SOLUTIONS THEORY WITH ASSIGNMENT

TOPIC 1 : SOLUTIONS, EXPRESSING CONCENTRATION OF SOLUTIONS AND SOLUBILITY

1. A **solution** is a homogeneous mixture of two or more chemically non-reaching substances. Its composition can be varied within certain limits. All particles in a solution are generally of molecular size, i.e., 0.2 – 2nm. The components of a solution generally cannot be separated by filtration, settling or centrifuging.

2. A solution consists of two components: solute and solvent.

a. The component which is present in larger proportion is termed as the **solvent**. It is usually in the same physical state as the solution.

b. The component which is present in smaller proportion is called the **solute.**

3. A solution may be classified as solid, liquid or a gaseous solution. The different types of solutions along with examples are summarised below:

Types of Solution	Examples
Gaseous solution	
(a) Gas in gas	Air, mixture of oxygen and nitrogen, etc.
(b) Liquid in gas	Water vapour.
(c) Solid in gas	Camphor vapours in nitrogen gas.
Liquid solution	
(a) Gas in liquid	Carbo dioxide dissolved in water (aerated water) oxygen dissolved in water, etc.
(b) Liquid in liquid	Ethanol dissolved in water, vinegar, formalin, etc.
(c) Solid in liquid	Sugar dissolved in water, saline water, etc.
Solid solutions	
(a) Gas in solid	Solution of hydrogen in palladium.
(b) Liquid in solid	Amalgams, eg., sodium amalgam.
(c) Solid in solid	Gold ornaments (copper or silver dissolved in gold).

4. **Methods of expressing concentrations of solution**

a. Mass percentage: It is the amount of solute in grams present in 100g of solution.

$$\text{Mass percent of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

b. Molarity = It is defined as the number of moles of solute present in one litre of solution.

$$\text{Molarity (M)} = \frac{\text{Number of moles of solution}}{\text{Volume of solution in litre}} = \frac{n}{v} \quad ; \quad n = \frac{\text{Weight in grams}}{\text{Molecular weight of solute}}$$

$$\therefore \quad M = \frac{\text{Weight in grams}}{\text{Volume of solution in litres}} \times \frac{1}{\text{Molecular weight of solute}}$$

Strength: This is weight (in gms) of solute per litre of solution

$$\therefore \quad \text{xvMolarity} = \frac{\text{Strength}}{\text{Molecular weight of solute}}$$

or Strength = Molarity × Molecular weight

Note: Molarity is the most common way of expressing concentration of a solution in laboratory. However, it has one disadvantage. It changes with temperature because volume of a solution alters due to expansion and contraction of the liquid with temperature.

c. Molality: It is defined as the number of moles of a solute present in 1000g (1 kg) of a solvent.

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in kg}} = \frac{n}{W}$$

Note: Molality is considered better way of expressing concentration of solutions as compared to molarity because molarity does not change with change in temperature since the mass of solvent does not vary with temperature.

d. Volume percentage: It is the volume of solute in cm^3 present in 1000 cm^3 of solution.

$$\text{Volume percent of solute} = \frac{\text{Volume of solute}}{\text{Volume of solute}} \times 100$$

e. Parts per million: When a solute is present in trace quantities it is convenient to express concentration in parts per million (ppm).

$$\text{Parts per million} = \frac{\text{Number of parts of solute}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

f. Mole fraction: It is defined as the ratio of the number of moles of the solute to the total number of moles in the solution. If n_A is the number of moles of solute dissolved in n_B moles of solvent, then

Mole fraction of solute $(X_A) = \dfrac{n_A}{n_A + n_B}$ ... (1)

Mole fraction of solvent $(X_B) = \dfrac{n_B}{n_A + n_B}$ ... (2)

Adding the above two equations, we get

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = \frac{n_A + n_B}{n_A + n_B} = 1$$

i.e., $X_A + X_B = 1$

$\therefore$ $X_A = 1 - X_B$ or $X_B = 1 - X_A$

Note: Even if three components make a solution, then $X_A + X_B + X_C = 1$.

5. **Solubility:** It is defined as the amount of solute in a saturated solution per 100g of a solvent. Solubility is guided by general principle of like dissolves like.

   Ionic and polar substances are generally soluble in polar solvents like water and are insoluble in non-polar solvents like benzene, chloroform, carbon disulphide, etc.

   Similarly, non-polar solutes like 'iodine', sulphur, phosphorus and organic substances are soluble in non-polar solvents like benzene, chloroform, etc., and are insoluble in polar solvents like water.

6. The solubility of a gas in a liquid depends upon

   a. the nature of the gas and the nature of the liquid, b. the temperature of the system, and

   c. the pressure of the gas.

7. The solubility of a gas in a given liquid varies considerably with the nature of the gas.

   a. Generally, the gases which can be easily liquefied are more soluble in common solvents. For example, CO_2 is more soluble in water as compared to oxygen or nitrogen.

   b. The gases which are capable of forming ions in aqueous solution are much more soluble in water than in any other solvent. For example, HCl and NH_3 are highly soluble in water in which they form ions but not in benzene.

   c. The solubility of a gas in a liquid decreases with rise in temperature of the solution.

   d. The effect of pressure on the solubility of a gas in a liquid is governed by Henry's Law. It states that the solubility of a gas in a liquid at a given temperature in directly proportional to the partial pressure of the gas Mathematically, $P = K_H X$

   where P is the partial pressure of the gas; and X is the mole fraction of the gas in the solution and K_H is Henry's Law constant.

8. **Applications of Henry's law :**

a. To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

b. Scuba divers much cope with high concentrations of dissolved gases while breathing air at high pressure under water. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases two dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

c. At high attitudes, the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

ILLUSTRATIONS

1. 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 of Na^+ ions in the lake.

Sol. Number of moles in 92 g of Na^+ ions $= \dfrac{\text{Mass}}{\text{Molecular mass}} = \dfrac{92}{23} = 4\text{ mol}$

Molality of Na^+ ions = $\dfrac{\text{Number of moles}}{\text{Mass of solvent (kg)}} = \dfrac{4}{1}$ = 4 mol kg^{-1}

2. If the solubility product of CuS is 6×10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

Sol. Maximum molarity of CuS in aqueous solution is the solubility (s) in mol L^{-1}.

$$CuS \rightleftharpoons \underset{s}{Cu^{2+}} + \underset{s}{S^{2-}}; \qquad K_{sp} = [Cu^{2+}]\,[S^{2-}] = s \times s \times s^2$$

$$\because \quad s^2 = 6 \times 10^{-16} \quad \text{(Given)} \qquad \therefore \quad s = \sqrt{6 \times 10^{-16}} = 2.45 \times 10^{-8}\text{ mol }L^{-1}$$

3. Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.

Sol. Since, the molal aqueous solution of urea is 0.25 m. ∴ Moles of urea = 0.25 mol and

Mass of solvent (water) = 1 kg = 1000 g

Molar mass of urea (NH_2CONH_2) = 14 + 2 + 12 + 16 + 14 + 2 = 60 g mol^{-1};

∴ 0.25 mole of urea = 0.25 mole × 60 g mol^{-1} = 15 g; Total mass of solution= 1000 + 15 g = 1015 g = 1.015 kg

Thus, 1.015 kg of solution contains urea = 15 g; ∴ 2.5 kg of solution will require urea

$$= \frac{15\text{g}}{1.015\text{ kg}} \times 2.5\text{ kg} = 37\text{ g}$$

4. Will the molarity of a solution at 50°C be same, less or more than at 25 °C?

Sol. Molarity at 50°C will be less than that at 25°C, because molarity decreases with increase in temperature.

Since, volume of the solution increases with increase in temperature but number of moles of solute remains the same.

PRACTICE PROBLEMS

1. State Henry's law. What is the effect of temperature on the solubility of a gas in a liquid?

2. 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 solutio is 1.2 g mL^{-1}, then what shall be the molarity of the solution?

3. Why do smaller particles dissolve faster than larger ones?

4. Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.

TOPIC 2 : VAPOUR PRESSURE OF LIQUID SOLUTIONS

1. The **vapour pressure** of a liquid is the pressure exerted by its vapour when it is in dynamic equilibrium with its liquid, in a closed container.

2. When a non-volatile solute is added to a solvent to make a solution, the vapour pressure of the solutions will be the vapour pressure of the solvent as there is no contribution from the solute.

3. According to **Raoults Law,** the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent (X_A). The proportionality constant being the vapour pressure of the pure solvent, i.e., $P \times X_A$ or $P = P°X_A$.

If the solution consists of two volatile liquids, then Raoult's Law is applicable to each component of the solution, i.e.,

$$P_A = P_A^0 X_A \text{ and } P_B = P_A^0 X_B$$

The total vapour pressure of the solution is equal to the sum of the partial pressures of each component

$$P = P_A + P_B = P_A^0 X_A + P_A^0 X_B$$

4. A solution which obeys Raoult's Law at all concentrations and temperatures is known as an **ideal solution.**

5. Characteristics of an ideal solution:

a. It obeys Raoults Law at all concentrations and temperature.

b. $\Delta_{sol} H = 0$; i.e., there is no change in volume when an ideal solution is formed.

c. $\Delta_{sol} H = 0$; i.e., heat is neither evolved nor absorbed during the formation of an ideal solution.

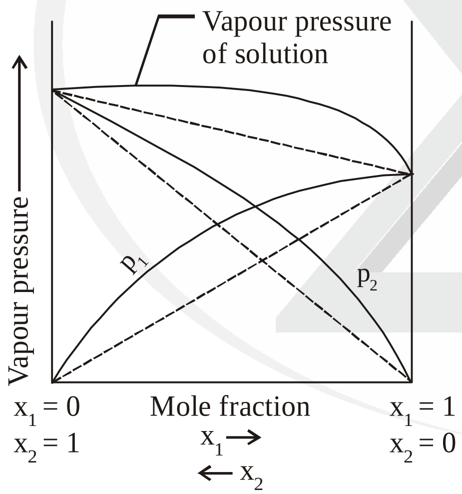
6. Solutions which do not obey Raoult's Law are known as **non-ideal solutions.**

a. The vapour pressure of a non-ideal solution is either higher or lower than that predicted by Raoult's Law.

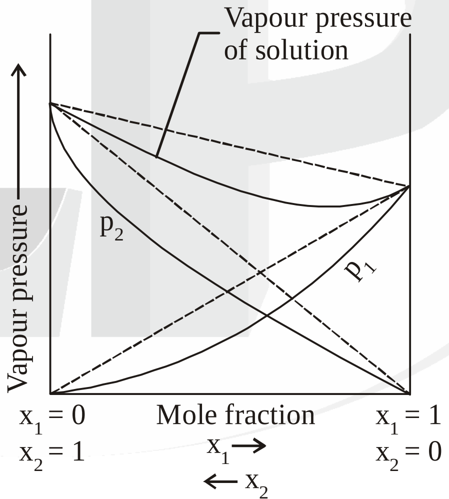
b. The solution shows **positive deviation** from Raoult' Law if its vapour pressure is higher than that predicted by Raoult's Law.

c. The solution shows **negative deviation** if its vapour pressure is lower than that predicted by Raoult's

It is important is know the graphical representations of ideal, positive deviating and negative deviating solutions. These are given below:



a.



b.

The ideal or non ideal behaviour of solutions depends on solvent-solute interactions. Let A represent the solvent and B represent the solute then we can write it as

- If A – B interactions = A – A & B –B then we get ideal solution.
- If A – B interactions > A – A & B – B then we get solution showing negative deviation having $\Delta_{sol}. V < 0$ & $\Delta_{sol}. H° > 0$.
- If A – B interactions < A – A & B – B then we get sol^n showing +ve deviation having $\Delta_{sol}. V > 0$ & $\Delta_{sol}. H° > 0$.

7. According to Raoult's Law, the vapour pressure of volatile component in a given solution is given by

$$P_A = P_A^0 X_A \qquad ...(i)$$

According to Henry's Law, the solubility of a gas (volatile component) in a liquid is governed by the expression.

$$P = K_H X \qquad ...(ii)$$

Note:

a. It can be seen from equations (i) and (ii) that the partial pressure of the volatile component or gas is directly proportional to its mole fraction in the solution. Only the proportionality constant K_H, in the Henry's Law equation, differs from P_A°, the proportionality constant in Raoult's Las equation.

b. If K_H becomes equal to P_A°, the Raoult's Law becomes a special case of Henry's Law.

8. In a very dilute solution of liquids, the solvent obeys Raoult's Law whereas the solute obeys Henry's Law.

ILLUSTRATIONS

1. Two liquids A and B boil at 155°C and 190°C, respectively. Which of them has a higher vapour pressure at 80 °C?

Sol. A is more volatile, therefore has higher vapour pressure.

2. What type of deviation is shown by a mixture of ethanol and acetone? Give reason.

Sol. A mixture of ethanol and acetone shows positive deviation because in this case, A—B interactions are weaker than A—A and B—B interactions. Due to this, vapour pressure increases which results in positive deviation.

3. At some temperature, the vapour pressure of pure C_6H_6 is 0.2456 bar and that of pure $C_6H_5CH_3$ (toluene) is 0.0925 bar. If the mole fraction of toluene in solution is 0.6. Then,

(i) what will be the total pressure of the solution? (ii) what will be the mole fraction in vapour phase?

Sol. (i) According to Raoult's law, $p_1 = p_1^\circ \times \chi_1$; For toluene, $p_1^\circ = 0.09256$ bar and $\chi_1 = 0.6$

Then, $p_1 = 0.925 \times 0.6 = 0.0555$ bar; For benzene, $p_2 = p_1^\circ \times \chi_2$; Mole fraction of benzene,

$\chi_2 = 1 - \chi_1 = 1 - 0.6 = 0.4$ and $p_2^\circ = 0.256$ bar; Then $p_2 = 0.256 \times 0.4 = 0.1024$ bar

Total vapour pressure of solution; $p_{total} = p_1 - p_2 = 0.1024 + 0.0555 = 0.158$ bar

(ii) Mole fraction of benzene in vapour phase $y_2 = \dfrac{p_2}{p_{total}} = \dfrac{0.1024}{0.158} = 0.648$

4. Benzene and toluene both have equal mole fractions in their mutual solution. What do you expect about their mole fraction in vapour phase at the same temperature. (Given, $p^\circ_{benzene} = 3p^\circ_{toluene}$)

Sol. $\because \chi_B = \chi_T$ [mole fractions are equal] $\therefore \dfrac{p_B}{p_T} = \dfrac{p_B^\circ}{p_T^\circ}$ But given that $\dfrac{p^\circ{}_B}{p^\circ{}_T} = 3 \therefore \dfrac{p_B}{p_T} = 3$

But $\dfrac{p_B}{p_T} = 3$ shows that $\dfrac{y_B}{y_T} = 3$ in vapour phase, since vapour pressures in vapour phase are in the ratio of their number of moles or mole fraction.

PRACTICE PROBLEMS

1. Two liquids x and y on mixing form an ideal solution. The vapour pressure of a solution containing 3 moles of x and 1 mole of y is 550 mm Hg. However, when 4 moles of x and 1 mole of y are mixed, the vapour pressure of solution thus formed is 560 mm Hg. What will be the vapour pressure of pure x and pure y at this temperature?

OR

Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

2. An aqueous solution containing 28% by mass of a liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 37°C. Find the vapour pressure of the pure liquid A. (The vapour pressure of water at 37°C is 150 mm)

3. Methanol and ethanol form nearly ideal solution at 300 K. A solution is made by mixing 32 g methanol and 23 g ethanol at 300 K. Calculate the partial pressures of its constituents and the total pressure of the solution.

4. Vapour pressure of two liquids A and B are 120 and 180 mm Hg at a given temperature. If 2 mole of A and 3 mole of B are mixed to form an ideal solution, calculate the vapour pressure of solution at the same temperature.

5. The vapour pressure of pure liquid A and pure liquid B at 20°C are 22 and 75 mm Hg respectively. A solution is prepared by mixing equal moles of A and B. Assuming the solution to be ideal, calculate the vapour pressure of the solution.

TOPIC 3 :

1. **Colligative properties** of solutions are those properties which depend only upon the number of solute particles in the solution and not on their nature. Such properties are

a. Relative lowering in vapour pressure, b. Elevation of boiling point,

c. Depression of freezing point and d. Osmotic pressure.

2. According to Raoult's Law, the vapour pressure of a solution containing a non-volatile solute is given by

$$P = P_A = P_A^o X_A$$

Lowering of vapour pressure = $P_A^o - P_A = P_A^o - P_A^o X_A$; $P_A^o - P_A = P_A^o (1 - X_A)$

Since for a binary mixture, $X_A + X_B = 1$ $X_B = 1 - X_A$ $\therefore$ $P_A^o - P_A = P_A^o X_B$

Relative lowering of vapour pressure = $\dfrac{P_A^o - P_A}{P_A^o}$; $\dfrac{P_A^o - P_A}{P_A^o} = X_B = \dfrac{n_B}{n_A + n_B}$

Thus, according to Raoult's Law, the relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute.

For a very dilute solution, $\dfrac{n_B}{n_A + n_B} \simeq \dfrac{n_B}{n_A}$; $\therefore$ $\dfrac{P_A^o - P_A}{P_A^o} = \dfrac{n_B}{n_A} = \dfrac{W_B/M_B}{W_A/M_A} = \dfrac{W_B M_A}{M_B W_A}$

3. The **boiling point** of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure. When a non-volatile solute is dissolved in a solvent, its vapour pressure decreases as there is no contribution from the non-volatile solute. Therefore, the boiling point of the solution is always higher than the boiling point of the pure solvent.

For a dilute solution, the elevation in boiling point is found to be proportional to the molality of the solution, i.e., $\Delta T_b \; \alpha \; m$ or $\Delta T_b = K_b m$

where ΔT_b is the elevation in boiling point, 'm' is the molality of K_b is the Molal elevation constant (boiling elevation constant) which is equal to the elevation in boiling point when one mole of the solute is dissolved in 1000g of the solvent. $\Delta T_b = K_b \dfrac{n_B}{W_A\,(g)} \times 1000$ $\Delta T_b = 1000 \dfrac{K_B W_B}{M_B W_A}$

4. **Freezing point** is the temperature at which the solid and the liquid state of the substance have the same vapour pressure. Since the presence of a non-volatile solute lowers the vapour pressure of the solvent, the freezing point of the solution is always less than that of the pure solvent. The depressions in freezing point (ΔT_f) is proportional to the molality of the solution.

$\Delta T_f \; \alpha \; m$ or $\Delta T_f = K_f m$

where K_f is **molal depression constant** (freezing point depression constant). It is the depression in freezing point when 1 mole of a solute is dissolved in 1000 g of the solvent

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

5. The spontaneous flow of solvent molecules from a dilute solution into a concentrated solution when the two are separated by a perfect semipermeable membrane is called osmosis.

6. **Osmotic pressure** (p) is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane.

Mathematically, $\pi = CRT = \frac{n_B}{V} RT$ where π is the osmatic pressure of the solution,

C is the concentration of solution ; n_B is the number of moles of solute,
V is the volume of the solution in litres, ; R is the gas constant, and
T is the temperature on the Kelvin scale.

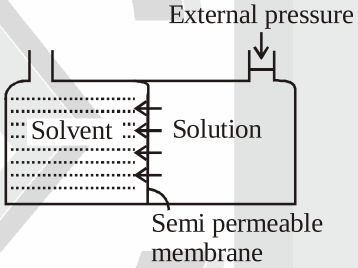
while solving the problems, we have to take proper care of units. If π is in atm, then R should be taken as 0.083 lit atm $mol^{-1}K^{-1}$.

7. **Isotonic solutions** are those solutions which have the same osmotic pressure. Also they have same molar concentration.

For isotonic solutions, $p_1 = p_2$ Also $C_1 = C_2$ or $\frac{n_1}{V_1} = \frac{n_2}{V_2}$ $\frac{W_1}{m_1 V_1} = \frac{W_2}{m_2 V_2}$

8. When two solutions have different osmotic pressures, the solution of lesser osmotic pressure in called **hypotonic solutions** and the solutions of higher osmotic pressure is called hypertonic solutions.

9. The movement of solvent particles from higher concentration to lower concentration through semipermeable membrane on applying pressure is known as **reverse osmosis**. If the external pressure greater than osmotic pressure is applied on more concentrated solution side, the solvent molecules start passing through semipermeable membrane from this solution to the solvent or less concentrated solution. This is known as reverse osmosis. It is used to purity the sea water.



ILLUSTRATIONS

1. Calculate the boiling point of a solution containing 1.8 g of a non-volatile solute dissolved in 90 g of benzene. The boiling point of pure benzene is 353.23 K. [K_b = 2.53 K kg mol^{-1} and molar mass of solute = 58 g mol^{-1}]

Sol. For boiling point elevation, we can use the relation, $\Delta T = K_{b_{1000}} \times \frac{w_B \times 1000}{m_B \times w_A}$

Given: K_b = 2.53 K kg mol^{-1}; w_B = 1.8 g; m_B = 58; w_A = 90 g.

$\therefore$ $\Delta T = 2.53 \times \frac{1.8 \times 1000}{58 \times 90} = 0.87$ K; $T = T_0 + 0.87 = 353.23 + 0.87 = 354.1$ K

2. The boiling point of water (100°C) becomes 100.52°C if 3 g of a non-volatile solute is dissolved in 20 mL of it. Calculate the molar mass of the solute. (K_b for water = 0.52 K m^{-1})

Sol. $m_B = \frac{1000 \times K_b \times w_B}{\Delta T \times w_A}$; Given: K_b = 0.52 K m^{-1}; w_B = 3 g; $w_A = 20 \times 1 = 20$ g;

$\Delta T = 100.52 - 100.0 = 0.52$ K; Putting these values in the above formula, $m_B = \frac{1000 \times 0.52 \times 3}{0.52 \times 20} = 150$

3. An aqueous solution freezes at –0.186°C. Find its elevation in boiling point. $K_f = 1.86\ Km^{-1}$, $K_b = 0.512\ Km^{-1}$

Sol. $\Delta T = K_f \times m$; $0.186 = 1.86$; $m = 0.1$; The elevation in boiling point of solution can be calculated as

$\Delta T = K_b \times m = 0.512 \times 0.1 = 0.0512$

4. Calculate the temperature at which a solution containing 54 g of glucose, $C_6H_{12}O_6$, in 250 g of water will freeze. (K_f for water = 1.86 K kg mol^{-1})

Sol. We know, $\Delta T = K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$ ....(i)

Given: $K_f = 1.86$ K kg mol^{-1}, $w_B = 54$ g, $w_A = 250$ g; $m_B = 180$ g/mol (molar mass of glucose)

Putting these values in eqn. (i) we get, $\Delta T = 1.86 \times \dfrac{54 \times 1000}{180 \times 250} = 2.232$; $T_0 - T = 2.232$; $273 - T = 2.232$;

$T = 273 - 2.232 = 270.768$ K or –2.232° C

5. The osmotic pressure of a solution of an organic substance containing 18 g in ne litre of solution at 293 K is $2.414 \times 10^5\ N\ m^{-2}$. Find the molecular mass of the substance if $S = 8.3\ J\ K^{-1}\ mol^{-1}$.

Sol. Applying the equation; $\pi V = \dfrac{w_B}{m_B}.ST$ or $m_B = \dfrac{w_B}{\pi V}.ST$

Given: $\pi = 2.414 \times 10^5\ Nm^{-2}$, V = 1.0 litre = $1 \times 10^{-3}\ m^3$, $S = 8.3\ J\ K^{-1}\ mol^{-1}$, $w_B = 18$ g and T = 293 K

$$m_B = \frac{18}{2.414 \times 10^5 \times 1 \times 10^{-3}} \times 8.3 \times 293 = 181.33$$

6. A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution.

Sol. Glucose and urea are non-electrolytes hence their solutions must have same molarity for the solutions to be isotonic.

$$\left(\frac{w_B \times 1000}{m_B \times V}\right)_{urea} = \left(\frac{w_B \times 1000}{m_B \times V}\right)_{glucose}; \qquad \frac{15 \times 1000}{60 \times 1000} = \frac{w_B \times 1000}{180 \times 1000}; \qquad w_B = \frac{15 \times 180}{60} = 45\,g$$

$\therefore$ 45 g glucose should be present in one litre of its solution.

PRACTICE PROBLEMS

1. Calculate the molal elevation constant of water of molar enthalpy of vaporisation of water at 373 K is 40.585 kJ mol^{-1}.

2. An aqueous solution of glucose boils at 100.02°C. What is the number of glucose molecules in the solution containing 100 g of water? (Given: K_b for $H_2O = 0.5\ K\ m^{-1}$; $N_A = 6.023 \times 10^{23}$)

3. The freezing point of cyclohexane is 279.65 K. A solution of 14.75 g of a solute in 500 g of cyclohexane has a freezing point of 277.33 K. Calculate the molar mass of the solute (given $K_f = 20.2$ K kg mol^{-1}).

4. At 10°C, the osmotic pressure of urea solution was found to be 500 mm. The solution is diluted and temperature is raised to 25°C. When osmotic pressure was noticed to be 105.3 mm, determine the extent of dilution.

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

TOPIC 4 :

1. **Abnormal Molar Masses** As all the colligative properties are proportional to the number of moles, of solute, we can use them to calculate molecular weight of solutes (M_g). If the solute undergoes association or dissociation then the value of colligative property will give us abnormal molecular weight of solute. To correct this abnormal molecular weight van't Hoff actor i is used. Van't Hoff factor, 'i' is used to express the extent of association or dissociation of solutes in solution. It is the ratio of the normal and observed molar masses of the solute, i.e.,

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} \quad \text{or} \quad i = \frac{\text{Calculated molar mass}}{\text{Experimental molar mass}}$$

2. In case of association, observed molar mass being more than the normal, the factor 'i' has a value less than one. But in case of dissociation, the Van't Hoff factor is more than one because the observed molar mass has a less value.

3. In case of solutes which do not undergo any association or dissociation in a solvent, the vant Hoff factor, 'i', will be equal to one because the observed and normal molar masses will be same.

4. Molar mass $\alpha \frac{1}{\text{Colligative property}}$

Therefore, van't Hoff factor may also be expressed as : $i = \frac{\text{Observed or calculated value of colligative property}}{\text{Normal or experimental value of colligative property}}$

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

Elevation in boiling point, $\Delta T_b = i\,K_b\,m$; Depression in freezing point, $\Delta T_f = i\,K_f\,m$

Osmotic pressure, $\pi = i\,CRT$

ILLUSTRATIONS

1. What mass of NaCl (molar mass = 58.5 g mol^{-1}) must be dissolved in 65 g of water to lower the freezing point by 7.5°C ? The freezing point depression constant, K_f, for water is 1.86 K kg mol^{-1}. Assume van't Hoff factor for NaCl is 1.87.

Sol. We know, $\Delta T = i \times K_f \times \frac{w_B \times 1000}{m_B \times w_A}$ ....(i)

Given: m_B = 58.5 g mol^{-1}; w_A = 65 g; i = 1.87, K_f = 1.86 K kg mol^{-1}; ΔT = 7.5

Putting these values in eqn. (i) we get : $7.5 = 1.87 \times 1.86 \times \frac{w_B \times 1000}{58.6 \times 65}$; w_B = 8.213 g = 8.2 g

$\therefore$ Mass of NaCl to be dissolved in 8.2 g.

2. Calculate the amount of KCl which must be added to 1 kg water so that the freezing point is depressed by 3 K.

Sol. We know, $\Delta T_{obs} = iK_f \times \frac{w_B \times 1000}{m_B \times w_A}$; where; i = van't Hoff factor = 2 for KCl

K_f = 1.86 K m^{-1} for water; w_B = ?; m_B = 74.5 (molar mass of KCl); w_A = 1000 g; ΔT_{obs} = 3 K

Substituting these values in the above equation, we get $3 = 2 \times 1.86 \times \frac{w_B \times 1000}{74.5 \times 1000}$; w_B = 60.08 g

3. The freezing point of a solution containing 0.3 g ethanoic acid in 30 g of benzene is depressed by 0.45 K. Calculate the van't Hoff factor of ethanoic acid. What can you say about the nature of ethanoic acid in benzene?
[$K_f(C_6H_6)$ = 5.12 K kg mol^{-1}; Molar mass of CH_3COOH = 60 g mol^{-1}]

Sol. The van't Hoff factor can be calculated by using following relation

$\Delta T = i \times K_f \times m$; $\Delta T = i \times K_f \times \frac{w_B \times 1000}{m_B \times 1000}$ ....(i)

Given: ΔT = 0.45 K; K_f = 5.12 K kg mol^{-1}; w_B = 0.3 g, w_A = 30 g; m_B = 60 g mol^{-1}

Putting these values in eqn. (i), we get $0.45 = i \times 5.12 \times \frac{0.3 \times 1000}{60 \times 30}$; $i = 0.527$

Since, i < 1, hence ethanoic acid should be associated in benzene.

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

Sol. We know, $\pi = iCST$ Given : $C = 0.1$ M; $T = 18 + 273 = 291$ K; $S = 0.0821$ litre atm K^{-1} mol^{-1}

Potassium ferrocyanide undergoes dissociation as, $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$; $n = 5$

We know, $\alpha = \frac{i-1}{n-1}$; $\alpha = \frac{46}{100} = 0.46$; $0.46 = \frac{i-1}{5-1}$; $i = 2.84$

From eqn. (i), $\pi = 2.84 \times 0.1 \times 0.0821 \times 291 = 6.785$ atm

5. Decinormal solution of NaCl developed an osmotic pressure of 4.6 atmosphere at 300 K. Calculate its degree of dissociation (S = 0.0821 litre atm K^{-1} and mol^{-1}).

Sol. Given: $C = 0.1$ M; $\pi = 4.6$ atm; $T = 300$ K; $C = 0.0821$ litre atm K^{-1} mol^{-1}

Substituting these values in the following equation, we can calculate van't Hoff factor.

$i = \frac{\pi}{CST} = \frac{4.6}{0.1 \times 0.0821 \times 300} = 1.87$; For dissociation, $\alpha = \frac{i-1}{n-1}$ for NaCl : $n = 2$ $= \frac{1.87-1}{2-1} = 0.87$

$\therefore$ % dissociation = 87

6. 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 ionization of salt. (K_f per 1000 g of water = 1.86°C)

Sol. We know, $\Delta T = i \times K_f \times \frac{w_B \times 1000}{m_B \times w_A}$ ....(i) $\Delta T = 0.24$, $K_f = 1.86$ Km^{-1}, $w_A = 100$ g

$w_B = 0.5$ g, $m_B = 74.5$. Putting these values in eqn. (i), we get $0.24 = i \times 1.86 \times \frac{0.5 \times 1000}{74.5 \times 100}$; $i = 1.922$

For KCl: $KCl \rightleftharpoons K^+ + Cl^-$ (n = 2) $\alpha = \frac{i-1}{n-1} = \frac{1.922-1}{2-1} = 0.922$

$\therefore$ Percentage ionization of salt = 0.922 × 100 = 92.2

PRACTICE PROBLEMS

1. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 2×10^{-2} kg of phenol of 1 kg of benzene has its freezing point decreased by 0.69 K. Calculate the degree of association of phenol. (K_f for benzene = 5.12 K kg mol^{-1}).

2. Calculate the amount of NaCl which must be added to 100 g of water, so that freezing point of water is depressed by 2K. ($K_f = 1.86$ Km^{-1}) (Assume complete dissociation of NaCl)

3. 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of the acid if it forms a dimer in solution?

4. Arrange the following solutions in the increasing order of their osmotic pressures.

a. 34.2 g/litre sucrose b. 60 g/litre of urea c. 90 g/litre of glucose d. 58.5 g/litre of sodium chloride

Give reason in support of your answer.

5. Benzoic acid completely dimerises in benzene. What will be the vapour pressure of solution containing 61 g benzoic acid per 500 g benzene when the vapour pressure of pure benzene at that temperature of experiment is 66.6 torr? What will be the vapour pressure in normal state.

6. 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 ionization of salt. ($K_f = 1.86$ K kg mol^{-1})

7. Calculate the freezing point depression for 0.0711 m aqueous solution of Na_2SO_4, if it is completely ionized in the solution. If this solution actually freezes at –0.32°C. What is the value of van't Hoff factor for it at freezing point? (K_f for water is 1.86 K kg mol^{-1})

IMPORTANT TIPS

1. **Grams per litre:** It is defined as the amount of the solute in grams present in one litre of the solution. Concentration or strength of solution = $\frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}} = \frac{W}{V}$ g/litre.

2. **Molarity of dilution:**

Before dilution	After dilution
M_1V_1	M_2V_2

3. **Molarity of mixing:** $M_1V_1 + M_2V_2 + M_3V_3 = M_R\,(V_1 + V_2 + V_3)$

where M_R = Resultant molarity,

$V_1 + V_2 + V_3$ = Resultant volume after mixing.

4. **Normality:** It is defined as the number of gram equivalents of a solute dissolved in one litre of solution.

$$\text{Normality (N)} = \frac{\text{Number of gram equivalents of a solute}}{\text{Volume of solution in litre}}\ ;$$

$$\text{Number of gram equivalents} = \frac{\text{Weight of solute in grams}}{\text{Equivalent weight}}$$

$$\therefore\ \ \text{Normality} = \frac{\text{Weight of solute in grams}}{\text{Volume of solution in litre}} \times \frac{1}{\text{Equivalent weight}} \qquad \therefore\ \text{Normality} = \frac{\text{Strength}}{\text{Equivalent weight}}$$

$$\therefore \qquad N = \frac{W}{V \times E} \qquad\qquad \therefore \qquad W = N \times E \times V.$$

Note: Normality is dependent on volume, therefore, it changes with temperature.

5. **Normality of dilution:**

Concentrated solution	Diluted solution
N_1V_1	N_2V_2

6. **Normality of mixing:**

$N_1V_1 + N_2V_2 + N_3V_3 = N_R\,(V_1 + V_2 + V_3)$

where N_R = Resultant normality, $V_1 + V_2 + V_3$ = Resultant volume after mixing.

7. **Relationship between normality and molarity of solution:**

$$\text{Normality} = \text{Molarity} \times \frac{\text{Molar mass}}{\text{Equivalent mass}} = \text{Molarity} \times n \qquad \text{where} \qquad n = \frac{\text{Molar mass}}{\text{Equivalent mass}}$$

For acids, Normality = Molarity × Basicity of acid. **For bases,** Normality = Molarity × Acidity of base.

For oxidising / reducing agents, Normality = Molarity × Change in oxidation number per molecule of reactant

Relation between mole fraction and molality:

8. **Relation between mole fraction and molality:**

$$X_A = \frac{n_A}{n_A n_B}, X_B = \frac{n_B}{n_A + n_B} \quad ; \quad \frac{X_B}{X_A} = \frac{n_B}{n_A} = \frac{W_B}{M_B} / \frac{W_A}{M_A} \quad \Rightarrow \quad \frac{X_B}{X_A} = \frac{W_B.M_A}{M_B.W_A}$$

$$\Rightarrow \quad \frac{X_B}{X_A.M_A} = \frac{W_B}{M_B} \times \frac{1}{W_A} \qquad \Rightarrow \quad \frac{1000X_B}{X_AM_A} = \frac{1000W_B}{M_B.W_A} = m \Rightarrow \frac{1000X_B}{(1-X_B).M_A} = m$$

Note: Mole fraction is independent of temperature of the solution as it is mass dependent only.

9. Expression relating molarity (M) and molality (m) of a solution:

Suppose we have 1000 ml of solution of molarity M and density d g/ml. 1000 ml solution has M moles of solutes i.e. MM_B grams of solute.

weight of solution = Volume × density = 1000 dg

$\therefore$ weight of solvent = weight of solution – weight of solute = 1000 d – MM_B.

$\therefore$ 1000 d – MM_B grass of solvent has M moles. $\therefore$ $m = \frac{m}{100d - MM_B} \times 1000$

10. K_f and K_b are characteristics of solvent and respectively depend on its heat of fusion and heat of vaporisation as given below:

$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H}$ M_1 = Mol. wt of solvent ; T_f = freezing point of solvent (K)

$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H}$ R = gas constant ; T_b = Boiling point of solvent (K)

11. Van’t Hoff factor is used to calculate the terms degree of dissociation or association of a substance in solution.

12. Degree of dissociation: It is defined as the fraction of total substance that undergo dissociation into ions.

$$\text{Degree of dissociation} = \frac{\text{No. of moles of the substance dissociated}}{\text{Total no. of moles of the substance taken}}$$

Suppose a molecule of an electrolyte gives ‘m’ ions after dissociation and α is the degree of dissociation, then

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

13. Degree of association: It is defined as the fraction of total number of molecules which combine to form associated molecules.

$$\text{Degree of association} = \frac{\text{No. of moles of the substance associated}}{\text{Total no .of moles of substance taken}}$$

If suppose ‘n’ molecules of a solute associate to form the associated molecule and α is its degree of association, then

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

14. Azeotropes are these liquid mixtures which boil at a constant temperature and distil over completely at the same temperature without change in composition.

a. The components of an azeotrope cannot be separated by fractional distillation.

b. Azeotropes arise due to very large deviations from Raoult’s Law.

c. The azeotropic mixture of ethanol-water contains approximately 95% by volume of ethanol.

15. There are two types of azeotropes.

a. **Minimum boiling point azeotropes:** These mixtures show a maximum in the vapour pressure curve and hence a minimum in the boiling point diagram, e.g., ethanol-water system. Exhibited by solutions showing positive deviation.

b. **Maximum boiling point azeotropes:** These mixtures show a minimum in the vapour pressure curve and hence a maximum in the boiling point diagram, e.g., HNO_3-H_2O system. Exhibited by solutions showing negative deviation.

An azeotrope of HNO_3 and H_2O contains approximately 68% HNO_3 by mass and boils at 393 K.

PART I VERY SHORT ANSWER QUESTIONS

1. Name two ways of measuring the concentration of a solution which are not temperature dependent.
2. Why semipermeable membrane of $Cu_2[Fe(CN)_6]$ is not used for osmosis in non-aqueous solution?
3. What types of membranes are used in reverse osmosis? Name one such membrane.
4. Why is the osmotic pressure considered to be a colligative property?
5. Which is the most suitable method for determining the molecular weights of proteins?
6. Arrange the following aqueous solutions in order of increasing freezing points.
   a. 0.10 M NH_2CONH_2 b. 0.10 M KCl c. 0.10 M CH_3COOH d. 0.10 M Na_2SO_4.
7. For which substances the value of van't Hoff factor (i) is equal to 1?
8. What is the expected value of vant Hoff factor for $K_3Fe\ (CN)_6$?
9. Among the following 0.1 M solutions, which will have the lowest freezing point?
   Potassium sulphate, sodium chloride, urea, glucose.
10. What is the vant Hoff factor (i) of the compound Na_2SO_4 if it is 100% dissociated.
11. Acetic acid associates in benzene to form double molecules. What is the value of vant Hoff factor for it?
12. Give one practical application of reverse osmosis.
13. What will happen if we place red blood cells in pure water?
14. Explain why the melting point of a substance gives an indication of the purity of the substance.
15. What is an antifreeze?
16. If glycerine $[C_3H_5\ (OH)_3]$ and ethylene glycol $(C_2H_6O_2)$ are sold at same price per kg, which would be cheaper for preparing in an antifreeze solution for the radiator of an automobile?
17. What does K_f stand for?
18. Define freezing point of a solution.
19. When a solution freezes, name the substance that separates out first.
20. Define molal elevation constant.
21. Define colligative property of a solution.
22. Define normal boiling point of a liquid.
23. If the atmospheric pressure is decreased, what will happen to the boiling point of water?
24. Can we separate an azeotropic mixture by distillation?
25. What role does the molecular interaction play in solution of alcohol and water?
26. How are the compositions of the vapour and the liquid phase related to each other in azeotropic mixtures?
27. What is the concentration of ethanol in an azeotropic mixture of ethanol and water?
28. What type of azeotrope is formed an mixing nitric acid with water?
29. Give one example of a
    a. minimum boiling point azeotrope. b. maximum boiling point azeotrope.
30. What is the enthalpy change and volume change when two liquids are mixed to form a non-ideal solution which shows negative deviation from Raoults Law?
31. Is the formation of a non-ideal solution showing positive deviation from Raoult's Law endothermic or exothermic?
32. When do we express the concentration of a solution in parts per million (ppm)?
33. Is smoke a solution?
34. Give an example of a solution that contains a gas dissolved in a liquid.
35. An old saying is that 'oil and water do not mix.' Why is this true?
36. Give an example of a solution containing a liquid solute in a solid solvent.
37. Why is the vapour pressure of a liquid constant at constant temperature?
38. Cutting onions taken from the fridge is more comfortable than cutting onions lying at room temperature. Explain why?

39. Why is liquid ammonia bottle first cooled in ice before opening it?

40. Why does the use of a pressure cooker reduce cooking time?

41. 10 cc of a liquid A were mixed with 10 cc of liquid B. The volume of the resulting solution was found to be 19.9 cc. What do you conclude?

42. Two liquids A and B on mixing produce a warm solution which type of deviation from Raoult's Law does it show?

43. What happen of pressure greater than osmotic pressure is applied on the solution separated by a semi permeable membrane from the solvent?

44. What will happen to the elevation in boiling point of a solution if the weight of the solute dissolved is doubled but the weight of solvent taken halved?

45. Why it is advised to add ethylene glycol to water in a car radiator while diving in a hill station?

46. 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? (K_H = Henry's constant).

47. What do you mean by 10% w/w aqueous solution of Na_2CO_3?

48. What is the relation between normality and morality of a given solution of H_2SO_4?

49. What type of liquids from ideal solutions?

50. What is the boiling point of an azeotrope of non-ideal solution showing positive deviations as composed to the boiling points of its components?

51. What are isotonic solutions? Give one example.

52. Define molal elevation constant or ebullioscopic constant.

53. Define molal depression constant or cryoscopic constant.

54. What is vant Hoff factor?

55. Why does water from the soil rise to the top of a tall tree?

56. Why NaCl solution freezes at lower temperature than water but boils at higher temperature than water?

57. Two liquids X and Y have boiling points 110 °C and 130 °C respectively. Which one of them has higher vapour pressure at 50 °C?

58. What freezes out first when a solution of common salt is cooled?

59. What is de-icing agent? How does it work?

PART II SHORT ANSWER QUESTIONS

1. Why there is an increase in vapour pressure when HgI_2 is added tot he aqueous solution of KI?

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

3. Will the elevation in boiling point be same if 0.1 mole of sodium chloride or 0.1 mole of sugar is dissolved in one litre of water?

4. CCl_4 and H_2O are immiscible whereas C_2H_5OH and H_2O are miscible in all proportions. Correlate this behaviour with the molecular structures of the three compounds.

5. When fruits and vegetables that have dried are placed in water, they slowly swell and return to original form why? Would a temperature increase accelerate the process? Explain.

6. The van't Hoff factor of a solute in the solution is 0.5. What do you infer about nature of solute in the solution?

7. a. Name the factors which affect the solubility of a solute in a solvent.
b. Which one the following has the lowest freezing point? 1 M urea solution, 1M Na_2SO_4 solution, 1 M NaCl

8. A deci molal solution of K_4 [Fe(CN)$_6$] is 50% dissociated at 300 K. Calculate the osmotic pressure of solution. [R = 0.0821 L atm K^{-1} mol^{-1}]

9. At 25 °C, the vapour pressure of pure water is 23.76 mm Hg and that of an aqueous dilute solution of urea is 22.98 mm Hg. Calculate the molality of this solution.

10. The vapour pressure of pure benzene at 25 °C is 639.7 mm Hg and vapour pressure of a solution of a non-volatile solute is benzene at some temperature is 631.9 mm Hg. Calculate mole fraction of solute and molality of solution.

11. A solution containing 2.56g of sulphur in 100g of CS_2 gave a freezing point of lowering of 0.383 K. Calculate molecular formula of sulphur (K_f for CS_2 = 3.83 K kg mol^{-1}, At. wt. of S = 32)

12. At 298 K, the vapour pressure of pure water is 23.75 mm Hg.

a. At same temperature calculate vapour pressure over 10% aqueous solution of an organic compound whose molecular weight is 60g mol^{-1}.

b. What will be the osmotic pressure of this solution at 298 K? [Given R = 0.082 Latim K^{-1} mol^{-1}].

13. An aqueous solution freezes at 272.4 K while pure water at 273K. Determine

a. the molality of solution

b. boiling point of solution

c. Lowering of vapour pressure of water at 298 K.

[Given K_f = 1.86 K kg mol^{-1}, K_b = 0 × 512 K mg mol^{-1}, vapour pressure of pure water is 23.756 mm Hg].

14. Explain why freezing point of a solvent is lowered on dissolving a non-volatile solute into it? Give on important application of the phenomenon of depression in freezing point.

15. With the help of suitable diagrams, illustrate the two types of non-ideal solutions.

16. Differentiate between molarity and molality of a solution. When and why is molality is preferred over molarity in handing solutions in chemistry.

17. What is molar concentration of solute particles in the human blood if the osmotic pressure is 7.2 atm at the body temperature of 37 °C? [R = 0.0821 L atm K^{-1} mol^{-1}].

18. How much glucose must be dissolved in one litre of an aqueous solution so that its osmotic pressure is 2.57 atm at 300 K. [R = 0.0821 L atm K^{-1} mol^{-1}].

19. Calculate the molar concentration of urea solution if it exerts an osmotic pressure of 2.45 atm at 300 K. [R = 0.0821 L atm K^{-1} mol^{-1}].

20. Vapour pressure of pure water at 35 °C is 31.82 mm Hg. When 27.0 g of solute is dissolved in 100 g of water (at same temperature), vapour pressure of solution thus formed is 30.95 mm Hg. Calculate molecular mass of the solute.

21. The vapour pressures of pure liquids A and B are 70 mm and 90mm Hg respectively at 25 °C. The mole fraction f 'A' in a solution of two is 0.3. Assuming that A and B form an ideal solution, calculate the partial pressure of each component is equilibrium with the solution.

22. a. Two liquids A and B oil at 145 °C and 190 °C respectively. Which of them has a higher vapour pressure at 80 °C?

b. Why is the vapour pressure of a solution of glucose in water lower than that of water?

23. Explain why are aquatic species are more comfortable in cold waters rather than warm waters?

24. What happens to the vapour pressure of a solution when

a. a volatile solute dissolves in the liquid, and

b. the dissolved solute is non-volatile?

25. What are non-ideal solutions? Explain as to why non-ideal solutions deviate from Raoult's Law.

26. Is the solution of ethanol in water an ideal solution? Justify your answer.

27. Explain why a solution of ethyl alcohol and water cannot be separated into pure components by fractional distillation?

28. A mixture of ethanol and acetone shows positive deviation from Raoult's Law whereas that of chloroform and acetone shows negative deviation. Explain.

29. What is meant by positive and negative deviations from Raoult's Law and how is the sign of Δ_{sol} H related to positive and negative deviations from Raoult's Law?

30. A solution contains two volatile components A and B. What will be the relative compositions of the vapour and liquid if a. $P_A^o = P_B^o$ b. $P_A^o > P_B^o$ c. $P_A^o < P_B^o$

31. Draw a suitable labelled diagram to express the relationships, for ideal solutions of A and B, between vapour pressures and mole fractions of components at constant temperature.

32. State Raoult's Law. It ΔT is the elevation of boiling point of a solvent and m is the number of moles of solute per kg of solvent, what is the relationship between ΔT and m?

33. Why does the boiling point of a solvent increase by the presence of solute is it? Write an expression showing the relationship between the elevation of boiling point and the molar mass of the solute.

34. Define osmotic pressure. How does it depend upon the temperature and atmospheric pressure?

35. What is reverse osmosis?

36. If 2g each of solutes A and B (Molecular mass of A > B) are dissolved separately in 20 g each of the same solvent C. Which will show greater lowering of vapour pressure and why?

37. After removing the outer shell of two eggs in dil. HCl, one is placed in distilled water and the other is placed in a saturated solution of NaCl. What will you observe and why?

38. What do you expect to happen when Red Blood Corpuscles (RBC's) are placed in following solutions:
(i) 1% NaCl solution (ii) 0.5% NaCl solution

39. Equimolal solutions of NaCl and $BaCl_2$ are prepared in water. Freezing point of NaCl is found to be –2 °C. What freezing point do you expect for $BaCl_2$ solution?

40. Why boiling point of water is increased on additional of sodium chloride into it?

PART III LONG ANSWER QUESTIONS

1. The molecular weight of KCl and glucose are determined by the depression of freezing point method. As compared to their theoretical molecular weights, what do you expect are the molecular weights determined by this experiment? Why?

2. Define osmotic pressure. Arrange the following in increasing order of osmotic pressure and give reasons in support of your answer:

a. 34.2 g per litre of sucrose (M. Wt = 342) b. 90.0 g per litre of glucose (M. Wt = 180)

c. 5.85 g per litre of glucose (M. Wt = 180) d. 5.585 g per litre of NaCl (M. Wt = 58.5)

3. a. State Raoult's Law for (i) a binary solution of two liquids (ii) a binary solution of non-volatile solute.

b. Comment on values, of P_{Total}, ΔH_{mix} and ΔV_{mix} for a solution showing negative deviation.

c. Why is vapour pressure of a solvent lowered on addition of non-volatile solute to it?

d. The normal boiling points of two pure liquids P and Q are 70 °C and 100 °C respectively. If these two are mixed in equimolar proportion to form a solution and this mixture is heated to 60 °C, which one have high partial vapour pressure?

4. a. Distinguish between ideal and non-ideal solution.

b. Show that for a binary solution of two volatile components A and B, the total vapour pressure of solution may be expressed as: $P = P_A^o + (P_B^o + P_A^o)\, X_B$

c. Calculate the molarity of pure water. (Density of water = 1 g/mol).

5. a. In a solution of three components A, B and C, mole fraction of A is 0.5 and that of C is 0.2. What is mole fraction of B?

b. Under what condition, molality and molarity of a solution are equal?

c. Calculate the osmotic pressure of mixture of 100 mL of 6% urea solution and 100 mol of 18% glucose solution at 27°C. [R = 0.0821 L atm mol^{-1} K^{-1}].

PART IV SKILL ANALYSER

Time: 30 min. **Max. Marks:** 15

Directions: (i) Attempt all questions (ii) Question 1 to 3 carry 1 mark each.
(iii) Question 4 and 5 carry 2 marks each. (iv) Question 6 carry 3 marks (v) Question 7 carry 5 marks

1. State Henry's Law.

2. What is the effect of temperature on the solubility of a gas in a liquid?

3. Why is osmotic pressure considered a colligative property?

4. Why does the molarity of a solution change with temperature?

5. Explain why are aquatic species more comfortable in cold waters rather than warm waters?

6. Give three biological phenomenon regulated by osmosis in plants and animals.

7. (i) Heptane and octane form ideal solution. At 373 K, the vapour pressure of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be vapour pressure, in bar of a mixture of 25.0g heptane and 35.0g of octane?

(ii) Why there is an increase in vapour pressure when HgI_2 is added to the aqueous solution of KI?

SOLUTIONS

PART I VERY SHORT ANSWER QUESTIONS

1. Molality and mole fraction.

2. This is because $Cu_2 [Fe (CN)_6]$ is soluble in non-aqueous solutions.

3. The pressures required for reverse osmosis are quite high. Hence, membranes which can withstand high pressures are used.

Cellulose acetate is permeable to water, but impermeable to impurities and ions present in sea water.

4. This because osmotic pressure depends only upon the number of solute particles per unit volume of solution and not on the nature of the solute.

5. Measurement of osmotic pressure.

6. d < b < c < a

7. For non-electrolytes such as urea, glucose and glycerol, i has a value of 1.

8. Four, $K_3 [Fe (CN)_6] \longrightarrow 3K^+ + [Fe(CN)_6]^-$.

9. Potassium sulphate.

10. Three, $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$.

11. 0.5.

12. To render sea water fit to drink, i.e., desalination of sea water.

13. The red blood cells will expand and eventually burst as a result of water entering the cells due to osmosis.

14. This is because impurities cause a depression in freezing point. The more the impurities the lower is the freezing point.

15. An antifreeze is a substance which on adding to the cooling system of an automobile, protects the coolant from freezing in cold weather, e.g., ethylene glycol.

16. Ethylene glycol ($C_2H_6O_2$). This is because, it has lower molecular weight and hence contains more moles for the same mass of glycerine.

17. K_f represents the freezing point depression of a molal solution, i.e. depression in freezing point for 1 m solution.

18. The freezing point of a solution is the temperature at which the solid solvent and the solution have the same vapour pressure.

19. Pure solid solvent.

20. It is the elevation in boiling point when 1 mole of a solute is dissolved in 1000g of the solvent.

21. A colligative property of a solution is that property which depends only on the number of particles of solute dissolved in the solvent and not the nature of solute.

22. It is the temperature at which its vapour pressure becomes equal to one bar.

23. The boiling point of water will also decrease.

24. No, we cannot separate the constituents of an azeotropic mixture by distillation.

25. The alcohol molecules are able to form hydrogen bonds with water molecules. As a result, alcohol and water are miscible with each other in all proportions.

26. The liquid and the vapour phase have the same composition.

27. 95% by volume of ethanol.

28. Maximum boiling point azeotrope.

29. a. Ethanol – water system. b. $HNO_3 - H_2O$ system.

30. $\Delta_{sol} H < O$, i.e., heat is evolved. $\Delta_{sol} V < O$, i.e., there is a decrease in volume.

31. The formation of a non-ideal solution showing positive deviation from Raoult's Law is endothermic, i.e., heat is absorbed.

32. When the solute is present in very minute amounts, the concentration of the solution is expressed in parts per million.

33. No. This is because smoke consists of carbon particles suspended in air and is not homogeneous.

34. Aerated water.

35. This is because oil-water forces are not strong enough to overcome oil-oil and water-water forces.

36. Hydrated salts, i.e., contain water of crystallisation $CuSO_4.5H_2O$.

37. This is because it reaches a state of equilibrium where rate of evaporation = rate of concentration.

38. This is because at lower temperature, the vapours pressure in low. Hence, lesser vapours of tear producing chemicals are produced.

39. At room temperature, the vapour pressure of liquid ammonia is very high. On cooling, vapour pressure decreases. Hence, the liquid ammonia will not splash out.

40. The weight over the lid does not allow the steam to go out. As a result, pressure inside the cooker is high. Higher the external pressure higher is the boiling point and faster is the cooking.

41. Decrease in volume means stronger intermolecular forces of attraction on mixing. This implies that the solution show negative deviation from Raoult's Law.

42. Warming up of a solution means that the process of mixing is exothermic, i.e., ΔH_{mixing} = negative. This implies that the solution shows a negative deviation.

43. Reverse osmosis, i.e., net flow of the solvent is from solution to solvent.

44. The elevation in boiling point will become four times because $\Delta T_b = K_b = \frac{W_2 \, 1000}{M_2 \, W_1}$

45. It is done to lower the freezing point of water so that it does not freeze.

46. As H_2 is more soluble than helium, H_2 will have lower value of K_H than that of helium.

47. It means that 10g of $Na_2 \, CO_3$ are present in 100g of the solution.

48. Normality = 2 × Molarity.

49. Liquids having similar structures and polarities.

50. The boiling point of such an azeotrope is lower than that of its components.

51. Solution having same osmotic pressure in called isotonic solutions, e.g., 0.1 M glucose and 0.1 M sucrose solutions.

52. The elevation in boiling point that takes place when molality of the solution is unity.

53. The depression in freezing point that takes place when the molality of the solution is unity.

54. It is the ratio of the observed colligative property to the theoretical value.

55. Due to osmosis through the roots because root cell walls are made up of semipermeable membrane.

56. When a solute is dissolved in a solvent the vapour pressure decreases. As a result, the solution boils at a higher temperature while solvent freezes at a lower temperature.

57. Lower the boiling point, more volatile it is. Hence, liquid X will have higher vapour pressure at 50° C.

58. Water as ice.

59. Common salt is called de-icing agent because it lowers the freezing point of water to such an extent that it does not freeze to form ice. Hence, it is used to clear show from roads.

PART II SHORT ANSWER QUESTIONS

1. When HgI_2 is mixed with KI (aq), a complex $K_2Hg \, I_4$ is formed and thus the number of particles in the solution are decreased.

$$2\,KI + Hg\,I_2 \longrightarrow K_2[Hg\,I_4] \longrightarrow 2K^+ + [HgI_4]^{2-}$$

Due to the decrease in number of particles, vapour pressure is increased.

2. Osmotic pressure, $\pi = \frac{n}{v}RT$. It is clear from the relation that osmotic pressure, π depends only on the number of moles of solute present in a definite volume of solution. Hence, it is a colligative property.

3. The elevation in boiling point of 0.1 mole of NaCl and 0.1 mole of sugar dissolved in water will not be same. Elevation in boiling point is a colligative property and depends upon the number of solute particles NaCl is ionic and gives more number of particles due to ionisation than sugar which consists of molecules.

4. CCl_4 is a non-polar compound, where as H_2O is a polar compound having hydrogen bonding. When CCl_4 is mixed with H_2O, CCl_4 is not able to break the hydrogen bonding of H_2O and hence remains immiscible.

However, both C_2H_5OH and H_2O are polar compounds and form hydrogen bonding. When C_2H_5OH is mixed with H_2O, the hydrogen bonding between the two takes place and thus mixing occurs.

5. It is due to osmosis that the dried fruits and vegetables slowly swell when placed in contact with water.

The outer layer of the fruits and vegetable (i.e., cell wall) acts as a semi-permeable membrane.

Yes, with a increase in temperature, the osmosis accelerates as the osmotic pressure of a solution increases with increase in temperature, $\pi \alpha T$.

6. van't Hoff factor, i $= \dfrac{\text{Number of particle of solute in solution}}{\text{Number of solute molecules in normal state}} = \dfrac{\text{Observed colligative property}}{\text{Number colligative property}}$

Since i = 0.5, it means that the number of particle (ions or molecules) of solute in solution is less than that in normal state. It indicates that the solute molecules undergo association.

7. a. Factors affecting the solubility of a solute are:

(i) Nature of solute and solvent (ii) Temperature and pressure

b. 1M Na_2SO_4 has lowest freezing point because the number of effective solute particles are maximum as one molecules dissociate into three ions.

8. Concentration, $C = \dfrac{n_B}{V} = 0.1\ M$; As degree of dissociation is 50%, $\alpha = 0.5$

T = 300 K $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$ $\therefore$ n = 5, van't Hoff factor 'i' can be calculated by relation,

degree of dissociation $= \dfrac{i-1}{n-1}$ $\therefore$ $0.5 = \dfrac{i-1}{5-1}$; $0.5 = \dfrac{i-1}{4}$; $i - 1 = 2$

$i = 3$; $\pi = iCRT = 3 \times 0.1 \times 0.0821 \times 300 = 7.389$ atm.

9. $P_A^o = 23.75mm$; $P_A = 22.98$ mm ; Let X_B mole fraction of solute

According to Raoult's Law, $\dfrac{P_A^o - P_A}{P_A^o} = X_B$ $\therefore$ $X_B = \dfrac{23.76 - 22.98}{23.76} = \dfrac{0.78}{23.76} = 0.0328$

For dilute solutions, $X_B = n_B/n_A$ or $n_B = n_A X_B$

If we consider 1 kg of water, then n_B becomes number of moles of solute per kg of solvent and thus molality of solution, $\therefore n_B = \dfrac{1000}{18} \times 0.0328 = 55.5 \times 0.0328 = 1.82$ mol/kg of solvent.

10. Using relation, $X_B = \dfrac{P_A^o - PA}{P_A^o} = X_B$

$X_B = \dfrac{639.7 - 631.9}{639.7} = 0.0122$; $X_{solute} = \dfrac{n_{solute}}{n_{solute} + n_{solvent}}$; $X_{solute} = \dfrac{n_B}{n_B + \dfrac{1000}{78}} = \dfrac{n_B}{n_B + 12.82}$

{when are consider weight of solvent equal to 1000 g then n_B obtained is molality}

$0.0122 = \dfrac{n_B}{n_B + 12.82}$; $n_B = 0.0122 n_B + 12.82 \times 0.0122$

$(1 - 0.0122)\ n_B = 12.82 \times 0.0122 = 0.1564$ $\therefore$ $n_B = \dfrac{0.1564}{0.9878}$ 0.158 moles/kg of benzene.

11. Using relation, $\Delta T_f = K_f m = K_f \dfrac{W_B \times 1000}{M_B \times W_A}$ $\therefore$ $M_B = \dfrac{3.82 \times 2.56 \times 1000}{0.383 \times 100} = 256\ g\ mol^{-1}$

Atomic weight of sulphur = 32 ; $\therefore$ No. of atoms in one molecule of sulphur $= \dfrac{\text{Mol. wt}}{\text{At. wt}} = \dfrac{256}{32} = 8.$

The molecular formula of sulphur is S_8

12. Let there is 100 g of solution i.e., 10 g of organic compound is 90 g of water

$$n_B = \frac{W_B}{M_B} = \frac{10}{60} = \frac{1}{6};\; n_A = \frac{W_A}{M_A} = \frac{90}{18} = 5.$$

$$\frac{P_A^o - PA}{P_A^o} = X_B;\; \frac{n_B}{n_A + n_B} = \frac{1/6}{5+1/6} = \frac{1}{31}\;\; \frac{23.75 - P_A}{23.75} = \frac{1}{31}\;;\;\; 23.75 - P_A = \frac{23.75}{31} = 0.766 \Rightarrow P_A = 22.98 \text{ mm Hg.}$$

b. Osmotic pressure, $\pi = \frac{n_B}{V} RT = \frac{1 \times 0.082 \times 298}{6 \times 0.1}$; $\pi = 40.73$ atm.

13. a. $\Delta T_f = 273 - 272.4 = 0.6$ K $\quad \Delta T_f = K_f m \quad \therefore$ molality, $m = \frac{\Delta T_f}{K_f} = \frac{0.6}{1.86} = 0.322$ mol/kg.

b. $\Delta T_b = K_b \times m = 0.512 \times 0.322 = 0.165$ K. Boiling point of solution $= 373 + \Delta T_b = 373 + 0.165$ K $= 373.165$ K

c. $\frac{P_A^o - P_A}{P_A^o} = X_B = \frac{n_B}{n_A + n_B}$

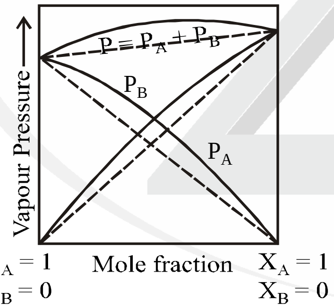
Moles of solute per kg of solvent = $n_A = 0.322$; Moles of solvent per kg of solvent $= n_B = \frac{1000}{18} = 55.55$

Mole fraction of solute, $X_B = \frac{0.322}{55.55 + 0.322} = 0.0057$ $\therefore$ Lowering of vapour pressure,

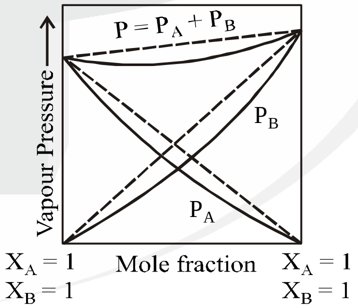
$P_A^o - P_A = P_A^o\, X_B = 23.756 \times 0.0057$ = 0.137 mm Hg.

14. Lowering of vapour pressure is the basic cause of depression in freezing point. Since the vapour pressure of a solution is lower than that of pure solvent, the temperature of freezing of the solution is lower than that of pure solvent. Liquid freezes at a vapour pressure at which solid form can also exist with in equilibrium, i.e., at freezing point there exists an equilibrium between liquid phase and solid phase of solvent.

15. The use of freezing mixtures (salts + ice) in making of kulfis, use of antifreeze into water especially in very cold regions, determination of molar mass, etc., are important applications of depression in freezing point.



A vapour pressure graph showing a positive deviation (solid lines) from ideal behaviour (dotted lines).



A vapour pressure graph showing a negative deviation (solid lines) from ideal behaviour (dotted lines).

16. Molarity is the number of moles of solute dissolved per litre of solution. $M = \frac{n_B}{V\text{ (in litres)}}$

Molality is the number of moles of solute dissolved per kg of solvent. $m = \frac{n_B}{W_B\text{ (in kg)}}$

Molality does not change with temperature whereas molarity change with temperature. Therefore, molality is used in study of elevation in boiling point, depression in freezing point and in very accurate analytical measurements involving variation of temperature.

17. $\pi = CRT$; $C = \frac{\pi}{RT} = \frac{7.2}{0.0821\times 310} = \frac{7.2}{25.45} = 0.283 \text{ mol L}^{-1}$.

18. Using relation, $\pi = CRT = \frac{n_B}{V}RT = \frac{W_B\,RT}{VM_B}$ $\therefore\ \pi = \frac{W_B\,RT}{VM_B}$; $W_B = \frac{\pi VM_B}{RT}$ $W_B = \frac{2.57\times 1\times 180}{0.0821\times 300} = 18.79\text{ g}$.

19. Using relation, $\pi = CRT$; $C = \frac{\pi}{RT} = \frac{2.45}{0.0821\times 300} = 0.099\text{ mol L}^{-1}$.

20. $\frac{P_A^o - P_A}{P_A^o} = X_B = \frac{W_B/M_B}{W_A/M_A} = \frac{27/M_B}{18/100}$; $\frac{31.82-30.95}{31.82} = \frac{27}{M_B}\times\frac{18}{100}$; $M_B = \frac{27\times 18\times 31.82}{100\times 0.87} = 177.38\text{ g mol}^{-1}$

21. Here P_A^o = 70 mm Hg. P_B^o = 90 mm Hg.

X_A = 0.3 $\therefore$ X_b = $1 - X_A = 1 - 0.3 = 0.7$

According to Raoult's Law, $P_A = P_A^o\ X_A$ = 70 × 0.3 = 21 mm Hg. $P_B = P_B^o\ X_B$ = 90 × 0.7 = 63 mm Hg.

22. a. Liquid A will have higher vapour pressure at 80 °C.

b. When any solute, i.e., glucose is dissolved in water, the surface of the solution is occupied of (non-volatile) molecules. Whereas in case of pure water whole surface is occupied by solvent molecules. Therefore, the number of solvent molecules escaping from the surface is correspondingly reduced as compared to the pure solvent and thus results in the decrease of vapour pressure.

23. Aquatic species are comfortable in cold water as they get the oxygen needed from the water containing dissolved oxygen. Also, the amount of oxygen dissolved in warm water is more than in cold water. This is because the solubility of a gas decrease with increase in temperature.

24. a. If the added solute is more volatile than the liquid (solvent), then the vapour pressure will increase.

b. When the dissolved solute is non-volatile, the vapour pressure of the solution will decrease.

25. The solutions which do not obey Raoult's Law are called non-ideal solutions. The vapour pressure of such solutions are either higher or lower than that predicted by Raoult's Law, e.g., ethane and acetone, acetone and chloroform.

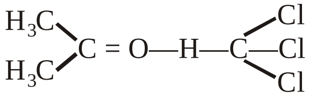
Non-ideal solutions deviate from Raoult's Law because in a non-ideal solution of two components A and B, the A – B interactions are not of the same strength as A – A and B – B interactions. The A – B interactions are either stronger or weaker than the A – A and B – B interaction.

26. The solution of ethanol in water is not an ideal solution because the forces operating between the molecules of water and ethanol are weaker than the forces (i.e., Hydrogen bonds) operating between the ethanol – ethanol and H_2O – H_2O molecules. This results in positive deviation from Raoult's Law.

27. Ethyl alcohol and water form an azeotropic mixture which distills without change in composition at a constant temperature. And this constant temperature is lower than the boiling points of either pure ethyl alcohol or water.

28. (i) In ethanol, there is intermolecular hydrogen bonding between ethanol molecules. When acetone is added to ethanol, the molecules of acetone get in between the ethanol molecules by breaking the hydrogen bonds of the host molecules. This results in increase of escaping tendency of ethanol molecules. Consequently, the vapour pressure of the solution increases resulting in position deviation.

(ii) When chloroform is mixed with acetone, if forms hydrogen bonds with acetone molecules.



As a result of hydrogen bonds between the molecules of chloroform and acetone, the escaping tendency of both chloroform and acetone decreases. Consequently, the vapour pressure of the solution decreases resulting in negative deviation from Raoult's Law.

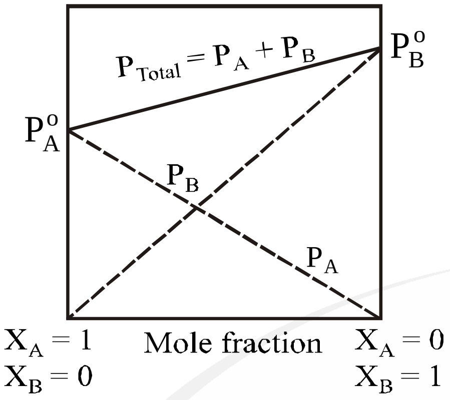
29. Positive deviation from Raoult's Law is exhibited when the measured vapour pressure is higher than the predicted vapour pressure. It occurs when A – B interactions are weaker than those between A – A and B – B interactions. Δ_{sol} H is +ve i.e., > O.

Negative deviation from Raoult's Law is exhibited when the measured vapour pressure is lower than the predicted vapour pressure. It occurs when A – B interactions are stronger than those between A – A and B – B interactions. Δ_{Sol} H is –ve i.e., < O.

30. a. $P_A^o = P_B^o$. It means that the composition of A and B will be same in both the liquid and the vapour phase $P_A^o > P_B^o$. It means that the vapour phase is richer in A component.

b. $P_A^o < P_B^o$. It means that the vapour phase is richer in B component whereas the liquid phase is richer in A component.

31.



32. According to Raoult's Law, the vapour pressure of a solution containing a non-volatile solution is directly proportional to the mole fraction of the solvent (X_A), P α X_A . P = P°X_A, where P° = Vapour pressure of pure solvent.

If the solution consists of two volatile liquids, then Raoults Law in $P_A = P_A^o X_A$ and $P_B = P_B^o X_B$. And the total vapour pressure of the solution is equal to the sum of the partial vapour pressure of each component.

$P = P_A + P_B = P_A^o X_A + P_B^o X_A$. Relation between ΔT and m, ΔT α m

$\Delta T = K_b m$ where K_b is a proportionality constant called molal elevation constant.

33. The boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure. When a non-volatile solute is dissolved in a solvent, the vapour pressure of the solvent is decreased, i.e., the temperature at which the vapour pressure of the solution will equal the atmospheric pressure will be higher than the temperature at which the vapour pressure of the pure solvent equals the atmospheric pressure. In other words, the boiling point of a solvent increases by the presence of a solute in it.

Relationship between the elevation of boiling point and the molal mass of the solute, $\Delta T_B = K_b m = \dfrac{K_b\, W_B\, 1000}{M_B\, W_A}$

34. Osmotic pressure (π) is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane. $\pi = CRT = \dfrac{n_B}{V} RT$

As can be seen from the above expression, osmotic pressure, π is directly proportional to the temperature on the Kelvin, scale, i.e., the osmotic pressure increases with rise in temperature.

Osmotic pressure is independent of atmospheric pressure.

35. Consider a solution separated from the pure solvent by a semipermeable membrane. If the pressure applied to the solution side is more than the osmotic pressure, the solvent will flow from the solution to the solvent side. This phenomenon is called reverse osmosis.

36. For dilute solutions, $\dfrac{P° - Ps}{P°} = \dfrac{W_2\, M_1}{W_1\, M_2}$; $\dfrac{\Delta P}{P°} = \dfrac{W_2\, M_1}{W_1\, M_2}$

For same, P°, i.e., P° constant and M_1 is also constant. $W_2 = W_A = W_B = 2g$; $W_1 = W_C = 20$ g

Hence $\frac{\Delta P_A}{\Delta P_B} = \frac{M_B}{M_A}$· As $M_A > M_B$, therefore, $\Delta P_B > \Delta P_A$.It means B will show greater lowering of vapour pressure.

37. Egg in water will swell while egg in NaCl solution will shrink. This is because as a result of osmosis, the net flow of solvent is from less concentrated to more concentrated solution.

38. (i) They will shrink due to plasmolysis.

(ii) They will smell and may even burst.

RBC's are isotonic with 0.9% NaCl solution.

39. van't Hoff Factor (i) for NaCl is 2 ; van't Hoff Factor (i) for $BaCl_2$ is 3.

$$\frac{(\Delta T_f)_{NaCl}}{(\Delta T_f)_{BaCl_2}} = 2/3 \quad ; \quad \therefore \quad (\Delta T_f)_{BaCl_2} = \frac{3}{2} \times (-2°C) \quad \therefore \quad (\Delta T_f)_{BaCl_2} = -3°C.$$

40. When NaCl which is non-volatile is dissolved in water, vapour pressure of water decreases because some of the solvent molecules on the surface are replaced by the molecules of the solute which are non-volatile. The solution has to be heated more to make vapour pressure equal to the external pressure. Hence, boiling point is increased.

PART III LONG ANSWER QUESTIONS

1. Glucose when dissolved in water does not associate or dissociate in water, so its experimental molecular weight is equal to its theoretical molecular weight whereas KCl is a strong electrolyte, each molecule of KCl dissociates in water to give two ions (particles), i.e., $KCl \rightleftharpoons K^+ + Cl^-$.

Hence, its depression in freezing point found experimentally is double its calculated value, i.e., its van't Hoff factor = 2.

As, colligative property $\alpha \ \frac{1}{\text{Molecular Mass}}$, therefore experimental molecular mass is half its theoretical value.

2. The external pressure applied to solution in order to stop the osmosis of solvent into solution separated by semipermeable membrane is called osmotic pressure.

$$\pi = CRT$$

Osmotic pressure is a colligative property and depends upon the number of particles of solute in solution. Glucose and sucrose are non-electrolytes, therefore, they do not dissociate or associate in solution while NaCl is an electrolyte and on dissolving in water it dissociates to give two ions:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$\pi = i\left(\frac{n}{V}\right)RT = i\,CRT$$

a. For sucrose, i = 1 (as it neither dissociates nor associates in solution)

$C = \frac{34.2}{342} = 0.1\,\text{moles/litre}$ $\quad \therefore \ \pi_{sucrose} = 1 \times 0.1 \times RT = 0.1\ RT$ atm.

b. For glucose, i = 1 (as it neither dissociation nor associates in solution) $C = \frac{90}{180} = 0.5\,\text{moles/litre}$

$\therefore \ \pi_{glucose} = 1 \times 0.5 \times RT = 0.5\ RT$ atm.

c. For NaCl, i = 2 (as it dissociates in solution to give 2 ions) $C = \frac{5.85}{585} = 0.1\,\text{moles/litre}$

$\pi_{Nacl} = 2 \times 0.1 \times RT = 0.2\ RT$ atm

Thus, the increasing order of osmotic pressure of the above solutions is as follows: Sucrose < NaCl < Glucose

3. a. Refer to brief resume

b. Vapour pressure of solution will be less than expected from Raoult's law. Values of $\Delta H_{sol.}$ and $\Delta V_{sol.}$ will also be less than zero i.e., heat is released and there is contraction in volume.

c. When solvent contains solute particles, the effective surface area available to solvent molecules to escape decreases. A part of surface area gets occupied by non-volatile solute particles.

d. Liquid P with lower boiling point high higher partial vapour pressure.

4. a

Ideal solutions	Non-ideal solutions
(i) A – B interactions are very much similar to A – A and B – B interactions.	(i) A – B interactions are very much different (either stronger or weaker) from A – A and B – B interactions.
(ii) There is no change in volume in the formation of solution, i.e., $\Delta V_{mix} = 0$.	(ii) The volume of solution is either less or more than the total volume of components, i.e., $\Delta V_{mix} \neq 0$.
(iii) No heat change takes place, i.e., $\Delta H_{mix} = 0$.	(iii) Enthalpy change takes place, i.e., $\Delta H_{mix} \neq 0$. Heat is evolved or absorbed in the process of solution formation.
(iv) They obey Raoult's Law at all temperature and concentrations.	(iv) They do not obey Raoult's Law.

b. By Raoult's Law, $P_A = P_A^o\ X_A$ and $P_B = P_B^o\ X_B$

Total vapour pressure, i.e., $P = P_A + P_B = P_A^o\ X_A + P_B^o\ X_B$

We know that $X_A = 1 - X_B$; $P_A = P_A^o\ (1 - X_B) + P_B^o\ X_B = P_A^o - P_A^o\ X_B + P_B^o\ X_B = P_A^o + (P_B^o - P_A^o)\ X_B$.

c. Consider 1 litre of pure water, i.e., 1000 mL

Weight of 1000 mL of water = Volume × Density = 1000 × 1 = 1000 g.

Moles of water $= \frac{1000}{18} = 55.55$ moles. Hence, 55.55 moles of water are present in one litre of water.

$\therefore$ Molarity of water = 55.55 M.

5. a. In a solution, sum of mole fractions of all components is unity.

$\therefore\ X_A + X_B + X_C = 1 \qquad \therefore\ X_B = 1 - (X_A + X_C) = 1 - (0.5 + 0.2) = 0.3.$

b. $M = \frac{n_B}{V \text{ in litres}}$ and $m = \frac{n_B}{W \text{ in kg}}$

Where M is molarity and m is molality. M and m will be equal if 1 litre of solution has mass of 1 kg.

This is generally true in case of very dilute aqueous solutions at room temperature when density of solution can be taken as 1g cm^{-3}.

c. Total volume of solution = V = 100 + 100 = 200 mL = 0.2 L

After mixing of two solutions, 6g of urea is present in 200 mL solution.

$$\therefore\ \pi_1 = \frac{n_B}{V}RT = \frac{6/60}{0.2} \times \frac{0.0821 \times 300}{1} = 12.315 \text{ atm}$$

(When molar mass of urea $NH_2CONH_2 = 2 \times 14 + 12 + 16 + 4 \times 1 = 60$)

Similarly, 18g of glucose ($C_6H_{12}O_6$) is present in 200 ml solution.

Osmotic pressure due to glucose,

$$\pi_2$$

$$= \frac{n_B}{V} RT = \frac{18 \times 0.0821 \times 300}{180 \times 0.2} \text{ atm} = 12.315 \text{ atm}$$

The two solutes behave independently and total osmotic pressure is the sum of two.

Osmotic pressure of mixture, $\pi = \pi_1 + \pi_2 = 12.315 + 12.315 = 24.630$ atm.

PART IV SKILL ANALYSER

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

2. The solubility of a gas in a liquid decreases with increase in temperature.

3. This is because the value of osmotic pressure of a solution depends upon the number of particles of solute per litre of solution.

4. The molarity of a solution is the number of moles of solute present in one litre of the solution.

The molarity of a solution changes, with temperature because the volume of the solution changes with change in temperature.

5. Aquatic species get their requirement of oxygen from water containing dissolved oxygen.

Since the solubility of a gas in liquid decreases with rise in temperature (1 mark) warm water dissolve less amount of oxygen as compared to cold water. Hence, aquatic species are more comfortable in cold water rather than warm water.

6. (1) Plants absorb water from the soil through their roots due to osmosis.

(2) In animals water moves into different parts of body due to osmosis.

(3) Movements in plants like opening and closing of flowers etc., are regulated by osmosis.

7. (i) No. of moles of heptane ($C_7 H_{10}$) in the solution

$$= \frac{\text{Mass}}{\text{Molar Mass}} = \frac{25}{(7 \times 12 + 1 \times 16)} = \frac{25}{100} = 0.25 \text{ mol}$$

No. of moles of octane ($C_8 H_{18}$) in the solution $= \frac{\text{Mass}}{\text{Molar Mass}} = \frac{35}{8 \times 12 + 1 \times 18} = \frac{35}{114} = 0.307 \text{ mol}$

Mole fraction of heptane $= \frac{0.25}{0.25 + 0.307} = 0.4488$; Mole fraction of octave $= \frac{0.307}{0.25 + 0.307} = 0.5512$

$P_{Heptane} = P°_{Heptane} X_{Heptane} = 105.2 \times 0.4488 = 47.2$; $P_{Octane} = P°_{Octane} X_{Octane} = 46.8 \times 0.5512 = 25.8$

Vapour pressure of a mixture = 47.2 +25.8 = 73.0 kPa

We know that 1 bar = 100 kPa $\therefore$ 73.0 kPa $= \frac{1 \text{ bar}}{100 \text{ kPa}} \times 73.0$ kPa = 0.73

(ii) When HgI_2 is mixed with KI (aq), a complex $K_2Hg\ I_4$ is formed and thus the number of particles in the solution are decreased.

$$2\ KI + Hg\ I_2 \longrightarrow K_2\ [HgI_4] \longrightarrow 2K^+ + [HgI_4]^{2-}$$

Due to the decrease in number of particles, vapour pressure is increased.