-1}$$

$$K_{f} = 3.9 \text{ K kg mol}^{-1}$$

$$M_{2} = \frac{1000K_{f}W_{2}}{W_{1}\Delta T_{f}}$$

$$W_{2} = \frac{M_{2} \times W_{1} \times \Delta T_{f}}{1000 \times K_{f}} = \frac{176 \text{ g mol}^{-1} \times 75 \text{ g} \times 1.5 \text{ °C}}{1000 \times 3.9 \text{ K kg mol}^{-1}} = 5.077 \text{ g}$$

or

2.12. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

50 Chemistry-XII –

Ans.

$$\pi = CRT = \frac{n}{V}RT$$

Here, number of moles of solute dissolved $(n) = \frac{1.0 \text{ g}}{185,000 \text{ g mol}^{-1}} = \frac{1}{185,000} \text{ mol}^{-1}$ V = 450 mL = 0.450 L $T = 37^{\circ}\text{C} = 37 + 273 = 310 \text{ K}$ $R = 8.314 \text{ Pa L K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{3} \text{ Pa L K}^{-1} \text{ mol}^{-1}$

Substituting these values we get

$$\pi = \frac{1}{185000} \times \frac{1 \times 8.314 \times 10^3 \text{ Pa } \text{LK}^{-1} \text{ mol}^{-1}}{0.45} \times 310 \text{ K}$$

= 30.96 Pa

NCERT TEXTBOOK QUESTIONS SOLVED

- **2.1.** Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.
- **Ans.** A solution is a homogeneous mixture of two or more substances which are chemically non–reacting. On the basis of physical component solutions are of the following types:

S.No.	Solute	Solvent	Types of solution	Examples
1.	Solid	Solid	Solid in solid	All Alloys like brass
2.	Liquid	Solid	Liquid in solid	Amalgam of mercury with Na
3.	Gas	Solid	Gas in solid	Solution of ${\rm H_2}$ in Pd

Solid Solutions

Liquid Solutions

S.No.	Solute	Solvent	Types of solution	Examples
1.	Solid	Liquid	Solid in liquid	Sugar solution
2.	Liquid	Liquid	Liquid in Liquid	Benzene in toluene
3.	Gas	Liquid	Gas in liquid	CO ₂ in water

Gaseous solutions

S.No.	Solute	Solvent	Types of solution	Examples		
1.	Solid	Gas	Solid in Gas	Iodine vapours in air		
2.	Liquid	Gas	Liquid in Gas	Water vapours in air		
3.	Gas	Gas	Gas in Gas	Air $(O_2 + N_2)$		

2.2. Give an example of a solid solution in which the solute is a gas.

- Ans. Solution of hydrogen in palladium.
- **2.3.** Define the following terms:
 - (*i*) Mole fraction

(*ii*) Molality

[Delhi 2017]

Γ

(*iii*) Molarity (*iv*) Mass percentage

Solutions **51**

Ans. (i) Mole fraction: It is the ratio of number of moles of a particular component to the total number of moles of all the components.Example: Mole fraction of component A

 $x_{\rm A} = \frac{x_{\rm A}}{x_{\rm A} + x_{\rm B}}$

where x_A is the number of moles of component 'A' and x_B is the number of moles of component B.

(*ii*) **Molality:** Molality of a solution is defined as the number of moles of the solute dissolved in 1000 g (1 kg) of the solvent. It is denoted by '*m*'.

Molality(m) =
$$\frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

For example, 1.00 mol kg⁻¹ (or 1.00 m) solution of KCl means that 1 mol of KCl dissolved in 1 kg of water.

(*iii*) **Molarity:** Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution.

Molarity
$$=$$
 $\frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}}$

(iv) Mass percentage: The mass percentage of a component of a solution is defined as:

 $\frac{\text{Mass of the component in the solution} \times 100}{\text{Mass of the component in the solution} \times 100}$

2.4. Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1} ?

Ans. 68% nitric acid by mass means that

Mass of nitric acid = 68 g Mass of solution = 100 g Molar mass of $HNO_3 = 63$ g mol⁻¹

68 g HNO₃ =
$$\frac{68}{63}$$
 mole = 1.079 mole

Density of solution = 1.504 g mL^{-1}

$$\therefore \text{ Volume of solution} = \frac{100}{1.504} \text{ mL} = 66.5 \text{ mL} = 0.0665 \text{ L}$$

Molarity of the solution = $\frac{\text{Moles of the solute}}{\text{Volume of solution}} = \frac{1.079}{0.0665} \text{ M} = 16.23 \text{ M}$

2.5. A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of the solution is 1.2 g mL^{-1} then what shall be the molarity of the solution?

Ans. 10 g glucose is present in 100 g solution, i.e. 90 g of water or 0.090 kg of water

10 g glucose =
$$\frac{10}{180}$$
 mol = 0.0555 mol
90 g H₂O = $\frac{90}{18}$ = 5 moles

52 Chemistry-XII –

...

Molarity = $\frac{0.0555}{0.090 \text{ kg}}$ = 0.617 m Mole fraction of Glucose, $x_{\rm B} = \frac{0.0555}{5+0.0555} = 0.01$ Mole fraction of water $(x_A) = 1 - 0.01 = 0.99$ 100 g of solution = $\frac{100}{1.2}$ mL = 83.33 mL = 0.08333 L Molarity = $\frac{0.0555 \text{ mol}}{0.08333 \text{ L}}$ = 0.67 M 2.6. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na₂CO₃ and NaHCO₃ containing equimolar amounts of both? Ans. To calculate the number of moles of the components in the mixture. Suppose Na_2CO_3 present in the mixture = x g :. NaHCO₃ present in the mixture = (1 - x) g Molar mass of $Na_2CO_3 = 23 \times 2 + 12 + 3 \times 16 = 106 \text{ g mol}^{-1}$ Molar mass of $NaHCO_3 = 23 + 1 + 12 + 3 \times 16 = 84 \text{ g mol}^{-1}$ Moles of Na₂CO₃ in x g = $\frac{x}{106}$ Moles of NaHCO₃ in $(1 - x) g = \frac{1 - x}{84}$ As mixture contains equimolar amounts of the two: $\frac{x}{106} = \frac{1-x}{84}$ 84 x = 106 - 106 x84 x + 106 x = 106 $190 \ x = 106$ $x = \frac{106}{190}$ g = 0.558 g moles of $Na_2CO_3 = \frac{0.558}{106} = 0.00526$ Thus, Moles of NaHCO₃ = $\frac{1 - 0.558}{84} = \frac{0.442}{84} = 0.00526$ To calculate the moles of HCl required $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$ 2 Moles 1 Mole $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$ 1 Mole 1 Mole 1 mole of Na_2CO_3 require HCl = 2 moles $0.00526 \text{ moles of Na}_2^{\circ} \text{CO}_3^{\circ}$ require HCl = $0.00526 \times 2 = 0.01052$ mole 1 mole of NaHCO₃ require HCl = 1 mole 0.00526 mole of NaHCO₃ require HCl = 0.00526 mole Total HCl required = 0.01052 + 0.0052 = 0.01578 moles

Π

Solutions 🔳 53

To calculate the volume of 0.1 M HCl 0.1 mole of 0.1 M HCl are present in 1000 mL of HCl

0.01578 mole of 0.1 M HCl will be present in $\frac{1000}{0.1} \times 0.01578 = 157.8$ mL of HCl.

2.7. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

Ans. 300 g of 25% solution contains solute = 75 g

400 g of 40% solution contains solute = 160 g Total mass of solute = 160 + 75 = 235 g Total mass of solution = 300 + 400 = 700 g % of solute in the final solution = $\frac{235}{700} \times 100 = 33.5\%$

% of water in the final solution =
$$100 - 33.5 = 66.5\%$$

- **2.8.** An antifreeze solution is prepared from 222.6 g of ethylene glycol $(C_2H_6O_2)$ and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL⁻¹ then what shall be the molarity of the solution?
- **Ans.** Mass of the solute $C_2H_4(OH)_2 = 222.6 \text{ g}$

Molar mass of
$$C_2H_4(OH)_2 = 62 \text{ g mol}^{-1}$$

Moles of the solute =
$$\frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59$$

Mass of the solvent = 200 g = 0.200 kg

Molality =
$$\frac{3.59 \text{ moles}}{0.200 \text{ kg}}$$
 = 17.95 mol kg⁻¹

Total mass of the solution = 422.6 g

Volume of the solution =
$$\frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}}$$
 = 394.2 ml = 0.3942 L

Molarity =
$$\frac{3.59 \text{ moles}}{0.3942 \text{ L}}$$
 = 9.11 mol L⁻¹

- **2.9.** A sample of drinking water was found to be severely contaminated with chloroform (CHCl₃) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass)
 - (*i*) express this in percentage by mass
 - (ii) determine the molality of chloroform in the water sample.
- Ans. 15 ppm means 15 parts in million (10⁶) parts by mass in the solution

:. % by mass =
$$\frac{15}{10^6} \times 100 = 1.5 \times 10^{-3}$$

Taking 15 g chloroform in 10⁶ g of the solution, mass of the solvent = 10^6 g Molar mass of CHCl₃ = $12 + 1 + 3 \times 35.5 = 119.5$ g mol⁻¹

$$Molality = \frac{\frac{15}{119.5}}{10^6} \times 1000 = 1.25 \times 10^{-4} \,\mathrm{m}.$$

2.10. What role does the molecular interaction play in solution of alcohol and water? **Ans.** There is strong hydrogen bonding in alcohol molecules as well as water molecules.

54 Chemistry-XII —

The intermolecular forces both in alocohol and water are H-bonds. When alcohol and water are mixed they form solution because of the formation of H-bonds the between alcohol and H₂O molecules but these interactions are weaker and less extensive than those in between pure water molecules. Hence, they show positive deviation from the ideal behaviour.

- **2.11.** Why do gases always tend to be less soluble in liquids as the temperature is raised?
- Ans. Mostly dissolution of gases in liquids is an exothermic process. It is because of the fact that this process involves decrease of entropy. Thus, increase of temperature tends to push the equilibrium towards backward direction as a result, of which solubility of gases decreases with rise in temperature.

 $(Gas + Solvent \rightleftharpoons Solution + Heat)$

- **2.12.** State Henry's law and mention some of its important applications.
- Ans. Henry's law: The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas.

Applications of Henry's law:

- (i) In the production of carbonated beverages (as solubility of CO_2 increases at high pressure).
- (ii) In deep sea diving.
- (iii) In functioning of lungs.
- (iv) In breathing for climbers or people living at higher altitudes.
- **2.13.** The partial pressure of ethane over a solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial [Delhi 2013 C] pressure of the gas?

Ans. Applying the relationship:

$$m = K_{\rm H} \times P$$

In the first case, ase, $6.56 \times 10^{-2} \text{g} = \text{K}_{\text{H}} \times 1 \text{ bar}^{-1}$

$$K_{\rm H} = 6.56 \times 10^{-2} \, {\rm g \ bar}$$

or

٦

In the second case, $5.00 \times 10^{-2} \text{ g} = 6.56 \text{ g} \times 10^{-2} \text{ g} \text{ bar}^{-1} \times \text{ P}$

$$P = \frac{5.00 \times 10^{-2} g}{6.56 \times 10^{-2} g \text{ bar}^{-1}} = 0.7621 \text{ bar.}$$

- 2.14. What is meant by positive and negative deviations from Raoult's law and how is the
- sign of ΔH_{mix} related to positive and negative deviations from Raoult's law? Ans. Positive deviations: In these type of deviations, the partial vapour pressure of each component A and B of solution is higher than the vapour pressure calculated from Raoult's law. For example: Water and ethanol, chloroform and water.

In case of positive deviation, A - B interactions are weaker than those between A - Aor B – B interactions. This means that in such solutions molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapour pressure and results in positive deviation from Raoult's law.

$\Delta H_{mix} = +ve$

Negative Deviations: In this type of deviations the partial vapour pressure of solution is less than that of the ideal solution of same composition. Boiling point of such a solution is relatively higher than the boiling point of both of the components. This type of behaviour is known as negative deviation from Raoult's law.

Here, the intermolecular attractive forces between A - A and B - B are weaker than those between A – B interactions and this leads to decrease in the vapour pressure.

In case of solutions showing negative deviations, a slight decrease in volume and evolution of heat takes place on mixing.

$$\Delta H_{mix} = -ve$$
$$\Delta V_{mix} = -ve$$

- **2.15.** An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at normal boiling point of the solvent. What is the molar mass of the solute?
- Ans. Vapour pressure of pure water at the boiling point,

$$(P^0) = 1 \text{ atm} = 1.013 \text{ bar}$$

Vapour pressure of solution, $P_s = 1.004 \text{ bar}$
 $M_1 = 18 \text{ g mol}^{-1}$
 $M_2 = ?$
Mass of solute = $W_2 = 2 \text{ g}$
Mass of solution = 100 g
Mass of solvent, $W_1 = 98 \text{ g}$
Applying Raoult's law for dilute solutions:

$$\frac{\mathbf{P}^{0} - \mathbf{P}_{s}}{\mathbf{P}_{0}} = \frac{n_{2}}{n_{1} + n_{2}} = \frac{n_{2}}{n_{1}} = \frac{\frac{\mathbf{W}_{2}}{\mathbf{M}_{2}}}{\frac{\mathbf{W}_{1}}{\mathbf{M}_{1}}}$$

$$\frac{\frac{P^{0} - P_{s}}{P_{0}} = \frac{W_{2}}{M_{2}} \times \frac{M_{1}}{W_{1}}$$

$$\frac{1.013 - 1.004}{1.013} = \frac{2 g}{M_{2}} \times \frac{18 \text{ g mol}^{-1}}{98 \text{ g}}$$
or
$$M_{2} = \frac{2 \times 18 \times 1.013}{98 \times 0.009} = 41.35 \text{ g mol}^{-1}.$$

- **2.16.** Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?
- Ans. Molar mass of heptane $(C_7H_{16}) = 100 \text{ g mol}^{-1}$ Molar mass of octane $(C_8H_{18}) = 114 \text{ g mol}^{-1}$

$$n_{\text{heptane}} = \frac{26 \text{ g}}{100 \text{ g mol}^{-1}} = 0.26 \text{ mol}$$

$$n_{\text{octane}} = \frac{35 \text{ g}}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$$

$$n_{\text{heptane}} = \frac{0.26}{0.26 + 0.31} = 0.456$$

$$n_{\text{octane}} = \frac{0.31}{0.26 + 0.31} = 0.544$$

$$P_{\text{heptane}} = 0.456 \times 105.2 \text{ kPa}$$

$$= 47.97 \text{ kPa}$$

$$P_{\text{octane}} = 0.544 \times 46.8 \text{ kPa} = 25.46 \text{ kPa}$$

$$P_{\text{total}} = 47.97 \text{ kPa} = 73.43 \text{ kPa}.$$

56 Chemistry-XII -

Γ

 \square

2.17. The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

Ans. 1 molal solution means 1 mole of the solute is dissolved in 1 kg of the solvent (water)

.77

Mole fraction of solute =
$$\frac{1}{1+55.5}$$
 = 0.01
Now $\frac{P^0 - P_s}{P^0} = x_2$
 \therefore 12.3 - P_s 0.0177

 $\frac{2.0}{12.3} = 0.0177$ $P_s = 12.08 \text{ kPa}$ i.e.

2.18. Calculate the mass of a non-volatile solute (molar mass 40 g mol⁻¹) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

Ans.

$$P_{s} = 80\% \text{ of } P^{0} = 0.80 P^{0}$$
Moles of solute =
$$\frac{W}{40 \text{ g mol}^{-1}}$$
Moles of solvent (octane) =
$$\frac{114 \text{ g}}{114 \text{ g mol}^{-1}}$$
(Molar mass of $C_{8}H_{18} = 114 \text{ g mol}^{-1}$)
Now
$$\frac{P^{0}-P_{s}}{P^{0}} = x_{2}$$

$$\frac{P^{0} - 0.80 P^{0}}{P^{0}} = \frac{\frac{W}{40}}{\frac{W}{40} + 1}$$

or

Γ

$$\frac{0.8 \text{ W}}{40} = 0.2$$

W = 10 g

- w = 10 g. **2.19.** A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is then added to solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate:
 - (*i*) molar mass of the solut
 - (ii) vapour pressure of water at 298 K.
- **Ans.** (i) Suppose the molar mass of the solute = M g mol⁻¹

$$n_{2}(\text{solute}) = \frac{30}{\text{M}} \text{ moles}$$

$$n_{1}(\text{solvent, H}_{2}\text{O}) = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ moles}$$

$$\frac{P^{0} - P_{s}}{P^{0}} = \frac{\frac{30}{\text{M}}}{5 + \frac{30}{\text{M}}}$$

Solutions **57**

 \square

$$1 - \frac{2.8}{P^0} = \frac{\frac{30}{M}}{5 + \frac{30}{M}}$$

$$\frac{2.8}{P^0} = 1 - \frac{\frac{30}{M}}{5 + \frac{30}{M}} = \frac{5 + \frac{30}{M} - \frac{30}{M}}{5 + \frac{30}{M}}$$

$$\frac{P^0}{2.8} = \frac{5 + \frac{30}{M}}{5} = 1 + \frac{6}{M} \qquad \dots (i)$$
18 g of water $P = 2.9$ kPa

L

 \square

On further adding 18 g of water, $P_s = 2.9$ kPa 30

$$\therefore \qquad \frac{P^{0}-2.9}{P^{0}} = \frac{\frac{30}{M}}{6+\frac{30}{M}} \qquad [\because 1 \text{ mole of } H_{2}O = 18 \text{ g mol}^{-1}]$$

$$1 - \frac{2.9}{P^{0}} = \frac{\frac{30}{M}}{6+\frac{30}{M}}$$

$$\frac{2.9}{P^{0}} = 1 - \frac{\frac{30}{M}}{6+\frac{30}{M}} = \frac{6+\frac{30}{M}-\frac{30}{M}}{6+\frac{30}{M}}$$
or
$$\frac{P^{0}}{2.9} = \frac{6+\frac{30}{M}}{6} \text{ or } \frac{P^{0}}{2.9} = 1 + \frac{5}{M} \qquad \dots (ii)$$
Dividing equation (i) by equation (ii) we get

Dividing equation (i) by equation (ii) we get

$$\frac{2.9}{2.8} = \frac{1 + \frac{6}{M}}{1 + \frac{5}{M}}$$
or
$$2.9 \left(1 + \frac{5}{M}\right) = 2.8 \left(1 + \frac{6}{M}\right)$$
or
$$2.9 + \frac{14.5}{M} = 2.8 + \frac{16.8}{M}$$
or
$$\frac{2.3}{M} = 0.1$$
M = 23 g mol⁻¹
M = 23 in equation (i)
We get
$$\frac{P^{0}}{2.8} = 1 + \frac{6}{23}$$

58 Chemistry-XII —

Γ

$$\frac{P^{0}}{2.8} = \frac{29}{23}$$
$$P^{0} = \frac{29}{23} \times 2.8 = 3.53 \text{ kPa}$$

- 2.20. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.Ans. Molar mass of cane sugar,
 - $C_{12}H_{22}O_{11} = 342 \text{ g mol}^{-1}$ Molality of sugar = $\frac{5 \times 1000}{342 \times 100} = 0.146$ ΔT_f for sugar solution = 273.15 - 271 = 2.15° $\Delta T_f = K_f \times m$ $K_f = \frac{2.15}{0.146}$ Molality of glucose solution = $\frac{5}{180} \times \frac{1000}{100} = 0.278$ ΔT_f for glucose solution = $\frac{2.15}{0.146} \times 0.278 = 4.09 \text{ K}$
 - \therefore Freezing point of glucose solution = 273.15 4.09 = 269.06 K.
- **2.21.** Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol⁻¹. Calculate atomic masses of A and B.
- Ans. Applying the formula,

$$\begin{split} M_2 &= \frac{1000 \times K_f \times W_2}{W_1 \times \Delta T_f} \\ M_{AB_2} &= \frac{1000 \times 5.1 \times 1}{20 \times 2.3} = 110.87 \text{ g mol}^{-1} \\ M_{AB_4} &= \frac{1000 \times 5.1 \times 1}{20 \times 1.3} = 196.15 \text{ g mol}^{-1} \\ \text{Suppose atomic masses of A and B are 'a' and 'b' respectively.} \\ \text{Then Molar mass of } AB_2 &= a + 2b = 110.87 \text{ g mol}^{-1} \\ \text{Molar mass of } AB_4 &= a + 4b = 196.15 \text{ g mol}^{-1} \\ \text{Molar mass of } AB_4 &= a + 4b = 196.15 \text{ g mol}^{-1} \\ \text{Equation (ii)} - \text{Equation (i) gives} \\ 2b &= 85.28 \\ b &= 42.64 \\ \text{Substituting in equation (i) we get} \\ a + 2 \times 42.64 &= 110.87 \\ a &= 25.59 \text{ u} \\ A &= 25.59 \text{ u} \\ \text{Atomic mass of B} &= 42.64 \text{ u.} \\ \text{At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of} \end{split}$$

2.22. At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature what would be its concentration?

Solutions **59**

Ans.

$$4.98 = \frac{36}{180} \times R \times 300$$

$$4.98 = 60 R$$

$$1.52 = C \times R \times 300$$

...(i)

...(ii)

In the second case $1.52 = C \times R \times$ Dividing (*ii*) by (*i*),we get, C = 0.061 M.

- **2.23.** Suggest the most important type of intermolecular attractive interaction in the following pairs:
 - (*i*) *n*-hexane and *n*-octane (*ii*) I_2 and CCl_4
 - (*iii*) NaClO₄ and water (*iv*) \tilde{M} ethanol and acetone
 - (v) acetonitrile (CH₃CN) and acetone (C₃H₆O).
- Ans. (i) Both are non-polar. Hence, there will be London dispersion forces
 - (*ii*) London dispersion forces. (*iii*) ion-dipole interactions.
 - (*iv*) dipole-dipole interactions. (*v*) dipole-dipole interactions.
- **2.24.** Based on solute-solvent interactions arrange the following in order of increasing solubility in *n*-octane, and explain: cyclohexane, KCl, CH₃OH, CH₃CN.
- **Ans.** (*i*) Cyclohexane and *n*-octane both are non-polar. Hence, they mix completely in all proportions.
 - (*ii*) KCl is an ionic compound while *n*-octane is non-polar. Hence, KCl will not dissolve at all in *n*-octane.
 - (*iii*) CH_3OH and CH_3CN both are polar but CH_3CN is less polar than CH_3OH . As the solvent is non-polar, CH_3CN will dissolve more than CH_3OH in *n*-octane. Thus, the order of solubility will be

 $KCl < CH_3OH < CH_3CN < Cyclohexane$

- **2.25.** Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?
 - (*i*) Phenol (*ii*) Toluene (*iii*) Formic acid
 - (*iv*) ethylene glycol (*v*) chloroform (*vi*) pentanol
- Ans. (i) Phenol—Partially soluble in water (ii) Toluene—Insoluble in water
 - (iii) Formic acid—Soluble in water (iv) Ethylene glycol—Soluble in water
 - (v) CHCl₃—Insoluble in water (vi) Pentanol—Partially soluble in water
- **2.26.** If the density of some lake water is 1.25 g mL⁻¹ and it contains 92 g of Na⁺ ions per kg of water, calculate the molality and molarity of Na⁺ ions in the lake.
- Ans.

Molality =
$$\frac{\text{Moles of Na}^+ \text{ ions}}{\text{Mass of water (kg)}}$$

92 g of Na⁺ ions =
$$\frac{92 \text{ g}}{22 \text{ g mol}^{-1}}$$
 = 4 moles

 23 g mol^{-1}

Therefore, molality = 4 m.

Molarity =
$$\frac{\text{Moles of Na}^+ \text{ ions}}{\text{Vol. of water (L)}} = \frac{92(g)/23 \ (g \ \text{mol}^{-1})}{1000 \ (g)/1.25 \times 10^3 \ (g \ \text{L}^{-1})} = 5 \ \text{M}$$

- **2.27.** If the solubility product of CuS is 6×10^{-16} , calculate the maximum molarity of CuS in aqueous solution.
- **Ans.** Maximum molarity of CuS in aqueous solution = Solubility of CuS in mole L^{-1} . If S is the solubility of CuS in mol L^{-1} , then

60 Chemistry-XII —

- $CuS \rightleftharpoons Cu^{2+} + S^{2-}$ $S \qquad S$ $K_{sp} = [Cu^{2+}][S^{2-}]$ $S \qquad S$ $= S \times S = S^{2}$ $S^{2} = 6 \times 10^{-16}$ $S = \sqrt{6 \times 10^{-16}} = 2.45 \times 10^{-8} \text{ mol } \text{L}^{-1}.$
- **2.28.** Calculate the mass percentage of aspirin $(C_9H_8O_4)$ in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN .
- Mass percentage of aspirin $= \frac{\text{Mass of aspirin} \times 100}{\text{Mass of aspirin} + \text{Mass of acetonitrile}}$ Ans. $= \frac{6.5}{6.5 + 450} \times 100 = 1.424\%$
- **2.29.** Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene, generally given is 1.5 mg. Calculate the mass of 1.5×10^{-3} m aqueous solution required for the above dose.
- Ans. 1.5×10^{-3} m solution means that 1.5×10^{-3} moles of nalorphene is dissolved in 1 kg of water.

- Molar mass of $C_{19}H_{21}NO_3 = 19 \times 12 + 21 + 14 + 48 = 311 \text{ g mol}^{-1}$ ∴ 1.5 × 10⁻³ moles of nalorphene = 1.5 ×10⁻³ × 311 g = 0.467 g = 467 mg
- Mass of solution = 1000 g + 0.467 g = 1000.467 g...

Thus, for 467 mg of nalorphene, solution required is 1000.467 g

So, for 1.5 mg nalorphene = $\frac{1000.467 \times 1.5}{467}$ = 3.21 g of the dose is required.

- **2.30.** Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.
- **Ans.** 0.15 M solution means that 0.15 moles of C_6H_5COOH is present in 1 L or 1000 mL of the solution

Molar mass of $C_6H_5COOH = 72 + 5 + 12 + 32 + 1 = 122 \text{ g mol}^{-1}$

 \therefore 0.15 mole of benzoic acid = 0.15 × 122 g = 18.3 g

Thus,

 \therefore 1000 mL of 0.15 M solution contains benzoic acid = 18.3 g

 \therefore 250 mL of solution will contain benzoic acid = $\frac{18.3}{1000} \times 250 = 4.575$ g.

2.31. The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

Ans. The depression in freezing points are in the order:

Acetic acid < trichloroacetic acid < trifluoroactic acid

Fluorine, being the most electronegative, has the highest electron withdrawing tendency.

Consequently, trifluoroacetic acid is the strongest while acetic acid is the weakest acid. Hence trifluoroacetic acid ionises to the largest extent.

Thus depression in freezing point is maximum for the fluoroacetic acid.

Solutions **61**

2.32. Calculate the depression in the freezing point of water when 10 g of

 $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol⁻¹. Ans. Molar mass of CH₃CH₂CHClCOOH

> = 12 + 3 + 12 + 2 + 12 + 1 + 35.5 + 12 + 32 + 1 $= 122.5 \text{ g mol}^{-1}$

Number of moles of $CH_3CH_2CHClCOOH = \frac{10}{122.5} = 8.16 \times 10^{-2}$ mole

Molality of the solution (m) = $\frac{8.16 \times 10^{-2} \text{ mol}}{250} \times 1000 = 0.3264$ *.*.. If x is the degree of dissociation of $CH_3CH_2CH_2CHClCOOH$, then

$$CH_{3}CH_{2}CHClCOOH \rightleftharpoons CH_{3}CH_{2}CHClCOO^{-} + H$$

$$n \mod L^{-1} \qquad 0 \qquad 0$$

$$n (x - 1) \qquad nx \qquad nx$$

To calculate van't Hoff factor

Total moles of particles = n[1 - x + x + x] = n[1 + x] $i = \frac{n(1+x)}{n} = 1 + x$ $x = \sqrt{\frac{K_a}{m}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$ i = 1 + 0.065 = 1.065We know that

$$\Delta T_f = i K_f m = 1.065 \times 1.86 \times 0.3264 = 0.65^{\circ}C$$

2.33. 19.5 g of CH₂FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Ans.

$$\begin{split} & W_2 = 19.5 \text{ g} \\ & W_1 = 500 \text{ g} \\ & \Delta T_f \text{ (observed)} = 1.0^\circ\text{C} \\ & K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1} \\ & M_2 \text{(observed)} = \frac{1000 \times K_f \times W_2}{W_1 \times \Delta T_f} = \frac{1000 \times 1.86 \times 19.5}{500 \times 1.0} = 72.54 \text{ g mol}^{-1} \\ & M_2 \text{ (calculated)} = \text{CH}_2\text{FCOOH} \\ & = 12 + 2 + 19 + 12 + 32 + 1 = 78 \text{ g mol}^{-1} \\ & \text{van't Hoff factor (i)} = \frac{M_2 \text{ (calculated)}}{M_2 \text{ (observed)}} = \frac{78}{72.54} = 1.0753 \end{split}$$

Calculation of dissociation constant: Suppose degree of dissociation at the given concentration is x.

 $\begin{array}{ccc} \mathrm{CH}_{2}\mathrm{FCOOH} &\rightleftharpoons \mathrm{CH}_{2}\mathrm{FCOO^{-}} + \mathrm{H}^{+} \\ n \ \mathrm{mol} \ \mathrm{L}^{-1} & 0 & 0 \\ n(1-x) & nx & nx \end{array}$ Then Total no. of moles = n (1 - x + x + x) = n (1 + x) $i = \frac{n(1+x)}{n} = 1 + x$

62 Chemistry-XII –

$$x = i - 1 = 1.0753 - 1 = 0.0753$$

$$K_a = \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]} = \frac{n \ x \times n \ x}{n(1 - x)} = \frac{nx^2}{1 - x}$$

$$n = \frac{19.5}{78} \times \frac{1}{500} \times 1000 = 0.5 \text{ M}$$

$$K_a = \frac{(0.5)(0.0753)^2}{1 - 0.0753} = 3.07 \times 10^{-3}$$

2.34. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.

 $P^0 = 17.535 \text{ mm Hg}$ Ans. Here $W_{2} = 25 \text{ g}$ $W_{1} = 450 \text{ g}$ $M_{2} = C_{6}H_{12}O_{6} = 72 + 12 + 96 = 180 \text{ g mol}^{-1}$

For solvent (H_2O)

$$M_1 = 18 \ g \ mol^{-1}$$

Applying Raoult's law

$$\frac{P^{0} - P_{s}}{P^{0}} = \frac{n_{2}}{n_{1} + n_{2}}$$
or
$$\frac{P^{0} - P_{s}}{P^{0}} = \frac{n_{2}}{n_{1}} \quad \text{or} \qquad \frac{P^{0} - P_{s}}{P^{0}} = \frac{W_{2}}{M_{2}} \times \frac{M_{1}}{W_{1}}$$
or
$$1 - \frac{P_{s}}{P^{0}} = \frac{25 \times 18}{M_{2} \times 450}$$
or
$$1 - \frac{P_{s}}{P^{0}} = \frac{25 \times 18}{180 \times 450}$$
or
$$1 - \frac{P_{s}}{17.535} = \frac{25 \times 18}{180 \times 450}$$
or
$$\frac{17.535}{P_{s}} = 1 + \frac{25}{4500}$$
or
$$\frac{17.535}{P_{s}} = \frac{4525}{4500}$$
P_{s} = \frac{4500 \times 17.535}{4525} = 17.44 \text{ mm Hg}

2.35. Henry's law constant for the solubility of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Ans. Here
Applying Henry's law

$$K_{H} = 4.27 \times 10^{5} \text{ mm Hg}$$

 $P = 760 \text{ mm Hg}$
 $P = K_{H}x$
 $x = \frac{P}{K_{H}}$

Solutions **63**

Γ

$$x = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-3}$$

i.e. mole fraction of methane in benzene = 1.78×10^{-3} .

2.36. 100 g of liquid A (molar mass 140 g mol⁻¹) was dissolved in 1000 g of liquid B molar mass (180 g mol⁻¹). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr.

Ans. No. of moles of liquid A (Solute)
$$= \frac{100 \text{ g}}{140 \text{ g mol}^{-1}} = \frac{5}{7} \text{ mole}$$

No. of moles of liquid B (solvent) =
$$\frac{1000 \text{ g}}{180 \text{ g mol}^{-1}} = \frac{50}{9} \text{ mole}$$

Mole fraction of A

$$x_{A} = \frac{x_{A}}{x_{A} + x_{B}} = \frac{\frac{5}{7}}{\frac{5}{7} + \frac{50}{9}} = \frac{\frac{5}{7}}{\frac{395}{63}}$$

$$= \frac{5}{7} \times \frac{63}{395} = \frac{45}{395} = 0.114$$

Mole fraction of B in the solution,

 $x_{\rm B} = 1 - 0.114 = 0.886$

Applying Raoult's law

$$P_{A} = x_{A} P_{A}^{0} = 0.114 \times P_{A}^{0}$$

$$P_{B} = x_{B}P_{B}^{0} = 0.886 \times 500 = 443 \text{ torr}$$

$$P_{\text{total}} = P_{A} + P_{B}$$

$$475 = 0.114P_{A}^{0} + 443$$

$$P_A^0 = \frac{475 - 443}{0.114} = 280.7 \text{ torr}$$

$$P_{A} = 0.114 \times 280.7 \text{ torr} = 32 \text{ torr}.$$

2.37. Vapour pressure of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, Plot P_{total} , $P_{chloroform}$ and $p_{acetone}$ as a function of $x_{acetone}$. The experimental data observed for different compositions of mixture is

Ans.	$x_{acetone}$:	0.0	0.118	0.234	0.360	0.508	0.582	0.645	0.721
	P _{acetone} /mm Hg	:	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
	P _{chloroform} /mm Hg	:	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
	P _{total}	:	632.8	603.0	579.2	562.1	580.4	599.5	615.3	641.8

Γ

64 Chemistry-XII —



As the plot for P_{total} dips downwards, hence the solution show negative deviation from the ideal behaviour.

- **2.38.** Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of naphthalene.
- **Ans.** Molar mass of benzene $(C_6H_6) = 78 \text{ g mol}^{-1}$ Molar mass of toluene $(C_6H_5CH_3) = 92 \text{ g mol}^{-1}$

$$\therefore$$
 No. of moles in 80 g of benzene = $\frac{80 \text{ g}}{78 \text{ g mol}^{-1}}$ = 1.026 mole

No. of moles in 100 g of toluene =
$$\frac{100 \text{ g}}{92 \text{ g mol}^{-1}} = 1.087 \text{ mole}$$

In the solution, mole fraction of benzene = $\frac{1.026}{1.026 + 1.087} = 0.486$ Mole fraction of toluene = 1 - 0.486 = 0.514

Given:

$$P_{\text{Benzene}}^0 = 50.71 \text{ mm Hg}$$

 $P_{\text{Toluene}}^0 = 32.06 \text{ mm Hg}$

Applying Raoult's law

$$P_{\text{Benzene}} = x_{\text{Benzene}} \times P_{\text{Benzene}}^{0}$$

= 0.486 × 50.71 mm Hg = 24.65 mm Hg
$$P_{\text{Toluene}} = x_{\text{Toluene}} \times P_{\text{Toluene}}^{0}$$

= 0.514 × 32.06 mm Hg = 16.48 mm Hg

Mole fraction of Benzene in vapour phase = $\frac{P_{Benzene}}{P_{Benzene} + P_{Toluene}}$ $= \frac{24.65}{24.65 + 16.48} = \frac{24.65}{41.13} = 0.60.$

Solutions **65**

Г

- **2.39.** The air is a mixture of number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% and 79% by volume respectively, at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.
- **Ans.** Total pressure of air in equilibrium with water = 10 atm. As air contains 20% oxygen and 79% nitrogen by volume.

Partial pressure of oxygen $(P_{O_2}) = \frac{20}{100} \times 10 \text{ atm}$ $= 2 \text{ atm} = 2 \times 760 \text{ mm Hg} = 1520 \text{ mm Hg}$ Partial pressure of nitrogen $(P_{N2}) = \frac{79}{100} \times 10 \text{ atm.}$ $= 7.9 \times 760 \text{ mm Hg} = 6004 \text{ mm Hg.}$ $K_{H}(O_2) = 3.30 \times 10^7 \text{ mm Hg}$ $K_{H}(N_2) = 6.51 \times 10^7 \text{ mm Hg}$ Applying Henry's law $P_{O_2} = K_{H} \times x_{O_2}$ $x_{O_2} = \frac{P_{O_2}}{K_{H}} = \frac{1520 \text{ mm}}{3.30 \times 10^7 \text{ mm}} = 4.61 \times 10^{-5}$ $P_{N_2} = K_{H} \times x_{N_2}$ $x_{N_2} = \frac{P_{N_2}}{K_{H}}$ $x_{N_2} = \frac{6004 \text{ mm}}{6.51 \times 10^7} = 9.22 \times 10^{-5}.$

2.40. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75. atm at 27°C.

Ans.

 $\pi = i \text{ CRT}$ $\pi = i \frac{n}{V} \text{RT}$ $\pi = \frac{i \frac{n}{V} \text{RT}}{v}$ $\pi = \frac{\pi V}{i \frac{n}{K}}$ $x = \frac{\pi V}{2.47 \times 0.0821 \text{ L} \text{ atm } \text{K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2.47 \times 0.0821 \text{ L} \text{ atm } \text{K}^{-1} \text{ mol}^{-1}}$ Molar mass of CaCl₂ = 40 + 2 × 35.5 = 111 g mol^{-1} Amount dissolved = 0.0308 × 111 g = 3.42 g.

2.41. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25°C, assuming that it is completely dissociated.

[Delhi 2013]

66 Chemistry-XII -

...

$$\begin{array}{l} {\rm K_2SO_4\ dissolved\ =\ 25\ mg\ =\ 0.025\ g} \\ {\rm Volume\ of\ solution\ =\ 2\ litre} \\ {\rm T\ =\ 25^\circ C\ =\ 25\ +\ 273\ =\ 298\ K} \\ {\rm Molar\ mass\ of\ K_2SO_4\ =\ 2\ \times\ 39\ +\ 32\ +\ 64\ =\ 174\ g\ mol^{-1}} \\ {\rm As\ K_2SO_4\ dissociates\ completely\ as\ K_2SO_4\ \longrightarrow\ 2K^+\ +\ SO_4^{\ 2-}} \\ i.e.,\ ions\ produced\ (i)\ =\ 3 \\ \pi\ =\ i\ CRT \\ \pi\ =\ i\ {\rm CRT} \\ \pi\ =\ i\ {\rm K}\frac{W}{M} \times \frac{1}{V} {\rm RT} \\ =\ 3\times \frac{0.025\ g}{174\ g\ mol^{-1}}\ \times\ \frac{1}{2{\rm L}} \times\ 0.821\ {\rm L\ atm\ K^{-1}\ mol^{-1}} \times 298\ {\rm K} \\ =\ 3\times \frac{0.025\ g}{174\ g\ mol^{-1}}\ \times\ \frac{1}{2{\rm L}} \times\ 0.821\ {\rm L\ atm\ K^{-1}\ mol^{-1}} \times 298\ {\rm K} \\ =\ 5.27\ \times\ 10^{-3}\ {\rm atm}. \end{array}$$

ADDITIONAL QUESTIONS SOLVED

I. Very Short Answer Type Questions

Q1. What type of liquids form ideal solutions?

- **Ans.** Liquids having similar structures and polarities.
- **Q2.** Give an example of gaseous solution.
- Ans. Mixture of oxygen and nitrogen gas.
- **Q3.** What would be the value of van't Hoff factor for a dilute solution of K_2SO_4 in water? [AI 2005]
- **Ans.** *i* = 3

٦

Q4. How the molality of a solution is different from its molarity.

[Foreign 2005 F, AI 2004]

Ans. Molality =
$$\frac{\text{Moles of solute}}{1}$$

Molarity = $\frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}}$ [AI 2014]

- **Q5.** Define 'mole fraction' of a substance in a solution. [AI 2006]
- **Ans.** Mole fraction of a substance is defined as the ratio of number of moles of substances to the total number of moles of the solute and solvent.
- **Q6.** What is the effect of temperature on the solubility of sodium sulphate decahydrate?

- **Ans.** The solubility first increases upto 32.4°C (called transition temperature) and then it decreases.
- **Q7.** Two liquids A and B boil at 145°C and 190°C respectively. Which of them has higher vapour pressure at 80°C?

[CBSE 2006]

- **Ans.** Liquid A with lower boiling point is more volatile and hence will have higher vapour pressure.
- **Q8.** What happens when blood cells are placed in pure water? [*CBSE* 2006 *C*]
- **Ans.** Due to osmosis, water molecules move into the blood cells through the cell walls. As a result, blood cells swell up and may even burst.
- Q9. Define osmotic pressure. [CBSE 2007]
- **Ans.** Osmotic pressure is that extra pressure which can just stop the flow of solvent molecules into the solution when both are separated by semipermeable membrane.
- **Q10.** What is an antifreeze? [CBSE 2009]
- **Ans.** A substance which is added to water to lower its freezing point is called an antifreeze.
- **Q11.** Mention a large scale use of the phenomenon called reverse osmosis? [*CBSE* 2004]

Solutions **67**

Ans.

- **Ans.** Reverse osmosis is used in desalination of water to get drinking water from sea water.
- **Q12.** What is van't Hoff factor for a compound which undergoes tetramerisation in an organic solvent? [*CBSE* 2008]

Ans.
$$4A \rightarrow A_4$$

1 mole after dissociation gives $\frac{1}{4}$ mole of A₄.

Hence $i = \frac{1}{4}$

Q13. Why is osmotic pressure considered to be a colligative property?

Ans.
$$\pi = CRT$$
 or $\pi = \frac{n}{V}RT$

It shows that osmotic pressure (π) depends only on the number of moles 'n' of the solute present in a definite volume of the solution (V) and there is no factor involving the nature of the solute. Hence, it is a colligative property.

- **Q14.** What are isotonic solutions?
- **Ans.** Isotonic solutions are those which have the same osmotic pressure at a given temperature.
- Q15. State the condition resulting in reverse osmosis? [AI 2007]
- **Ans.** Reverse osmosis occurs when a pressure greater than osmotic pressure is applied on the solution.
- **Q16.** Name two factors on which the vapour pressure of the liquid depends?
- Ans. Vapour pressure depends upon
- (*i*) temperature (*ii*) external pressure
- **Q17.** Why is ether not miscible in water?
- **Ans.** Ether is not miscible in water because it cannot form H-bond with water.
- **Q18.** State Raoult's law for a binary solution containing volatile components. Write two differences between an ideal solution and a non ideal solution.

[Foreign 2007]

Ans. The partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction.

Q19. In the determination of molar mass of A⁺B⁻ using a colligative property, what may be the value of van't Hoff factor if the solute is 50% dissociated?

[Foreign 2005]

Ans.
$$\alpha = \frac{i-1}{n-1} \Rightarrow 0.5$$

 $\frac{i-1}{2-1} \Rightarrow i = 1.5$

Q20.10 mL of liquid A was mixed with 10 mL of liquid B. The volume of the resulting solution was found to be 19.9 mL. What do you conclude?

[*CBSE* 2005]

- **Ans.** Due to increase in extent of attractive forces between molecules A and B, there is a slight reduction in volume and mixture will show negative deviation from the Raoult's law.
- **Q21.** Define Henry's law about the solubility of a gas in a liquid.
- **Ans.** Henry's law states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas.
- **Q22.** Two liquids A and B on mixing produce a warm solution. Which type of deviation from Raoult's law does it show?
- **Ans.** Warming up of the solution means that the process of mixing is exothermic, *i.e.* $\Delta H_{\text{mixing}} = -\text{ve.}$ This implies that the solution shows a negative deviation.
- **Q23.** Why is the elevation in b.p. of water different in the following two solutions?
 - (a) 0.1 molar NaCl solution.
 - (b) 0.1 molar sugar solution.

[CBSE 2005 C]

Ans. NaCl is an electrolyte. It dissociates to give Na⁺ and Cl⁻ ions in the solution. Sugar is a non-electrolyte. It does not dissociate in the solution. Thus, the number of particles is greater in 0.1 M NaCl solution than in 0.1 M sugar solution. Hence elevation in boiling point is greater is case of NaCl solution.

68 Chemistry-XII –

- **Q24.** Under what condition do non-ideal solutions show negative deviations?
- **Ans.** When the new forces of attraction between the components are greater than those in between the pure components.
- **Q25.** Which substance is usually added to water in the car radiator to act as an antifreeze?
- **Ans.** Ethylene glycol.
- **Q26.** Give an example of compound in which hydrogen bonding results in the formation of a dimer.
- **Ans.** Benzoic acid (C₆H₅COOH) in benzene.
- **Q27.** Why is it advised to add ethylene glycol to water in a car radiator while driving in a hill station?
- **Ans.** It is done to lower the freezing point of water, so that it does not freeze.
- **Q28.** Sodium chloride or calcium chloride is used to clear snow from the roads. Why? [*CBSE* 2005]
- **Ans.** Sodium chloride depresses the freezing point of water to such an extent that it cannot freeze to form ice. Hence it melts off easily at the prevailing temperature.
- **Q29.** Give an example of nearly ideal solution? [AI 2014]
- **Ans.** Benzene and Toluene form nearly ideal solution.
- **Q30.** What are azeotropes? Give an example. [*AI* 2005 *C*, *Delhi* 2014]
- **Ans.** Azeotropes are constant boiling mixtures which distil out unchanged in their composition. For example, ethanol and H₂O.
- **Q31.** Give reason when 30 mL of ethyl alcohol and 30 mL of water are mixed, the volume of resulting solution is more than 60 mL. [AI 2006C]
- **Ans.** Forces of attraction become less in ethyl alcohol and water as compared to ethanol and water molecule.
- **Q32.** On mixing equal volume of water and ethanol, what type of deviation would you expect from Raoult's law?

٦

[CBSE 2003C]

- **Ans.** Due to decrease in intermolecular forces of attraction, it shows positive deviation from the Raoult's law.
- **Q33.** What is expected van't Hoff factor for $K_4[Fe(CN)_6]$?
- **Ans.** $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$ \therefore van't Hoff factor (i) = 5
- **Q34.** What factors are responsible for deviation for Raoult's law?
- **Ans.** If forces of attraction between A B are different from A A and B B, there will be deviation from Raoult's law.
- **Q35.** Why is osmotic pressure of 1M KCl is higher than that of 1M urea solution?
- Ans. 1 M KCl solution dissociates into K⁺ and Cl⁻ ions, therefore its osmotic pressure is higher than that of 1M solution of urea which does not dissociate or associate.
- **Q36.** What possible value of 'i' will it have if solute molecules undergo association in solution?
- **Ans.** i < 1, if solute molecules undergo association.
- **Q37.** When is the value of van't Hoff factor become more than one? [*CBSE* 2000 *F*]
- **Ans.** In case of electrolytes it is greater than one because they dissociate into ions.
- **Q38.** How is osmotic pressure dependent upon number of moles of solute?
- **Ans.** Osmotic pressure is directly proportional to the number of moles of solute.
- **Q39.**Why an increase in temperature is observed on mixing chloroform with acetone?
- **Ans.** It is because of H-bonding between acetone and CHCl₃, the force of attraction increases, therefore energy is released.
- **Q40.** Two liquids X and Y boil at 110 °C and 130 °C respectively. Which of these has higher vapour pressure at 50 °C?
- **Ans.** 'X' will have higher vapour pressure at 50 °C because it has lower boiling point?

Solutions **69**

- **Q41.** What are the values of ΔH and ΔV for an ideal solution of two liquids?
- **Ans.** $\Delta H = 0$, $\Delta V = 0$ for an ideal solution of two liquids.
- **Q42.** Define osmosis.
- **Ans.** Osmosis is a process in which solvent molecules enter the solution through semipermeable membrane.
- **Q43.** State any two characteristics of ideal solution.

Ans.

- (i) Ideal solutions follow Raoult's law.
- (*ii*) They can be separated by fractional distillation.
- **Q44.** What are hypertonic and hypotonic solutions?
- **Ans.** Hypertonic solution has higher concentration than body fluids whereas hypotonic solution has lower concentration than body fluids.
- **Q45.** What happens when pressure greater than osmotic pressure is applied on the solution separated by a semipermeable membrane from the solvent?
- **Ans.** Reverse osmosis occurs, *i.e.* net flow of solvent is from solution to solvent.
- **Q46.** What do you expect to happen when Red Blood Corpuscles (RBC's) are placed in
 - (i) 1% NaCl solution
 - (ii) 0.5% NaCl solution
- Ans.
 - (i) They will shrink due to plasmolysis.
 - (ii) They will swell and may even burst.
- **Q47.** Give an example of a solution containing a liquid solute in a solid solvent.
- Ans. Amalgam of mercury with sodium.
- **Q48.**Why is liquid ammonia bottle first cooled in ice before opening it?
- **Ans.** At room temperature, the vapour pressure of liquid ammonia is very high. On cooling, the vapour pressure decreases. Hence, the liquid ammonia will not splash out.
- **Q49.**Why do doctors advise gargles by saline water in case of sore throat?

- **Ans.** Saline water is hypertonic that is why fluids causing irritation in throat will come out.
- **Q50.** What are maximum boiling azeotropes? Give one example.
- **Ans.** The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Example: Nitric acid and water—68% nitric acid and 32% water by mass with a boiling point of 393.5 K.
- **Q51.** What are minimum boiling azeotropes? Give one example.
- **Ans.** The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotropes at a specific composition. For example, ethanol water mixture.
- **Q52.** A person suffering from high blood pressure should take less common salt, Why?
- **Ans.** Common salt contains Na⁺ and Cl⁻ which increases the osmotic pressure of blood, therefore it increases the blood pressure.
- **Q53.**Define molal elevation constant or ebullioscopic constant.
- **Ans.** Molal elevation constant is defined as increase in boiling point of a liquid when a solid is dissolved in it. The elevation is proportional to the number of particles dissolved and given by: ΔT = $K_b C$, where C is the molal concentration of solute. The constant, K_b is the ebullioscopic constant of the solvent.
- **Q54.**Define molal depression constant or cryoscopic constant.
- **Ans.** Molal depression constant is defined as the depression in freezing point when molality is equal to 1.
- **Q55.** What do you mean by 10% aqueous solution of sodium carbonate?
- **Ans.** It means that 10 g of Na_2CO_3 salt is present in 100 g of the solution.
- **Q56.** What do you mean by saying that the molality of a solution is 0.1?
- **Ans.** It means that 0.1 mol of the solute is dissolved in 1 kg of the solvent.

70 Chemistry-XII –

- **Q57.** What are constant boiling mixtures called?
- Ans. Azeotropes
- **Q58.** (*i*) Write the colligative property which is used to determine the molecular mass of macromolecules.
 - (*ii*) In non-ideal solutions what type of deviation shows the formation of minimum boiling azeotropes?

[CBSE 2016]

Ans. (i) Osmotic pressure

(*ii*) Large positive deviation from Raoult's Law. eg. Mixture of water and ethanol.

II. Short Answer Type Questions

 $\alpha = 0.5$

(2 or 3 Marks)

Q1. An electrolyte AB is 50% ionised in aqueous solution. Calculate the freezing point of 1 molal aqueous solution.

Ans.

$$n = 2$$

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

$$\Rightarrow \quad 0.5 = \frac{i-1}{2-1} = 1.5$$

$$\Delta T_f = i \times k_f \times m$$

$$= 1.5 \times 1.86 \times 1 = 2.79$$
Freezing point of the solution

$$= 273 - 2.79 = 270.21 \text{ K}$$

Q2. A solution of sucrose (Molecular weight 342 u) is prepared by dissolving 68.4 g of it per litre of solution. What is the osmotic pressure at 300 K? $[R = 8.314 \text{ kPa } \text{dm}^3 \text{ K}^{-1} \text{ mol}^{-1}]$

Ans.

here
$$V = 1$$
 L
 $R = 8.314$ kPa dm³ K⁻¹ mol⁻¹

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

 $\pi V = nRT$

$$\pi V = \frac{W}{M} \times RT$$

$$\pi \times 1 = \frac{68.4}{342} \times 8.314 \times 300$$

$$\pi = 498.84 \text{ kPa}$$

- **Q3.** What type of non-idealities are exhibited by cyclohexane-ethanol and acetone-chloroform mixture? Give reason for your answer.
- **Ans.** Ideal solutions are those which obey Raoult's law over extreme range of concentration.

Ideal solutions have another important properties.

(*i*) $\Delta H_{mix} = 0$ (*ii*) $\Delta V_{mix} = 0$ Here-forces of attraction between A – A, B – B and A – B are of the same order. Non ideal solutions do not obey Raoult's law over the entire range of concentration.

$$\Delta H_{mix} \neq 0$$
 and $\Delta V_{mix} \neq 0$

Cyclohexane-ethanol mixture shows positive deviation from Raoult's law because forces of attraction between cyclohexane and ethanol are less than in between pure cyclohexane as well as pure ethanol.

Acetone-Chloroform mixture shows negative deviation from Raoult's law because forces of attraction between acetone and chloroform are higher than that in between pure acetone and pure chloroform molecules.

- **Q4.** How is relative lowering of vapour pressure defined for a solution consisting of volatile solvent and non-volatile solute? How is this function related to the mole fraction of the solute of the solvent.
- **Ans.** Relative lowering of vapour pressure is equal to the mole fraction of solute if solute is non-volatile and only solvent molecules is volatile.

$$\frac{\mathbf{P}_{\mathrm{A}}^{\mathrm{o}} - \mathbf{P}_{\mathrm{A}}}{\mathbf{P}_{\mathrm{A}}^{\mathrm{o}}} = x_{\mathrm{B}}$$

where P_A^0 is vapour pressure of pure solvent and P_A is vapour pressure of solution and x_B is the mole fraction of solute.

Q5. Given below is the sketch of a plant for carrying out a process.



- (*i*) Name the process occurring in the above plant.
- (*ii*) To which container does the net flow of solvent take place?
- (*iii*) Name one SPM which can be used in this plant.
- (*iv*) Give one practical use of the plant. [CBSE Sample Paper-I 2008]

Ans.

- (i) Reverse osmosis
- (*ii*) In fresh water container from salt water container.
- (*iii*) Cellulose acetate is semipermeable membrane (SPM)
- (iv) Purification of water
- **Q6.** An aqueous solution of glucose is made by dissolving 10 g of glucose ($C_6H_{12}O_6$) in 90 g of water at 303 K. If the vapour pressure of pure water at 303 K is 32.8 mm Hg, what would be the vapour pressure of the solution? [*CBSE* 2000]

Ans.

$$\begin{split} & W_1 = 90 \text{ g} \\ & W_2 = 10 \text{ g} \\ & M_2 = 72 + 12 + 96 \\ & = 180 \text{ g mol}^{-1} \\ & P_1^0 = 32.8 \text{ mm Hg} \\ & M_1 = 18 \text{ g mol}^{-1} \\ & \frac{P_1^0 - P_1}{P_1^0} = \frac{n_2}{n_1 + n_2} = \frac{W_2}{M_2} \times \frac{M_1}{W_1} \\ & \frac{P_1^0 - P_1}{P_1^0} = \frac{10}{180} \times \frac{18}{90} \\ & 1 - \frac{P_1}{p_1^0} = \frac{10 \times 18}{180 \times 90} \\ & - \frac{P_1}{p_1^0} = \frac{10 \times 18}{180 \times 90} - 1 \end{split}$$

 $\frac{P_1}{p_1^0} = \left(1 - \frac{10 \times 18}{180 \times 90}\right)$ $\frac{P_1}{32.8} = 1 - \frac{10 \times 18}{180 \times 90}$

$$P_1 = 0.36 \text{ mm Hg}$$

Q7. Calculate the mole fraction of ethylene glycol (C₂H₆O₂) in a solution containing 20% of C₂H₆O₂ by mass. [CBSE 2001] **Ans.** Let total mass of solution = 100 g ∴ mass of ethylene glycol $W_2 = 20$ g Mass of solvent (water) $W_1 = 80$ g Molar mass of [C₂H₆O₂] $M_2 = 12 \times 2 + 6 + 16 \times 2$ ` = 24 + 6 + 32 = 62 g mol⁻¹ Molar mass of water (H₂O) $M_1 = 1 \times 2 + 16 = 18$ g mol⁻¹ Moles of water $n_1 = \frac{W_1}{M_1} = \frac{80}{18} = 4.44$ mole

$$n_2 = \frac{W_2}{M_2} = \frac{20}{62} = 0.322 \text{ mol}$$

Mole fraction of C₂H₆O₂ = $\frac{n_2}{n_1 + n_2}$ = $\frac{0.322}{4.44 + 0.322}$ = 0.068

Q8. A solution is made by dissolving 30 g of a non-volatile solute in 90 g of water. It has a vapour pressure of 2.8 kPa at 298 K. At 298 K, vapour pressure of pure water is 3.64 kPa. Calculate the molar mass of the solute. [*CBSE* 2005]

Ans.
$$\frac{P_A^0 - P_A}{P_A^0} = x_B$$

 P_A^0 = Vapour pressure of pure water P_A = Vapour pressure of solute

$$P_A = vapour pressure of solute$$

 $x_{\rm B}$ = mole fraction of solute

$$\frac{\mathbf{P}_{\mathrm{A}}^{\mathrm{o}} - \mathbf{P}_{\mathrm{A}}}{\mathbf{P}_{\mathrm{A}}^{\mathrm{o}}} = \frac{n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}}$$

72 Chemistry-XII

$$\begin{split} \frac{P_{A}^{0} - P_{A}}{P_{A}^{0}} &= \frac{n_{B}}{n_{A} + n_{B}} = \frac{W_{B}}{M_{B}} \times \frac{W_{A}}{M_{A}} \\ \frac{3.64 \, \text{kPa} - 2.8 \, \text{kPa}}{3.64 \, \text{kPa}} &= \frac{30}{M_{B}} \times \frac{90}{18} \\ M_{B} &= 26 \, \text{g mol}^{-1}. \end{split}$$

- **Q9.** Calculate the molality of a solution containing 20.7 g of potassium carbonate dissolve in 500 ml of solution, assume density of solution = 1 g/ml. [*CBSE* 2005]
- Ans. Molar mass of K_2CO_3 = 39 × 2 + 12 + 48 $M_2 = 138 \text{ g mol}^{-1}$ Amount of solute (K_2CO_3) $W_2 = 20.7 \text{ g}$ Amount of water mass of solvent = 500 - 20.7 $W_1 = 479.3 \text{ g}$ \therefore Molality = $\frac{W_2 \times 1000}{M_2 \times W_1}$ = $\frac{20.7 \times 1000}{138 \times 479.3}$ = 0.313 m
- **Q10.** State Henry's law for solubility of a gas in a liquid. Explain the significance of Henry's law constant (K_H). At the same temperature, hydrogen is more soluble in water than helium. Which of them will have a higher value of K_H and Why? [*CBSE* 2005, *AI* 2014] *Or*

State henry's law. Why do gases always tend to be less soluble in liquid as the temperature is raised? [*CBSE* 2015]

Ans. Henry's law states that the solubility of a gas in liquid at a given temperature is directly proportional to the partial pressure of the gas.

 $P = K_H x$

where P is the pressure of the gas, x is the mole fraction of the gas in the solution and K_H is the Henry's law constant. K_H is a function of the nature of gas. Higher the value of K_H at a given temperature, lower is the solubility of the gas in the liquid.

As helium is less soluble in water, so it has a higher value of K_H than hydrogen. **Henry's Law:** As dissolution of agar in liquid is an exothermic process, therefore, the solubility should decrease with in increase in temperature.

Q11. At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If osmotic pressure of solution is 1.52 bar at the same temperature, what would be its concentration? [CBSE 2005]

Ans.
$$\pi = \frac{n}{V} RT$$

 $\pi V = n RT$

If *n*, R and T are same in both case $\pi_2 V_2 = \pi_1 V_1$

$$V_2 = \frac{\pi_1 V_1}{\pi_2} = \frac{4.98 \times 1}{1.52} = 3.28 \text{ L.}$$

- **Q12.**What do you mean by azeotropic mixtures?
- **Ans.** The solutions (liquid mixtures) which boils at constant temperature and remains unchanged in composition are called azeotropes or azeotropic mixtures.
- Q13. (a) A 4% solution of sucrose is isotonic with 3% solution of an unknown organic substance. Calculate the molecular mass of unknown substance. (b) What is the mole fraction of a solute, in 2.5 m aqueous solution?

[AI 2006 C, 05 C]

Ans. (a)
$$M_{sucrose} = M_{unknown}$$

 $\frac{4}{342} \times \frac{1000}{100} = \frac{3}{x} \times \frac{1000}{100}$
 $x = \frac{3 \times 342}{4} = \frac{3 \times 171}{2}$
 $= 256.5 \text{ g mol}^{-1}.$

(b) 2.5 m aqueous solution contains2.5 moles of solute in 1000 g of water.Number of moles of water

Solutions **73**

 $= \frac{1000}{18 \text{ g mol}^{-1}} = 55.55$ Total no. of moles = 2.5 + 55.55 = 58.05Mole fraction of solute $= \frac{2.5}{58.05} = 0.043.$ Q14. Urea forms an ideal solution in water. Determine the vapour pressure of aqueous solution containing 10% by mass of urea at 4 °C. (Vapour pressure of water, at 40 $^{\circ}C$ = 55.3 mm Hg) [AI 2005] **Ans.** Mass of urea = 10 gMass of water = 90 gMoles of urea = $\frac{10 \text{ g}}{60 \text{ g mol}^{-1}} = \frac{1}{6}$ Moles of Water = $\frac{90}{18} = 5$ Mole fraction of water 30 5 x 31

$$A_{A} = \frac{1}{\frac{1}{6}+5} = \frac{1}{3}$$

Vapour pressure of solution

$$P = P_A^0 \cdot x_A = 55.3 \times \frac{30}{31}$$

P = 53.52 mm Hg.

Q15. (*a*) Why is the vapour pressure of a solution of glucose in water lower than that of water?

(*b*) A 6.90 M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the KOH solution?

[Molar mass of KOH = 56 g mol⁻¹] [CBSE 2006]

Ans. (a) A part of the water surface is occupied by non-volatile glucose molecules. This decreases the effective surface area for the vaporisation of water molecules consequently, the vapour pressure of a solution of glucose in water is lower than that of water.
(b) A 6.90 M solution contains 6.90 mol of KOH in 1000 cm³ of the solution.

Mass of 6.90 moles of KOH = $6.90 \times 56 = 386.4$ g A 30% solution contains 30 g of KOH present in 100 g of solution. \therefore 386.4 g of KOH is present in

$$= \frac{100 \times 386.4}{30}$$

= 1288 g of solution.
Density of KOH solution
$$= \frac{Mass}{Volume}$$

$$= \frac{1288 \text{ g}}{1000 \text{ cm}^3} = 1.288 \text{ g cm}^{-3}.$$

Q16. A 0.2 percent aqueous solution of a non-volatile solute exerts vapour pressure of 1.004 bar at 100 °C. What is the molar mass of the solute?

[Foreign 2006]

Ans. According to Raoult's law

$$\frac{P^{0} - P}{P^{0}} = n_{B} \text{ (mole fraction of solute)}$$

$$= \frac{n_{B}}{n_{A} + n_{B}} = \frac{n_{B}}{n_{A}} = \frac{W_{B} \times M_{A}}{M_{B} \times W_{A}}$$
(For dilute solution, $n_{B} < << n_{A}$)
$$M_{B} = \frac{W_{B} \times M_{A}}{W_{A}} \cdot \frac{P^{0}}{P^{0} - P}$$

$$= \frac{0.2 \times 18}{99.8} \times \frac{1.013}{1.013 - 1.009}$$

$$= 4.06 \text{ g mol}^{-1}$$

Q17. Calculate the freezing point of a solution containing 0.520 g glucose $(C_6H_{12}O_6)$ dissolved in 80.20 g of water. For water $K_f = 1.86$ K kg mol⁻¹. **Ans.** Molecular mass of glucose $(C_2H_2O_2)$

$$M_{\rm B} = 72 + 12 + 96 = 180 \text{ g mol}^{-1}$$
$$\Delta T_{f} = \frac{K_{f} \times W_{\rm B} \times 1000}{M_{\rm B} \times 1000}$$

$$f = M_{\rm B} \times W_{\rm A}$$

= $\frac{1.86 \times 0.520 \times 1000}{180 \times 80.20} = 0.067.$

Q18.A 0.1539 molal aqueous solution of cane sugar (mol mass = 342 g mol⁻¹) has a freezing point of 271 K while the freezing point of pure water is 273.15 K. What will be the freezing point of

74 🔳 Chemistry-XII –

an aqueous solution containing 5 g of glucose (molar mass = 180 g mol⁻¹) per 100 g of solution. [CBSE 2007] Ans. Molality = 0.1539 m $\Delta T_f = 273.15 - 271 \text{ K} = 2.15 \text{ K}$ $\Delta T_f = K_f \cdot m$ $m = \frac{\Delta T_f}{K_f}$ $0.1539 = \frac{2.15}{K_f}$ $\Rightarrow K_f = \frac{2.15}{0.1539}$ $W_2 = 5g$ $M_2 = 180 \text{ g mol}^{-1}$ $\Delta T_f = K_f \times m$ $= \frac{2.15}{0.1539} \times \frac{5}{180} \times \frac{1000}{95}$ = 4.08 KFreezing point of solution

$$= 273.15 - 4.08 \text{ K}$$

Q19. State Henry's law correlating the pressure of a gas and its solution in a solvent and mention two applications for the law.

- **Ans. Henry's law:** It states that at constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas. Applications: It is used:
 - (*i*) in the production of carbonated beverages.
 - (ii) in deep sea diving
- (*iii*) in the functioning of lungs.
- **Q20.** A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86°C, whereas pure ether boils at 35.60 °C. Determine the molecular mass of the solute (For ether $K_b = 2.02K$ kg mol⁻¹) [Foreign 2008]
- Ans. We have, mass of solute,

 $W_2 = 8 \text{ g}$ Mass of solvent, $W_1 = 100 \text{ g}$

٦

Elevation of boiling point, $\Delta T_b = 36.86 - 35.60 = 1.26 \ ^{\circ}C$ $K_b = 2.02$ Molecular mass of the solute $M_2 = \frac{1000 \times W_2 \times K_b}{\Delta T_b \times W_1}$ $= \frac{1000 \times 8 \times 2.02}{1.26 \times 100} = \frac{161.6}{1.26}$ $= 128.25 \ \text{g mol}^{-1}.$ **Q21.** Calculate the temperature at which of solution containing 54 g of glucose, $C_6 H_{12}O_6 \text{ in } 250 \text{ g of water will freeze.}$ $(K_f \text{ for water } = 1.86 \text{ K kg mol}^{-1})$ [CBSE 2008]

Ans. Molecular mass of glucose

$$M_{\rm B} = 72 + 12 + 96$$

= 180 g mol⁻¹

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_B}$$

$$= \frac{1.86 \times 54 \times 1000}{180 \times 250} = 2.23$$

Freezing point of solution

= 0 - 2.23 = -2.23 °C.

- **Q22.** Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure? [CBSE 2008]
- **Ans. Osmotic pressure:** Osmotic pressure is equal to the extra pressure which must be applied on solution side so as to prevent the flow of solvent molecules into solution.

$$\pi = CRT$$

$$\pi = \frac{n}{V}RT$$

or $\pi V = nRT$
or $\pi V = \frac{W_B}{M_B}RT$

r
$$M_{\rm B} = \frac{W_{\rm B}RT}{\pi V}$$

Osmotic pressure is inversely proportional to the molecular mass of the solute.

Solutions **75**

Q23. The boiling point elevation of 0.30 g acetic acid in 100 g benzene is 0.0633 K. Calculate the molar mass of acetic acid from this data. What conclusion can you draw about the molecular state of the solute in the solution? [Given K_b for benzene = 2.53 K kg mol⁻¹]

Ans. Here

W₁ = 100 g W₂ = 0.30 g $\Delta T_b = 0.0633$ K K_b = 2.53 K kg mol⁻¹ ∴ Molar mass of acetic acid M = K_b × W₂ × 1000

$$M_2 = \Delta T_b \times W_1$$

= $\frac{2.53 \times 0.30 \times 1000}{0.0633 \times 100} = 119.90$

van't Hoff factor (i)

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$
$$= \frac{60}{119.90} = 0.5$$

Hence i < 1, therefore the solute (acetic acid) is associated in the solution.

- **Q24.** The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45 °C, calculate:
 - (*i*) the molar mass of acetic acid from this data.
 - (*ii*) van't Hoff factor [For benzene, $K_f = 5.12$ K kg mol⁻¹] What conclusion can you draw from the value of van't Hoff factor obtained?

Ans. Here $W_1 = 20.0 \text{ g}$

$$W_2 = 0.2 \text{ g}$$

 $\Delta T_2 = 0.45^{\circ}\text{C}$

$$\Delta I_f = 0.43$$
 C
 $K = 5.12$ K kg mg

 $K_f = 5.12 \text{ K kg mol}^{-1}$ Molar mass of acetic acid

$$M_{2} = \frac{K_{f} \times W_{2} \times 1000}{\Delta T_{f} \times W_{1}}$$
$$= \frac{5.12 \times 0.2 \times 1000}{0.45 \times 20.0}$$
$$= 113.77 \text{ g mol}^{-1}$$

76 Chemistry-XII -

Actual molar mass of acetic acid. = 60 g mol⁻¹

(ii) van't Hoff factor

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$
$$i = \frac{60}{113.77} = 0.52$$

Here i < 1, therefore the non-volatile solute (acetic acid) is associated in the solution.

Q25. 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein? (R = 0.0821 L atm mol⁻¹ K⁻¹,

760 mm Hg = 1 atm [*CBSE* 2009] **Ans.** Here W = 100 mg = 0.100 g

$$V = 10.0 \text{ mL} = 0.01 \text{ L}$$

$$\pi = 13.33 \text{ mm Hg} = \frac{13.3}{760} \text{ atm}$$
$$T = 25 \text{ }^{\circ}\text{C} = 25 + 273 = 298 \text{ K}$$
$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$
$$M = ?$$

Molar mass

$$M = \frac{WRT}{\pi V} = \frac{0.1 \times 0.0821 \times 298}{\frac{13.3}{760} \times 0.01}$$
$$= \frac{0.1 \times 0.0821 \times 298 \times 760}{13.3 \times 0.01}$$
$$= \frac{1859 \times 4008}{0.133}$$
$$= 13980.4 \text{ g mol}^{-1}$$
or 13.98 kg mol^{-1}

Q26. Calculate the freezing point depression expected for 0.0711 m aqueous solution of Na₂SO₄. If this solution actually freezes at 0.320 °C, what would be the value of van't Hoff factor? (K_f for water is 1.86 K kg mol⁻¹) [*CBSE* 2009] **Ans.** Here m = 0.0711 m $\Delta T_c = 0.320$ °C or 0.320 K

$$\Delta T_f = 0.320 \text{ °C or } 0.320 \text{ I}$$
$$K_f = 1.86 \text{ K Kg mol}^{-1}$$
$$\Delta T_f = iK_f m$$

$$i = \frac{\Delta T_f}{K_f \times m} = \frac{0.320}{1.86 \times 0.0711}$$
$$= \frac{0.320}{0.132} = 2.4$$

Q27. Ethylene glycol (molar mass = 62 g mol⁻¹) is a common automobile antifreeze. Calculate the freezing point of a solution containing 12.4 of this substance in 100 g of water. Would it be advisable to keep this substance in the car radiator during summer? (K_f for water = 1.86 k kg/mol) (K_b for water = 0.512 K kg/mol.)

Ans.
$$\Delta T_b = K_b \times \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

$$= 0.512 \times \frac{12.4}{62} \times \frac{1000}{100}$$

= 1.024 K

Since water boils at 100°C, so a solution containing ethylene glycol will boil at 101.04 °C, so it is advisable to keep this substance in car radiator during summer.

Q28. 1.00 molal aqueous solution of trichloroacetic acid (CCl₃COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid. (k_b for water = 0.512 Kkgmol⁻¹). [CBSE 2013]

Ans.

(vant

$$\Delta T_b = ik_b \times m$$

$$\Delta T_b = 100.18 - 100$$

$$0.18 = (0.512 \times 1)$$

Hoff factor):

$$i = \frac{0.18}{0.512} = 0.351$$

[AI 2014]

Q29. 15.0 g of an unknown molecular material is dissolved in 450g of water. The resulting solution freezes at -0.34° C. What is the molar mass of the material? K_f for water = 1.86 K kg mol⁻¹.

W = 15.0 g

Ans.

٦

W (solvent) = 450 g

$$\Delta T_f = T_f^0 - T_f$$
= 0 - (-0.34)
= 0.34 °C

$$\Delta T_f = k_f m$$
0.34 = 1.86 × $\frac{15}{M} \times \frac{1000}{450}$
M = $\frac{1.86 \times 15 \times 1000}{0.34 \times 450}$
= 182.35 g mol⁻¹.

Q30. A solution of glycerol $(C_3H_8O_3)$ in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C. What mass of glycerol was dissolved to make this solution $(k_b \text{ for water} = 0.512 \text{ K kg mol}^{-1})$ [AI 2014]

Ans. $\Delta T_b = k_b m$

$$(100.42-100^{\circ}) = \frac{0.512 \times W \times 1000}{92 \times 500}$$

$$0.42 = \frac{0.512 \times W \times 1000}{92 \times 500}$$
$$W = \frac{92 \times 500 \times 0.42}{0.512 \times 1000}$$

Q31. Calculate the amount of $CaCl_2$ (molar mass – 111 g mol⁻¹) which must be added to 500 g as water to lower its freezing point by 2K, assuming $CaCl_2$ is completely dissociated (k_f for water = 1.86 K kg mol⁻¹). (*CBSE* 2015)

Ans. CaCl
$$\longrightarrow$$
 Ca²⁺ + 2Cl⁻
 $i = 3$
 $\Delta T_f = i \times k_f \times m$
 $2k = 3 \times 1.86 \frac{W_2}{111 \times 500} \times 1000$
 $W_2 = \frac{111 \times 2}{2 \times 3 \times 1.86}$
 $= \frac{222}{11.16} = 19.89 \text{ g}$

Solutions 🔳 77

Q32. Calculate the boiling point of solution when 2 g of Na_2SO_4 (M = 142 g/mol) was dissolved in 50 g assuming Na₂SO₄ undergoes complete ionization. (K_b for water = 0.52 K kg mol⁻¹) [CBSE 2016] Ans. Wt of solute $(W_2) = 2 g$ Molar mass $(M_2) = 142 \text{ g/mol}$ Wt. of solvent $(W_1) = 50 g$ $K_b = 0.52$ K kg/mol $\Delta T_{h} = i K_{h} m$ *.*.. $= 3 \ \times \ 0.52 \ \times \ \frac{W_2 \times 1000}{M_2 \times W_1}$ $= 3 \times 0.52 \ \frac{2 \times 1000}{142 \times 50}$ = 0.439 K

III. Long Answer Type Questions

(5 Marks)

Q1.

- (i) Benzoic acid completely dimerises in benzene. What will be the vapour pressure of a solution containing 61 g of benzoic acid per 500 g benzene when the vapour pressure of pure benzene at the temperature of experiment is 66.6 torr?
- (*ii*) What would have been the vapour pressure in the absence of dimerisation?
- (*iii*) Derive the relationship between mole fraction and vapour pressure of a component of an ideal solution in the liquid phase and vapour phase?

Ans.

(i)
$$\frac{\Delta P}{P^0} = ix_{B_i} i = \frac{1}{2}$$
$$x_B = \frac{n_B}{n_A + n_B} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$= \frac{\frac{61}{122}}{\frac{500}{78} + \frac{61}{122}}$$

$$x_{\rm B} = \frac{0.5}{6.91}$$

$$\frac{\Delta P}{66.6} = \frac{1}{2} \times \frac{0.5}{6.91}$$

$$\Delta P = \frac{50 \times 66.6}{2 \times 691} = 2.41$$

$$P^{0} - P = 2.41$$

$$P = 66.6 - 2.41 = 64.19 \text{ torr.}$$
In the absence of dimerisation. (*i* = 1)

$$\frac{\Delta P}{P^{0}} = x_{\rm B}$$

$$\Delta P = \frac{50}{691} \times 66.6 = 4.82$$

$$P = 66.6 - 4.82 = 61.78 \text{ torr.}$$
From Raoult's law

$$x_{1} = \text{mole fraction of liquid 1}$$

$$x_{2} = \text{mole fraction of liquid 2}$$

$$P_{1} = x_{1}P_{1}^{0}$$

$$P_{2} = x_{2}P_{2}^{0}$$

 $y_1^2 = {\text{mole}} {\text{fraction of component}}$ 1 in vapour phase $y_2 = {\text{mole fraction of component}}$

2 in vapour phase

$$y_1 = \frac{P_1}{P_{\text{total}}} = \frac{P_1}{P_1 + P_2}$$

$$y_1 = \frac{P_2}{P_2} = \frac{P_2}{P_2}$$

$$y_{2} = \frac{1}{P_{\text{total}}} = \frac{1}{P_{1} + P_{2}}$$
$$y_{1} = \frac{x_{1}P_{1}^{0}}{x_{1}P_{1}^{0} + x_{2}P_{2}^{0}} = \frac{x_{1}P_{1}^{0}}{x_{1}P_{1}^{0} + (1 - x_{1})P_{2}^{0}}$$
$$y_{2} = \frac{x_{2}P_{2}^{0}}{x_{1}P_{1}^{0} + x_{2}P_{2}^{0}}$$

Q2.

(ii)

(iii)

- (a) Which aqueous solution has higher concentration -1 molar or 1 molal solution of the same solute? Give reason.
- (b) 0.5 g KCl was dissolved in 100 g water and the solution originally at 20°C, froze at -0.24 °C. Calculate the percentage ionisation of salt. (K_f per 1000 g of water = 1.86 K.)

78 🔳 Chemistry-XII

Ans.

(a) 1 M has higher concentration than 1 m. 1 m solution = 1 mole in 1000 g solvent or 1 mole in 1000 cm³ of solvent. But 1 M solution = 1 mole in 1000 cm³ of solution, *i.e.* solvent is less here.
(b) ΔT_f = 0 - (-0.24 °C) = 0.24 °C 1000 K_c W_c

$$M_{2} = \frac{1000 K_{f} W_{2}}{\Delta T_{f} W_{1}}$$

$$= \frac{1000 \times 1.86 \times 0.5}{0.24 \times 100} \text{g mol}^{-1}$$

$$= 38.75 \text{ g mol}^{-1}$$
Theoretical molar mass of KCl
$$= 39 + 35.5 = 74.5 \text{ g mol}^{-1}$$

$$i = \frac{\text{Calculated mol mass}}{\text{Theoretical mol mass}}$$

$$= \frac{74.5}{38.75} = 1.92$$
KCl $\longleftrightarrow K^{+} + \text{Cl}^{-}$

$$1 \text{ mole } 0 \quad 0$$

$$1 - \alpha \qquad \alpha \qquad \alpha$$
Total no. of moles after dissociation
$$= 1 + \alpha$$

$$i = \frac{1 + \alpha}{1}$$

$$i - 1 = \alpha = 1.92 - 1 = 0.92$$
Percentage dissociation = 0.92 × 100
$$= 92\%$$

Q3. What are ideal and non-ideal solutions? Explain with suitable diagram the behaviour of ideal solutions.

[CBSE 2015, AI 2003]

Ans. Ideal solutions: The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. Ideal solutions are formed by mixing the two components which are identical in molecular size, in structure and have almost identical intermolecular forces.

Examples:

٦

- (*i*) Benzene and toluene
- (ii) n-Hexane and n-heptane
- (*iii*) Chlorobenzene and bromobenzene. **Characteristics:**
- (i) They must obey Raoult's law.

- (*ii*) ΔH mixing should be zero.
- (*iii*) ΔV mixing should be zero, *i.e.* volume change on mixing is zero.

Non-ideal solutions: The solutions which do not obey Raoult's law are called non-ideal solutions. In case of non-ideal solutions there is a change in volume and heat energy when the two components are mixed.

Characteristics:

- (i) They does not obey Raoult's law.
- (*ii*) $\Delta V \min \neq 0$
- (iii) △H mix ≠ 0 Behaviour of Ideal Solutions:

A plot of P_1 or P_2 versus the mole fraction x_1 and x_2 for an ideal solution gives a linear plot.



These Lines (I and II) pass through the points and respectively when x_1 and x_2 is equal to unity. Similarly the plot (Line III) of P_{total} versus x_2 is also linear. The minimum value of P_{total} is P_1^0 and the maximum value is P_2^0 , assuming that component 1 is less volatile than component 2, *i.e.* $P_1^0 < P_2^0$

- **Q4.** Explain with a suitable diagram and appropriate example, why some non-ideal solution shows positive deviation from Raoult's law. [CBSE 2004]
- **Ans.** Some non-ideal solutions show positive deviation from Raoult's law. Consider a solution of two components A and B. If A-B interactions in the solution are weaker than the A-A and B-B interactions in the two liquids forming the solution, then the escaping tendency of molecules A and B from the

Solutions **79**

solution become more than in pure liquids. The total vapour pressure will be greater than the corresponding vapour pressure as expected on the basis of Raoult's law. This type of behaviour of solution is called positive deviation from Raoult's law. The boiling point of such solutions are lowered. Mathematically,



The total vapour pressure is less than $P_A + P_B$

$$\begin{array}{ccc} & & P < P_A + P_B \\ & & P < P_A^0 \cdot x_A + P_B^0 x_B \\ \text{Hence} & & P_1 = P_A \\ & & P_2 = P_B \end{array}$$

Examples of solutions showing positive deviations:

- (i) Ethyl alcohol and water
- (*ii*) Benzene and acetone
- (iii) Ethyl alcohol and cyclohexane
- (*iv*) Carbon tetrachloride and chloroform.
- **Q5**.
- (*i*) What is Osmotic pressure and how is it related to the molecular mass of a non volatile substances?
- (*ii*) What advantage the osmotic pressure method has over the elevation of boiling point method for determining the molecular mass?

[AI 2004] [CBSE 2011]

Ans.

٦

(*i*) **Osmotic pressure:** It is the pressure of the solution column that can prevent

80 Chemistry-XII -

the entry of solvent molecules through a semi-permeable membrane, when the solution and the solvent are separated by the same. It is denoted by π . Its unit is mm of Hg or atmosphere.

We know that $\pi = CRT$

where π is the osmotic pressure and R is the gas constant

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

where V is volume of solution per litre containing n_2 moles of solute.

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

By the above relation molar mass of solute can be calculated.

- (ii) The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and molarity of the solution is used instead of molality. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperature and polymers have poor solubility.
- **Q6.** Calculate the molarity and molality of a 15% solutions (by weight) of sulphuric acid. (density-1.020 g cm⁻³) (Atomic masses H = 1, O = 16, S = 32 *amu*). [CBSE 2006]

Ans.
$$M = \frac{W}{M}$$

_

 $M_B \times V_L$ Molecular weight of H_2SO_4 = 2 × 1 + 32 + 64 = 98 g mol⁻¹ Molarity (M)

$$\frac{15 \text{ g} \times 1000}{98 \text{ g/mol} \times 115 \text{ g} \times 1.02 \text{ g/cm}^3}$$
$$= \frac{15,000}{11495.4} \text{ moles} = 1.3048 \text{ moles}$$

m (molality) =
$$\frac{W_B \times 1000}{M_B \times 100 \text{ g}}$$

= $\frac{15 \text{ g} \times 10}{98 \text{ g} \text{ mol}^{-1}} = \frac{150}{98}$
= 1.53 molal.

Q7.

(a) Define the following terms:

(i) Mole fraction

- (ii) van't Hoff factor [CBSE 2014, 17]
- (b) 100 mg of a protein is dissolved in enough water to make 10.0 mL of a solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25 °C, what is the molar mass of protein?

Ans. (*a*)

٦

(i) Mole fraction (x): Mole fraction of a component in a mixture is the ratio between the number of moles of that component to the total number of moles of all the component of the mixture.

 \therefore Mole fractions of component A is given by:

$$n_{\rm A} = \frac{1}{\text{Total moles of all the components}}$$
 of the mixture

(*ii*) **van't Hoff factor** '*i*' is a correction factor defined as

$$i = \frac{\text{Observed value of colligative property}}{1}$$

(b)
$$V = 10.0 \text{ mL}$$

$$\pi = 13.3 \text{ mm Hg} = \frac{13.3}{760} \text{ atm}$$

$$T = 25 ^{\circ}\text{C} = 25 + 273 = 298 \text{ K}$$

$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$M = ?$$
Molar mass (M) = $\frac{\text{WRT}}{\pi \text{V}}$

$$= \frac{0.1 \times 0.0821 \times 298}{\frac{13.3}{760} \times 0.01}$$

$$= \frac{0.10 \times 0.0821 \times 298 \times 760}{13.3 \times 0.01}$$

$$=\frac{1859.4008}{0.133}$$

= 13980.4 g mol⁻¹ or 13.98 kg mol⁻¹

Q8.

- (a) What is meant by:
- (*i*) Colligative properties?
- (ii) Molality of a solution? [CBSE 2017]
- (b) What concentration of nitrogen should be present in a glass of water at room temperature. Assume a temperature of 25 °C, a total pressure of atmosphere and mole fraction of nitrogen in air of 0.78 [K_H for nitrogen = 8.42×10^{-7} M/mm Hg] [AI CBSE 2009]

Ans. (*a*)

[CBSE 2009]

 (i) Colligative properties: The properties of solution which depends upon the number of solute particles and not upon the nature of the solute particles are known as colligative properties.

There are four colligative properties:

- (a) Relative lowering of vapour pressure.
- (*b*) Elevation of boiling point
- (c) Depression of freezing point
- (d) Osmotic pressure.
- (*ii*) Molality (m): It is the number of moles of solute dissolved per kilogram (kg) of the solvent. It is denoted by m. Mathematically,

Molality (m) =
$$\frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

 $\therefore \qquad m = \frac{W_2 \times 1000}{M_2 \times W_1}$

where

$$x(N_2) = \frac{P_{N_2}}{K_H} = \frac{1}{8.42 \times 10^{-7}}$$

Solutions **81**

$$\begin{aligned} x(N_2) &= \frac{n(N_2)}{n(N_2) + n(H_2O)} \\ x(N_2) &= \frac{n(N_2)}{n(H_2O)} \\ n(N_2) &= x(N_2) \cdot n(H_2O) \\ n(N_2) &= x(N_2) \cdot \frac{1000}{18} \\ &= \frac{1}{8.42 \times 10^{-7}} \times 55.5 \\ &= 6.59 \times 10^7 \text{ moles.} \end{aligned}$$

Hence concentration of nitrogen (N₂)
$$&= 6.59 \times 10^7 \text{ mol L}^{-1}. \end{aligned}$$

Q9. Explain by giving examples the term colligative molality. Why do we sometimes get abnormal molecular mass of the substances using colligative properties of the solution?

The freezing point depression of 0.1 molal solution of benzoic acid in benzene is 0.256 K. For benzene K_f is 5.12 K kg mol⁻¹. Calculate the value of van't Hoff factor (*i*) for benzoic acid in benzene. What conclusion can you draw about the molecular state of benzoic acid in benzene? [*CBSE* 2003 *I*]

Ans. The colligative properties like elevation in boiling point and depression in freezing point depends upon the molality of solution, this concentration (in molality) is called colligative molality. We get abnormal molecular mass if the solute either undergoes association or dissociation.

$$\Delta T_f = iK_f \times m$$

$$0.256 = i \times 5.12 \times 0.1$$

$$i = \frac{0.256}{0.256} = \frac{1}{2}$$

$$=\frac{1}{0.512}=\frac{1}{2}$$

 \therefore Benzoic acid exists as a dimer in benzene.

IV. Value-Based Questions

Q1. Water is a universal solvent. But alcohol also dissolves most of the substances soluble in water. And also many more. Boiling point of water is

82 Chemistry-XII –

٦

100 $^\circ C$ and that of alcohol is 80 $^\circ C.$ The specific heat of water is much higher than the specific heat of alcohol.

- (*a*) List out three possible differences if instead of water as the liquid in our body we had alcohol.
- (b) What value can you derive from this special property of water and its innumerable uses in sustaining life on earth?

Ans.

- (a) (i) Even a small rise in temperature in the surroundings will raise the temperature of the body because the specific heat of alcohol is much less than the specific heat of water. So, in order to cool the body, more sweating will take place.
- (*ii*) As there is less H bonding in alcohol, it will get evaporated faster. The alcohol will be evaporated at such a faster rate that the liquid has to be ingested all the time.
- (*iii*) Ice which floats on water helps aquatic life to exist even in winter as water insulates the heat from liquid below it to go back to the surroundings. Solid alcohol does not have such special properties.
- (b) Praise is to the almighty that has so thoughtfully given such special properties to water and made it a liquid that could sustain life on earth.
- **Q2.** Bharath went to his grandfather's house in winter this year. As usual he went for fishing. His grandmother told him there will be no fishes in the lake. He noticed that it was more difficult to find fishes in winter. The fishes were deep inside the river. Whereas in summer they were on the surface and hence he was able to catch fishes.
- (*a*) Why are fishes on the surface in summer and in the depth in winter?
- (b) What value can be derived from this?

Ans.

- (a) According to Henry's law, at low temperature gases are more soluble and hence as more oxygen gets dissolved in water fishes survive better even in depth of the river water. In summer, as the oxygen level is less in water, the fishes come to the surface.
- (b) The value that can be derive from this is that wisdom is superior to knowledge.
- **Q3.** Srisha wanted to keep ice creams without melting. So he had to keep it on ice taken in a container. His grandmother advised him to pour salt on the ice.
- (a) Why?
- (b) What is the value in this?

Ans.

- (a) Adding salt to ice decreases the melting point of ice. Hence the ice-creams can be easily kept without melting.
- (*b*) Obey your elders.
- **Q4.** Sneha's grandmother lives in Shimla. In winter there is a lot of snow in front of their house. She asked Sneha to clear their snow from the front of the house. Sneha added salt to snow to clear it.
- (a) Why?
- (b) What is the value in this?

Ans.

٦

- (a) Adding salt to show decreases the melting point of snow. Thus snow melts down and it can be easily removed.
- (b) Scientific knowledge is the value associated with Sneha.

V. HOTS Questions

- **Q1.** Why is the freezing point depression of 0.1M NaCl solution nearly twice that of 0.1M glucose solution?
- **Ans.** NaCl is an electrolyte and it dissociates completely whereas glucose being a non-electrolyte does not dissociate. Hence, the number of particles in 0.1M NaCl solution is nearly double for NaCl

solution than that for glucose solution of same molarity. Therefore depression in freezing point being a colligative property is nearly twice for NaCl solution than that for glucose solution of same molarity.

- **Q2.** When X and Y are mixed, the solution becomes warm and when Y and Z are mixed the solution becomes cool. Which of this solution will exhibit positive deviation and which one will exhibit negative deviation?
- **Ans.** X and Y solution shows the negative deviation while Y and Z solution shows the positive deviation.
- **Q3.** A solution contains 0.8960 g of K_2SO_4 in 500 ml solution. Its osmotic pressure is found to be 0.690 atm. at 27°C. Calculate the value of van't Hoff factor.

$$M_{B} = \frac{W_{B}RT}{\pi V}$$

$$W_{B} = 0.8960 \text{ g}$$

$$V = 500 \text{ ml} = 0.5 \text{ L}$$

$$R = 0.082 \text{ L} \text{ atm } \text{K}^{-1} \text{ mol}^{-1}$$

$$\pi = 0.69 \text{ atm, } \text{T} = 300 \text{ K}$$

$$\therefore \qquad M_{B} = \frac{0.8960 \times 0.082 \times 300}{0.69 \times 0.5}$$

$$= 63.9 \text{ g mol}^{-1}$$
Normal molar mass
$$= 2 \times 39 + 32 + 4 \times 32$$

$$= 174 \text{ g mol}^{-1}$$

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

$$= \frac{174 \text{ g mol}^{-1}}{63.9 \text{ g mol}^{-1}}$$

Q4.

Ans.

(a) Menthol is a crystalline substance with peppermint taste. A 6.2% solution of menthol in cyclohexane freezes at -1.95°C. Determine the formula mass of menthol. The freezing point and molal depression constant of cyclohexane are 6.5°C and 20.2K m⁻¹, respectively.

i = 2.72

- (*b*) State Henry's Law and mention its two important applications.
- (c) Which of the following has higher boilling point and why?0.1 M NaCl or 0.1 M Glucose

Ans. (*a*)

$$\Delta T_f = K_f m$$

$$W_B$$

$$\frac{W_B}{M_B} \times \frac{1000}{W_A}$$

$$\therefore \qquad 8.45 \mathrm{K} = \frac{20.2 \times 6.2 \times 1000}{\mathrm{M}_{_{B}} \times 93.8}$$

 $M_{\rm B} = 158 {\rm g \ mol^{-1}}$

(b) **Henry's Law:** The solubility of a gas in a liquid is directly proportional to the pressure of the gas.

Applications:

1. Solubility of CO_2 is increased at high pressure.

2. Mixture of He and O_2 are used by deep sea divers because He is less soluble than nitrogen.

- (c) 0.1M NaCl, because it dissociates in solution and furnishes greater number of particles per unit volume while glucose being a non-electrolyte does not dissociate.
- **Q5.** Why a person suffering from high blood pressure is advised to take minimum quantity of common salt?
- **Ans.** Osmotic pressure is directly proportional to the concentration of solutes. Our body fluid contains a number of solutes. On taking large amount of salt, ions entering into the body fluid thereby raises the concentration of solutes. As a result, osmotic pressure increases which may rupture the blood cells.