ALLEN
CAREER INSTITUTE
KOTA (RAJASTHAN)
path to success

PRE-MEDICAL

PHYSICAL CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER

STUDY MATERIAL

Solutions

ENGLISH MEDIUM

Copyright Statement

SOLUTIONS

3.0 INTRODUCTION

3.1 Definition of Solution :

When two or more chemically non-reacting substances are mixed together forming homogeneous mixture the mixture is called solution.

When the solution is composed of only two chemical substances, it is termed as binary solution, similarly, it is called ternary and quaternary if it is composed by three and four components respectively.

For binary solution : Solution = solute + solvent

• Generally the component present in lesser amount than, other component in solution, is called solute.

• Generally, the component present in greater amount than all other components, is called the solvent.

• Physical state of solvent and solution is same.

Solution	Solute + Solvent	
	(B)	(A)
moles	n	N
mass	$w_{(g)}$	$W_{(g)}$
molar mass	m	M
mole fraction	$x_{(B)}$	$x_{(A)}$

Ex.1 In a syrup (liquid solution) containing 60 g sugar (a solid) and 40 g water (a liquid) same aggregation as solution water is termed as the solvent.

Ex.2 : In a solution of alcohol and water ; having 10 mL alcohol and 20 mL water, water is solvent and alcohol will be solute.

• On the basis of amount of solute, solutions can be classified in two ways.

(a) Dilute Solution

A solution in which relatively a small amount of solute is dissolved in large amount of solvent is called a dilute solution.

(b) Concentrated Solution

A solution in which relatively a large amount of the solute is present is called a concentrated solution.

3.2 CONCENTRATION TERMS

(a) Normality (N)

The *number of equivalents* or *gram equivalents* of solute present in *one litre* of the solution is known as normality (N) of the solution.

$$= \frac{\text{Number of gram equivalents of solute (g)}}{\text{Volume of solution (L)}}$$

$$= \frac{\text{Mass of solute (g)}}{\text{Equivalent mass} \times \text{Volume of solution (L)}}$$

(b) Molarity (M)

The *number of moles* of solute present in *one litre* solution is called its molarity(M).

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{volume of solution (L)}} = \frac{n}{V_{(L)}}$$

(c) Formality (F)

It is the number of *gram formula mass units* present per litre of solution. Formality is generally used for solutions of ionic compounds.

$$\text{Formality} = \frac{\text{Mass of solute (g)}}{\text{Formula mass of solute (g)} \times \text{Volume of solution (L)}}$$

(d) Molality (m)

The *number of moles* of solute present in *1000 gram* of the solvent is called molality of the solution.

$$\text{Molality of a solution} = \frac{\text{Number of moles of solute}}{\text{Amount of solvent(kg)}} = \frac{\text{Number of moles of solute} \times 1000}{\text{Amount of solvent(g)}}$$

(e) Strength of a Solution (S)

The mass of solute in g dissolved in 1L solution is known as its strength in g L^{-1}

$$S = \frac{\text{Mass of solute (g)}}{\text{Volume of solution (L)}}$$

$S(gL^{-1})$ = Molarity of solution × Molar mass of solute

$S(gL^{-1})$ = Normality of solution × Equivalent mass of solute

(f) Concentration in terms of percentage

(i) Percent By Mass (w/W)

Mass of solute (in g) present in 100 g of solution (g) is called mass percent of the solute.

Where 'w' gram of solute is dissolved in W gram of solvent.

$$\text{Mass percent} = \frac{\text{Mass of solute(g)} \times 100}{\text{Mass of solution(g)}} = \frac{w \times 100}{w + W}$$

Mass percent is independent of temperature.

(ii) Percent By Volume (v/V)

This method is used for solutions of liquid in a liquid. The volume of liquid (solute) in mL present in 100 mL of solution in is called volume percent.

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

(iii) Percent by strength /percentage mass by volume $\left(\dfrac{w}{V}\right)$: Mass of solute (in g) present in

100 mL solution is called mass by volume.

$$\% \left(\frac{w}{V}\right) = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100$$

(g) Parts Per Million (ppm)

This method is used for expressing the concentration of very dilute solutions such as hardness of water, air pollution etc.

$$\text{ppm of substance (by mass)} = \frac{\text{Mass of solute(g)} \times 10^6}{\text{Mass of solution(g)}}$$

$$\text{ppm (by volume)} = \frac{\text{Volume of solute(mL)} \times 10^6}{\text{Volume of solution(mL)}}$$

$$\text{ppm}\left(\text{by}\frac{w}{V}\right) = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 10^6$$

(h) **Mole Fraction**

The ratio of the number of moles of one component to the total number of moles of all the components present in the solution, is called the mole fraction of that component.

Mole fraction of solute $\quad X_B = \dfrac{\text{moles of solute}(n)}{\text{moles of solute }(n) + \text{moles of solvent}(N)}$

Mole fraction of solvent $\quad X_A = \dfrac{\text{moles of solvent}(N)}{\text{moles of solute }(n) + \text{moles of solvent}(N)}$

$$\boxed{X_A + X_B = 1}$$

(i) (i) **Relation Between Molarity and Normality**

$S = \text{Molarity} \times \text{Molar mass of solute}$ and $S = \text{Normality} \times \text{Equivalent mass of solute}$.

So we can write

$\text{Molarity} \times \text{Molar mass of solute} = \text{Normality} \times \text{Equivalent mass of solute}$.

$\text{Normality} = \dfrac{\text{Molarity} \times \text{Molar mass of solute}}{\text{Equivalent mass of solute}}$

$\qquad\qquad = \dfrac{\text{Molarity} \times \text{Molar mass of solute}}{(\text{Molar mass of solute/valency factor})}$

$\text{Normality} = \text{Molarity} \times \text{Valency factor}$

$N = M \times n \text{ factor}$

(ii) **Relation Between Molality (m) and Mole fraction**

$$\dfrac{x_B}{x_A} = \dfrac{n_B}{N_A} = \dfrac{n_B \times M_A \times 1000}{w_A \times 1000}$$

$$\dfrac{x_B}{x_A} = \dfrac{\text{molality} \times M_A}{1000}$$

$$\dfrac{x_B}{1 - x_B} = \dfrac{\text{molality} \times M_A}{1000} : \text{if } x_B <<< 1 \text{ for very dilute } x_B = \dfrac{\text{molality} \times M_A}{1000}$$

(j) **VOLUME STRENGTH OF H_2O_2 SOLUTION :**

Volume of O_2 (L) produced by decomposition of unit volume solution of H_2O_2 at NTP/STP; is called its volume strength.

Relationship between volume strength of H_2O_2 and Molarity/Normality / (g/L) / % (w/V)

Let volume strength of H_2O_2 solution be 'X V', it means 1L solution of H_2O_2, can produce X L of O_2 at NTP.

$$\underset{2\,\text{mole}}{2H_2O_2} \rightarrow 2H_2O + \underset{1\,\text{mole}}{O_2(g)}$$
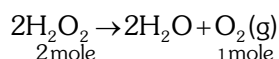
$\because$ 1 mol O_2 can be produced by = 2 mol H_2O_2 solution

$\therefore \quad \dfrac{X}{22.4}$ mol of O_2 can be produced by $\dfrac{2X}{22.4}$ = mol H_2O_2 solution

$$= \dfrac{X}{11.2} \text{ mol of } H_2O_2 \text{ solution}$$

(a) $\text{Molarity} = \dfrac{\text{number of moles of solute}}{\text{volume of solution(L)}} = \dfrac{2X}{22.4} = \dfrac{X}{11.2}$

Hence $\boxed{M = \dfrac{X}{11.2}}$

(b) $\text{Normality} = \text{molarity} \times \text{valence factor} = \dfrac{X}{11.2} \times 2 = \dfrac{X}{5.6}$

Hence $\boxed{N = \dfrac{X}{5.6}}$

(c)   Strength (g/L) : $S = N \times E$

Hence $\boxed{S = \dfrac{X}{5.6} \times 17}\ gL^{-1}$

(d) $\boxed{\%\left(\dfrac{w}{V}\right) = \dfrac{X}{5.6} \times \dfrac{17}{10}}$

GOLDEN KEY POINTS

- If the density of solution is approximately 1g/cc then Molality > Molarity

- ppm unit is used to represent concentration of very dilute solutions like pollutants in environment and salts present in sea water.

- Those concentration terms which involves volume of solution are temperature dependent.

- Molarity, normality, formality, % by volume, % w/V, are temperature dependent.

- Molality, % w/W, mole fraction are temperature independent.

──────────────── **Illustrations** ────────────────

Illustration 1.   If 0.4 g of NaOH is present in 40 mL of solution. What is the molarity and normality of solution

[Molecular mass of NaOH = 40]

Solution.   We know that

$$\text{Molarity} = \dfrac{\text{Mass of solute} \times 1000}{\text{Molar Mass of solute} \times \text{Volume of solution (mL)}}$$

$$M = \dfrac{0.4}{40 \times 40} \times 1000 = 0.25\ M$$

$$\text{Normality} = \dfrac{\text{Mass of solute}}{\text{Equivalent mass of solute} \times \text{volume of solution(mL)}} \times 1000$$

Equivalent mass of NaOH = 40

$$N = \dfrac{0.4}{40 \times 40} \times 1000 = 0.25N$$

Illustration 2.   The normality of 1.5M H_3PO_4 is –

Solution.   Basicity of H_3PO_4 is 3

We know that $N = M \times n$ $\Rightarrow$ Normality = $1.5 \times 3 = 4.5\ N$

Illustration 3. Find out the mass of H_2SO_4 in 150 mL, $\frac{N}{7} H_2SO_4$.

Solution. $N = \dfrac{\text{Mass in gram}}{\text{Equivalent mass} \times \text{Volume(L)}}$

Mass in gram = Equivalent mass $\times$ N $\times$ Volume (L) = $49 \times \dfrac{1}{7} \times \dfrac{150}{1000} = \dfrac{21}{20} = 1.05g$

Illustration 4. Find out the molarity of 93% (w/W) H_2SO_4 (density = 1.84 g/ml).

Solution. $\text{Molarity} = \dfrac{\text{Moles of solute}}{\text{Volume of solution(L)}} = \dfrac{\text{Mass in gram} \times \text{Density} \times 1000}{\text{Molar mass} \times \text{mass of solution (g)}}$

$= \dfrac{93 \times 1.84 \times 1000}{98 \times 100} = 17.46 \text{ M}$

Illustration 5. A 100 cm³ solution is prepared by dissolving 2g of NaOH in water. Calculate the normality of the solution.

Solution. $2g \ NaOH = \dfrac{2}{40} g \ eq ; \quad N = \dfrac{\frac{1}{20}}{100} \times 1000 = \dfrac{1}{2}$

Normality of solution = $\dfrac{N}{2}$

Illustration 6. Find the percentage by mass and mass fraction of aspirin in the solution prepared by dissolving 3.65 g of aspirin in 25.08 g of water .

Solution. Mass of solution = 3.65 + 25.08 = 28.73 g

Mass fraction = $\dfrac{3.65}{28.73} = 0.127$

Mass percent = $0.127 \times 100 = 12.7\%$

Illustration 7. A solution was prepared by adding 125 cm³ of isopropyl alcohol to water until the volume of the solution was 175 cm³. Find the volume fraction and volume percent of isopropyl alcohol in the solution.

Solution. Volume of solute = 125 cm³

Volume of solution = 175 cm³

$\therefore$ Volume fraction = $\dfrac{125}{175} = 0.714$

Volume percent = $\dfrac{125}{175} \times 100 = 71.4\%$

Illustration 8. Calculate volume strength of H_2O_2 in 5L solution which yields 100 L of O_2 at NTP.

Solution 5L H_2O_2 gives = 100 L O_2

1L H_2O_2 gives = 20 L O_2

i.e. 20 V H_2O_2 solution

BEGINNER'S BOX-1

1. What is the normality of 2M H_3PO_2 solution?

(1) 0.5 N   (2) 1.0N   (3) 2.0 N   (4) 3.0 N

2. 23 g ethanol is dissolved in 36 g water. Find mole fraction of ethanol?

(1) 2   (2) 0.5   (3) 0.2   (4) 0.8

3. How many gram of HNO_3 is required to prepare 400 mL solution of 0.2 M HNO_3?

(1) 5.04 g   (2) 5040 g   (3) 25.2 g   (4) 2.52 g

4. Calculate normality of 2.1% (w/V) H_2SO_4 solution?

(1) 2.14 N (2) 4.28 N (3) 0.428 N (4) 0.214 N

5. What is the molarity of 1N H_2SO_4 solution?

(1) 1 M (2) 2M (3) 0.5 M (4) 3M

6. 20.6 g NaBr is dissolved in 500 mL solution what is the molarity of resulting solution?

(1) 0.6 (2) 0.4 (3) 1 (4) None

7. Calculate molality of the solution obtained by dissolving 11.7 g NaCl in 500 g water

(1) 0.1 m (2) 0.3 m (3) 0.2m (4) 0.4m

8. Density of 2.03 M aqueous solution of acetic acid is 1.017 g mL^{-1} molecular mass of acetic acid is 60. Calculate the molality of solution?

(1) 2.27 (2) 1.27 (3) 3.27 (4) 4.27

9. A molar solution is one that contains one mole of solute in

(1) 1000 g of the solvent (2) one litre of the solution
(3) 1000 g of the solution (4) 22.4 litres of the solution

10. Calculate the mole percentage of CH_3OH and H_2O respectively in 60% (by mass) aqueous solution of CH_3OH

(1) 45.8, 54.2 (2) 54.2, 45.8 (3) 50, 50 (4) 60, 40

3.3 SOLUBILITY

Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is solubility. Solubility is affected by nature of solute and solvent as well as by temperature and pressure.

(a) Solubility of Solid in Liquid

Polar solutes are soluble in polar solvent and non polar solutes are soluble in non polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent then following equilibrium exists.

$$\text{Solute + Solvent} \xrightleftharpoons[\text{Crystallization}]{\text{Dissolution}} \text{Solution}$$
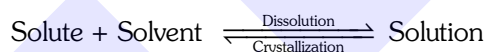
Solubility of solids is affected by temperature and pressure according to Le-chatlier's principle. If dissolution is exothermic then solubility decreases with increase in temperature and if endothermic then solubility increases with increase in temperature.

Solubility of solids is not affected by pressure significantly since solids are highly incompressible.

(b) Solubility of Gases in Liquid

Certain gases are highly soluble in water like NH_3, HCl etc. and certain gases are less soluble in water like O_2, N_2, He etc. Solubility of gases is affected by pressure and temperature. Increasing pressure increases solubility and increase in temperature decreases solubility. During dissolution of gas pressure of gas decrease and dissolution of gas is exothermic in nature.

HENRY'S LAW

It can be stated as at constant temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

or

Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

or

The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (X) in the solution. (This is most common definition)

$P = K_H X$ K_H = Henry's Constant

Henry's Constant is not a universal constant. It depends on nature of gas and temperature. K_H increases with increase in temperature therefore solubility of gas decreases.

───────────────── **Illustrations** ─────────────────

Illustraion 9.   Henry's Law Constant for CO_2 in water is 1.67×10^8 Pa at 298K. Calculate the quantity of CO_2 in 1 L of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Solution. $P = K_H X_{gas}$

$$X_{gas} = \frac{P}{K_H} = \frac{2.5 \times 10^5}{1.67 \times 10^8} = 1.5 \times 10^{-3}$$

$$\frac{n}{n+N} = X$$

$$\frac{n}{N} = X \quad \because \ n << N \quad \therefore \ n + N \simeq N$$

$$\frac{n}{55.55} = 1.5 \times 10^{-3} = 8.3 \times 10^{-2} \ \text{mol L}^{-1}$$

$$= 3.65 \ \text{g L}^{-1}$$

3.4   VAPOUR PRESSURE

At a constant temperature, the pressure exerted by the vapours of a liquid on its surface when they (liquid and its vapours) are in equilibrium, is known as vapour pressure.

Factor affecting vapour pressure :

     (a) Nature of liquid   (b) Temperature

Raoult's Law

(a)   **For liquid-liquid system :** For a solution of volatile liquids the partial vapour pressure of any component at constant temprature is equal to vapour pressure of pure component multiplied by mole fraction of that component in the solution.

	Liquid (B)	Liquid (A)
Vapour pressure in pure state	P_B^0	P_A^0
Partial vapour pressure	P_B	P_A
Mole fraction in solution	X_B	X_A
Moles	n moles	N moles
Mass	w g	W g
Molar mass	m	M

$$P_A \propto X_A \ \text{so} \ P_A = P_A^0 X_A \quad …(i)$$

$$P_B \propto X_B \ \text{so} \ P_B = P_B^0 X_B \quad …(ii)$$

At constant temperature partial vapour pressure of component is directly proportional to mole fraction of component in solution.

According to Dalton's law given below :

• $P_{total} = P_A + P_B + ...$

     $\boxed{P_S = X_A P_A^0 + X_B P_B^0}$; $X_A + X_B = 1$

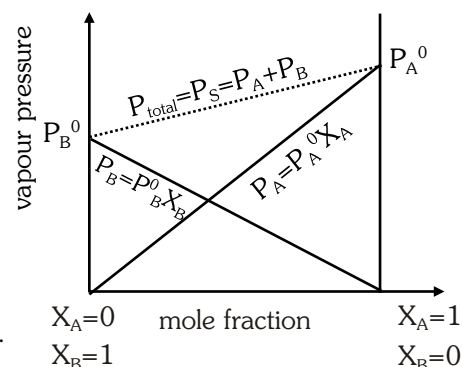 $P_S \quad = (1 - X_B) P_A^0 + X_B P_B^0$

     $P_S \quad = P_A^0 - X_B P_A^0 + X_B P_B^0$

     $P_S \quad = P_A^0 + X_B (P_B^0 - P_A^0)$

$$\boxed{\begin{array}{cccc} P_S = & P_A^0 + & X_B & (P_B^0 - P_A^0) \\ \downarrow & \downarrow & \downarrow & \downarrow \\ y & c & x & m \end{array}}$$

slope can be positive or negative.

when $P_B^0 > P_A^0$ when $P_A^0 > P_B^0$

• **Dalton's Law**

Partial pressure of gas = mole fraction $\times$ total pressure of gas

$$P_A = Y_A P_T$$
$$P_B = Y_B P_T$$
$$P_A + P_B = P_T$$

Y_A and Y_B gives mole fraction in vapour phase

$$\boxed{\begin{aligned} X_A P_A^0 &= Y_A P_T \\ X_B P_B^0 &= Y_B P_T \end{aligned}}$$ X_A and X_B gives mole fraction in liquid phase.

──────────── **Illustrations** ────────────

Illustration 10. Methanol and C_2H_5OH form an ideal solution. Solution is prepared by mixing 32 g of CH_3OH and 23 g of C_2H_5OH at 300K. At 300K $P^0_{methanol}$ = 90 mm of Hg and $P^0_{ethanol}$ = 51 mm of Hg. Calculate

(i) partial vapour pressure of its constitutents and total vapour pressure of solution.

(ii) Mole fraction of each component in vapour phase.

Solution (i) $n_{CH_3OH} = \dfrac{32}{32} = 1$; $n_{C_2H_5OH} = \dfrac{23}{46} = 0.5$

$X_{CH_3OH} = \dfrac{1}{1.5} = \dfrac{2}{3}$; $X_{C_2H_5OH} = \dfrac{0.5}{1.5} = \dfrac{1}{3}$

$p_{CH_3OH} = p_m^0 . X_m = 90 \times \dfrac{2}{3}$

$P_{CH_3OH} = 60$ mm of Hg

$p_{C_2H_5OH} = p_e^0 . X_e = 51 \times \dfrac{1}{3}$

$P_{C_2H_5OH} = 17$ mm of Hg

$p_S = p_{CH_3OH} + p_{C_2H_5OH}$

$P_S = 77$ mm of Hg

(ii) $60 = Y_A \times 77$ $17 = Y_B \times 77$

$Y_{CH_3OH} = \dfrac{60}{77} = 0.78$; $Y_{C_2H_5OH} = 0.22$

(b) **For solid - liquid system** : non-volatile solute (B) and volatile solvent (A)

$$P_B^0 = 0$$

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

$$\boxed{P_S = X_A P_A^0 = \dfrac{N}{n+N} P_A^0}$$ ...(i)

For solution of non-volatile solute : At constant temperature vapour pressure of solution containing non-volatile solute is proportional to mole fraction of solvent.

$\therefore$ $P_S \propto \dfrac{N}{n+N}$; $X_A + X_B = 1$

$P_S = (1 - X_B) P_A^0$; $P_S = P_A^0 - X_B P_A^0$

$X_B P_A^0 = P_A^0 - P_S$ $\Rightarrow$ $\boxed{\dfrac{P_A^0 - P_S}{P_A^0} = X_B = \dfrac{n}{n+N}}$ ....(ii)

• When a non-volatile solute is added to a volatile liquid its vapour pressure decrease because less number of solvent particles present in solution at surface. (as compare to pure solvent)

∴ less vapour is formed and vapour pressure of solution decreases

$P_A^0 - P_S = \Delta P$ (lowering of vapour pressure)

$\dfrac{P_A^0 - P_S}{P_A^0}$ = relative lowering of vapour pressure.

$\dfrac{P_A^0}{P_A^0 - P_S} = \dfrac{n+N}{n} \Rightarrow \dfrac{P_A^0}{P_A^0 - P_S} = 1 + \dfrac{N}{n}$

$\Rightarrow \dfrac{P_A^0 - P_A^0 + P_S}{P_A^0 - P_S} = \dfrac{N}{n} \Rightarrow \dfrac{P_S}{P_A^0 - P_S} = \dfrac{N}{n}$

$\Rightarrow \boxed{\dfrac{P_A^0 - P_S}{P_S} = \dfrac{n}{N}}$ ...(iii)

$\Rightarrow \Delta P \propto \dfrac{n}{N}$

Ex. The vapour pressure of pure liquid A is 40 torr at 310 K. The vapour pressure of this liquid in solution with solid B is 32 torr. Calculate X_A in solution.
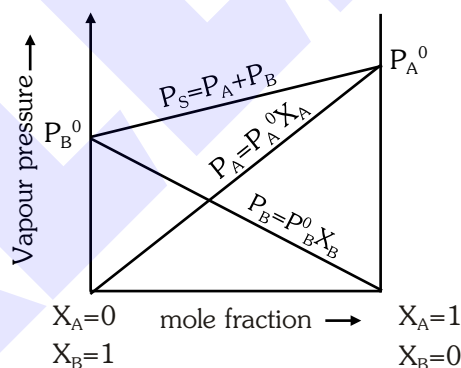
Sol. $32 = X_A \times 40$

$X_A = 0.8$

3.5 IDEAL SOLUTIONS (mixture of two liquids A and B)

- A solution which obeys Raoult's law exactly at all concentrations and at all temperatures is called an ideal solution.

- For ideal solutions; A-A interactions = B-B interactions = A-B interactions.

  An ideal solution possesses the following characteristics :

- Volume change on mixing should be zero. $\Delta V_{mix} = 0$, i.e., ($V_{solute} + V_{solvent} = V_{solution}$)

- Heat change on mixing should be zero. $\Delta H_{mix} = 0$ (Heat is neither absorbed nor evolved)

- There should be no chemical reaction between liquid A and liquid B.

- Ideal solution must obey Raoult's law at all concentrations.

  $P_A = P_A^0 . X_A , \quad P_B = P_B^0 . X_B$

- observed VP = calculated VP

- observed BP = calculated BP

- $\Delta S_{mix} > 0$

- $\Delta G < 0$

Example

(i) Benzene and toluene (ii) CCl_4 and $SiCl_4$ (iii) n-hexane and n-heptane

(iv) C_2H_5Br and C_2H_5Cl (v) PhCl and PhBr (vi) n-butylchloride and n-butylbromide

3.6 NON-IDEAL SOLUTIONS

- For non ideal solutions ; A–A interactions or B-B interactions ≠ A-B interactions.

- Those solutions which do not obey Raoult's law are called non-ideal solutions.

- For such solutions ; $P_A \neq P_A^\circ X_A$; $P_B \neq P_B^\circ X_B$

- Non ideal solutions are formed when the components differ much in their structures and polarities.
  So $\Delta H_{mixing} \neq 0$ and $\Delta V_{mixing} \neq 0$

- Non ideal solutions show either positive or negative deviations from Raoult's law.

(a) Non ideal solutions having positive deviation from Raoult's law.
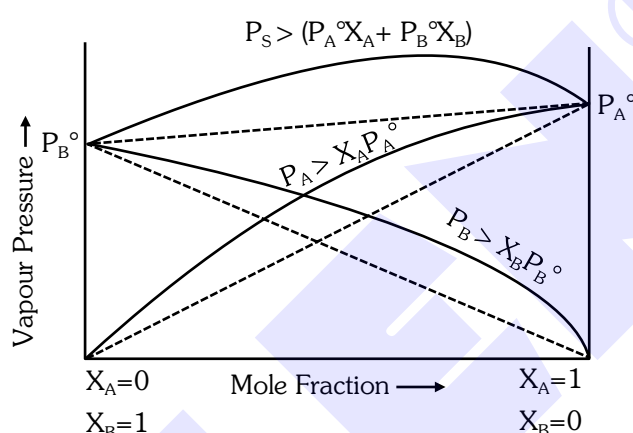
- In these solutions A-B interactions are less than A-A and B-B molecular interactions.

$$P_A > P_A^\circ X_A$$

$$P_B > P_B^\circ X_B$$

- The total vapour pressure of the solution will be greater than the corresponding vapour pressure expected in case of an ideal solution of same composition. i.e.

$$P_{total} > (P_A^\circ X_A + P_B^\circ X_B)$$

- $\Delta H_{mix} > 0$; endothermic dissolution ; heat is absorbed.

- $\Delta V_{mix} > 0.$; volume increases after dissolution, i.e., ($V_{solute} + V_{solvent} < V_{solution}$).

- 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

$$(B.P.)_{th} > (B.P.)_{exp}$$

- $(\Delta S)_{mix} = +ve$, $\Delta G = -ve$

Entropy change in mixing is positive.

Examples : (i) Ethanol and cyclohexane (v) CCl_4 and Benzene (ix) Benzene and Acetone

(ii) Ethanol and Water (vi) CCl_4 and Toluene (x) CS_2 and Acetone

(iii) Ethanol and Acetone (vii) CCl_4 and $CHCl_3$ (xi) CS_2 and Acetaldehyde

(iv) Methanol and H_2O (viii) CCl_4 and Methanol

(b)   **Non ideal solutions having negative deviation from Raoult's Law**
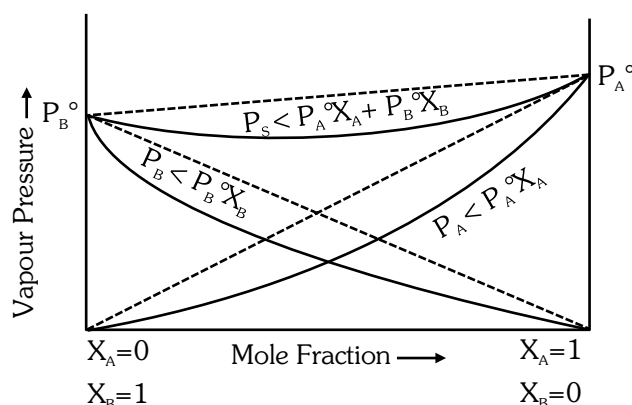
- In these solutions the A–B interactions are stronger than the A–A and B–B molecular interactions.

$$P_A < P_A^\circ X_A \quad ; \quad P_B < P_B^\circ X_B$$

- $P_{total} < (P_A^\circ X_A + P_B^\circ X_B)$

   Total vapour pressure is less than sum of individual vapour pressure.

- $\Delta H_{mix} < 0$; exothermic dissolution heat is evolved.

- $\Delta V_{mix} < 0$; volume decreases during dissolution, i.e., $(V_{solute} + V_{solvent} > V_{solution})$.

- Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

   Examples   (i) $CHCl_3$ and CH_3COCH_3 (vi) H_2O and HCl

                   (ii) $CHCl_3$ and C_6H_6 (vii) H_2O and HNO_3

                   (iii) $CHCl_3$ and $C_2H_5OC_2H_5$ (viii) CH_3COOH and CH_3OH

                   (iv) $CHCl_3$ and HNO_3 (ix) CH_3COOH and C_5H_5N

                   (v) $CHCl_3$ and CH_3COOH (x) CH_3COCH_3 and Aniline

AZEOTROPIC MIXTURES :

Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature, the liquid and vapour have the same composition, and no further separation occurs.

Components form azeotrope can't be separated by fractional distillation but can be separated by azeotropic distillation.

Solutions showing Positive deviation form minimum boiling azeotrope and solutions showing negative deviation form maximum boiling azeotrope.

There are two types of azeotropes :

(a) Minimum boiling azeotrope   (b) Maximum boiling azeotrope

(a)   The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition. For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95.57% v/v ethanol.

(b)   The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

GOLDEN KEY POINTS

- Those gases which can react with solvent do not follow Henry's Law. e.g. NH_3 in water.

- Raoult's Law is special case of Henry's Law.

- ΔS is positive and ΔG is negative for ideal as well as non ideal solutions.

- The vapour phase is richer in more volatile component than the less volatile component. This is called as Konowaloff's rule.

Illustrations

Illustraion 11.   1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole. Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

Solution.   Total mole = 1 + 4 = 5

Mole fraction of heptane $X_A = 1/5$

Mole fraction of octane $X_B = 4/5$

$P_S = X_A P_A^0 + X_B P_B^0 = \dfrac{1}{5} \times 92 + \dfrac{4}{5} \times 31 = 43.2$ mm of Hg.

Illustraion 12.   At 88^0C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88^0C at 1 atm pressure (benzene – toluene form an ideal solution).

Solution. $P_S = 760$ torr, because solution boils at 88^0C

$P_S = P_B^0 X_B + P_t^0 X_t$

∴   760 = 900 a + 360 − 360 a

a = 0.74 where 'a' is mole fraction of $C_6H_6 (X_B)$

BEGINNER'S BOX-2

1.   Which of the gas will not follow Henry's law?

(1) HCl   (2) He   (3) O_2 (4) H_2

2.   If solubility of gas 'X' is 0.5 gL^{-1} at 1 bar then its solubility at 3 bar pressure will be

(1) 0.5 gL^{-1} (2) 1.5 gL^{-1} (3) 3.0 gL^{-1} (4) 2 gL^{-1}

3.   Among the following that forms an ideal solution?

(1) water and methanol   (2) acetone and ethanol   (3) benzene and toluene   (4) water and HCl

4.   On mixing 10 mL of acetone with 40 ml of chloroform the total volume of the solution is

(1) < 50 mL   (2) > 50 mL   (3) = 50 mL   (4) cannot be predicted

5.   The mixture of n-hexane and n-heptane is an example of

(1) ideal solution   (2) non-ideal solution   (3) dilute solution   (4) none

3.7   COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS (CP)

Those physical properties of a solution which depends upon the relative number of particles of solute and do not depend on nature of solute particles are called colligative properties.

CP   ∝   Number of solute particles

      ∝   Number of molecules (in the solution of non electrolyte)

      ∝   Number of ions (in the solution of electrolytes)

      ∝   Number of moles of solute

      ∝   Mole fraction of solute

The following four properties are CP :

(a) Relative lowering in vapour pressure of solvent

(b) Elevation in boiling point (ΔT_b) of solvent

(c) Depression in freezing point (ΔT_f) of solvent

(d) Osmotic pressure (π or P) of solution

(a) Relative Lowering in Vapour Pressure

• When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases (due to lesser solvent molecules per unit surface area).

If at a certain temperature $P°$ is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then

According to Raoult's law :

Relating lowering in vapour pressure = $\dfrac{P_A^0 - P_S}{P_A^0} = \dfrac{n_B}{N_A + n_B}$

For a dilute solution $n_B << N_A$ $\therefore \dfrac{P_A^0 - P_S}{P_A^0} \approx \dfrac{n_B}{N_A}$ so $\Delta P \propto \dfrac{n_B}{N_A}$

• Relative lowering depends upon relative number of solute particles. Therefore it is called colligative properties.

(b) Elevation in Boiling Point

• The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure.

• When a non-volatile solute is dissolved in a pure solvent, its vapour pressure is decreased and boiling point increases. The difference of boiling points of the solution and pure solvent is called elevation in boiling point.(ΔT_b)

• If T_b^0 is the boiling point of pure solvent and T_b is the boiling point of the solution then, $T_b > T_b^0$ and the elevation in boiling point $\Delta T_b = T_b - T_b^0$

• The elevation in boiling point (ΔT_b) is directly proportional to lowering of vapour pressure of the solution i.e.

$\Delta T_b \propto (P°-P_s)$ from graph and

$\Delta T_b \propto \Delta P \propto \dfrac{n_B}{N_A}$

T_b = Boiling point of solution
T_b = Boiling point of solution

The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.
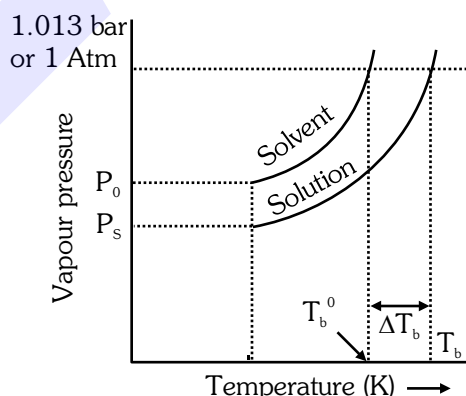
$\therefore$ $\Delta T_b \propto \dfrac{n_B}{N_A} = \dfrac{w_B M_A}{m_B W_A}$ for a solvent P^0 & M_A = constant

$\therefore$ $\Delta T_b \propto \dfrac{w_B}{m_B W_A}$ or $\Delta T_b = \dfrac{K w_B}{m_B W_A}$

where K = elevation constant

if $\dfrac{w_B}{m_B} = 1$ mole and $W_A = 1$ g

then $\Delta T_b = K$ (Elevation constant or molecular elevation constant)

if $\quad \dfrac{w_B}{m_B} = 1$ and $W_A = 1000$ gram; Then $\Delta T_b = K_b$ (molal elevation constant)

$\therefore \quad \dfrac{K}{1000} = K_b$ (molal elevation constant or Ebullioscopic constant)

$\Delta T_b = \dfrac{K_b \times w_B \times 1000}{m_B \times W_A}$; $\quad \Delta T_b = \dfrac{w_B}{m_B} \times \dfrac{1000}{W_A} \times K_b$

$\therefore \quad \boxed{\Delta T_b = \text{molality} \times K_b} \quad \therefore \Delta T_b \propto \text{molality}$

hence elevation in boiling point (ΔT_b) is a colligative property.

- K_b depends only on nature of solvent which can be explained by thermodynamic relation.

$$\boxed{K_b = \dfrac{R\left(T_b^0\right)^2}{1000 L_v} = \dfrac{M_w R\left(T_b^0\right)^2}{1000 \Delta H_{vap}}}$$

Where $\quad T_b^{\;0}$ = Boiling point of solvent.

M_w = Molar mass of solvent.

ΔH_{vap} = Enthalpy of vapourisation per mole of solvent

L_v = Latent heat of vapourisation per gram of solvent

- **The molal elevation constant for some common solvents are given in the following table**

| Solvent	B.P. (^{0}C)	Molal elevation constant (K_b)
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.63
Carbon tetra chloride	76.8	5.03
Benzene	80.0	2.53
Ethyl alcohol	78.4	1.20

(c) Depression in Freezing Point

- The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other.

- It may be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.

- When a non-volatile is dissolved in a pure solvent the vapour pressure of the solvent is lowered.

- If T_f^0 is the freezing point of pure solvent and T_f is the freezing point of its solution then, $\quad T_f < T_f^0$

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

  $\Delta T_f = T_f^0 - T_f$; the depression in freezing point is directly proportional to lowering in vapour pressure (ΔP)

  $\Delta T_f \propto \Delta P \propto \dfrac{n_B}{N_A}$; $\quad \Delta T_f \propto \dfrac{n_B}{N_A}$ so $\boxed{\Delta T_f = K_f \times \text{molality}}$

K_f = molal depression constant or Cryoscopic constant.
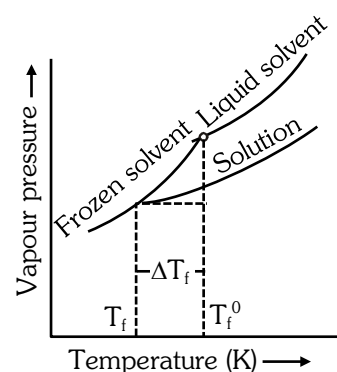
- K_f depends only on nature of solvent which can be explained by thermodynamic relation

$$K_f = \frac{R\left(T_f^0\right)^2}{1000 L_f} = \frac{R\left(T_f^0\right)^2 M_w}{1000 \Delta H_f}$$

Where T_f^0 = Freezing point of solvent
     M_w = Molar mass of solvent
 ΔH_f = Enthalpy of fusion per mole of solvent
     L_f = latent heat of fusion per gram of solvent

- **The molal depression constant for some common solvents are given in the following table**

Solvent	F.P.(ºC)	Molal depression constant (K_f)
Water	0.0	1.86
Ethyl alcohol	– 114.6	1.99
Chloroform	– 63.5	4.79
Carbon tetra chloride	– 22.8	31.80
Benzene	5.5	5.12
Camphor	179.0	39.70

(d) Osmosis and Osmotic Pressure

Osmosis : Osmosis is defined as the spontaneous net flow of solvent molecules through semipermeable membrane from a solvent to a solution or from a dilute solution to a concentrated solution.
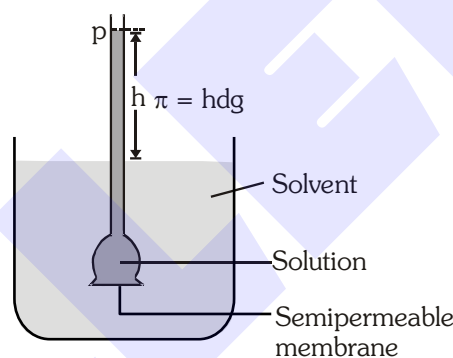
Level of solution rises in the thistle
funnel due to osmosis of solvent

Osmotic Pressure (p or π)

- The external pressure which must be applied on the solution in order to stop the flow of solvent into the solution through semipermeable membrane is equal to osmotic pressure

or

- Hydrostatic pressure developed in a vertical column when solution and solvent are separated by SPM.

Osmotic pressure = hydrostatic pressure ; $\boxed{\pi = hdg}$

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

Van't Hoff law for Dilute Solution

According to it Gas equation PV = nRT is also followed by dilute solution when pressure of gas is replaced by osmotic pressure of solution.

π = osmotic pressure of solution (atm)
V = volume of solution (L)
n = moles of solute

$$\begin{array}{c} PV = nRT \\ \downarrow \downarrow \quad \downarrow \\ \pi V = nRT \end{array}$$

R = (S) gas constant / solution constant = 0.0821 L atm mol^{-1}K^{-1};   0.083 L bar mol^{-1}K^{-1}

$$\pi = \left(\frac{n}{V}\right)RT \quad \boxed{\pi = CRT}$$

At constant temperature $\pi \propto C$ $\quad \therefore \pi$ is a colligative property.

• On the basis of osmotic pressure solution can be classified by following ways :

(i) **Isotonic solutions :** Solutions having same osmotic pressure are called isotonic solution.

$$\boxed{\pi_1 = \pi_2}$$; primary condition

$$C_1RT = C_2RT \quad \text{(at same temperature)}$$

$$\boxed{C_1 = C_2}$$ (secondary condition) ; means

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$; such solutions are known as **isotonic**

(ii) $\pi_1 > \pi_2$ or $C_1 > C_2$ then solution 1 is called **hypertonic** and solution 2 is called **hypotonic**

Reverse Osmosis

If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.
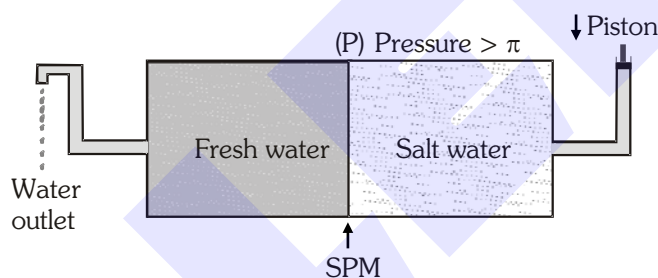
─────────── **Illustrations** ───────────

Illustration 13. The vapour pressure of benzene at 90^0C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. The molecular weight of the solute is?

Solution. $\dfrac{P^0 - P_S}{P_S} = \dfrac{w \times M}{m \times W} \Rightarrow \dfrac{1020 - 990}{990} = \dfrac{5 \times 78}{m \times 58.5} \Rightarrow$ m = 220

Illustration 14. A 5% $\left(\dfrac{w}{V}\right)$ solution of cane sugar is isotonic with 0.877% $\left(\dfrac{w}{V}\right)$ solution of unknown solute. Find out molecular weight of unknown solute.

Solution $\dfrac{5 \times 10}{342} = \dfrac{0.877 \times 10}{x}$

$x = \dfrac{0.877 \times 342}{5}$

$x = 0.877 \times 68.4 = 60$

Illustration 15. 0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216 °C than that of the pure solvent. What is the molar mass of the substance. [K_b for solvent = 2.16 °Cm^{-1}]

Solution. Given $K_b = 2.16^0 C$, w = 0.15 g, $\Delta T_b = 0.216^0 C$, W = 15 g

ΔT_b = Molality $\times K_b$

$\Delta T_b = \dfrac{w}{m \times W} \times 1000 \times K_b \Rightarrow 0.216 = \dfrac{0.15}{m \times 15} \times 1000 \times 2.16$

$\Rightarrow m = \dfrac{0.15 \times 1000 \times 2.16}{0.216 \times 15} = 100$

Illustration 16. The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1^{0}C. The molal elevation constant of the liquid is –

Solution. ΔT_b = Molality $\times K_b$

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

given $\Delta T_b = 0.1^0 C$, m = 180, W = 100, w = 1.8

$K_b = \dfrac{180 \times 0.1 \times 100}{1000 \times 1.8} = 1.0 \quad °Cm^{-1}$

Illustration 17. If freezing point of a solution prepared from 1.25 g of a non electrolyte and 20 g of water is 271.9 K, the molar mass of the solute will be

Solution. Given : $(T_f)_s$ = 271.9 K, w = 1.25 g, W = 20 g, K_f = 1.86 K kg mol^{-1}

$\Delta T_f = T_b^0 - (T_f)_s = 273 - 271.9 = 1.1$

ΔT_f = Molality $\times K_f$ or $\Delta T_f = \dfrac{w}{m \times W} \times 1000 \times K_f$

$m = \dfrac{w \times 1000 \times K_f}{\Delta T_f \times W} = \dfrac{1.25 \times 1000 \times 1.86}{1.1 \times 20} = 105.68$

Illustration 18. Molal depression constant for water is 1.86 °Cm^{-1}. The freezing point of a 0.05 molal solution of a non electrolyte in water is –

Solution. ΔT_f = Molality $\times K_f$ = $0.05 \times 1.86 = 0.093^0 C$

$(T_f)_s = T_0 - 0.093 = 0 - 0.093$

$(T_f)_s = -0.093°C$

Illustration 19. A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

Solution. $\pi V = nST$ or $\pi = \dfrac{n}{V} ST$ = CST or $C = \dfrac{\pi}{ST} = \dfrac{2.46}{300 \times 0.0821} = 0.1 M$

Illustration 20. What is the osmotic pressure of 12% solution of cane sugar (molecular weight 342) at 17 °C.

Solution. 12 g sugar is dissolved in 100 mL

thus 342 g sugar is dissolved in $\dfrac{100 \times 342}{12 \times 1000} = 2.85$ L

Now $\pi V = RT$ $\{\because n = 1\}$

$\pi = \dfrac{RT}{V} = \dfrac{0.0821 \times 290}{2.85} = 8.35$ atm

Illustration 21. A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (weight/volume) solution of an organic, non-volatile solute. Calculate molar mass organic compound.

Solution. Solutions are isotonic

so $\quad \pi_1 = \pi_2 \quad$ or $\quad \dfrac{n_1}{V_1}RT = \dfrac{n_2}{V_2}RT \quad$ { R & T are constant}

so, $\quad \dfrac{n_1}{V_1} = \dfrac{n_2}{V_2} \quad$ or $\quad \left(\dfrac{w_1}{m_1 \times v_1}\right)_{urea} = \left(\dfrac{w_2}{m_2 \times v_2}\right)_{organic}$

or $\quad \dfrac{8.6}{60 \times 1000} = \dfrac{0.5}{m_2 \times 100} \Rightarrow m_2 = 34.89$

GOLDEN KEY POINTS

- (i) $\dfrac{\Delta P}{P^0} \approx \dfrac{n}{N} \Rightarrow \Delta P = \dfrac{wM}{mW} \times P^0$ (ii) $\Delta T_b = \left(\dfrac{w \times 1000}{m \times W}\right)K_b$ (iii) $\Delta T_f = \left(\dfrac{w \times 1000}{m \times W}\right)K_f$ (iv) $\pi = CRT$

- Best method to determine molecular weight of biomolecules like protein and polymers is osmotic presure. Because it is a colligative property also as no temprature change is involved so there is no chance of change in nature of biomolecule. In other methods changes are very less and it is difficult to measure very small changes accurately. But osmotic pressure can be easily measured at room temperature at which biomolecules remain in original state.

- $0.91\% \left(\dfrac{w}{V}\right)$ NaCl solution is isotonic with blood.

- Intravenous injections need to be isotonic with blood to prevent damage to RBC.

- Magnitude of osmotic pressure is independent with the nature of solvent.

- Berkley Hartley's method and Funnel experiment (π = hdg) are used to determine osmotic pressure.

- Ostwalds process is used to determine elevation in boiling point.

- Camphor is the best solvent for determination of molar mass of solute by using depression in freezing point since its K_f is very high.

BEGINNER'S BOX-3

1. An example of colligative property

(1) freezing point   (2) boiling point   (3) vapour pressure   (4) osmotic pressure

2. The freezing point order of the solution of glucose is

(1) 10% > 3% > 2% > 1%   (2) 1% > 2%> 3%> 10%

(3) 1% > 3% > 10% > 2%   (4) 10% > 1% > 3% > 2%

3. In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It result in reducing

(1) viscoity   (2) specific heat   (3) freezing point   (4) boiling point

4. Calculate the molal depression constant of a solvent, which has freezing point 16.6 °C and latent heat of fusion 180.75 Jg^{-1}

(a) 2.68   (2) 3.86   (3) 4.68   (4) 2.86

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

(1) 4 atm   (2) 2 atm   (3) 8 atm   (4) 1 atm

3.8 ABNORMAL COLLIGATIVE PROPERTIES

• It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.

• **Van't hoff factor (i)** : Tells about relationship between normal colligative properties and abnormal colligative properties.

• $i = \dfrac{\text{number of particles after dissociation or association}}{\text{number of particles before dissociation or association}} = \dfrac{\text{observed colligative properties}}{\text{calculated colligative properties}}$

$= \dfrac{\text{calculated molecular mass}}{\text{observed molecular mass}}$

• If i = 1 Neither dissociation nor association ; Ex. glucose, urea, sugar

• if i > 1 Dissociation will occur ; Ex. NaCl, KCl, $BaCl_2$

• if i < 1 Association will occur ; Ex. CH_3COOH, PhCOOH in benzene

CASE I :

DISSOCIATION OF SOLUTE : Molecules of electrolytes undergo ionization or dissociation in polar solvents to give two or more particles in solution. This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher. As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.

Number of solute particles in solution increses.

• observed / experimental C.P. > calculated C.P. (normal)

• observed /experimental molecular weight of solute < calculated (normal) moleclar weight of solute

$$\therefore \ C.P. \propto \dfrac{1}{\text{molecular weight of solute}}$$

• Calculation of 'i' : Let solute be A_xB_y (electrolyte)

$$A_xB_y \rightarrow xA^{y+} + yB^{x-} \ ; \qquad x + y = n \text{ (total number of ions)}$$
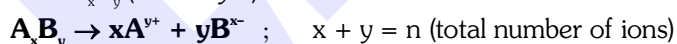
Initially   1 mol   0   0

After dissociation   (1−α)   xα   yα

Total number of solute particles = 1−α + xα + yα

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

$$= (1 - \alpha + n\alpha)\text{mol}$$

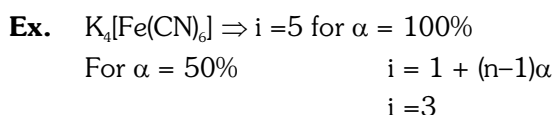Observed colligative property is proportional to observed number of solute particles (1−α + nα)

$$i = \dfrac{\text{number of particles after dissociation}}{\text{number of particles before dissociation}} = \dfrac{1 - \alpha + n\alpha}{1}$$

$$\boxed{i = 1 + (n-1)\alpha}$$

where α is the degree of dissociation

• For strong electrolytes

if   α=1 or 100% ⇒ then $\boxed{i = n}$

Ex.   NaCl ⇒ i =2;   α = 100%

K_2SO_4 ⇒ i = 3   α = 100%

Ex. $K_4[Fe(CN)_6]$ ⇒ i =5 for α = 100%

For α = 50%   i = 1 + (n−1)α

i =3

CASE II :

ASSOCIATION OF SOLUTE : The formation of a bigger molecule by the union of two, three or more solute molecules is called association. As a result, the total number of particles in solution becomes less than the number of molecules initially dissolved in the solution and hence the colligative properties will have lower value. As the molar mass of solute is inversely proportional to the colligative properties, so the molar mass of solute will be greater than theoretical value.

Number of solute particles in solution decreases.

• Observed /experimental C.P. < calculated C.P.

• Observed / experimental molecular weight of solute > normal molecular weight of solute

$\therefore$ C.P. $\propto \dfrac{1}{\text{Molecular weight of solute}}$; i < 1 for association.

• Calculation of i

$$\text{nA} \longrightarrow [\text{A}]_n$$

Initially   1   0

After association $(1-\alpha)$ $\dfrac{\alpha}{n}$

Total number of solute particles = $\left(1 - \alpha + \dfrac{\alpha}{n}\right)$ mol

Observed C.P. $\propto$ observed number of solute particles $\left(1 - \alpha + \dfrac{\alpha}{n}\right)$
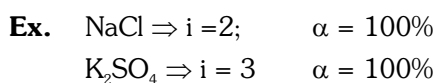
Van't hoff factor (i) = $\dfrac{\text{number of particles after association}}{\text{number of particle before association}}$; $i = \dfrac{1 - \alpha + \dfrac{\alpha}{n}}{1}$

$$\boxed{i = 1 - \alpha + \dfrac{\alpha}{n}}$$

α = degree of association

n = number of solute particles which are associated.

• If α = 100% or 1 or α is not specified $\boxed{i = \dfrac{1}{n}}$

──────────────── **Illustrations** ────────────────

Illustraion 22. A 5% solution of anhydrous $CaCl_2$ at 0^0C developed 15 atm osmotic pressure. What is the degree of dissociation of $CaCl_2$?

Solution. 5 g. of $CaCl_2$ are present in 100 mL, so 111 g (M_W of $CaCl_2$) will be present in

$\dfrac{100 \times 111}{5 \times 1000} = 2.22$ L

Now $\pi V = ST$ { $\because$ n = 1}   or $\pi = \dfrac{0.082 \times 273}{2.22} = \dfrac{22.47}{2.22} = 10.09$ atm

We know that Van't Hoff factor $i = \dfrac{\text{observed colligative property}}{\text{Normal colligative property}} = \dfrac{15}{10.09}$

and $\alpha = \dfrac{i-1}{n-1}$ or $\alpha = \dfrac{\dfrac{15}{10.09} - 1}{3 - 1} = \dfrac{4.91}{10.09 \times 2} = 0.2433$ or 24.33%

Illustraion 23. Calculate the osmotic pressure of 20% (wt/Vol.) anhydrous $CaCl_2$ solution at 0℃ assuming 100% ionisation.

Solution

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$$

Before dissociation 1   0   0

After dissociation $1 - \alpha$ α 2α

Given, w = 20 g, V = 100 mL, T = 273 K,

mol, wt. of $CaCl_2$ = 111
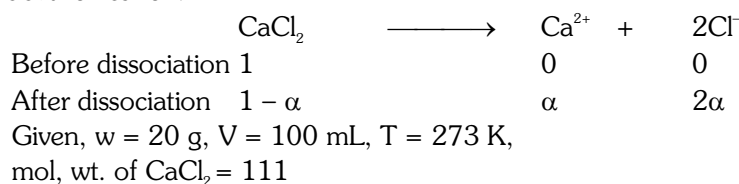
$$\pi_{Normal} = \frac{w}{mV} \times S \times T = \frac{20 \times 1000 \times 0.0821 \times 273}{111 \times 100} = 40.38 \text{ atm.}$$

Now, $i = \dfrac{1+2\alpha}{1} = 1 + 2 = 3 \; (\because \alpha = 1)$

$$\pi_{exp} = i \times \pi_{Normal}$$

$\therefore$ $\pi_{exp} = 40.38 \times 3 = 121.14 \text{ atm}$

BEGINNER'S BOX-4

1. Calculate the percentage degree of dissociation of an electrolyte AB_2(normal molar mass = 164) in H_2O if observed molar mass is 65.6

(1) 50%   (2) 25%   (3) 75%   (4) None

2. Which of the following solution will have highest freezing point

(1) 1M urea   (2) 1M Na_2SO_4 (3) 1M NaCl   (4) 1M $Al_2(SO_4)_3$

3. A 1.17% solution of NaCl is isotonic with 7.2% solution of glucose calculate the value of i of NaCl

(1) 1   (2) 2   (3) 3   (4) 4

4. Van't hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution)

(1) 1.6   (2) 2.6   (3) 3.6   (4) 4.6

ANSWER'S KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	3	3	1	3	3	2	4	1	2	1

BEGINNER'S BOX-2	Que.	1	2	3	4	5
	Ans.	1	2	3	1	1

BEGINNER'S BOX-3	Que.	1	2	3	4	5
	Ans.	4	2	3	2	3

BEGINNER'S BOX-4	Que.	1	2	3	4
	Ans.	3	1	2	2