Solutions And Colligative Properties

1. INTRODUCTION

A solution is a homogeneous mixture of two or more substances which are chemically non-reacting. We come across many types of solutions in our daily life. e.g., solid-liquid, liquid-liquid, gas-gas. In this chapter we will learn several properties of solutions and their applications.

Solution : A homogeneous mixture of two or more substances is known as solution.

Solute : The substance present in smaller amount in a solution is called solute.

Solvent : The substance present in larger amount in a solution is called solvent.

Binary solutions : *Those solutions which contain two components are called binary solutions,* e.g., salt solution, benzene and toluene.

Ternary solutions : *Those solutions which contain three components are called ternary solutions,* e.g., ethanol + water + acetic acid.

Aqueous solution : *When solute is dissolved in water, it is called aqueous solution,* e.g., sugar solution, ethanol in water.

Non-aqueous solution : *When solute is dissolved in solvent other than water, it is called non-aqueous solution,* e.g., iodine dissolved in alcohol (Tincture of iodine).

Miscible liquids : Those liquids which mix with each other and form homogeneous mixture are called miscible liquids.

Immiscible liquids : Those liquids which do not mix with each other are called immiscible liquids.

Table 1

Alloys : Solid solutions of the two or more metals are called alloys. One of them can be a non-metal also.

2. TYPES OF SOLUTIONS :

			- •			
S.No.	Solute	Solvent	Types of Solutions	Examples		
	Solid Solutions					
1	Solid	Solid	Solid in solid	All alloys like brass, bronze, an alloy of copper and gold, etc.		
2	Liquid	Solid	Liquid in solid	Amalgam of mercury with Na, CuSO ₄ .5H ₂ O. FeSO ₄ .7H ₂ O		
3	Gas	Solid	Gas in solid	Solution of H_2 in Pd, dissolved gases in minerals.		
			Liquid	d Solutions		
4	Solid	Liquid	Solid in liquid	Sugar solution, salt solution, I_2 in CCl ₄		
5	Liquid	Liquid	Liquid in liquid	Benzene in toluene, alcohol in water.		
6	Gas	Liquid	Gas in liquid	CO ₂ in water, NH ₃ in water etc.		
	Gaseous Solutions					

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7	Solid	Gas	Solid in gas	lodine vapours in air, camphor vapours in N_2 .
8	Liquid	Gas	Liquid in gas	Water vapours in air, $CHCI_3$ vapours in N_2 .
9	Gas	Gas	Gas in gas	Air (O ₂ + N ₂)

The concentration of a solution can be expressed by different concentration terms which are described as follows.

Section (A) : Concentration terms

3. **CONCENTRATION TERMS:**

% Concentration

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

weight of solute (g)

% w/w =
$$^{\text{weight of solution }(g)} \times 100$$

Ex. 10% w/w urea solution = 10 g of urea is present in 100 g of solution.

= 10 g of urea is present in 90 g of water.

Mass by volume percentage (% w/v) : It is defined as mass of solute dissolved per 100 ml of solution. It is commonly used in medicine and pharmacy.

% wt/vol. (w/v)

% w/v = wt. of solute/100 mL of solution

$$% w/v = {gram of solutes} {volume of solution in mL} \times 100$$

Ex. 10% (w/v) urea solution = 10 g of urea is present in 100 mL of solution.

But not 10 g of urea present in 90 ml of water

for dilute solution : volume solution = volume solvent.

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

volume of solute

 $% v/v = volume of solution \times 100$

Strength of solution in g/L : Weight of solute (in gram) per litre (1000 mL) of solution.

10% (w/v) sucrose solution, then specify its concentration in g/L Ex.

100 mL 10 g
∴ 1000 mL
$$\frac{10}{100} \times 1000$$
 = 100 g/L

Example-1

If we have 6% w/w urea solution with density 1.060 g/mL, then calculate its strength in g/L? Solution. 6 g urea is present in 100 g solution.

> 100 6 g in ^{1.060} mL 100 $1.060 \text{ mL} \longrightarrow 6 \text{ g}.$ 6 $1000 \text{ mL} = \frac{100}{100} \times 1.060 \times 1000 = 10.6 \times 6 = 63.6$

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

n = No. of moles of solute ; N = No. of moles of solvent ; V = volume of solution Let

$$\begin{array}{l} \prod_{M=1}^{n} \frac{(M)}{(n-L)} = \left(\frac{W}{M}\right)_{X} \frac{1000}{\sqrt{((n-mL)}} \\ \text{no. of moles of solute = molarity volume (in L)} \\ \text{no. of moles of solute = molarity volume (in mL)} \end{array} \\ \hline M = \sqrt{(n-L)} \left(\frac{W}{M}\right)_{X} \frac{1000}{\sqrt{((n-mL)}} \\ \text{If } V_1 \text{ mL of } C_1 \text{ molarity solution is mixed with } V_2 \text{ mL of } C_2 \text{ molarity} \\ \text{Solution (same substance or solute)} \\ \hline \text{EMBED Equation.DSMT4 } C_r (V_1+V_2) = C_1V_1 + C_2V_2 \\ \hline \text{Molality not depends on temperature.} \\ \hline \text{Soluced Examples} \\ \hline \text{Example-2} \\ \text{If } 20 \text{ ml of } 0.5 \text{ M } \text{Na}_{S}\text{O}_4 \text{ is mixed with } 50 \text{ ml of } 0.2 \text{ M } \text{H}_2\text{SO}_4 \& 30 \text{ ml of } 0.4 \text{ M } \text{Al}_2(\text{SO}_4)_3 \\ \text{solution.} \\ \hline \text{Molarity} = \frac{100}{100 \text{ moles of Na}_2\text{SO}_4} \Rightarrow 20 \text{ m. moles of Na^+} \\ \hline \left(\frac{20}{(0)} + \frac{20}{(N^+)^2} + \frac{100}{100} = 0.2 \text{ M} \\ (\text{ii)} \quad (\text{H}^+) = 7 \\ 10 \text{ m. moles } \text{H}^+ 0 \\ \left(\frac{20}{(10)} + \frac{100}{100} = 0.2 \text{ M} \\ (\text{iii)} \quad (\text{SO}_4^-) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.2 \text{ M} \\ (\text{iv)} \quad (\text{A}^{34}) = \frac{100}{100} = 0.24 \text{ M} \\ \text{Example-3} \end{aligned}$$
(a) Derive a relationship between molality & molarity of a solution in which w g of solute of molar mass M g'mol is dissolved in W g solvent & density of resulting solution = 'd' g'mt. \\ (\text{b) Calcutate molality} - 12 \text{ M H_SOA solution ? If its } p = 1.4 \text{ g/mL} \\ \text{Solution.} \\ \text{(a) Say 1 L solution taken,} \\ \text{mass of solute = (molarity)} \\ \frac{12

Mole-fraction (x) : It is the ratio of number of moles of a particular component to the total number of

n_A

moles of all the components. e.g., mole-fraction of component A, $x_A = {n_A + n_B}$, where n_A is the number of moles of component 'A' and n_B is the number of moles of component 'B'.

For binary mixture.

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		moles	of	solute	n
X _{solute} =	total	moles	in	solutions	$=\overline{n+N}$
X _{solute} +	X _{Solv}	_{ent} = 1			

 $\frac{\text{moles of solvent}}{X_{\text{Solvent}}=} \frac{\text{moles in solutions}}{\text{Total moles in solutions}} = \frac{N}{n+N}$

Parts per million (ppm) : The number of parts of solute present in 1 million parts of solution are called *its ppm.* When a solute is present in small quantities (very minute amounts), it is easier to express the concentration in parts per million.

;

(a) ppm (w/w) = $\frac{\text{wt. of solute (in g)}}{\text{wt. of solution (in g)}} \times 10^{6}$ (b) moles of solute

ppm (w/v) = $\frac{\text{wt. of solute (in g)}}{\text{vol. of solution (in mL)}} \times 10^{6}$

(c) ppm (moles/moles) = $\frac{\text{moles of solution}}{\text{moles}} \times 10^6$

Table : 2

Name	Units	Advantage		Disadvantages
Molarity (M)	Mole/litre	Useful in stoichiometry; volume	measure by	Temperature-dependent; must know density to find solvent mass
Mole fraction (x)	None	Temperature-independent; special applications	useful ir	Measure by mass ; must know density to convert to molarity
Mass %	%	Temperature-independent; small amounts	useful fo	r Measure by mass ; must know density to convert to molarity
Molality (m)	Mole/ kg	Temperature-independent special applications	useful ir	Measure by mass ; must know density to convert to molarity

Note : All volume related concentration terms are temperature dependent.

-Solved Examples -

Example-4 If we have 10 molal urea solution, Calculate mole fraction of urea in this solution & also calculate % w/w of urea (MW = 60).

Solution. 10 moles urea in 1000 g of water

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 $\frac{1}{100} = 2$ moles of CaCO₃ in 10³ liters of water. (density =1g/mL)

So molarity =
$$\frac{2}{10^3} = 2 \times 10^{-3} \text{ M}.$$

Section (B) : Vapour Pressure

4. VAPOUR PRESSURE OF A PURE LIQUID OR PURE SOLID

(1) Vapour pressure of a pure liquid : The pressure exerted by the vapours over the liquid surface at equilibrium is called vapour pressure. It increases with the increase in temperature.

Note: Volatile solids (like lodine) also evaporate and have a vapour pressure at any given temperature, just like liquids.

(2) Vapour pressure of solution : The pressure exerted by the vapours of solvent 'A' and solute 'B' in equilibrium with the liquid phase is called the vapour pressure of solution.

(3) Definition of vapour pressure : The partial pressure of vapours in equilibrium with pure solid or pure liquid at a given temperature.

At equilibrium the rate of evaporation = rate of condensation

e.g.
$$H_2O(I) \stackrel{eq}{\longrightarrow} H_2O(g)$$

 $K_p = {}^{p_{H_2O,g}^{eq}}$

Hence V.P is equilibrium constant (K_P) of the reaction, liquid $\overrightarrow{}$ vapours.

(4) Since vapour pressure is an equilibrium constant. so it's value is dependent only on temperature.

Factors affecting vapour pressure of liquid

(a) Nature of liquid: The value of a liquid's vapour pressure depends on the magnitude of the intermolecular forces in the liquid. The smaller the intermolecular forces, higher the vapour pressure becuause loosely held molecules escape more easily into vapour phase.

(b) Temperature of the given liquid : At higher temperature, more molecules from the liquid have enough KE to escape from the surface of the liquid. That will increase the saturated vapour pressure.

Vapourization (liquid to vapour) is always endothermic. It needs heat to convert the liquid into the vapour. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means that increasing the temperature increases the amount of vapour present, and so increases the saturated vapour pressure.

The dependence of vapour pressure with temperature is given by Clausius-Clapeyron equation

$$\ln \left(\frac{p_2}{p_1}\right) = -\frac{\Delta H v}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

 $\Gamma_2 = \Gamma_1$, where $\Delta H_v =$ molar enthalpy of vapourisation of the given liquid,

 p_2 = vapour pressure of the liquid at T_2 and p_1 = vapour pressure of the liquid at T_1 .

(c) Vapour pressure of a liquid does not depend on :

- (i) the amount of liquid taken
- (ii) surface area of the liquid
- (iii) volume or shape of the container

(5) Partial vapour pressure : The pressure of vapours of a component 'A' over a solution of 'A' and 'B' is called partial vapour pressure of component A. It is denoted by p_A.

(6) Partial pressure of vapours: If vapours of a liquid are present in a gaseous mixture then,

Pressure of vapours

Partial pressure of vapours of the liquid = Total pressure

Saturation: A gas or gaseous mixture is said to be saturated with the vapours of a liquid if the partial pressure of the liquid vapours is equal to its (saturated) vapour pressure.

(7) (a) Saturated (Equillibrium) Vapour pressure of water, at a given temprature, is called aqueous tension.

The value of aqueous tension is different at different temprature.

Partial pressure of water vapour at given temperature

Vapour pressure of water at the same temperature (b) Relative Humidity (R.H.) = × 100%

(8) Saturated vapour pressure and boiling point:

A liquid boils when its saturated vapour pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapour to form throughout the liquid. If the external pressure is higher than the saturated vapour pressure, these bubbles are prevented from forming, and we just get evaporation at the surface of the liquid.

* $P_{ext} > P_{sat} \Rightarrow$ evaporation

* $P_{ext} = P_{sat} \Rightarrow Boiling$

If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapour pressure becomes equal to 1 atmosphere. This happens with water when the temperature reaches 100°C. But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C.

(a) Boiling point : The boiling point is the temperature at which the vapour pressure of a liquid is equal to the external pressure.

(b) At boiling temperature, vapour pressure of the pure liquid i.e. $P^{o} = P_{ext}$

(c) At normal boiling point, vapour pressure of the pure liquid i.e. $P^0 = 1$ atm

(9) Saturated vapour pressure and solids: Sublimation

Solids can also loose particles from their surface to form a vapour, except that in this case we call the effect sublimation rather than evaporation. Sublimation is the direct change from solid to vapour without going through the liquid stage.

The forces of attraction in many solids are too high to allow much loss of particles from the surface. However, there are some solids which easily form vapours.

Naphthalene (used in "moth balls") has guite a strong smell. Molecules must be breaking away from the surface as a vapour, because otherwise we wouldn't be able to smell it.

Solid carbon dioxide never forms a liquid at atmospheric pressure and always converts directly from solid to vapour. That's why it is known as dry ice.

(10) If partial pressure of vapours of a liquid is increased beyond the saturated (equillibrium) vapour pressure value (Pº), its vapours begin to condense till their partial pressure becomes equal to the saturated vapur pressure.

(11) If the partial pressure of vapour is less than v.p. of liquid, the liquid (if present) will vaporize till (a) its v.p. is attained or (b) the liquid completely gets vaporized

(12) If a volatile solid/ liquid is brought in contact with a gas (or vaccuum), vapours of that solid/ liquid occupy the gas phase till the gas phase becomes saturated with that solid /liquid vapours.

Solved Examples -

Example-6 :

The vapor pressure of water at 80° C is 355 torr. A 100 ml vessel contained water-saturated oxygen at 80° C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 ml, vessel at the same temperature. What were the partial pressures of oxygen and of water vapor, what was the total pressure in the final equilibrated state ? Neglect the volume of any water which might condense.

 P_{O_2} = 810 mm Hg, P_{H_2O} = 355 mm Hg , P_{total} = 1165 mm Hg Ans.

Solution :

In 100 ml vessel which contained water - saturated oxygen, the pressure of O_2 gas = 760 - 355 = 405 torr when the contents of this vessel were pumped into 50 ml vessel, at the same

temperature, the pressure of oxygen gets doubled i.e. $P_{O_2} = 810$ torr. But pressure of water vapour will remain constant, as some vapour in this 50 ml vessel, gets

condensed.

So. $P_{H_2O} = 355$ torr & Total pressure = 810 + 355 = 1165 torr.

Section (C) : Solutions of Solid and Gases in Liquids

5. SATURATED SOLUTION

A solution in which no more solute can be dissolved at the same temperature is called saturated solution. Unsaturated solution : It is a solution in which more amount of solute can be dissolved at the same temperature.

Supersaturated solution : It is a solution which contains more mass of the dissolved solute than the saturated solution at the same temperature and pressure. It should be prepared in a dust-free vessel and at a higher temperature. It is metastable. Mechanical stress, such as shaking or addition of solute, causes deposition of solute.

Solubility : Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent (generally 100 g of solvent) at a specified temperature to form a saturated solution.

Solubility of one substance into another depends on

(i) nature of the solute and solvent. (ii) Temperature (iii) Pressure

5.1 Solubility of a solid in a liquid :

Like dissolves like: Polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents. Sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not.

Dissolution : When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution.

Crystallisation : Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation.

At equilibrium, rate of dissolution is equal to rate of crystallisation. At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Such a solution is said to be saturated with the given solute.

Solute + Solvent - Solution

Effect of temperature on solubility of a solid in a liquid 5.2

Consider the equilibrium: Solute + Solvent Solution. By Le Chatelier's Principle:

If above process is exothermic i.e. $\Delta H < 0$, then as T increases, solubility decreases.

If above process is endothermic i.e. $\Delta H > 0$, then as T increases, solubility increases.

5.3 Effect of pressure on solubility of a solid in a liquid (no effect)

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

6. Solubility of gases in liquids :

Factors Affecting Solubility of Gas In Liquid : 6.1

(ii) Nature of liquid (iii) Temperature (iv) Pressure (i) Nature of gas

6.2 Henry's Law (effect of pressure on solubility of gases in liquids) :

Statement : The solubility of a gas in a liquid at a given temperature is directly proportional to its partial pressure at which it is dissolved

Let x = Mole fraction of unreacted gas in solution at a given temperature as a measure of its solubility.

p = Partial pressure of gas in equilibrium with the solution.

erature.

(IV) Higher the value of $\mathbf{k}_{\rm H}$ of a gas, lower will be its solubility. Since, x = 11

Plot of p Vs x is a straight line passing through the origin with slope equal to K_{H} .



Plot of p Vs x for solution of HCl in cyclohexane.

Note : If a mixture of gases is brought in contact with solvent each constituent gas dissolves in proportion to its partial pressure. It means Henry's law applies to each gas independent of the pressure of other gas.

Solved Examples

Example-7: Henry's law constant for O₂ dissolved in water is 4.34×10^4 atm at 25°C. If the partial pressure of oxygen in air is 0.4 atm. Calculate the concentration (M) of dissolved oxygen in water in equilibrium with air at 25°C :

Solution :

equilibrium with air at 25°C : Given $K_H = 4.34 \times 10^4$ atm

 $p_{O_2} = 0.4 \text{ atm}$ acc. to Henry's Law $p = K_H X$ $X_{O_2} = \frac{0.4}{4.34 \times 10^4} = 9.2 \times 10^{-6}$ Moles of water $\binom{n_{H_2O}}{18} = 55.8 \text{ mol}$

n_{O2}

$$X_{O_2} = \overline{n_{O_2} + n_{H_2O}}$$

Since n_{O_2} is very small in comparison to n_{H_2O}

$$X_{O_2} = \frac{n_{O_2}}{n_{H_2O}}$$

or $X_{O_2} \times n_{H_2O} = n_{O_2}$

So $n_{O_2} = 9.2 \times 10^{-6} \times 55.55 = 5.11 \times 10^{-4} \text{ mol}$

So $M = 5.11 \times 10^{-4}$





Solution : $P_T = P_x + P_{H2O}$ $P_x = 1.5 - 0.5 = 1$ atm slope of graph = $K_H = 5 \times 10^3$ n_x n_{H_2O} $P_x = K_H$

$$1 = 5 \times 10^{3} \times \frac{n_{x}}{10}$$
$$n_{x} = \frac{1}{500} = 2 \times 10^{-3}$$

The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the Example-9 solution contains 5.00 × 10^{-2} g of ethane, then what shall be the partial pressure of the gas ? 0.762 bar

- 6.4 Effect of temperature : Solubility of gases in liquids decreases with rise in temperature. Explanation: When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's principle. As dissolution of gases in liquids is an exothermic process, the solubility should decrease with increase of temperature.
- Note : K_H values for both N₂ and O₂ increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature. It is due to this reason that aquatic spcies are more comfortable in cold water rather than warm water.

6.5 Applications of Henry's law :

Ans.

It has several applications in biological and industrial phenomena.

(i) To increase the solubility of CO₂ in soft drinks and soda water the bottle is sealed under high pressure. (ii) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmosphere gases in blood. When the divers come towards surface, the pressure is gradually decreased. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as **bends**, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

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

6.6 Limitation of Henry's law :

Henry's law is valid only under following condition.

- (i) The pressure of gas is not too high. (ii) The temperature is not too low.
- (iii) The gas should not undergo any chemical reaction with the solvent.
- (iv) The gas should not undergo dissociation in solution.

Section (D) : Raoult's law (for volatile Liq. Mixture)

VOLATILE SOLVENT Liq. solution

7. SOLUTIONS CONTAINING VOLATILE SOLUTE $\int Liq$. solution

Statement of Raoult's law (for volatile liq. mixture): In solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction.

 $p_A \propto x_A \qquad => \qquad p_A = x_A P_A^o$

pA = Partial vapour pressure of component A

 x_A = Mole fraction of component 'A' in solution.

PA° = Vapour pressure of pure component 'A' at given temperature

Derivation of total pressure over solution using Raoult's law and Dalton's law:

Let A, B be to two volatite liquids in a closed container as shown

$$p_A = x_A P_A^{C}$$

Similarly, for liquid B we have,

 $p_B = x_B P_B^0$

Total pressure over the solution PT, according to Dalton's law is

$$P_{T} = p_{A} + p_{B} = x_{A}P_{A}^{0} + x_{B}P_{B}^{0}$$



Determining composition of vapour phase:

Let, y_A = mole fraction of A in vapour phase above the solution and y_B = mole fraction of B in vapour phase above the solution

Now, we have, $p_A = y_A P_T$ Dalton's law of partial pressure for a gaseous mixture

Thus,

 $p_A = y_A P_T = x_A P_A^o$

Also.

$$p_{\rm B} = y_{\rm B} P_{\rm T} = x_{\rm B} P_{\rm B}^{\rm o}$$

$$x_{A} + x_{B} = 1 = \frac{\frac{y_{A}P_{T}}{P_{A}^{0}} + \frac{y_{b}P_{T}}{P_{B}^{0}}}{P_{B}^{0}}; \qquad \text{Thus,} \quad \frac{1}{P_{T}} = \frac{\frac{y_{A}}{P_{A}^{0}} + \frac{y_{B}}{P_{B}^{0}}}{P_{B}^{0}}$$

Graphical Representation of Raoult's Law:

$$p_{A} = x_{A}P_{A}^{0} \qquad \& \qquad p_{B} = x_{B}P_{B}^{0}$$

$$P_{T} = x_{A}P_{A}^{0} + x_{B}P_{B}^{0}$$

$$P_{T} = (P_{A}^{0} - P_{B}^{0}) x_{A} + P_{B}^{0}$$

$$P_{T} = (P_{B}^{0} - P_{A}^{0}) x_{B} + P_{A}^{0}$$

This represents equation of straight line. $P_T v.s. x$

Note: If $P_{A^{\circ}} > P_{B^{\circ}}$, A is more volatile than B. B.P. of A < B.P. of B.

Solved Examples.

Example-10	1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mol. Octane (V.P. = 31 mm of Hg), from
	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 = $X_B = 4/5$



$$P_{S} = X_{A}P_{A}^{0} + X_{B}P_{B}^{0} = \frac{1}{5} \times 92 + \frac{4}{5} \times 31 = 43.2 \text{ mm og Hg}$$

Example-11

An equimolar mix of benzene & toluene is prepared the total V.P. of this mix as a function of mole fraction of benzene is found to be

 $P_T = 200 + 400 X_{ben}$.

(i) Calculate composition of vapours of this mix. [Assume that the no. of moles going into vapour phase is negligible in comparison to no. of moles present in liq. phase].

 $P^{0}_{Benzene}$ = 600 mm of Hg $P^{0}_{Toluene}$ = 200 mm of Hg

(ii) If the vapour above liq in part A are collected & are condensed into a new liquid, calculate composition of vapours of this new liq.



This process is known as fractional distillation.

7.1 Limitations of Raoult's Law: Raoult's Law only works for ideal solutions. Very dilute solutions obey Raoult's Law to a reasonable approximation.

Section (E) : Ideal & nonideal solutions

7.2 Ideal Solutions : Those solutions which obey Raoult's law over the entire range of conc. are called ideal solutions. When the forces of attraction between A—A, B—B is similar to A—B, then A and B will form ideal solution.

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Thatmeans that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Properties of ideal solution :

(i) Raoult's law is obeyed

(ii) $\Delta H_{mix} = 0$, i.e., there should not be enthalpy change when components of ideal solutions are mixed.

(iii) $\Delta V_{mix} = 0$, (1L + 1L = 2L) i.e., there should not be change in volume on mixing.

e.g.; n-hexane and n-heptane;

Ethyl bromide and ethyl iodide;

Benzene and toluene;

Chlorobenzene and bromobenzene

7.3 Non-Ideal Solutions :

Those solutions which do not obey Raoult's over the entire range of concentration are called non-ideal solutions.

When the forces of attraction between A—A, B—B is different from A—B then 'A' and 'B' form non-ideal solutions. For these solutions :

(i) Raoult's law is not obeyed. (ii) $\Delta H_{mix} \neq 0$; (iii) $\Delta V_{mix} \neq 0$.

Types of Non-Ideal Solutions : Non-ideal solution can be two types.

O Non ideal solutions showing positive deviation

O Non ideal solutions showing negative deviation

(A) Non-Ideal Solutions Showing Positive Deviation From Raoult's Law :

(i) In this case, partial pressure of each component A and B is higher than that calculated from Raoult's law, and hence total pressure over the solution is also higher than if the solution were ideal, as shown in figure.

(ii) Boiling point of such a solution is relatively lower than the boiling points of both A and B.



Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution **Examples:** water and ethanol, chloroform and water, ethanol and CCl₄, methanol and chloroform, benzene and methanol, acetic acid and toluene, acetone and ethanol, methanol and H_2O , C_2H_5OH + cyclohexane.

Explanation: The fact that the vapour pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids. That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

You can see this when you mix the liquids. Less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic.

(B) Non-Ideal Solutions Showing Negative Deviation From Raoult's Law :

(i) In this case, partial pressure of each component A and B is lower than that calculated from Raoult's law, and hence total pressure over the solution is also lower than if the solution were ideal, as shown in figure.

(ii) Boiling point of such a solution is relatively higher than the boiling points of both A and B.



Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution. **Examples:** chloroform and acetone, chloroform and methyl acetate, H₂O and HCI, H₂O and HNO₃, acetic

acid and pyridine, Phenol & Aniline.

Explanation: These are cases where the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids. You can recognise this happening because heat is evolved when you mix the liquids-more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones.

Table 3

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Positive deviation solution

(i)
$$P_T > (X_A P_A^0 + X_B P_B^0)$$
 (i

(ii) The inter molecular interaction is weaker as interaction found in any one of the pure components.

A.....A molecular interaction A.....B B.....B

(iii) There is increase in volume on mixing and absorption of heat.

$$\label{eq:shared_mix} \begin{split} \Delta V_{mix} &= positive & \Delta H_{mix} = positive \\ \Delta S_{mix} &= +ive & \Delta G_{mix} = -ive \end{split}$$

Ex. $H_2O + CH_3OH$, $C_2H_5OH + Hexane$ $C_2H_5OH + Cyclohexane$, $CHCI_3 + CCI_4$

Negative deviation solution

(i)
$$P_T < X_A P_A^0 + X_B P_B^0$$

(ii) The inter molecular interaction is more than the interaction found in any of the pure components

A.....B molecular interaction A.....A is more than B.....B

(iii) There is decrease in volume on mixing and evolution of heat takes place on mixing

	$\Delta V_{mix} = -ve$	$\Delta H_{mix} = -ive$
	$\Delta S_{mix} = +ive$	$\Delta G_{mix} = -ive$
Ex.	H₂O + HCOOH,	H ₂ O + CH ₃ COOH
	$H_2O + HNO_3$	CHCl ₃ + CH ₃ OCH ₃

(8) Azeotropic Mixtures : Very large deviations from ideality lead to a special class of mixtures known as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

Azeotropes : Liquid mixtures which distill over without changes in composition are called constant boiling mixtures or Azeotropes or Azeotropic mixtures.

A boiling liquid mixture at the azeotropic composition produces a vapour of exactly the same composition, and the liquid does not change its composition as it evaporates. Two types of azeotropes are known.

- **Minimum Boiling Azeotropes :** Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes which boil at temperature lower than boiling point of its components 'A' and 'B', e.g., water and benzene, chloroform and methanol.
- Maximum Boiling Azeotropes : Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which boil at temperature higher than the boiling point of its components A and B respectively, e.g., a mixture of HCl and H₂O containing 20.2% HCl by weight boils at 108.5°C higher than either pure HCl (– 85°C) or water (100°C).

Section (F) : Colligative properties & constitutional properties :

• Constitutional Properties :

Properties which are dependent on nature of particles are constitutional properties like electrical conductance.

• Colligative properties :

The properties of the solution which are dependent only on the total no. of particles relative to solvent/solution or total concentration of particles in the solution and are not dependent on the nature of particle i.e. shape, size, neutral /charge etc. of the particles.

There are 4 colligative properties of solution.

 ΔP

1. Relative lowering in vapour pressere

3. Depression in freezing pt. (ΔT_f)

2. Elevation in boiling point (ΔT_b)

SOLUTIONS & COLLIGATIVE PROPERITES

4. Osmotic pressure (π)

9.1 ABNORMAL COLLIGATIVE PROPERTIES :

Vant–Hoff correction :

• For electrolytic solutes the number of particles would be different from the number of particles actually added, due to dissociation or association of solute.

• The actual extent of dissociation/association can be expressed with a correction factor known as vant Haff factor (*i*).

moles of particles in solution after dissociation/association

Vant–Hoff factor : *i* = moles of solute dissolved

• If solute gets associated or dissociated in solution then experimental / observed / actual value of colligative property will be different from theoretically predicted value so it is also known as **abnormal** colligative property.

• This abnormality can be calculated in terms of Vant-Hoff factor.

exp/observed/actual/abnormal value of colligative property

Theoretical value of colligative property

i =

exp./observed no. of particles or concentration (Theoretical molar mass of substance)

_ Theoretical no. of particles or concentration _ (Experimental molar mass of the substance)

- i > 1 dissociation
- i < 1 association

Case - I : Electrolyte dissociates

. :0 5 (1-- **f** - l' - -Case - II : Electrolyte associates Relation between degree of association 2 & i. nA EMBED Equation.DSMT4 the An. t = 0С 0 of C (1-2) EMBED Equation.DSMT4 tea our Net concentration = C - CP + EMBED Equation.DSMT4= C [1 + EMBED Equation.DSMT4 2] i = 1 + EMBED Equation.DSMT4 2 if dimerise n = 2; trimerise n = 3; tetramerise n = 4. e.g. CH₃COOH 100% dimerise in benzene, i = EMBED Equation.DSMT4 ; $C_6H_5COOH 100\%$ dimerise in benzene, i = EMBED Equation DCMTA

SOLUTIONS & COLLIGATIVE PROPERITES



Lowering in Vapour pressure = $P^0 - P_S = \Delta P$ ΔP

Relative lowering in Vapour Pressure = $\overline{P^0}$

Raoult's law (For non-volatile solutes): The vapour pressure of a solution of a non-volatile solute is equal to the vapour pressure of the pure solvent at that temperature multiplied by its mole fraction.

OR Relative Lowering in Vapour Pressure = mole fraction of the non volatile solute in solution.

$$P_{S} = x_{solvent}P^{0} = (1 - x_{solute})P^{0}$$
$$RLVP = \frac{P^{0} - P_{s}}{P^{0}} = x_{Solute} = \frac{n}{n + N}$$

where n = number of moles of non-volatile solute and N = number of moles of solvent in the solution.

$$\frac{P^{0}}{P^{0}-P_{s}} = \frac{n+N}{n} = \frac{N}{1+n}$$

$$\frac{N}{n} = \frac{P^{0}-P_{s}}{P^{0}} = \frac{P_{s}}{-1} = \frac{P_{s}}{P^{0}-P_{s}}$$

$$\frac{P^{0}-P_{s}}{P_{s}} =$$

$$= x = x \times x = x \times x$$

= (molality) ×

where w and W = mass of non-volatile solute and volatile solvent respectively m and M = molar mass of non-volatile solute and volatile solvent respectively

If solute gets associated or dissociated; = that is = i x (molality) x action (H) + Elevation in bailing point

Section (H) : Elevation in boiling point

(iii) Elevation in Boiling point (ΔT_b)

- **Boiling point of a Liquid :** The temprature at which vapour pressure of a liquid becomes equal to the external pressure present at the surface of the liquid is called b.p of liquid at that pressure.
- Normal boiling point : The temperature at which boiling ocuurs when the external pressure is exactly 1 atm is called the normal boiling point of the liquid. (T_b).

 $H_2O(\ell)$ $H_2O(g)$ $\Delta H = +ve$ $K_p =$



Boiling pt of any solution :

• Since V.P. of solution is smaller then V.P. of pure solvent at any temperature hence to make it equal to Pext. we have to increase the temp. of solution by greater amount in comparision to pure solvent.

 $\Delta H_{vapour of solvent} = \Delta H_{vapour solution}$

As only solvent particles are going into vapours.

 $\Delta T_s > \Delta T$:.

Graphical :

• If solution are dilute then BE & CD can be approximated as straight lines.

;

 $\therefore \Delta ABE \& \Delta ACD$ will be similar.

; ∴ ΔT_bαΔP

Using Raoult's law :

or

ΔP =

		⇒	$\Delta T_b \; \alpha$	=		;	$\Delta T_{b} = K$	$f_{\rm b} \times {\rm molality}$
•	K⋼is de It is also K⋼ = ele	pendent o known evation in	on property as ebulliosc boiling poir	of solvent and k opic constant. nt of 1 molal solu	nown as molal i	elevation cor	nstant of	solvent
•	Units :		=	K kg mol ⁻¹				
	Using t ∴	thermody L _{Vap} – is	namics : latent heat	K _b = of vapourization	in cal/g or J/g			
		R = 2 ca K _b = K k	al mol ⁻¹ K ⁻¹ (ag mol ⁻¹	or 8.314 J mol ^{−1}	≺ −1. ;	$T_b = b.$	p. of liqu	id (in kelvin)
•	Also K _b	=		Here : ΔH_{va}	_⊮ = molar entł M ⇒	nalpy of vap mole wt. of :	orisation solvent	in cal/mole of J/mole
•	If solute	L _{vap} = e gets ass	sociated/dis	sociated :	ΔT _b = i × K	ь × molality		
Examp	le-12	Calculat	te K_b of wate	er if L _{vap} = 540 Ca	al/g T _b = 100° C			
Solutio	on.	K _b =	=	0.52 K kg mol ^{_1}				
Examp	<i>le-</i> 13	A soluti Assumir benzene	on of 122 g ng that solu e. given mol	g of benzoic ac te is dimerized to ar enthalpy of va	d in 1000 g o o the extent of p. of benzene =	f benzene s 80 percent (= 7.8 Kcal/mo	shows a (80ºC) ca ble.	b.p. elevation of 1.4°. alculate normal b.p. of
Solutio	on.	T _b – T _i =	:	× K _b	0.8			
	⇒	Kb						
		T _b — T _i =	= K _b × 0.4	(i)				
		K _b = Now from	m eq (i)	=> K _b = 1.4 = 0.4 × 2	- 20 × 10 ^{_6} T₀²		SO	$T_{b} = 418.33 \text{ K}$ ans.

Section (I) : Depression in freezing point

(iv) Depression in freezing pt (ΔT_f)

Freezing point : Temperature at which vapour pressure of solid becomes equal to v.p of liquid is called freezing point of liquid or melting point of solid.

H₂O(s) H₂O (g)

K_p = /eq. = vapour pressure of solid

for ice at $0^{\circ}C$ K_p = V_p of ice 4 mm of Hg.

∴ In =

- For dil. solutions BE & CD can be assumed to be straight lines.
 - \therefore using similar triangles
 - $\Delta T_f \alpha \Delta P$
 - $\therefore \qquad \Delta T_f = K_f . \text{ Molality}$
- K_f = molal depression constant = cryoscopic constant

K_f =

• for water
$$T_f = 273 \text{ K} \text{ \& } L_{Fusion} = 80 \text{ cal } / \text{ g}$$

=

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

Solved Examples

Example-14 Calculate the freezing point of a solution of a non-volatile solute in a unknown solvent of molar mass 30 g/mole having mole freezing of solvent equal to 0.8. Given that latent heat of fusion of solid solvent = 2.7 kcal mol⁻¹, freezing point of solvent = 27° C and R = 2cal mol⁻¹ k⁻¹.

Solution.	k _f = mole fraction o mole fraction o	= of water = of solute =	0.8 = 0.2	= 2.00 K kg mol ⁻¹
or	0.2 =	and	0.8 =	
:	= = =	:		
or	=			=
 	$\Delta T_f = F.P. of solutior$	= 1. = 10.3 3	= °C.	= 16.67

Ans. 10.33°C

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Example-15	A 0.01 mola	I solution of ammo	nia freezes at – (0.02ºC. C	Calculate the var	n't Hoff factor, i and the
Solution.	percentage Experimenta Theoretical	dissociation of amr al ∆T = 0.02º ∆T = 1.86 × 0.01 =	nonia in water. 0.0186º	=	1.86 deg molal ⁻¹	
	i = van't Ho	ff factor =	= 1.075			
	Degree of d	issociation , $\alpha =$	(v = no. of spe	cies form	ned on dissociat	ion)
		= = = 0.0 % dissociation	75 = 7.5.		Ans.	1.075, 7.5.
Example-16	Van't Hoff fa equal conce (1) b.p. : X <	actors of aqueous entrations in all thre < Y < Z	solutions of X, Y e cases)	, Z are 1 (2) f. p.	I.8, 0.8 and 2.5 Z < X < Y	. Hence, their (assume
Solution.	(3) osmotic As van't Hof Elevation in Depresion ir	pressure : X = Y = . ff factor increases F b.p. increases i.e., n f.p increases i.e.,	Z RLVP increases b.p. increases f.p decreases	(4) v. p. i.e., y < x < y > x >	: Y < X < Z V.P. decreases z z	y > x > z
Example-17	Osmotic pre A 0.001 mo depression complex, wr	essure increases olal solution of a c of 0.0054°C. Giver ite the ionisation na	so omplex reprsente K_f for H ₂ O = 1. ature and formula	y < x < ed as Pt(86 molal of comp	z. Ans. (2) NH ₃) ₄ Cl ₄ in wat lity ⁻¹ . Assuming llex.	er had a freezing point 100% ionisation of the
Solution.	Let n atoms	of CI be the acting	as ligand. Then f	formula c	of complex and i	ts ionisation is :
Example-18 Solution.	Thus particle and ther Now ΔT_f 0.00 ∴ n = Thus comple [Pt(NH ₃) ₄ Cl ₂ Depression solution free (1) 2 For urea,	es after dissocation refore, van't Hoff fac = K' _f × molality × v 054 = 1.86 × 0.001 2.1 \approx 2 (integer val ex and its ionisation clCl ₂ [Pt(NH ₃ of freezing point c ezes at – 1.86°C. A (2) 3 $\Delta T_f = k_f \times m$	$0 = 4 - n + 1 = 5 - n$ $an't Hoff factor$ $x (5 - n)$ $ue)$ $n is :$ $an't Cl_2]^{2+} + 2Cl^{-1}$ of 0.01 molal aq. $an't molal = 100$	(4 – n) (4 – n) - n CH₃CO equal to (3) 3.2 =	OH solution is (molarity, pH of (= 1.86	0.02046°. 1 molal urea CH₃COOH solution is : (4) 4.2
Solution.	Now for CH ₃	ΔTf = kf x m 3COOH = i kf m	OI Kf =	=	= 1.00	
	so $i =$ Now $i = 1$ so $\alpha =$	= 1.1 I + α 1.1 – 1 = 0.1				
	Now CH ₃	COOH	CH₃COO⁻ 0	+	H⁺ 0	

SOLUTIONS & COLLIGATIVE PROPERITES

	$C - C \alpha$	Cα	Cα
	$[{\rm H}^{+}] = {\rm C}\alpha = 0.01 \times 0.1 =$	0.001	
SO	pH = 3.		Ans. (2)

Section (J) : Osmosis and osmotic pressure

Diffusion : Spontaneous flow of particles from high concentration region to lower concentration region is known as diffusion.

Ex.

Osmosis: The spontaneous flow of solvent particles from solvent side to solution side or from solution of low concentration side to solution of high concentration side through a semipermeable membrane (SPM) is known as osmosis.

Semipermeable Membrane(SPM): A membrane which allows only solvent particles to move across it.

 (a) Natural : Semi permeable membrane Animal/plant cell membrane formed just below the outer skins.
 (b) Artificial membranes also : A copper ferrocyanide.

Cu₂[Fe(CN)₆] & Silicate of Ni, Fe, Co can act as SPM.

Ex.

Conclusion : After some time in (A) grape or egg will shrink and in (B) grape or egg will swell.

e.g. (i) A raw mango placed in concentrated salt solution loses water & <u>shrivel</u> into pickle.

(ii) People taking lot of salt, experience water retention in tissue cells. This results in puffiness or swelling called edema.

The phenomenon of osmosis : A solution inside the bulb is separated from pure solvent in the beaker by a semipermeable membrane, Net passage of solvent from the beaker through the memberane occurs, and the liquid in the tube rises untill equilibrium is reached. At equilibrium, the osmotic pressure exerted by the column liquid in the tube is sufficient to prevent further net passage of solvent.

takes place in both direction, passage from the pure solvent side to the solution side is more favoured and occurs faster. As a result, the amount of liquid on the pure solvent side decreases, the amount of liquid on the solution side increases, and the concentration of the solution decreases.

Osmotic Pressure : The equilibrium hydrostatic pressure developed by solution column when it is seperated from solvent by semipermeable membrane is called O.P. of the solution.

$\pi = \rho g h$,	ρ = density of soln.
g = acceleration due to gravity	;	h = eq. height

 $1 \text{ atm} = 1.013 \text{ x} 10^5 \text{ N/m}^2$

Definition : The external pressure which must be applied on solution side to stop the process of osmosis is called osmotic pressure of the solution.

If two solutions of concentration C_1 and C_2 are kept separated by SPM, and $C_1 > C_2$ then particle movement take place from lower to higher concentration. So, extra pressure is applied on higher concentration side to stop osmosis. And $P_{ext.} = (\pi_1 - \pi_2)$

Reverse Osmosis : If the pressure applied on the solution side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is known as reverse osmosis.

Berkely : Hartely device/method uses the above pressure to measure osmotic pressure.

e.g. used in desalination of sea-water.

Vant – Hoff Formula (For calculation of osmotic pressure)

• π concentration (molarity) T $\pi = CST$ S = ideal solution constant = 8.314 J mol⁻¹ K⁻¹ (exp value) = R (ideal gas) constant

= CRT = RT (just like ideal gas equation)

In ideal solution solute particles can be assumed to be moving randomly without any interactions.
 C = total concentration of all types of particles.

= atm.

 $= C_1 + C_2 + C_3 + s....$

= Solved Examples —

Example-19 If V₁ mL of C₁ solution + V₂ mL of C₂ solution are mixed together then calculate final concentration of solution and final osmotic pressure. If initial osmotic pressure of two solutions are π_1 and π_2 respectively?

Solution. C_f =

 $\pi_1 = C_1 RT, C_1 = ; \pi_2 = C_2 RT, C_2 =$

 $\pi = RT$; $\pi =$

Type of solutions :

- (a) Isotonic soution : Two solutions having same osmotic pressure are consider as isotonic solution. $\pi_1 = \pi_2$ (at same temperature)
- (b) Hypotonic & Hypertonic solutions : If two solutions 1 and 2 are such that $\pi_2 > \pi_1$, then 2 is called hypertonic solution and 1 is called hypotonic solution.

Conclusion : Pressure is applied on the hypertonic solution to stop the flow of solvent partices, this pressure become equal to $(\pi_2 - \pi_1)$ and if hypotonic solution is replaced by pure solvent then pressure becomes equal to π_2 .

Note : Osmotic pressure of very dilute solutions is also quite significant. So, its measurement in lab is very easy.

Plasmolysis : When the cell is placed in solution having osmotic pressure greater than that of the cell sap, water passes out of the cell due to osmosis. Consequently, cell material shrinks gradually. The gradual shrinking of the cell material is called plasmolysis.

Solved Examples.

Example-20	Calculate π of a solutions having 0.1 M NaCl & 0.2 M Na ₂ SO ₄ and 0.5 HA (weak acid which is 20% dissociation solutions at 300 K)
Solution.	$\pi = (0.2 + 0.6) \text{ RT} + i_3 \text{ C}_3 \text{ RT}$
Evenne la 04	$i_3 = 1+(1).2 = 1.2$ [0.8 + 0.6] RT = (1.4 × 0.083 × 300) = 1.162 × 30 = 34.86 atm
Example-21	disscociation) solutions calculate degree of disscociation of sodium sulphate.
Solution.	$i C_1 RT = i_2 C_2 RT$
	$[1+(2) \alpha] 0.042 = 2 \times$
	$1 + 2 \alpha = -1$
	2α =
	$\alpha = \times 100 = 75 \%.$

SOLUTIONS & COLLIGATIVE PROPERITES

Example-22 If 6 g of CH₃ COOH is dissolved in benzene to make 1 litre at 300 K π of solutions is found to be 1.64 atm. If it is known that CH₃COOH in benzene forms a dimer.

Solution.

Calculate degree of association of acetic acid in benzene

i = 1 + β.

 $1.64 = 0.0823 \times 300 \times [1 + \beta]$

 $1.64 = 0.0823 \times 300 [1 -]0.1$

= = $4 = 6 - 3\beta$

 $3\beta = 2$ $\beta =$

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. A 6.90 M solution of KOH in water has 30% by weight of KOH. Calculate density of solution.

Sol. Let V = 1 It, then moles of solute = 6.9

wt of solute = 6.9×56 g

So wt. of solution = $6.9 \times 56 \times g$

So density = $6.9 \times 56 \times x = 1288$ g/ lt Ans.

- **2.** 10 ml of sulphuric acid solution (sp. gr. = 1.84) contains 98% by weight of pure acid. Calculate the volume of 2.5 M NaOH solution required to just neutralize the acid.
- **Sol.** Wt of solute = $10 \times 1.84 \times g$

So moles of solute = \times = 0.184

So 0.184 = M ×

So Vml = 147.2 Ans.

- The density of 3M solution of Na₂S₂O₃ is 1.25 g mL⁻¹. Calculate.
 (a) the % by weight of Na₂S₂O₃ (b) mole fraction of Na₂S₂O₃
- **Ans.** (a) 37.92 (b) 0.065
- 4. Calculate Molality of aqueous urea solution which has X_{urea} = 0.2
- Sol. = 0.2 0.2 moles of urea in 0.8 moles water

x 1000 =

= m Ans.

- 5. If 10 g of an unknown substance (non-electrolyic) is dissolved to make 500 mL of soln then OP at 300 K is observed to be 1.23 atm find m.wt. ?
- **Sol.** $\pi = CRT \text{ so } 1.23 = \times 0.082 \times 300$, so M 400 g/mol **Ans.**
- 6. If 6 g of urea, 18 g glucose & 34.2 g sucrose is dissolved to make 500 mL of a soln at 300 K calculate π
- **Sol.** p = × 0.082 × 300 = 14.76 atm**Ans.**
- 7. If 200 ml of 0.2 M BaCl₂ solutions is mixed with 500 ml of 0.1 M Na₂SO₄ solutions. Calculate π of resulting solutions.
- **Ans.** $\pi = 6.685$ atm.
- **Sol.** $C_{net} = Now \quad \pi = C_{net} RT$
- 8. V.P. of solute containing 6 g of non volatile solute in 180 g of water is 20 Torr/mm of Hg. If 1 mole of water is further added in to the V.P. increses by 0.02. Torr calculate V.P of pure water & molecular wt. of non volatile solute.

Ans. m = 54 g/mol.

9. If 0.1 M solutions of K₄ [Fe (CN)₆] is prepared at 300 K then its density = 1.2 g/mL . If solute is 50% dissociated calculate ΔP of solutions if P of pure water = 25 mm of Hg. (K = 39, Fe = 56)

Ans. $\Delta p = 25 - 24.82 = 0.18$ mm of Hg

SOLUTIONS & COLLIGATIVE PROPERITES

- **10.** 1 Lit. of aq. solution of urea having density = 1.060 g/mL is found to have $\Delta T_b = 0.5^{\circ}$ C, If temp. of this solution increase to 101.5°C then calculate amount of water which must have gone is vapour state upto this pt. given K_b = 0.5 K kg mol⁻¹ for water
- **Ans.** W_{water} = g. = 666.67 g
- **11.** Find the molality of a solution containing a non-volatile solute if the vapour pressure is 2% below the vapour pressure of pure water.
- Ans. Given, If $P^\circ = 100$ than $P_S = 98$

Now, = =

= molality ×

 \therefore molality = \times = 1.133

- **12.** An aqueous solution of 2 percent non-volatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute ?
- Ans. Given $P_s = 1.004$ bar, $P^\circ = 1.013$ bar (at boiling point P = P = 1.013 bar.) Note : 2 % solution should be reported in terms of w/W and not simply 2%

From Raoult's law : =

 $m = 41 \text{ g mol}^{-1}$

- **13.** The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a solute in it.
- Ans. 1 molal = 1000 g solvent contains 1 mole of solute, moles of solvent = \therefore n = 1

 $\begin{array}{ll} \therefore \ \mathsf{P}_{s} = & \mathsf{P}^{\circ} \\ \therefore \ \mathsf{P}_{s} = 12.08 \ \mathsf{kPa} \end{array}$

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

Ans. = = (Given m = 40, w = 114g, M_{octane} = 114) = w = 10 g

- **Note :** By = (only for dilute solution, the answer comes 8 g)
- **15.** A solution containing 30 g of a non-volatile solute exactly in 90 g water has a vapour pressure of 2.8 kPa at 298 K. Further 18 g of water is then added to solution, the new vapour pressure becomes 2.9 kPa at 298 K. Calculate : (i) Molecular mass of the solute, (ii) vapour pressure of water at 298 K.

=

Ans.

For I case : = = (1)

For II case : = (2) By (1) and (2) $P^{\circ} = 3.53 \text{ kPa}$ m = 23 g mol⁻¹

Note : Answer will be 3.4 kPa and 34 g mol⁻¹ if = is used which is only valid for dilute solutions.

16. The boiling point of CHCl₃ was raised by 0.323° when 0.5143 g of anthracene was dissolved in 35 g CHCl₃. Calculate the molecular weight of anthracene. K_b for CHCl₃ = 3.9 K mol⁻¹ kg.
Ans. Given that, w = 0.5143 g, W = 35 g, K_b = 3.9 K mol⁻¹ kg, ΔT_b = 0.323°C

- $\therefore \qquad \Delta T_b =$
- ∴ 0.323 = m = 177.42
- **17.** What will be the boiling point of bromine when 174.5 mg of octa-atomic sulphur is added to 78 g of bromine, K_b for Br₂ is 5.2 K mol⁻¹ kg and boiling point of Br₂ is 332.15 K.
- **Ans.** Given, $w = 174.5 \times 10^{-3}$, W = 78g, $m = 8 \times 32 = 256$ (: octa-atomic), $K'_b = 5.2$
 - $\therefore \qquad \Delta T = = = 0.045$
 - :. Boiling point of Br₂ solution = $332.15 + \Delta T_b$ = 332.15 + 0.045 = 332.195 K