

## Syllabus

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## 2.1 Introduction

1. What is a mixture? Give an example.

Ans:

- i. The mixture is a combination of two or more substances.
- ii. Air is a mixture of gases, rock is a mixture of two or more minerals and so forth.

Q.2 What is the different between homogenous mixture and heterogenous mixture?

Ans: In homogenous mixture. The mixing of component is uniform whereas in heterogenous mixture. The mixing of component is ununiform.

Q.3 How are homogenous mixture classified?

Ans: Homogeneous mixtures are classified according to the size of their constituent particles as colloids or as true solutions.

Q.4 What is the size of particles of colloids and those of true solutions.

Ans:

- i. Colloids contains particle size of the dispersed phase ranges from 1 nm to 1 mm.
- ii. True solution the substance dissolved (solute) in solvent has the particle size of less than  $10^{-9}$ m or 1nm.

+5. What is a solution and what are the two components of solutions?

Ans:

- i. The solution is a homogeneous mixture of two or more pure substances.
- ii. A true solution consists of a solvent and one or more solutes.

+6 Where are solutions commonly found?

Ans:

- i. The solutions are commonly found in all life processes. The body fluids are solutions.
- ii. The solutions are also important for industrial processes, and many other areas.

Q.7

Define the term solute and solvent.

Ans:

- i. The component of solution which is in smaller proportion is called solute.
- ii. The component of solution which is in larger proportion is called solvent.

## 2.2 Types of solutions

Q.8 What are the different types of solutions.

Ans:

- i. The solute and the solvent may be in any of three states namely, solid, liquid or gas.
- ii. The solutions thus may involve any combination of these three states of their components.

- iii. This gives rise to nine types of solutions depending on the states of solute and solvent.

**Q.9 What are the different units used to express the concentrations of solutions.**

**Ans:** Different units used to express the concentration of solutions are

- Mass percent or weight percent (w/w%)
- Mole fraction
- Molarity (M)
- Molality (m)

### 2.3 Capacity of solution to dissolve solute

**Q.10 Explain the following terms.**

- Saturated solution.**
- Superstaturated solution.**

**Ans:**

- A saturated solution contains maximum amount of solute dissolved in a given amount of solvent at a given temperature.
  - The solution at this point is said to be saturated. A dynamic equilibrium can be reached where the number of solute molecules leaving the crystal to pass into solution is equal to the number returning from the solution to the crystal.
- $$\text{Solute} + \text{solvent} \xrightleftharpoons[\text{crystallization}]{\text{dissolution}} \text{Solution}$$
  - A solution containing greater than the equilibrium amount of solute is said to be supersaturated solution.
  - Such solutions are unstable.
  - The precipitation occurs by the addition of a tiny crystal of solute and the supersaturated solution changes to saturated solution.

### 2.4 Solubility

**Q.11 What is solubility. Give the unit used to express solubility**

**Ans:**

- The solubility of a solute is its amount per unit volume of saturated solution at a specific temperature.
- The solubility of a solute is its maximum concentration and expressed in the concentration units mol L<sup>-1</sup>.

**Q.12 How does the nature of solute and solvent affect solubility?**

**Ans:**

- Generally the compounds with similar chemical character are more readily soluble in each other than those with entirely different chemical characters.
- The saying that 'like dissolves like' guides to predict the solubility of a solute in a given solvent.
- Thus, substances having similar intermolecular forces are likely to be soluble in each other.
- Generally polar solutes dissolve in polar solvents. This is because in these, solute-solute, solute-solvent and solvent-solvent interactions are all of similar magnitude.
- For example, NaCl dissolves in water. The strong ion-dipole interactions of Na<sup>+</sup> and Cl<sup>-</sup> ions with water molecules, hydrogen bonding between water molecules and ion-ion attractions between Na<sup>+</sup> and Cl<sup>-</sup> ions are comparable.
- Nonpolar organic compounds like cholesterol dissolves in nonpolar solvent such as benzene.
- Sugar dissolves in water! The dissolution of sugar in water is due to intermolecular hydrogen bonding between sugar and water.

**Q.13 Why naphthalene dissolves in benzene but not in water?**

**Ans:**

- The 'like dissolve like' principle guides to predict the solubility of a solute in a given solvent. Thus substance having similar intermolecular forces are likely to be soluble in each other.
- Naphthalene and benzene both are nonpolar while water is polar.  
Hence, naphthalene dissoves in benzene but not in water.

**★ Q.14 What is the effect of temperature on solubility of solids in water? Give examples.**

**Ans:** The effect of temperature on solubility of solids in water.

- When the substance dissolves in water by an exothermic process its solubility increases with an decrease of temperature.

Example - KCl dissolve in water by endothermic process.

- ii. On the other hand, when the substance dissolves in water by an exothermic process its solubility decreases with an increase of temperature.

Example - The substances such as  $\text{CaCl}_2$  and  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  dissolve in water releasing heat.

- iii. It is important to understand that there is no direct correlation between solubility and exothermicity or endothermicity.

For example, dissolution of  $\text{CaCl}_2$  in water is exothermic and that of  $\text{NH}_4\text{NO}_3$  is endothermic. The solubility of these increases with the temperature.

**+Q.15 Le-Chatelier priciple, exothermic process and endothermic process.**

**Ans:** According to Le-Chatelier priciple, in exotheric reactions, an increase in temperature decreases the equilibrium constant,  $K$ , whereras in endothermic reactions an increase in tempertraure.

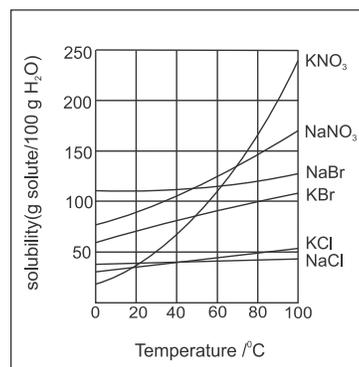
**+Q.17 Can you tell?**

**Anhydrous sodium sulphate dissolves in water with the evolution of heat. What is the effect of temperature on its solubility.**

- Ans:**
- Since anhydrous sodium sulphate dissolves in water with evolution of heat, it is an exothermic reaction.
  - When the substance dissolves in water by an exothermic process, with the release of heat, the solubility of substance decreases with increase in temperature.
  - Therefore, the solubility of anhydrous sodium sulphate in water decreases with increase in temperature.

**Q.18 The following graph shows the experimental determination of solubilities of some ionic solids in water at various temperatures. Comment on the effect of temperature on solubilities of these compounds in water.**

**Ans:**



- Solubilities of NaBr, NaCl and KCl change slightly with temperature.
- Solubilities of  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{KBr}$  increase appreciably with increasing temperature.
- Solubility of  $\text{Na}_2\text{SO}_4$  decreases with increase of temperature.

**Q.19 Why does the solubility of gases in water usually decreases with increase of temperature.**

**Ans:**

- When gases are dissolved in water, the gas molecules in liquid phase are condensed.
- The condensation is an exothermic process.

**Q.20 What is the effect of pressure on solubility?**

**Ans:**

- Pressure has no effect on the solubilities of solids and liquids as they are incompressible.
- However pressure greatly affects solubility of gases in liquids.
- The solubility of gases increases with increasing pressure.

**Q.21 State and explain Henry's law.**

**Ans:**

- It states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution. Thus,

$$S \propto P \text{ or } S = K_H P \dots\dots\dots (i)$$

- where,  $S$  is the solubility of the gas in  $\text{mol L}^{-1}$ ,  $P$  is the pressure of the gas in bar over the solution.  $K_H$ , the proportionality constant is called Henry's law constant.

$$K_H : K_H = \frac{S}{P} = \frac{\text{mol L}^{-1}}{\text{bar}} = \text{mol L}^{-1} \text{ bar}^{-1}$$

- iii. When  $P = 1$  bar,  $K_H = S$ . Thus,  $K_H$  is the solubility of the gas in a liquid when its pressure over the solution is 1 bar.

**Q.22 Why CO<sub>2</sub> effervescence is observed, when the bottle of soft drink is opened.**

**Ans:**

- Before sealing the bottle of soft drink, it is pressurised with a mixture of air, CO<sub>2</sub> saturated with water vapour.
- Because of high partial pressure of CO<sub>2</sub>, its amount dissolved in soft drink is higher than the solubility of CO<sub>2</sub> under normal conditions.
- When the bottle of soft drink is opened, excess dissolved CO<sub>2</sub> comes out with effervescence.

**Q.23 Give reason: Why gases like NH<sub>3</sub> and CO<sub>2</sub> do not obey Henry's law.**

**Ans:**

- Gases like NH<sub>3</sub> and CO<sub>2</sub> do not obey Henry's law.
- The reason is that these gases react with water.
- $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$
- Because of these reactions, NH<sub>3</sub> and CO<sub>2</sub> gases have higher solubilities than expected by Henry's law.

### Type - 1

#### Numericals based on Henry's law

1. The solubility of N<sub>2</sub> gas in water at 25 °C and 1 bar is  $6.85 \times 10^{-4} \text{ mol L}^{-1}$ . Calculate (a) Henry's law constant (b) molarity of N<sub>2</sub> gas dissolved in water under atmospheric conditions when partial pressure of N<sub>2</sub> in atmosphere is 0.75 bar.

**Solution:**

$$\begin{aligned} \text{a. } K_H &= \frac{S}{P} = \frac{6.85 \times 10^{-4} \text{ mol dm}^{-3}}{1 \text{ bar}} \\ &= 6.85 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1} \\ \text{b. } S &= K_H P = 6.85 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1} \\ &\quad \times 0.75 \text{ bar} \\ &= 5.138 \times 10^{-4} \text{ mol L}^{-1} \end{aligned}$$

2. The Henry's law constant of methyl bromide (CH<sub>3</sub>Br), is  $0.159 \text{ mol L}^{-1} \text{ bar}^{-1}$  at 25°C. What is the solubility of methyl bromide in water at 25°C and at pressure of 130 mmHg?

**Solution:**

According to Henry's law

$$S = K_H P$$

$$\text{a. } K_H = 0.159 \text{ mol L}^{-1} \text{ bar}^{-1}$$

$$\text{b. } P = 130 \text{ mm Hg} \times \frac{1}{760 \text{ mm Hg / atm}}$$

$$= 0.171 \text{ atm} \times 1.013 \text{ bar/atm}$$

$$= 0.173 \text{ bar}$$

$$\text{Hence, } S = 0.159 \text{ mol L}^{-1} \text{ bar}^{-1} \times 0.173 \text{ bar}$$

$$= 0.271 \text{ M}$$

3. Fish generally needs O<sub>2</sub> concentration in water atleast 3.8 mg/L for survival. What partial pressure of O<sub>2</sub> above the water is needed for the survival of fish? Given the solubility of O<sub>2</sub> in water at 0 °C and 1 atm partial pressure is  $2.2 \times 10^{-3} \text{ mol/L}$

**Solution :**

O<sub>2</sub> concentration in water required for fishes = 3.8 mg/L

Solubility of O<sub>2</sub> in water =

$$2.2 \times 10^{-3} \text{ mol / L}$$

$$\text{Pressure} = 1 \text{ atm}$$

To find : Partial pressure of O<sub>2</sub> above the water needed for the survival of fish.

Formula :  $S = K_H P$

Calculation : Pressure = 1 atm = 1.013 bar

Now, using formula and rearranging,

$$K_H = \frac{S}{P} = \frac{2.2 \times 10^{-3} \text{ mol / L}}{1.013 \text{ bar}}$$

$$= \frac{2.2 \times 10^{-3}}{1.013}$$

$$= \text{Antilog} [ (\log 2.2 + \log 10^{-3}) - \log 1.013 ]$$

$$= \text{Antilog} [ (0.3424 - 3) - 0.0055 ]$$

$$= \text{Antilog} [ -2.6576 - 0.0055 ]$$

$$= \text{Antilog} (-2.6631)$$

$$= 2.17 \times 10^{-3} \text{ mol / L}$$

O<sub>2</sub> concentration in water required for fishes = 3.8 mg/L

$$= \frac{3.8 \times 10^{-3}}{32 \text{ g/mol}} = 1.19 \times 10^{-4} \text{ molL}^{-1}$$

$$= \frac{3.8 \times 10^{-3}}{32}$$

$$= \text{Antilog} [(\log 3.8 + \log 10^{-3}) - \log 32]$$

$$= \text{Antilog} [(0.5797 - 3) - 1.5051]$$

$$= \text{Antilog} [-2.4203 - 1.5051]$$

$$= \text{Antilog} [-3.9254]$$

$$= 1.1874 \times 10^{-4}$$

$$= 1.19 \times 10^{-4}$$

Now, using formula and rearranging,

$$P = \frac{S}{K_H} = \frac{1.19 \times 10^{-4} \text{ molL}^{-1}}{2.17 \times 10^{-3} \text{ molL}^{-1} \text{ bar}^{-1}} = 0.0548 \text{ bar}$$

$$= \frac{1.19 \times 10^{-4}}{2.17 \times 10^{-3}} = \frac{1.19 \times 10^{-1}}{2.17}$$

$$= \frac{0.119}{2.17} = \text{Antilog} [\log 0.119 - \log 2.17]$$

$$= \text{Antilog} (-0.9244 - 0.3364)$$

$$= \text{Antilog} (-1.2608)$$

$$= 0.0548$$

**Ans :** The partial pressure of O<sub>2</sub> above the water needed for the survival of fish is 0.0548.

### 2.5 Vapour pressure of solutions of liquids in liquids

**Q.24** State and explain Raoult's law.

**Ans:**

i. It states that the partial vapour pressure of any volatile component of a solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.

ii. Suppose that for a binary solution of two volatile liquids A<sub>1</sub> and A<sub>2</sub>, P<sub>1</sub> and P<sub>2</sub> are their partial vapour pressures and x<sub>1</sub> and x<sub>2</sub> are their mole fractions in solution. Then according to Raoult's law,

iii.  $P_1 = x_1 P_1^0$  and  $P_2 = x_2 P_2^0$  .....(i)

iv. where P<sub>1</sub><sup>0</sup> and P<sub>2</sub><sup>0</sup> are vapour pressures of pure liquids A<sub>1</sub> and A<sub>2</sub>, respectively.

v. According to Dalton's law of partial pressures, the total pressure P above the solution is,  
 $P = P_1 + P_2$

$$= P_1^0 x_1 + P_2^0 x_2 \text{ .....(ii)}$$

vi. Since x<sub>1</sub> = 1 - x<sub>2</sub>, the Eq. (i) can also be written as

$$P = P_1^0 (1 - x_2) + P_2^0 x_2$$

$$= P_1^0 - P_1^0 x_2 + P_2^0 x_2$$

$$= (P_2^0 - P_1^0) x_2 + P_1^0 \text{ ..... (iii)}$$

vii. Because P<sub>1</sub><sup>0</sup> and P<sub>2</sub><sup>0</sup> are constants, a plot of P versus x<sub>2</sub> is a straight line as shown in the diagram.

viii. The figure also shows the plots of P<sub>1</sub> versus x<sub>1</sub> and P<sub>2</sub> versus x<sub>2</sub> according to the equations (i).

xi. These are straight lines passing through origin.

x. a. For P<sub>1</sub><sup>0</sup> versus x<sub>2</sub> straight line,

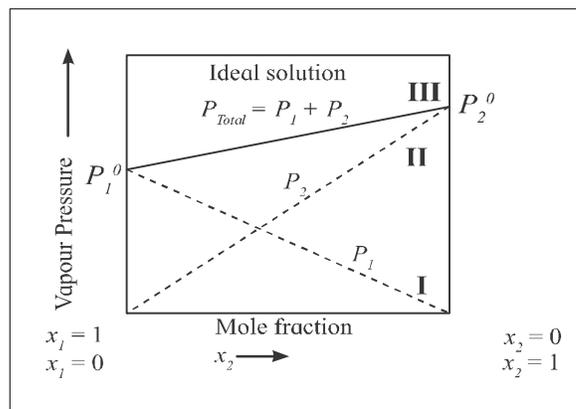
$$P = P_1^0 \text{ at } x_2 = 0 \text{ and } P = P_2^0 \text{ at } x_2 = 1$$

b. For P<sub>1</sub> versus x<sub>1</sub> straight line,

$$P_1 = 0 \text{ at } x_1 = 0 \text{ and } P_1 = P_1^0, \text{ at } x_1 = 1$$

c. For P<sub>2</sub> versus x<sub>2</sub> straight line,

$$P_2 = 0 \text{ at } x_2 = 0 \text{ and } P_2 = P_2^0 \text{ at } x_2 = 1$$



**Q.25** How the composition of vapour phase in liquid - liquid phase can be determined?

**Ans:**

i. The composition of vapour in equilibrium with the solution can be determined by Dalton's law of partial pressures.

ii. If we take y<sub>1</sub> and y<sub>2</sub> as the mole fractions of two components in the vapour, then

$$P_1 = y_1 P \text{ and } P_2 = y_2 P$$

iii. where P<sub>1</sub> and P<sub>2</sub> are the partial pressures of two components in the vapour and P is the total vapour pressure.

**Q.26 State the characteristics of ideal solution.**

**Ans:**

- Ideal solutions obey Raoult's law over entire range of concentrations.
- No heat is evolved or absorbed when two components forming an ideal solution are mixed. Thus, the enthalpy of mixing is zero.

$$\Delta_{\text{mix}} H = 0$$

- There is no volume change when two components forming an ideal solution are mixed. Thus volume of an ideal solution is equal to the sum of volumes of two components taken for mixing.

$$\Delta_{\text{mix}} V = 0$$

- In an ideal solution solvent-solute, solute-solute and solvent-solvent molecular interactions are comparable.
- The vapour pressure of ideal solution always lies between vapour pressures of pure components,

**Note -**

It is important to understand that perfectly ideal solutions are uncommon and solutions such as benzene + toluene behave nearly ideal.

**Q.27 Give the characteristics of non - ideal solution.**

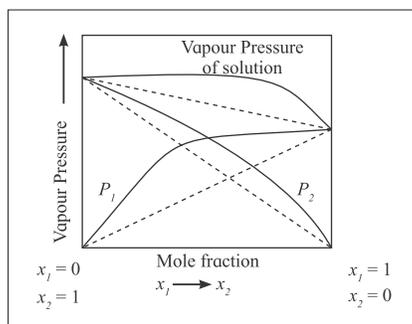
**Ans:**

- These solutions do not obey Raoult's law over the entire range of concentrations.
- The vapour pressures of these solutions can be higher or lower than those of pure components.

**Q.28 Explain positive deviations from Raoult's law using a neat labelled diagram.**

**Ans:**

i.



- The above diagram represents a plot of vapour pressure vs mole fraction for a non ideal solution showing positive deviation from Raoult's law.

**Q.29 Distinguish between ideal and non ideal solution.**

**Ans:**

	Ideal Solutions	Nonideal Solutions
i.	Ideal solutions obey Raoult's law over entire range of concentrations.	These solutions do not obey Raoult's law over the entire range of concentrations
ii.	The vapour pressure of ideal solution always lies between vapour pressures of pure components.	The vapour pressures of these solutions can be higher or lower than those of pure components.
iii.	The proportion of solvent particles that change into their vapour forms remains unchanged even when solute particles are added.	The vapour pressure of solvent significantly decreases when solute particles are added to the solvent.
iv.	For example solutions of benzene-toluene, n hexanen heptane and ethyl bromide-ethyl iodide.	For example solutions of sugar-water, alkane and kerosene etc.

### Type-2

#### Numerical based on vapour pressure of solutions of liquids in liquids

- The vapour pressures of Pure liquids A and B are 450 mm Hg and 700 mm Hg, respectively at 350 K. Find the composition of liquid and vapour if total vapour pressure is 600 mm.

**Solution :**

- Composition of A and B in the solution are  $x_1$  and  $x_2$ .

$$P = (P_2^{\circ} - P_1^{\circ})x_2 + P_1^{\circ}$$

$$P_1^{\circ} = 450 \text{ mm Hg}, P_2^{\circ} = 700 \text{ mm Hg},$$

$$P = 600 \text{ mm Hg}$$

$$\begin{aligned} \text{Hence, } 600 \text{ mm Hg} &= \\ (700 \text{ mmHg} - 450 \text{ mmHg})x_2 + 450 \text{ mmHg} &= \\ &= 250x_2 + 450 \quad 600 - 450 = 150 = 250 \\ x_2 \text{ or } x_2 &= \frac{150}{250} = 0.6 \\ x_1 &= 1 - x_2 = 1 - 0.6 = 0.4 \end{aligned}$$

ii. Compositions of A and B in vapour are  $y_1$  and  $y_2$  respectively.

$$P_1 = y_1 P \text{ and } P_2 = y_2 P, \quad P_1 = P_1^\circ x_1 \text{ and}$$

$$P_2 = P_2^\circ x_2$$

$$y_1 = \frac{P_1}{P} = \frac{P_1^\circ x_1}{P} = \frac{450 \text{ mmHg} \times 0.4}{600 \text{ mmHg}}$$

$$y_2 = 1 - y_1 = 1 - 0.3 = 0.7$$

2. A mixture of benzene and toluene contains 30% by mass of toluene. At 30 °C, vapour pressure of pure toluene is 36.7 mm Hg and that of pure benzene is 118.2 mm Hg. Assuming that the two liquids form ideal solutions, calculate the total pressure and partial pressure of each constituent above the solution at 30 °C.

**Solution :**

Given : Mass percentage of toluene = 30% W/W

Vapour pressure of liquid toluene ( $P_1^\circ$ ) = 36.7 mm Hg

Vapour pressure of liquid benzene ( $P_2^\circ$ ) = 118.2 mm Hg

To find : i. Partial pressures of each constituent

ii. Total pressure

Formulae : i.  $P_1 = P_1^\circ x_1$  and  $P_2 = P_2^\circ x_2$

ii.  $P = P_1 + P_2$

Calculation : Molar mass of toluene,

$$C_7H_8 = (7 \times 12) + (8 \times 1) = 92 \text{ g mol}^{-1}$$

Molar mass of benzene,

$$C_6H_6 = (6 \times 12) + (6 \times 1) = 78 \text{ g mol}^{-1}$$

Now, 30 % W/W toluene means 30 g toluene in 100 g solution.

Thus, mass of benzene = 100 - 30 = 70 g

Number of moles of toluene,

$$C_7H_8 = n_A = \frac{30 \text{ g}}{92 \text{ mol}} = 0.326 \text{ mol}$$

$$= \frac{30}{92} = \text{Antilog}(\log 30 - \log 92)$$

$$= \text{Antilog}(1.4771 - 1.9637)$$

$$= \text{Antilog}(-0.4866)$$

$$= 0.3261$$

Number of moles of benzene,

$$C_6H_6 = n_A = \frac{70 \text{ g}}{78 \text{ mol}} = 0.897 \text{ mol}$$

$$= \frac{70}{78} = \text{Antilog}(\log 70 - \log 78)$$

$$= \text{Antilog}(1.8450 - 1.8920)$$

$$= \text{Antilog}(-0.047)$$

$$= 0.8974$$

Total number of moles ( $n_A + n_B$ ) = 0.326 mol + 0.897 mol = 1.223 mol

$$\text{Mole fraction of toluene } (x_{C_7H_8}) = \frac{n_A}{n_A + n_B}$$

$$= \frac{0.326}{1.223} = \text{Antilog}(\log 0.326 - \log 1.223)$$

$$= \text{Antilog}(-0.4867 - 0.0874)$$

$$= \text{Antilog}(-0.5741)$$

$$= 0.2666$$

Mole fraction of benzene ( $x_{C_6H_6}$ ) = 1.0 - 0.2666

$$= 0.7334$$

Now using the formula (i),

$$P_{C_7H_8} = P_{C_7H_8}^\circ \times x_{C_7H_8} = 36.7 \text{ mm Hg} \times 0.2666$$

$$= 9.78 \text{ mm Hg}$$

$$P_{C_6H_6} = P_{C_6H_6}^\circ \times x_{C_6H_6} = 118.2 \text{ mm Hg} \times 0.7334$$

$$= 86.7 \text{ mm Hg}$$

Now, using formula (ii),

Vapour pressure of the solution,

$$P = P_{C_7H_8} + P_{C_6H_6} = 9.78 + 86.7 = 96.48 = 96.5 \text{ mm Hg}$$

**Ans :** Partial pressures of toluene and benzene are 9.78 mm Hg and 86.7 mm Hg, respectively.

Total pressure above the solution is 96.5 mm Hg.

**2.6 Colligative properties of nonelectrolyte solutions**

**Q.30 Define colligative properties and give examples.**

**Ans:**

- The physical properties of solutions that depend on the number of solute particles in solutions and not on their nature are called colligative properties.
- Examples of Colligative properties are
  - vapour pressure lowering
  - boiling point elevation
  - freezing point depression
  - osmotic pressure

**Note -**

While dealing with colligative properties of nonelectrolyte solutions, the relatively dilute solutions with concentrations 0.2 M or less are considered.

**2.7 Vapour pressure lowering**

**Q.31 Define vapour pressure of a liquid.**

**Ans:** When a liquid in a closed container is in equilibrium with its vapours, the pressure exerted by the vapour on the liquid is its vapour pressure.

**Q.32 Explain why the vapor pressure of solution is equal to the vapour pressure of solvent above the solution.**

**Ans:**

- Experiments have shown that when a nonvolatile, nonionizable solid is dissolved in a liquid solvent, the vapour pressure of the solution is lower than that of pure solvent.
- In other words the vapour pressure of a solvent is lowered by dissolving a nonvolatile solute into it.
- When the solute is nonvolatile it does not contribute to the vapour pressure above the solution.
- Therefore, the vapour pressure of solution is equal to the vapour pressure of solvent above the solution.

**Q.33 Express lowering of vapour pressure in terms of vapour pressure of pure solvent and that of solution.**

**Ans:**

- If  $P_1^0$  is the vapour pressure of pure solvent and  $P_1$  is the vapour pressure of solvent above the solution, then
- $P_1 < P_1^0$
- The vapour pressure lowering is  

$$\Delta P = P_1^0 - P_1$$

**★ Q.34 Why the vapour pressure of solution containing non volatile solute is lower than that of pure solvent?**

**Ans:**

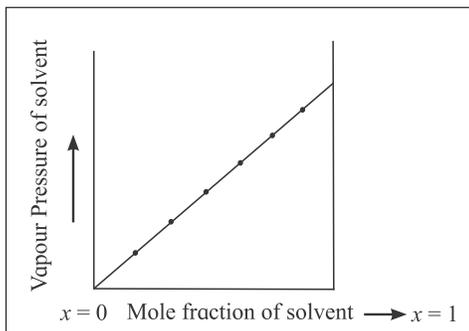
- Vapour pressure of a liquid depends on the ease with which the molecules escape from the surface of liquid.
- When non volatile solute is dissolved in a solvent, some of the surface molecules of solvent are replaced by non volatile solute molecules.
- These solute molecules do not contribute to vapour above the solution. Thus, the number of solvent molecules available for vaporization per unit surface area of solution is less than the number at the surface of pure solvent.
- As a result the solvent molecules at the surface of solution vaporize at a slower rate than pure solvent.
- This results in lowering of vapour pressure.

**★ Q.35 State Raoult's law of solution containing a non volatile solute.**

**Ans:**

- In solutions of nonvolatile solutes, the law is applicable only to the volatile solvent.
- The law states that the vapour pressure of solvent over the solution is equal to the vapour pressure of pure solvent multiplied by its mole fraction in the solution.
- Thus  

$$P_1 = P_1^0 x_1$$
- A plot of  $P_1$  versus  $x_1$  is a straight line as shown in the diagram below.



★ Q.36 Using Raoult's law, how will you show that  $\Delta P = P_1^0 x_2$ ? Where,  $x_2$  is the mole fraction of solution in the solution and  $P_1^0$  vapour pressure of pure solvent.

Ans:

- i. For a binary solution containing one solute,  
 $x_1 = 1 - x_2$
  - ii. It therefore, follows that  
 $P_1 = P_1^0 x_1$   
 $= P_1^0 (1 - x_2)$
- or  $= P_1^0 - P_1 = P_1^0 x_2$

Q.37 Show that lowering of vapour pressure is a colligative property.

Ans:

- i.  $\Delta P = P_1^0 - P_1$  defines  $P_1^0 - P_1$  as  $\Delta P$ , The lowering of vapour pressure. Hence  
 $\Delta P = P_1^0 x_2$
- ii. The above equation shows that  $\Delta P$  depends on  $x_2$  that is on number of solute particles. Thus,  $\Delta P$ , the lowering of vapour pressure is a colligative property.

Q.38 Define: Relative lowering of vapour pressure.

Ans: The ratio of vapour pressure lowering of solvent divided by the vapour pressure of pure solvent is called relative lowering of vapour pressure.

Q.39 Show that relative lowering of vapour pressure is a colligative property.

Ans:

- i. Relative vapour pressure lowering

$$= \frac{\Delta P}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} \dots\dots\dots (i)$$

ii. We know that  $\Delta P = P_1^0 x_2$  Therefore

$$\frac{\Delta P}{P_1^0} = x_2 = \frac{P_1^0 - P_1}{P_1^0} \dots\dots\dots (ii)$$

iii. Thus, relative lowering of vapour pressure is equal to the mole fraction of solute in the solution. Therefore, relative vapour pressure lowering is a colligative property.

Q.40 Derive the relationship between relative lowering of vapour pressure and molar mass of solute.

Ans:

i. We studied that the relative lowering of vapour pressure is equal to the mole fraction  $x_2$  of solute in the solution.

$$\frac{\Delta P}{P_1^0} = x_2 = \frac{P_1^0 - P_1}{P_1^0}$$

ii. The mole fraction of a component of solution is equal to its moles divided by the total moles in the solution.

$$x_2 = \frac{n_2}{n_1 + n_2}$$

where  $n_1$  and  $n_2$  are the moles of solvent and solute respectively, in the solution.

iii. We are concerned only with dilute solutions hence  $n_1 \gg n_2$  and  $n_1 + n_2 \approx n_1$ . The mole fraction  $x_2$  is then given by

$$x_2 = \frac{n_2}{n_1} \text{ and}$$

$$\frac{\Delta P}{P_1^0} = \frac{n_2}{n_1} \dots\dots\dots (ii)$$

vi. Suppose that we prepare a solution by dissolving  $W_2$  g of a solute in  $W_1$  g of solvent. The moles of solute and solvent in the solution are then,

$$n_2 = \frac{W_2}{M_2} \text{ and } n_1 = \frac{W_1}{M_1} \dots\dots\dots (iii)$$

vi. where  $M_1$  and  $M_2$  are molar masses of solvent and solute, respectively. Substitution of Eq. (iii) into Eq. (ii) yields

$$x_2 = \frac{\Delta P}{P_1^0} = \frac{W_2 / M_2}{W_1 / M_1}$$

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1}$$

**Type-3**

**Numerical based on the vapour pressure of a solution.**

1. A solution is prepared by dissolving 394g of a non volatile solute in 622 g of water. The vapour pressure of solution is found to be 30.74 mm Hg at 30 °C. If vapour pressure of water at 30 °C is 31.8 mm Hg, what is the molar mass of solute?

**Solution :**

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1}$$

$$W_2 = 394 \text{ g}, W_1 = 622 \text{ g}, M_1 = 18 \text{ g mol}^{-1}$$

$$P_1 = 30.74 \text{ mm Hg}, P_1^0 = 31.8 \text{ mm Hg}$$

Substituting of these quantities into the equation gives

$$\frac{31.8 \text{ mmHg} - 30.74 \text{ mmHg}}{31.8 \text{ mmHg}} = \frac{394 \text{ g} \times 18 \text{ g mol}^{-1}}{M_2 \times 622 \text{ g}}$$

$$0.0333 = \frac{11.4 \text{ g mol}^{-1}}{M_2}$$

$$M_2 = \frac{114 \text{ g mol}^{-1}}{0.0333} = 342 \text{ g mol}^{-1}$$

2. The vapour pressure of pure benzene (molar mass 78 g/mol) at a certain temperature is 640 mm Hg. A non volatile solute of mass 2.315 g is added to 49 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of solute ?

**Solution :**

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

$$P_1^0 = 640 \text{ mm Hg}, P_1 = 600 \text{ mm Hg},$$

$$W_1 = 49 \text{ g}, W_2 = 2.315 \text{ g}$$

Hence,

$$\frac{640 \text{ mmHg} - 600 \text{ mmHg}}{640 \text{ mmHg}}$$

$$= \frac{2.315 \text{ g} - 78 \text{ g/mol}}{40 \text{ g} \times M_2}$$

$$\frac{40 \text{ mmHg}}{640 \text{ mmHg}} = \frac{2.315 \text{ g} - 78 \text{ g/mol}}{40 \text{ g} \times M_2}$$

$$M_2 = \frac{2.315 \text{ g} - 78 \text{ g/mol} \times 640 \text{ mmHg}}{40 \text{ mmHg} \times 40 \text{ g}}$$

$$= 72.23 \text{ g mol}$$

3. The vapour pressure of water at 20 °C is 17 mm Hg. What is the vapour pressure of solution containing 2.8 g urea in 50 g of water?

**Solution :**

Given :

Vapour pressure of pure water =  $P_1^0 = 17 \text{ mm Hg}$

Mass of urea ( $W_2$ ) = 2.8 g

Mass of water ( $W_1$ ) = 50 g

To find : Vapour pressure of the solution ( $P_1$ )

$$\text{Formula : } \frac{P_1^0 - P_1}{P_1^0} = \frac{W_2 M_1}{M_2 W_1}$$

Calculation :

Molar mass of urea ( $\text{NH}_2\text{CONH}_2$ ) = 14+2+

12+ 16+ 14 +2 = 60 g mol<sup>-1</sup>

Molar mass of water = 18 g mol<sup>-1</sup>

Now, using formula,

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{W_2 M_1}{M_2 W_1}$$

$$\frac{17 \text{ mmHg} - P_1}{17 \text{ mmHg}} = \frac{2.8 \text{ g} \times 18 \text{ g mol}^{-1}}{50 \text{ g} \times 60 \text{ g mol}^{-1}}$$

$$17 - P_1 = \frac{2.8 \times 18 \times 17}{50 \times 60}$$

$$= \text{Antilog} [(\log 2.8 + \log 18 + \log 17) - (\log 50 + \log 60)]$$

$$= \text{Antilog} [(0.4471) + 1.2552 + 1.2304] - (1.6989 + 1.7781)]$$

$$= \text{Antilog} [2.9327 - 3.477]$$

$$= \text{Antilog} (-0.5443)$$

$$= 0.2856$$

$$\therefore 17 \text{ mm Hg} - P_1 = 0.2856 \text{ mm Hg}$$

$$P_1 = 17 \text{ mm Hg} - 0.2856 \text{ mm Hg} = 16.71 \text{ mm Hg}$$

**Ans :** Vapour pressure of the given solution is 16.71 mm Hg.

**2.8 Boiling point elevation**
**Q.41 What is boiling point of liquid?**
**Ans:**

- The boiling point of liquid is the temperature at which its vapour pressure equals the applied pressure.
- For liquids in open containers the applied pressure is atmospheric pressure.

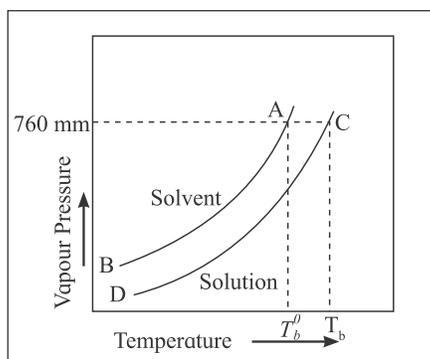
**Q.42 What is boiling point elevation?**
**Ans:**

- The difference between the boiling point of solution and that of pure solvent at any given constant pressure is called the boiling point elevation.
- If  $T$  is the boiling point of a pure solvent and  $T_b$  that of a solution,  $T_b > T_b^0$ .
- $\Delta T_b = T_b - T_b^0$

★ **Q.43 Explain with diagram the boiling point elevation in terms of vapour pressure lowering.**

**Ans:**

- The vapour pressures of solution and of pure solvent are plotted as a function of temperature as shown in diagram below.



- At any temperature the vapour pressure of solution is lower than that of pure solvent. Hence, the vapour pressure-temperature curve of solution (CD) lies below that of solvent (AB).
- The difference between the two vapour pressures increases as temperature and vapour

pressure increase as predicted by the equation.

$$\Delta P = x_2 P_1^0$$

- The intersection of the curve CD with the line corresponding to 760 mm is the boiling point of solution.
- The similar intersection of the curve AB is the boiling point of pure solvent. It is clear from the figure that the boiling point ( $T_b$ ) of the solution is higher than that of pure solvent ( $T_b^0$ ).
- At the boiling point of a liquid, its vapour pressure is equal to 1 atm.
- In order to reach boiling point, the solution and solvent must be heated to a temperature at which their respective vapour pressures attain 1 atm.
- At any given temperature the vapour pressure of solution is lower than that of pure solvent.
- Hence, the vapour pressure of solution needs higher temperature to reach 1 atm than that needed for vapour pressure of solvent.
- In other words the solution must be heated to higher temperature to cause it to boil than the pure solvent.

★ **Q.44 How vapour pressure lowering is related to a rise in boiling point of solution.**

**Ans:**

- At the boiling point of a liquid, its vapour pressure is equal to 1 atm.
- In order to reach boiling point, the solution and solvent must be heated to a temperature at which their respective vapour pressures attain 1 atm.
- At any given temperature the vapour pressure of solution is lower than that of pure solvent.
- Hence, the vapour pressure of solution needs higher temperature to reach 1 atm than that needed for vapour pressure of solvent.

★ **Q.45 Write the equation relating boiling point elevation to the concentration of solution.**

**Ans:**

- The boiling point elevation is directly

proportional to the molality of the solution.

- ii.  $\Delta T_b \propto m$  or  $\Delta T_b \propto K_b m$
- iii. where  $m$  is the molality of solution. The proportionality constant  $K_b$  is called boiling point elevation constant or molal elevation constant or ebullioscopic constant.
- iv. If  $m = 1$ ,  $\Delta T_b = K_b$

**Q.46 What is ebullioscopic constant and give its units.**

**Ans:** Ebullioscopic constant is the boiling point elevation produced by 1 molal solution.

$$\Delta T_b = K_b m$$

If  $m = 1$  and  $\Delta T_b = K_b$

Units of

$$K_b = \frac{\Delta T_b}{m} = \frac{K}{\text{mol Kg}^{-1}} = K \text{ kg mol}^{-1}$$

**Remember-**

$K_b$  and  $\Delta T_b$  are the differences between two temperatures. Hence, their values will be the same in  $K$  or in  $^{\circ}\text{C}$ .

**Note-**

We are dealing with the systems whose temperature is not constant. Therefore, we cannot express the concentration of solution in molarity which changes with temperature whereas molality is temperature independent. Therefore the concentration of solute is expressed in mol/kg (molality) rather than mol/L (molarity).

**Q.47 Derive a relationship between elevation of boiling point and molar mass of the solute.**

**Ans:**

- i. The boiling point elevation is directly proportional to the molality of the solution. Thus,  
 $\Delta T_b \propto m$  or  $\Delta T_b = K_b m$  ..... (i)
- ii. Suppose we prepare a solution by dissolving  $W_2$  g of solute in  $W_1$  g of solvent.
- iii. Moles of solute in  $W_1$  g of solvent =  $\frac{W_2}{M_2}$   
where  $M_2$  is the molar mass of solute.
- iv. Mass of solvent =

$$W_1 \text{ g} = \frac{W_1 \text{ g}}{1000 \text{ g/kg}} = \frac{W_1}{1000} \text{ kg}$$

v. the expression of molality,  $m$ .

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

$$= \frac{W_2 / M_2 \text{ mol}}{W_1 / 1000} = \frac{1000 W_2}{M_2 W_1} \text{ mol kg}^{-1} \dots\dots (ii)$$

vi. Substitution of this value of  $m$  in Eq. (i) gives

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

Hence,  $M_2 = \frac{1000 K_b W_2}{\Delta T_b W_1}$

**Q.48 What is the effect on the boiling point of water if 1 mole of methyl alcohol is added to 1 dm<sup>3</sup> of water? Why?**

**Ans:**

- i. Methyl alcohol is a volatile liquid.
- ii. When 1 mole of methyl alcohol is added to 1 dm<sup>3</sup> of water. The boiling point of water decreases.
- iii. Therefore, it increases the vapour pressure of a solution at a given temperature.

**Type-4**

**Numrical based on boiling point elevation**

**1. The normal boiling point of ethyl acetate is 77.06 °C. A solution of 50 g of a non volatile solute in 150 g of ethyl acetate boils at 84.27 °C. Evaluate the molar mass of solute if  $K_b$  for ethyl acetate is 2.77 °C Kg mol<sup>-1</sup>.**

**Solution :**

$$M_2 = \frac{100 K_b W_2}{\Delta T_b W_1}$$

$W_2 = 50 \text{ g}, W_1 = 150 \text{ g}$

$$\Delta T_b = T_b - T_B^{\circ} = 84.27^{\circ}\text{C} - 77.06^{\circ}\text{C} = 7.21^{\circ}\text{C} = 7.21 \text{ K}$$

$K_b = 2.77^{\circ}\text{C Kg mol}^{-1} = 2.77 \text{ K Kg mol}^{-1}$

Substituting of these in above equation

$$M_2 = \frac{1000 \text{ g Kg}^{-1} \times 2.77 \text{ K Kg mol}^{-1} \times 50 \text{ g}}{7.21 \text{ K} \times 150 \text{ g}}$$

= 128 g mol<sup>-1</sup>

2. 3.795 g of sulphur is dissolved in 100 g of carbon disulfide. This solution boils at 319.81 K. What is the molecular formula of sulphur in solution? The boiling point of the solvent is 319.45 K. (Given that  $K_b$  for  $CS_2 = 2.42 \text{ K Kg mol}^{-1}$  and atomic mass of S = 32 u)

**Solution :**

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

$$W_1 = 100 \text{ g}, W_2 = 3.795 \text{ g}$$

$$\Delta T_b = (319.81 - 319.45) \text{ K} = 0.36 \text{ K}$$

$$M_2 = \frac{1000 \text{ g Kg}^{-1} \times 2.42 \text{ K Kg mol}^{-1} \times 3.795 \text{ g}}{0.36 \text{ K} \times 100 \text{ g}}$$

$$= 255.10 \text{ g mol}^{-1}$$

Atomic mass of S = 32 u

Therefore number of atoms in a molecule of sulphur

$$= \frac{\text{molar mass of S}}{\text{atomic mass of S}} = \frac{255.1}{32}$$

$$= 7.92 \approx 8$$

The molecular formula would be  $S_8$  in  $CS_2$ .

3. A solution of citric acid  $C_6H_8O_7$ , in 50 g of acetic acid has a boiling point elevation of 1.76K. If  $K_b$  for acetic acid is  $3.07 \text{ K kg mol}^{-1}$ , what is the molality of solution?

**Solution :**

Given : Boiling point elevation =  $\Delta T_b = 1.76 \text{ K}$

$K_b$  of acetic acid =  $3.07 \text{ K kg mol}^{-1}$

Mass of acetic acid = 50 g

To find : Molality of the solution

Formula :  $\Delta T_b = K_b m$

Calculation :

Using formula and rearranging, we get,

$$m = \frac{\Delta T_b}{K_b} = \frac{1.76 \text{ K}}{3.07 \text{ K kg mol}^{-1}} = 0.573 \text{ mol kg}^{-1}$$

$$= \frac{1.76}{3.07}$$

$$= \text{Antilog} (\log 1.76 - \log 3.07)$$

$$= \text{Antilog} (0.2455 - 0.4871)$$

$$= \text{Antilog} (-0.2416)$$

$$= 0.573 \text{ m}$$

**Ans:** The molality of the solution is 0.573 m.

## 2.9 Depression in freezing point

**Q.49** Define freezing point of a liquid.

**Ans:** Freezing point of a liquid is the temperature at which liquid and solid are in equilibrium and the two phases have the same vapour pressure.

**Q.50** What is depression in freezing point?

**Ans:**

i. The difference between the freezing point of pure solvent and that of the solution is depression in freezing point.

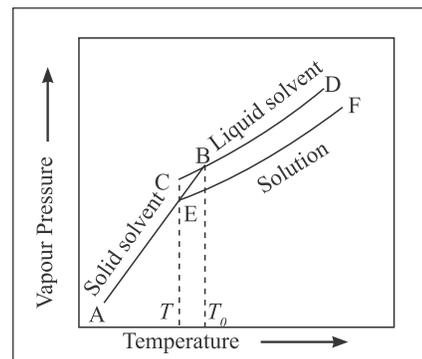
ii. Thus  $\Delta T_f = T_f^0 = T_f^0 - T_f$

iii. Here  $T_f^0$  is the freezing point of pure solvent and  $T_f$  that of a solution in which non volatile solute is dissolved,  $T_f^0 > T_f$ .

**Q.51** Explain the freezing point depression in terms of lowering of vapour pressure.

**Ans:**

i. Consider the vapour pressure temperature diagram as shown in below.



ii. The diagram consists of three curves. AB is the vapour pressure curve of solid solvent while CD is the vapour pressure curve of pure liquid solvent.

iii. EF is the vapour pressure curve of solution that always lies below the pure solvent.

iv. It is important to note that solute does not dissolve in solid solvent.

v. The curves AB and CD intersect at point B where solid and liquid phases of pure solvent are in equilibrium.

vi. The two phases have the same vapour pressure at B. The temperature corresponding to B is the freezing point of

- solvent ( $T_f^0$ ).
- vii. Similarly at E, the point of intersection of EF and AB, the solid solvent and solution are in equilibrium.
- viii. They have the same vapour pressure at E. The temperature corresponding to E is the freezing point of solution,  $T_f$ .
- xi. It is clear from the figure that freezing point of solution  $T_f$  is lower than that of pure solvent  $T_f^0$ . It is obvious because the vapour pressure curve of solution lies below that of solvent.

**★Q.52 Why freezing point of solvent is lowered by dissolving a non volatile solute into it?**

**Ans:**

- At the freezing point of a pure liquid the attractive forces among molecules are large enough to cause the change of phase from liquid to solid.
- In a solution, the solvent molecules are separated from each other because of solute molecules.
- Thus, the separation of solvent molecules in solution is more than that in pure solvent.
- This results in decreasing the attractive forces between solvent molecules. Consequently, the temperature of the solution is lowered below the freezing point of solvent to cause the phase change.

**Q.53 Give the equation for freezing point depression to the concentration of solution.**

**Ans:**

- For a dilute solution the freezing point depression ( $\Delta T_f$ ) is directly proportional to the molality of solution. Thus,  
$$\Delta T_f \propto m \quad \Delta T_f = K_f m$$
- The proportionality constant  $K_f$  is called freezing point depression constant or cryoscopic constant.
- If  $m = 1$ ,  $\Delta T_f = K_f$ . The cryoscopic constant thus is the depression in freezing point

produced by 1 molal solution of a nonvolatile solute.

**Q.54 What is cryoscopic constant ? Give its unit.**

**Ans:** Unit of  $K_f : \frac{\Delta T_f}{m} = \frac{K \text{ or } ^\circ C}{\text{mol kg}^{-1}}$   
 $= K \text{ kg mol}^{-1} \text{ or } ^\circ C \text{ kg mol}^{-1}$

**Q.55 Obtain the relationship between freezing point depression of a solution containing non volatile - non electrolyte solute and its molar mass.**

**Ans:**

- For a dilute solution. The freezing point depression ( $\Delta T_f$ ) is directly proportional to the molality of solution. Thus,

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m \dots\dots\dots(i)$$

- Suppose we prepare a solution by dissolving  $W_2$  g solution in  $W_1$  g of solvent.

$$\text{Moles of solvent in } W_1 \text{ g of solvent} = \frac{W_1}{M_2}$$

Mass of solvent =

$$W_1 \text{ g} = \frac{W_1 \text{ g}}{1000 \text{ g/kg}} = \frac{W_1}{1000} \text{ kg}$$

- The expression of molality, m.

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

$$= \frac{W_2 / M_2 \text{ mol}}{W_1 / 1000 \text{ kg}} = \frac{1000 W_2}{M_2 W_1} \text{ mol kg}^{-1} \dots\dots\dots(ii)$$

(iv) substituting eq (ii) in eq (i) we get.

$$\Delta T_f = K_f \frac{1000 W_2}{M_2 W_1}$$

Hence,

$$M_2 = \frac{1000 K_f W_2}{\Delta T_f W_1}$$

**Q.56 While considering boiling point elevation and freezing point depression a solution concentration is expressed in molality and not in molarity . Why?**

Ans:

- It has been found that the boiling point of a solvent is elevated by dissolving a non volatile solute into it.
- Thus, the solutions containing non volatile solutes boil at temperatures higher than the boiling point of a pure solvent.
- Therefore, while considering boiling point elevation and freezing point depression a solution concentration is expressed in molality and not in molarity.

**Type - 5**

**Numerical based on depression in freezing point**

- 1.02 g of urea when dissolved in 98.5 g of certain solvent decreases its freezing point by 0.211 K. 1.609 g of unknown compound when dissolved in 86 g of the same solvent depresses the freezing point by 0.34 K. Calculate the molar mass of the unknown compound. (Molar mass of urea = 60 g mol<sup>-1</sup>)

**Solution :**

Urea compound	Unknown
W <sub>2</sub> = 1.02 g	
W <sub>2</sub> ' = 1.609 g	
W <sub>1</sub> = 98.5 g	
W <sub>1</sub> ' = 86 g	
ΔT <sub>f</sub> = 0.211 K	
ΔT <sub>f</sub> ' = 0.34 K	
M <sub>2</sub> = 60 g mol <sup>-1</sup>	
M <sub>2</sub> ' = ?	
$1000 K_f = \frac{M_2 \times \Delta T_f \times W_1}{W_2}$	
$1000 K_f = \frac{M_2' \times \Delta T_f' \times W_1'}{W_2'}$	
$= \frac{60 \text{ g mol}^{-1} \times 0.211 \text{ K} \times 98.5 \text{ g}}{1.02 \text{ g}}$	
$= \frac{M_2' \times 0.34 \text{ K} \times 86 \text{ g}}{1.609 \text{ g}}$	

$$\frac{1247.01 \text{ g K mol}^{-1}}{1.02} = \frac{M_2' \times 29.24 \text{ K}}{1.609}$$

$$1222.55 \text{ g K mol}^{-1} = M_2' \times 18.173$$

$$M_2' = \frac{1222.55 \text{ g K mol}^{-1}}{18.173 \text{ K}} = 67.3 \text{ g mol}^{-1}$$

- A 5% aqueous solution (by mass) of cane sugar (molar mass 342 g/mol) has freezing point of 271 K. Calculate the freezing point of 5% aqueous glucose solution.**

**Solution :**

Given :

Percentage by mass of cane sugar solution = 5 %

Percentage by mass of glucose solution = 5 %,

Freezing point of cane sugar solution = 271 K

Molar mass of cane sugar = 342 g mol<sup>-1</sup>

To find : Freezing point of glucose solution

Formula :

Calculation : 5 % solution (by mass) of cane sugar

means that mass of cane sugar (W<sub>2</sub>) =

5g, and mass of solvent (W<sub>1</sub>) = 95 g.

5 % glucose solution means that mass of glucose = 5 g,

and mass of solvent = 95g

Molar mass of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)

= 180 g mol<sup>-1</sup>

for cane sugar solution

= 273.15 K – 271 K = 2.15 K

Now, using the formula,

$$M_2 = \frac{1000 \times K_f \times W_2}{\Delta T_f \times W_1}$$

Rearranging the formula, we get

$$1000 K_f = \frac{M_2 \times \Delta T_f \times W_1}{W_2} \dots\dots\dots(i)$$

$$1000 K_f = \frac{M_2' \times \Delta T_f' \times W_1'}{W_2'} \dots\dots\dots(ii)$$

From equations (1) and (2),

$$\frac{M_2 \times \Delta T_f \times W_1}{W_2} = \frac{M_2' \times \Delta T_f' \times W_1'}{W_2'}$$

$$\therefore \frac{342 \text{ g mol}^{-1} \times 2.15 \text{ K} \times 95 \text{ g}}{5 \text{ g}} = \frac{180 \text{ g mol}^{-1} \times \Delta T_f' \times 95 \text{ g}}{5 \text{ g}}$$

$$\Delta T'_f = \frac{342 \text{ g mol}^{-1} \times 2.15 \text{ K}}{180 \text{ g mol}^{-1}} = 4.085 \text{ K}$$

$$= \frac{342 \times 2.15}{180}$$

$$= \text{Antilog} [(\log 342 + \log 2.15) - \log 180]$$

$$= \text{Antilog} [(2.5340 + 0.3324) - 2.2552]$$

$$= \text{Antilog} [2.8664 - 2.2552]$$

$$= \text{Antilog} (0.6112)$$

$$= 4.085$$

Freezing point of glucose solution

$$(T_f) = T_f^\circ - \Delta T'_f = 273.15 \text{ K} - 4.085 \text{ K}$$

$$= 269.065 \text{ K}$$

**Ans:** Freezing point of glucose solution is 269.065K.

### 2.10 Osmotic pressure

**Q.57** Write a short note on semipermeable membrane.

**Ans:**

- It is a film such as cellophane which has pores large enough to allow the solvent molecules to pass through them.
- These pores are small enough not to allow the passage of large solute molecules or ions of high molecular mass through them.
- The semi permeable membrane selectively allows passage of solvent molecules.

★ **Q.58** A solvent and its solution containing a non volatile solute are separated by a semipermeable membrane. Does the flow of solvent occur in both directions? Comment giving reason.

**Ans:**

- When a solution and pure solvent or two solutions of different concentrations are separated by a semipermeable membrane, the solvent molecules pass through the membrane.
- The passage of solvent molecules through the semipermeable membrane takes place in both directions, since solvent is on both sides of the membrane.
- However, the rate of passage of solvent molecules into the solution or from more dilute solution to more concentrated solution is found to be greater than the rate in the

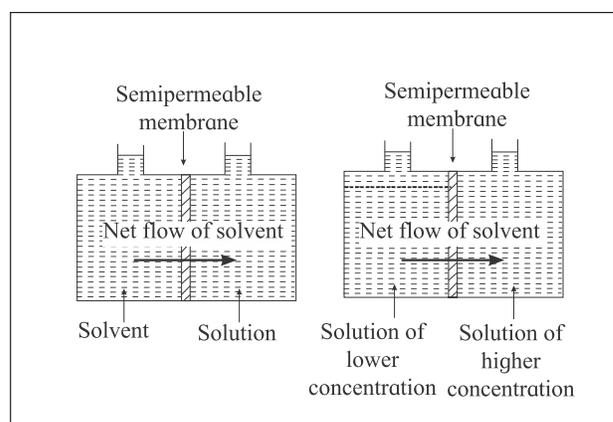
reverse direction.

- This is favourable since the vapour pressure of solvent is greater than that of solution.

**Q.59** Write a short note on osmosis.

**Ans:**

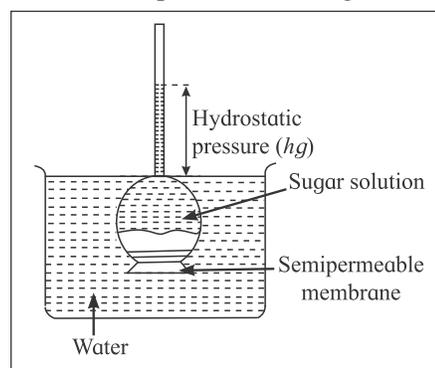
- The net spontaneous flow of solvent molecules into the solution or from more dilute solution to more concentrated solution through a semipermeable membrane is called osmosis.
- As a result of osmosis, the amount of liquid on the pure solvent side or more dilute solution side decreases.
- the amount of liquid on the other side increases. This results in decrease of the concentration of solution.



**Q.60** Explain the phenomenon of osmosis in terms of osmotic pressure using a neat labelled diagram.

**Ans:**

- Osmosis can be demonstrated with experimental set up shown the diagram below.



- Semipermeable membrane is firmly fastened across the mouth of thistle tube. The solution of interest is placed inside an inverted thistle tube. This part of the tube and the membrane

- are then immersed in a container of pure water.
- iii. As a result, some of the solvent passes through the membrane into the solution. It causes the liquid level in the tube to rise. The liquid column in the tube creates hydrostatic pressure that pushes the solvent back through the membrane into the container.
  - iv. The column of liquid in the tube continues to rise and eventually stops rising.
  - v. At this stage hydrostatic pressure developed is sufficient to force solvent molecules back through the membrane into the container at the same rate they enter the solution.
  - vi. An equilibrium is thus established where rates of forward and reverse passages are equal. The height of liquid column in the tube remains constant.
  - vii. This implies that the hydrostatic pressure has stopped osmosis.
  - viii. The hydrostatic pressure that stops osmosis is an osmotic pressure ( $p$ ) of the solution.
  - xi. The hydrostatic pressure is equal to  $h\rho g$  where  $h$  is the height of liquid column in the tube,  $\rho$  is density of solution and  $g$  is acceleration due to gravity.

**★ Q.61 What is osmotic pressure ?**

**Ans:** The excess of pressure on the side of the solution that stops the net flow of solvent into the solution through a semipermeable membrane is called osmotic pressure.

**Remember-**

It is important to note that osmotic pressure is not the pressure produced by a solution. It exists only when the solution is separated from the solvent by a suitable kind of semipermeable membrane.

**★ Q.62 What is isotonic and hypertonic solution.**

**Ans:**

- i. **Isotonic solutions :**
  - a. Two or more solutions having the same osmotic pressure are said to be isotonic solutions.
  - b. For example, 0.1 M urea solution and 0.1

M sucrose solution are isotonic because their osmotic pressures are equal. Such solutions have the same molar concentrations but different concentrations in g/L. If these solutions are separated by a semi permeable membrane, there is no flow of solvent in either direction.

ii. **Hypertonic and hypotonic solutions :**

- a. If two solutions have unequal osmotic pressures, the more concentrated solution with higher osmotic pressure is said to be hypertonic solution.
- b. For example, if osmotic pressure of sucrose solution is higher than that of urea solution, the sucrose solution is hypertonic to urea solution.

**Q.62 What is isotonic and hypertonic solution.**

**Ans:**

- i. If two solutions having unequal osmotic pressure. The more dilute solution exhibiting lower osmotic pressure is said to be hypotonic solution.
- ii. For example - If osmotic pressure of sucrose solution is higher than that of urea solution. The urea solution is hypotonic to sucrose solution.

**★ Q.64 How molar mass of a solute is determined by osmotic pressure measurement?**

**Ans:**

- i. For very dilute solutions, the osmotic pressure follows the equation,

$$\pi = \frac{n_2 RT}{V} \dots\dots\dots (i)$$

- ii. where  $V$  is the volume of a solution in  $\text{dm}^3$  containing  $n_2$  moles of non volatile solute.  $R$  is the gas constant equal to  $0.08206 \text{ dm}^3\text{atm K}^{-1}\text{mol}^{-1}$  and  $\pi$  is osmotic pressure in atm.

- iii. The term  $n_2/V$  is concentration in molarity (M). Eq. (i) thus can be written as  $\pi = MRT \dots\dots\dots (ii)$

**★ Q.65 A solution concentration is expressed in molarity and not in molality while considering osmotic pressure. Why?**

**Ans:**

- i. The solute concentration is expressed in

- molarity while calculating osmotic pressure rather than molality.
- The reason is that osmotic pressure measurements are made at a specific constant temperature.
  - It is not necessary to express concentration in a temperature independent unit like molality.

★ **Q.66 Which of the four colligative properties is most often used for molecular mass determination? Why?**

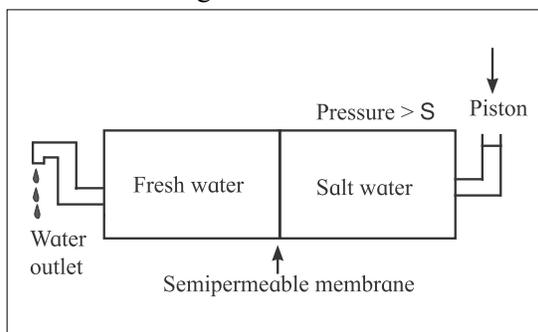
**Ans:**

- Among the four colligative properties osmotic pressure is most often used for molecular mass determination.
- Osmotic pressure is much larger and therefore more precisely measurable property than other colligative properties.
- It is therefore, useful to determine molar masses of very expensive substances and of the substances that can be prepared in small quantities.

**Q.67 Explain reverse osmosis.**

**Ans:**

- The direction of osmosis can be reversed by applying a pressure larger than the osmotic pressure.
- The pure solvent then flows from solution into pure solvent through semi permeable membrane. This phenomenon is called reverse osmosis.
- For example shows the schematic set up for reverse osmosis. Fresh water and salty water are separated by a semipermeable membrane. When the pressure larger than the osmotic pressure of solution is applied to solution, pure water from salty water passes into fresh pure water through the membrane.


**Type 6**
**Numerical based on osmotic pressure**

- What is the molar mass of a solute if a solution prepared by dissolving 0.822 g of it in 300 dm<sup>3</sup> of water has an osmotic pressure of 149 mm Hg at 298 K ?**

**Solution :**

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

$$W_2 = 0.822 \text{ g}$$

$$R = 0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\pi = 149 (\text{mm Hg}) = \frac{149 (\text{mm Hg})}{760 (\text{mm Hg} / \text{atm})}$$

$$= 0.196 \text{ atm}$$

$$V = 300 \text{ mL} = 0.3 \text{ dm}^3$$

$$M_2 = \frac{0.822 \text{ g} \times 0.08205 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.196 \text{ atm} \times 0.3 \text{ dm}^3}$$

$$= 342 \text{ g mol}^{-1}$$

- An aqueous solution of a certain organic compound has a density of 1.063 g mL<sup>-1</sup>, an osmotic pressure of 12.16 atm at 25 °C and a freezing point of -1.03 °C. What is the molar mass of the compound?**

**Solution :**

Given: Density of a solution =  $d = 1.063 \text{ g mL}^{-1}$

Osmotic pressure of solution =  $\pi = 12.16 \text{ atm}$

Temperature =  $T = 25 \text{ °C} = 298.15 \text{ K}$

Freezing point of solution =  $T_f = -1.03 \text{ °C}$

To find : Molar mass of a compound

Formulae : i.  $\Delta T_f = K_f m$     ii.  $\pi = MRT$

$$\text{iii. } m = \frac{1000 W_2}{M_2 W_1}$$

Calculation :  $R = 0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

$$\Delta T_f = T_f^\circ - T_f = 0 \text{ °C} - (-1.03 \text{ °C}) = 1.03 \text{ °C} = 1.03 \text{ K}$$

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

Using formula (i),

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{1.03 \text{ K}}{1.86 \text{ K kg mol}^{-1}} = 0.554 \text{ mol kg}^{-1} = 0.554 \text{ m}$$

$$= \frac{1.03}{1.86}$$

$$= \text{Antilog} [\log 1.03 - \log 1.86]$$

$$= \text{Antilog} [0.0128 - 0.2695]$$

$$= \text{Antilog} [-0.2567]$$

$$= 0.554 \text{ mol kg}^{-1}$$

Using formula (ii),

$$\pi = MRT$$

$$M = \frac{\pi}{RT} = \frac{12.16 \text{ atm}}{0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= \frac{12.16}{0.08205 \times 298.15}$$

$$= \text{Antilog} [\log 12.16 - (\log 0.08205 + \log 298.15)]$$

$$= \text{Antilog} [1.0849 - 1.3885]$$

$$= \text{Antilog} [-0.3036]$$

$$= 0.497$$

$$= 0.497 \text{ mol dm}^{-3} = 0.497 \text{ M}$$

Mass of solvent =

$$\frac{0.497 \text{ mol dm}^{-3}}{0.554 \text{ mol kg}^{-1}} \times 1 \text{ dm}^3 = 0.897 \text{ kg} = 897 \text{ g units}$$

$$= \frac{0.497}{0.554}$$

$$= \text{Antilog} [\log 0.497 - \log 0.554]$$

$$= \text{Antilog} [-0.3036 - (-0.2564)]$$

$$= \text{Antilog} [-0.3036 + 0.2564]$$

$$= \text{Antilog} [-0.0472]$$

$$= 0.897$$

$$\text{Mass of solution} = 1.063 \text{ g mL}^{-1} \times 1000 \text{ mL} \\ = 1063 \text{ g}$$

$$\text{Mass of solute} = 1063 \text{ g} - 897 \text{ g} = 166 \text{ g}$$

Now, using formula (iii),

$$m = \frac{1000 W_2}{M_2 W_1}$$

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

$$\frac{1000 \text{ g kg}^{-1} \times 166 \text{ g}}{0.554 \text{ mol kg}^{-1} \times 897 \text{ g}} = 334 \text{ g mol}^{-1}$$

$$= \frac{1000 \times 166}{0.554 \times 897}$$

$$= \frac{166000}{0.554 \times 897}$$

$$= \text{Antilog} [\log 166000 - (\log 0.554 + \log 897)]$$

$$= \text{Antilog} [5.2201 - (-0.2564 + 2.9527)]$$

$$= \text{Antilog} [5.2201 - 2.6963]$$

$$= \text{Antilog} (2.5238)$$

$$= 334.0 \text{ g mol}^{-1}$$

**Ans:** The molar mass of the compound is 334 g mol<sup>-1</sup>.

### 2.11 Colligative properties of electrolytes

**+Q.68 Can you recall?**

**Electrolytes and non electrolytes.**

**Ans:**

- Electrolytes:  
Electrolytes are salts or molecules that ionizes completely in solution.
- Nonelectrolytes:  
Non electrolytes are molecules that do not dissociate in solutions.

**Q.69 Give the experimental observations for the colligative behaviour of electrolytes.**

**Ans:** Following are the experimental observations for the colligative behavior of electrolytes.

- The solutions of electrolytes also exhibit colligative properties which do not obey the relations of non electrolytes.
- The colligative properties of the solutions of electrolytes are greater than those to be expected for solutions of non electrolytes of the same concentration.
- The molar masses of electrolytes in aqueous solutions determined by colligative properties are found to be considerably lower than the formula masses.

**Q.70 Why the colligative properties of electrolyte solutions are greater than those for non electrolyte solutions of the same concentrations?**

**Ans:**

- Electrolytes dissociate into two or more ions when dissolved in water whereas nonelectrolytes do not.
- One unit of electrolyte dissolved in water produces two or more ions.

- iii. Consequently number of particles in solution increases.
- iv. The colligative properties of electrolyte solutions are thus higher than the non electrolyte solutions.
- v. For example, when NaCl is dissolved in water, it produces two ions, Na<sup>+</sup> and Cl<sup>-</sup>, whereas sucrose does not dissociate. It is expected then that the colligative property of 0.1 m NaCl is twice that of 0.1 m sucrose solution.

**Q.71 What is van't Hoff factor?**
**Ans:**

It is defined as the ratio of colligative property of a solution of electrolyte divided by the colligative property of nonelectrolyte solution of the same concentration. Thus

$$i = \frac{\text{colligative property of electrolyte solution}}{\text{Colligative property of non electrolyte solution of the same concentration}}$$

$$= \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{(\Delta T_b)}{(\Delta T_b)_0} = \frac{(\Delta P)}{(\Delta P)_0} = \frac{(\pi)}{(\pi)_0}$$

where quantities without subscript refer to electrolytes and those with subscript to nonelectrolytes

**Q.72 How is van't Hoff factor related to formula mass and observed molar mass?**
**Ans:**

- i. The van't Hoff factor  $i$  is also defined in an alternative but exactly equivalent manner as

$$i = \frac{\text{actual moles of particles in solution after dissociation}}{\text{moles of formula units dissolved in solution}}$$

$$= \frac{\text{formula mass of substance}}{\text{observed molar mass of substance}}$$

$$= \frac{M_{\text{theoretical}}}{M_{\text{observed}}}$$

**Q.73 Explain: At high concentrations. The colligative properties of strong electrolytes and their van't Hoff factor ( $i$ ) values are usually smaller than expected.**
**Ans:**

- i. At high concentrations, the colligative properties of strong electrolytes and their  $i$  values

are usually smaller than expected.

- ii. At high concentration the electrostatic forces between oppositely charged ions bring about the formation of ion pairs.
- iii. Each ion pair consists of one or more cations and one or more anions held together by electrostatic attractive forces.
- iv. This results in decrease in the number of particles in solution causing reduction in the expected  $i$  value and colligative properties.
- v. Therefore in reality especially at high concentrations the colligative properties of strong electrolytes and their  $i$  value are usually smaller than expected.

**Q.74 Give modified equations of colligative properties.**
**Ans:** The modified equations are

$$i. \quad \Delta P = i P_1^0 x_2 = i \frac{W_2 M_1}{M_2 W_1}$$

$$ii. \quad \Delta T_b = i K_b m = i \frac{1000 K_b W_2}{M_2 W_1}$$

$$iii. \quad \Delta T_f = i K_f m = i \frac{1000 K_f W_2}{M_2 W_1}$$

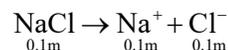
$$iv. \quad \pi = i MRT = i \frac{W_2 RT}{M_2 V}$$

**★ Q.75 Which of the following solution will have higher freezing point depression and why?**

- i. 0.1 NaCl:
- ii. 0.05 m Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

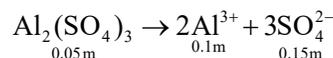
**Ans:**

- i. For 0.1 m NaCl:



Total particles in solution = 0.2

- ii For 0.05m Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>:



Total particles in solution = 0.25 mol

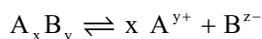
Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution contains more number of particles than NaCl solution. Hence, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution has maximum  $\Delta T_f$ .

Therefore, the freezing point depression of 0.05 m Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution will be higher than 0.1 m NaCl solution.

★ Q.76 Derive the relationship between degree of dissociation of an electrolyte and van't Hoff factor.

Ans:

i. Consider an electrolyte  $A_xB_y$  that dissociates in aqueous solution as



ii. 

Initially	1 mol	0	0
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iii. At equilibrium:

a.  $(1-\alpha)$  mol  $(x\alpha)$  mol  $(y\alpha)$  mol

b. If  $\alpha$  is the degree of dissociation of electrolyte, then the moles of cations are  $\alpha x$  and those of anions are  $\alpha y$  at equilibrium. We have dissolved just 1 mol of electrolyte initially.  $\alpha$  mol of electrolyte dissociates and  $(1-\alpha)$  mol remains undissociated at equilibrium.

c. Total moles after dissociation

$$= (1-\alpha) + (x\alpha) + (y\alpha)$$

$$= 1 + \alpha(x+y-1)$$

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

iv. where,  $n = x+y$  = moles of ions obtained from dissociation of 1 mole of electrolyte.

★ Q.77 How is van't Hoff factor related to degree of ionization?

Ans: The van't Hoff factor is related to degree of ionization as follows:

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

or

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

Where,  $\alpha$  = Degree of ionization / dissociation

$i$  = van't Hoff factor

$n$  = Moles of ions obtained from ionization of 1 mole of electrolyte.

### Type-7

#### Numericals based on van't Hoff factor

1. Which of the following solution will have maximum boiling point elevation and which have minimum freezing point depression assuming the complete dissociation? (a) 0.1m KCl (b) 0.05 m NaCl (c) 1m  $AlPO_4$  (d) 0.1 m  $MgSO_4$

Solution :

Boiling point elevation and freezing point depression are colligative properties that depend on number of particles in solution. The solution having more number of particles will have large boiling point elevation and that having less number of particles would show minimum freezing point depression.

i.  $KCl \rightarrow K^{\oplus} + Cl^{\oplus}$  Total particles in  
 $\begin{matrix} 0.1m & 0.1m & 0.1m \end{matrix}$  solution = 0.2 mol

ii.  $NaCl \rightarrow Na^{\oplus} + Cl^{\oplus}$  Total particles in  
 $\begin{matrix} 0.05m & 0.05m & 0.05m \end{matrix}$  solution = 0.1 mol

iii.  $AlPO_4 \rightarrow Al^{3\oplus} + PO_4^{3\ominus}$  Total particles in  
 $\begin{matrix} 1m & 1m & 1m \end{matrix}$  solution = 2.0 mol

iv.  $MgSO_4 \rightarrow Mg^{2+} + SO_4^{2-}$  Total particles in  
 $\begin{matrix} 0.1m & 0.1m & 0.1m \end{matrix}$  solution = 2.0 mole

$AlPO_4$  solution contains highest moles and hence highest number particles and in turn, the maximum  $\Delta T_b$ . NaCl solution has minimum moles and particles. It has minimum  $\Delta T_f$ .

2. Arrange the following solutions in order of increasing osmotic pressure. Assume complete ionization.

i. 0.5 m  $Li_2SO_4$

ii. 0.5 m KCl

iii. 0.5 m  $Al_2(SO_4)_3$

iv. 0.1 m  $BaCl_2$

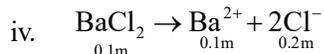
Solution:

Osmotic pressure is a colligative property that depends on number of particles in solution. The solution having more number of particles will have large osmotic pressure.

i.  $Li_2SO_4 \rightarrow 2Li^+ + SO_4^{2-}$   
 $\begin{matrix} 0.5m & 1.0m & 0.5m \end{matrix}$   
 Total particles in solution = 1.5 mol

ii.  $KCl \rightarrow K^+ + Cl^-$   
 $\begin{matrix} 0.5m & 0.5m & 0.5m \end{matrix}$   
 Total particles in solution = 1.0 mol

iii.  $Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$   
 $\begin{matrix} 0.5 & 1.0m & 1.5m \end{matrix}$   
 Total particles in solution = 2.5 mol



Total particles in solution = 0.3 mol

Ans: The increasing order of osmotic pressure :

$0.1 \text{ m BaCl}_2 < 0.5 \text{ m KCl} < 0.5 \text{ m Li}_2\text{SO}_4 < 0.5 \text{ m Al}_2(\text{SO}_4)_3$ .

3. A 0.1 m solution of  $\text{K}_2\text{SO}_4$  in water has freezing point of  $-4.3^\circ\text{C}$ . What is the value of van't Hoff factor if  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ ?

**Solution :**

Given: Molality of  $\text{K}_2\text{SO}_4$  solution =  $m = 0.1 \text{ m}$

Freezing point of solution =  $T_f = -4.3^\circ\text{C}$

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

To find : van't Hoff factor

Formula :  $\Delta T_f = iK_f m$

Calculation :

$$\Delta T_f = T_f^\circ - T_f = 0^\circ\text{C} - (-4.3^\circ\text{C}) = 4.3^\circ\text{C} = 4.3 \text{ K}$$

Now, Using formula,

$$\Delta T_f = iK_f m$$

$$\therefore i = \frac{\Delta T_f}{K_f m}$$

$$= \frac{4.3 \text{ K}}{1.86 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1}}$$

$$= \frac{4.3}{1.86 \times 0.1}$$

$$= \text{Antilog} [\log 4.3 - \log 0.186]$$

$$= \text{Antilog} [0.6334 - (-0.7304)]$$

$$= \text{Antilog} [0.6334 + 0.7304]$$

$$= \text{Antilog} [1.3638]$$

$$= 23.1$$

Ans: The value of van't Hoff factor is 23.1.

[ Note : The expected van't Hoff factor for  $\text{K}_2\text{SO}_4$  in water is 3. However, in the above numerical the value is 23.1, which is very high.]

4. If 1.25 m sucrose solution has  $\Delta T_f$  for  $2.32^\circ\text{C}$ , what will be the expected value of  $\Delta T_f$  for 1.25 m  $\text{CaCl}_2$  solution?

**Solution:**

Given: Molality of  $\text{K}_2\text{SO}_4$  solution =  $m = 0.1 \text{ m}$

Freezing point of solution =  $T_f = -4.3^\circ\text{C}$

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

To find: Van't Hoff factor

Formula:  $\Delta T_f = iK_f m$

Calculation:

$$\Delta T_f = T_f^\circ - T_f = 0^\circ\text{C} - (-4.3^\circ\text{C}) = 4.3^\circ\text{C} = 4.3 \text{ K}$$

Now using formula,

$$\Delta T_f = iK_f m$$

$$i = \frac{\Delta T_f}{K_f m}$$

$$= \frac{4.3 \text{ K}}{1.86 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1}}$$

$$= 23.1$$

Ans: The value of van't Hoff factor is 23.1.

4. 3.4 g of  $\text{CaCl}_2$  is dissolved in 2.5 L of water at 300 K. What is the osmotic pressure of the solution? van't Hoff factor for  $\text{CaCl}_2$  is 2.47.

**Solution :**

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

$$i = 2.47, W_2 = 3.4 \text{ g}, R = 0.08206 \text{ dm}^3 \text{ atm}$$

$$\text{K}^{-1} \text{mol}^{-1}, T = 300 \text{ K}, M_2 = 40 + 71 = 111 \text{ g mol}^{-1},$$

$$V = 2.5 \text{ dm}^3$$

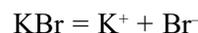
$$\pi = 2.47 \times$$

$$\frac{3.4 \cancel{\text{g}} \times 0.08206 \cancel{\text{dm}^3} \text{ atm} \cancel{\text{K}^{-1} \text{mol}^{-1}} \times 300 \cancel{\text{K}}}{111 \cancel{\text{g}} \cancel{\text{mol}^{-1}} \times 2.5 \cancel{\text{dm}^3}}$$

$$= 0.745 \text{ atm}$$

5. Assuming complete dissociation, calculate the molality of an aqueous solution of  $\text{KBr}$  whose freezing point is  $-2.95^\circ\text{C}$ .  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ .

**Solution :**



$$i = \frac{\text{moles of particles after dissociation}}{\text{moles of particles dissolved}}$$

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

$$\Delta T_f = iK_f m$$

$$\Delta T_f = 0^\circ\text{C} - (-2.95^\circ\text{C}) = 2.95^\circ\text{C}.$$

$$m = \frac{\Delta T_f}{iK_f} = \frac{2.95 \text{ K}}{2 \times 1.86 \text{ K kg mol}^{-1}}$$

$$= 0.793 \text{ mol kg}^{-1}.$$

6. **0.2 m aqueous solution of KCl freezes at  $-0.680^\circ\text{C}$ . Calculate van't Hoff factor and osmotic pressure of solution at  $0^\circ\text{C}$ . ( $K_f = 1.86 \text{ K kg mol}^{-1}$ )**

**Solution :**

$$\Delta T_f = K_f m$$

$$\Delta T_f = 0.680 \text{ K}, m = 0.2 \text{ mol kg}^{-1}$$

$$(\Delta T_f)_0 = 1.86 \text{ K kg mol}^{-1} \times 0.2 \text{ mol kg}^{-1}$$

$$= 0.372 \text{ K}$$

$$i = \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{0.680 \text{ K}}{0.372 \text{ K}} = 1.83$$

$$(\pi)_0 = MRT$$

$$\frac{n^2}{V} RT$$

$$= \frac{0.2 \text{ mol} \times 0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}}{1 \text{ L}}$$

$$= 4.48 \text{ atm}$$

$$i = 1.83 = \frac{\pi}{\pi_0}$$

$$\pi = 1.83 \times 4.48 \text{ atm}$$

$$\pi = 8.2 \text{ atm}$$

7. **A 0.15 m aqueous solution of KCl freezes at  $-0.510^\circ\text{C}$ . Calculate  $i$  and osmotic pressure at  $0^\circ\text{C}$ . Assume volume of solution equal to that of water.**

**Solution :**

Given : Molality of solution =  $m = 0.15 \text{ m}$

Freezing point of solution =  $T_f = -0.510^\circ\text{C}$

Temperature =  $0^\circ\text{C} = 273 \text{ K}$  To find :

- The value of van't Hoff factor ( $i$ )
- Osmotic pressure of solution

Formulae :

$$i. \Delta T_f = K_f m$$

$$ii. i = \frac{(\Delta T_f)}{(\Delta T_f)_0}$$

$$iii. \pi = MRT = \frac{n^2 RT}{V}$$

$$iv. i = \frac{\pi}{\pi_0}$$

Calculation :

$$\Delta T_f = T_f^0 - T_f = 0^\circ\text{C} - (-0.510^\circ\text{C}) = 0.510^\circ\text{C}$$

$$= 0.510 \text{ K}$$

$$m = 0.15 \text{ m} = 0.15 \text{ mol kg}^{-1}$$

Now, using formula (i),

$$\Delta T_f = K_f m$$

$$(\Delta T_f)_0 = 1.86 \text{ K kg mol}^{-1} \times 0.15 \text{ mol kg}^{-1}$$

$$= 0.279 \text{ K}$$

Now, using formula (ii),

$$i = \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{0.510 \text{ K}}{0.279 \text{ K}} = 1.83$$

$$= \frac{0.510}{0.279}$$

$$= \text{Antilog} [\log 0.510 - \log 0.279]$$

$$= \text{Antilog} [-0.2924 - (-0.5543)]$$

$$= \text{Antilog} [-0.2924 + 0.5543]$$

$$= \text{Antilog} [0.2619]$$

$$= 1.83$$

Now, using formula (ii),

$$\pi_0 = MRT$$

$$= \frac{n^2 RT}{V}$$

$$= \frac{0.15 \text{ mol} \times 0.08205 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1} \times 273 \text{ K}}{1 \text{ dm}^3}$$

$$= \frac{0.15 \times 0.08205 \times 273}{1}$$

$$= 0.15 \times 0.08205 \times 273$$

$$= \text{Antilog} [\log 0.15 + \log 0.08205 + \log 273]$$

$$= \text{Antilog} [-0.8239 + (-1.0859) + 2.4361]$$

$$= \text{Antilog} [-0.8239 - 1.0859 + 2.4361]$$

$$= \text{Antilog} (0.5263)$$

$$= 3.36 \text{ atm}$$

Now, using formula (iv),

$$i = \frac{\pi}{\pi_0} = 1.83$$

$$\pi = 1.83 \times 3.36 \text{ atm}$$

$$\pi = 6.15 \text{ atm}$$

**Ans:**

- i. The van't Hoff factor is 1.83.
- ii. The osmotic pressure of solution at 0 °C is 6.15 atm.

**8. The osmotic pressure of CaCl<sub>2</sub> and urea solutions of the same concentration at the same temperature are respectively 0.605 atm and 0.245 atm, calculate van't Hoff factor for CaCl<sub>2</sub>.**

**Solution :**

Given :

Osmotic pressure of CaCl<sub>2</sub> solution = 0.605 atm

Osmotic pressure of urea solution = 0.245 atm

To find : The value of van't Hoff factor

Formula :  $\pi = MRT$  ,  $\pi = iMRT$

Calculation : For urea solution,

$$\pi = MRT$$

$$0.245 \text{ atm} = MRT \quad \dots(i)$$

For CaCl<sub>2</sub> solution

$$\pi = iMRT$$

$$0.605 \text{ atm} = iMRT \quad \dots(ii)$$

From equations (i) and (ii),

$$\frac{0.605}{0.245} = \frac{iMRT}{MRT}$$

$$= \frac{0.605}{0.245}$$

$$= \text{Antilog} [ \log 0.605 - \log 0.245 ]$$

$$= \text{Antilog} [ -0.2182 - (-0.6108) ]$$

$$= \text{Antilog} ( -0.2182 + 0.6108 )$$

$$= \text{Antilog} ( 0.3926 )$$

$$= 2.3926$$

$$= 2.4694$$

$$\therefore i = 2.47$$

**Ans:** The value of van't Hoff factor is 2.47.

**9. At 25 °C, a 0.1 molal solution of CH<sub>3</sub>COOH is 1.35 % dissociated in an aqueous solution. Calculate freezing point and osmotic pressure of the solution assuming molality and molarity to be identical.**

**Solution :**

Given :

Molality of solution (m) = 0.1 m = 0.1 mol kg<sup>-1</sup>

Degree of dissociation ( $\alpha$ ) = 1.35% = 0.0135

Temperature = 25 °C = 25 °C + 273.15 = 298.15 K

Molarity of solution (M) = 0.1 M

To find : i. Freezing point of solution

ii. Osmotic pressure of solution

Formulae :

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

$$ii. \Delta T_f = iK_f m$$

$$iii. \pi = iMRT$$

Calculation : Using formula (i).

$$\alpha = \frac{i-1}{n-1} = i-1 \text{ because } n=2$$

$$i = 1 + \alpha = 1 + 0.0135 = 1.0135$$

Now, using formula (ii),

$$\Delta T_f = iK_f m$$

$$= 1.0135 \times 1.86 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1}$$

$$= 1.0135 \times 1.86 \times 0.1$$

$$= \text{Antilog} [ \log 1.0135 + \log 1.86 + \log 0.1 ]$$

$$= \text{Antilog} [ 0.0427 + 0.2695 - 1 ]$$

$$= \text{Antilog} ( -0.6879 )$$

$$= 0.2052$$

$$\text{Now, } \Delta T_f = T_f^\circ - T_f$$

$$T_f = T_f^\circ - \Delta T_f = 0^\circ \text{C} - (0.189^\circ \text{C}) = -0.189^\circ \text{C}$$

Now, using formula (iii),

$$\pi = iMRT =$$

$$1.0135 \times 0.1 \text{ mol dm}^{-3} \times 0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$\times 298.15 \text{ K} = 2.48 \text{ atm}$$

**Ans :**

- i. The freezing point of the solution is -0.189 °C.
- ii. The osmotic pressure of solution at 25 °C is 2.48 atm.

**10. 0.01 m aqueous formic acid solution freezes at -0.021 °C. Calculate its degree of dissociation. K<sub>f</sub> = 1.86 K kg mol<sup>-1</sup>**

**Solution :**

Given : Molality of solution = m = 0.01 m

Freezing point of solution = T<sub>f</sub> = 0.021 °C

K<sub>f</sub> = 1.86 K Kg mol<sup>-1</sup>

To find : Degree of dissociation of formic acid

Formulae : i.  $\Delta T_f = iK_f m$       ii.  $\alpha = \frac{i-1}{n-1}$

Calculation :  $\Delta T_f = T_f^\circ - T_f = 0^\circ\text{C} - (-0.021^\circ\text{C})$

$$= 0.021^\circ\text{C} = 0.021\text{ K}$$

$$m = 0.01\text{ mol kg}^{-1}$$

Using formula (i),

$$\Delta T_f = iK_f m$$

$$0.021\text{ K} = i \times 1.86\text{ K kg mol}^{-1} \times 0.01\text{ mol kg}^{-1}$$

$$\therefore i = \frac{0.021}{1.86 \times 0.01} = 1.13$$

$$= \frac{0.021}{1.86 \times 0.01}$$

$$= \frac{0.021}{1.86 \times 10^{-2}} = \frac{0.021 \times 10^2}{1.86}$$

$$= \frac{2.1}{1.86}$$

$$= \text{Antilog} [\log 2.1 - \log 1.86]$$

$$= \text{Antilog} [0.3222 - 0.2695]$$

$$= \text{Antilog} (0.0527)$$

$$= 1.1290$$

Using formula (iii),

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

$$\therefore \alpha = 1.13 - 1 = 0.13 = 13\%$$

**Ans :** The degree of dissociation is 13%.

○○○

**MCQ. from Textbook**

1. The vapour pressure of a solution containing 2 moles of a solute in 2 moles of water (vapour pressure of pure water = 24 mm Hg)
  - a. 24 mm Hg
  - b. 32 mm Hg
  - c. 48 mm Hg
  - d. 12 mm Hg
2. The colligative property of a solution is
  - a. Vapour pressure
  - b. boiling point
  - c. osmotic pressure
  - d. freezing point
3. In calculating osmotic pressure the concentration of solute is expressed in
  - a. molarity
  - b. molality
  - c. mole fraction
  - d. mass percent
4. Ebullioscopic constant is the boiling point elevation when the concentration of solution is
  - a. 1 m
  - b. 1M
  - c. 1 mass%
  - d. 1 mol fraction of solute.
5. Cryoscopic constant depends on
  - a. nature of solvent
  - b. nature of solute
  - c. nature of solution
  - d. number of solvent molecules
6. Identify the correct statement
  - a. vapour pressure of solution is higher than that of pure solvent.
  - b. boiling point of solvent is lower than that of solution
  - c. osmotic pressure of solution is lower than that of solvent
  - d. osmosis is a colligative property.
7. A living cell contains a solution which is isotonic with 0.3 M sugar solution. What osmotic pressure develops when the cell is placed in 0.1 M KCl solution at body temperature?
  - a. 5.08 atm
  - b. 2.54 atm
  - c. 4.92 atm
  - d. 2.46 atm
8. The osmotic pressure of blood is 7.65 atm at 310 K. An aqueous solution of glucose isotonic with blood has the percentage (by volume)
  - a. 5.41 %
  - b. 3.54%
  - c. 4.53 %
  - d. 53.4%
9. Vapour pressure of solution is
  - a. directly proportional to the mole fraction of the Solute
  - b. inversely proportional to the mole fraction of the solute
  - c. inversely proportional to the mole fraction of the solvent
  - d. directly proportional to the mole fraction of the solvent
10. Pressure cooker reduces cooking time for food because
  - a. boiling point of water involved in cooking is increased
  - b. heat is more evenly distributed in the cooking space
  - c. the higher pressure inside the cooker crushes the food material
  - d. cooking involves chemical changes helped by a rise in temperature.
11. Henry's law constant for a gas  $\text{CH}_3\text{Br}$  is  $0.159 \text{ mol dm}^{-3} \text{ atm}$  at  $250^\circ\text{C}$ . What is the solubility of  $\text{CH}_3\text{Br}$  in water at  $25^\circ\text{C}$  and a partial pressure of  $0.164 \text{ atm}$ ?
  - a.  $0.0159 \text{ mol L}^{-1}$
  - b.  $0.164 \text{ mol L}^{-1}$
  - c.  $0.026 \text{ M}$
  - d.  $0.042 \text{ M}$
12. Which of the following statement is NOT correct for 0.1 M urea solution and 0.05 M sucrose solution?
  - a. osmotic pressure exhibited by urea solution is higher than that exhibited by sucrose solution
  - b. urea solution is hypertonic to sucrose solution
  - c. they are isotonic solutions
  - d. sucrose solution is hypotonic to urea solution

**Answer Key**

1. d   2. c   3. a   4. a   5. d   6. b  
 7. b   8. a   9. b   10. a   11. c   12. c