



# Unit - 2

# Solutions

Homogeneous mixture of two or more than two substances is called as solution.

⇒ The substances making the solution are called as components of solution.

⇒ Solute :- The component of the solution which is present in small amount is called as solute.

⇒ Solvent :- The component of solution which is present in large amount in soln is called as solvent.

## Classification of Solutions:-

(I) Based upon No. of components present in soln:-

(i) Binary soln :- Solution made up of two components only.

i.e. Solute and Solvent

eg :- Sugar solution in water.



(2) Tertiary Soln :- Soln containing three components  
i.e. two solute and one solvent and vice versa  
eg :- Soln of sugar + NaCl + H<sub>2</sub>O.

(3) Quaternary Soln :- Soln containing 4 components.

(II) Based upon amount of solute :-

(i) Concentrated Soln :- Soln containing large amount of solute is called as conc. solution.

(ii) Dilute solution :- The solution which containing very small amount of solute in very large amount of solvent is called as dilute soln.

(III) Based upon physical state of solute and solvent :-

Solute	Solvent	eg.
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(A) Gaseous Solns.

(1) Gas + Gas ⇒ Air, mixture of gases.

(2) Liquid + Gas ⇒ water vapours in air

(3) Solid + Gas ⇒ dust or smoke particles  
Suspended in air.



(b) Liquid Solutions :-

Gas + Liquid  $\Rightarrow$  oxygen dissolved in  $H_2O$ ,  $CO_2$  in  $H_2O$ .

Liquid + liquid  $\Rightarrow$  Ethanol dissolved in  $H_2O$ .

Solid + Liquid  $\Rightarrow$  Sugar dissolved in  $H_2O$ .

(c) Solid solutions :-

Gas + Solid  $\Rightarrow$  Soln of  $H_2$  in palladium.

Liquid + Solid  $\Rightarrow$  Mercury with sodium (amalgam)

Solid + Solid  $\Rightarrow$  Copper dissolved in gold, alloys.

(IV) Depending upon type of solvent used :-

(i) Aqueous Solns :-

The Solns which are prepared by dissolving solute in  $H_2O$ .

(2) Non aq. soln :-

The Solns which are prepared by dissolving solute in organic solvent like Benzene, Toluene,  $CCl_4$ ,  $CS_2$  etc.



## Methods for Expressing the Conc. of Solution:-

Amount of the Solute present in the given quantity of the Solution is called as the Conc. of the Solution.

The diff ways to express the conc. of Soln are:-

### ① Mass percentage and volume % age:-

Mass % age of Component in a Soln is defined as mass of the Component present per 100 gm of the Soln.

$$\text{Mass \% age of Component} = \frac{\text{Mass of Component in Soln}}{\text{Total mass of the Soln}} \times 100$$

eg: if a Soln is made up of two Components A and B.

Let  $w_A$  = wt. of Component A.

$w_B$  = wt. of Component B.

Total wt. of Soln = wt. of Component A + wt. of Component B

$$\text{Mass \% age of A} = \frac{w_A}{w_A + w_B} \times 100.$$

⇒ volume % age :- It is defined as the volume of the Component per 100 by vol. of Soln.



Let the soln contains  $V_A$  ml and  $V_B$  ml of Component A and B respectively. then vol. percentage of component A :-

$$\text{Vol. \% age of 'A'} = \frac{V_A}{V_A + V_B} \times 100.$$

⇒ Mass by volume percentage :-

It is defined as the mass of the solute dissolved per 100 ml of the soln.

② Parts per million (ppm) :- It is defined as the mass of a component per present per million parts of the solution.

$$\text{eg: ppm} = \frac{\text{Mass of Component}}{\text{Total mass of the soln}} \times 10^6.$$

③ Molarity of Soln :- It is defined as the no. of moles of the solute dissolved per litre of the soln.

⇒ It is represented as M.

⇒ Units mole  $\text{lit}^{-1}$ .

$$\Rightarrow \text{Molarity (M)} = \frac{\text{No. of moles of Solute (n)}}{\text{Vol. of Soln in litre}}$$



$$M = \frac{\text{No. of moles of solute (n)}}{\text{Vol. of soln in ml}} \times 1000$$

$$M = \frac{\text{given wt. of solute}}{\frac{\text{Mol. wt}}{\text{Vol. of soln in 'ml'}}} \times 1000$$

⇒ It has one disadvantage that molarity of the soln changes with change in temp. becoz of contraction or expansion of vol. of liquid.

(4.) Molality of soln :- (m) :-

It is defined as the no. of moles of the solute present per kg. of the solvent.

⇒ It is represented by (m).

⇒ Its units are mol kg<sup>-1</sup>.

$$\Rightarrow m = \frac{\text{no. of moles of}}{\text{mass of solvent in kg}} = \frac{\text{no. of moles of solute (n)}}{\text{Mass of solvent in gm.}} \times 1000$$

⇒ Becoz mass of liquid remains Unchanged with change in temp. Hence molality of solution does not change with change in temp.

Hence it is a better way to express the conc. of the soln than molarity.



(5.) Mole fraction:- It is the ratio of no. of moles of the given component to that of total no. of moles of all the components present in the soln.

⇒ It is Unit less.

⇒ It is represented by  $x$ .

Let a soln made of two components A and B.

No. of moles of Component A =  $n_A$

No. of moles of Component B =  $n_B$   
In soln

then mole fraction of component (A) can be calculated as :-

$$x_A = \frac{n_A}{n_A + n_B} \quad x_B = \frac{n_B}{n_A + n_B}$$

⇒ Sum of mole fractions of all the components in a solution is always equal to one.

i.e

$$x_A + x_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

(6.) Normality:- It is defined as the no. of gm equivalents of the solute dissolved per litre of the soln.



⇒ It is represented by N.

⇒ Unit = gm eq/lit.

$$N = \frac{\text{no. of gm equivalents of solute (n)}}{\text{vol. of the soln in litres}}$$

$$N = \frac{\text{no. of gm eq. of the solute}}{\text{vol. of the soln in (ml)}} \times 1000$$

⇒ Normality of the soln also changes with change in temp. becoz of expansion or contraction of liquid with change in temp.

(7) Formality :- It is defined as the no. of formula masses of the solute dissolved per litre of the solution.

$$\text{formality} = \frac{\text{No. of formula masses of solute}}{\text{vol. of soln in litres.}}$$

Important relations:-

(1) Normality = Molarity  $\times$   $\frac{\text{Molar Mass}}{\text{equivalent wt.}}$

(2) for acids :- Normality = Molarity  $\times$  Basicity

(3) for bases :- Normality = Molarity  $\times$  Acidity





## Solubility of gases and Solids in liquids:-

Solubility of a sub. is defined as the amount of that sub. which can be dissolved in definite amount of solvent at a given temp.

### (A) Solubility of Solids in liquids:-

The Solubility of a solid in a solvent depends upon the following factors:-

#### (i) Nature of Solute and Solvent:-

According to the principle of like dissolves like, a polar solid can be dissolved in a polar solvent while non-polar solid can be dissolved in non-polar solvent.

(2) Effect of temp.:- The change in temp. may increase or decrease the solubility of a solid in a given solvent. This depends upon the nature of the reaction that occurs bet<sup>n</sup> solute and solvent. This is explained as follows:-

(a) If the process of dissolution of a solid in a given solvent is endothermic. then acc<sup>n</sup> to Le-Chatelier principle the solubility of solid will



↑ es with ↑ es in temp.

eg: dissolution of  $\text{NaNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{KCl}$ ,  $\text{KI}$ ,  $\text{AgCl}$



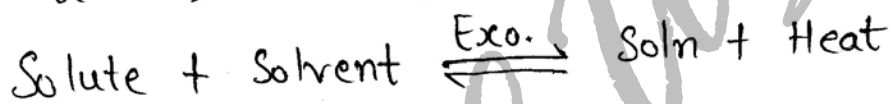
$$\Delta H = +ve.$$

(b.) If the process of dissolution of a solid in a given solvent is exothermic, then accn to Le-Chatelier's

principle, the solubility of solid will ↓ es with ↑ es

in temp. eg: In case of dissoln of  $\text{Li}_2\text{SO}_4$ ,

$\text{Ce}_2(\text{SO}_4)_3$ ,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  etc.



(c) For some substances the solubility does not show a regular behaviour with change in temp.

eg: Solubility of  $\text{Na}_2\text{SO}_4$  increases upto certain temp., then decreases as temp. is further increased.

This is due to change of the solid from one form to another with change in temp.

eg: below  $32.8^\circ\text{C}$   $\text{Na}_2\text{SO}_4$  exists as

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and above  $32.8^\circ\text{C}$  it changes

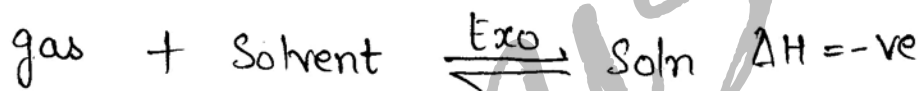
to  $\text{Na}_2\text{SO}_4$  i.e. anhydrous state.



## Solubility of gases in Liquids:-

The solubility of gases in liquids depends upon the following factors:-

- (1) Effect of temp :- The solubility of a gas decreases with increase in temp. This becoz the process of dissolution of a gas is always exothermic in nature. Hence solubility of a gas always decreases with ↑ in temp, accn to Le-Chatelier principle.



- (2) Effect of pressure :- Effect of pressure on the solubility of gas can be explained in terms of Henry's Law.

Accn to this Law, the mass of a gas dissolved per unit volume of the solvent at a constant temp. is directly proportional to the pressure of the gas in equilibrium with the soln.

if 'm' is the mass of gas dissolved in a unit volume of the solvent and 'p' is the pressure of the gas in equilibrium with the soln. then

$$m \propto p.$$

$$m = K \cdot p. \quad \text{Here } K = \text{Proportionality Constant.}$$



Magnitude of  $K$  depends upon nature of the gas, nature of solvent, temp. etc.

### Limitations of Henry's Law:-

It is found that Henry's law is valid if :-

- (1) Pressure is low. At High pressure Law becomes less accurate.
- (2) The temp. is not too low.
- (3) The gas is not Highly soluble.
- (4) The gas neither reacts chemically with the solvent nor dissociates or associates in the solvent.

⇒ Effect of pressure on the solubility of a gas can be explained in terms of Dalton's Law :-

Acc. to Dalton, mole fraction of the gas in the solution is proportional to the partial pressure of the gas over the soln. i.e.

$$x \propto P.$$

$$x = K'P$$

$$P = \frac{1}{K'} x$$

$$P = K_H x \quad \left( K_H = \frac{1}{K'} \right)$$

$K_H$  is called as Henry's law constant.  
Thus, In other words.



The partial pressure of a gas in the vapour phase is directly proportional to the mole fraction of the gas in the solution.

### Applications of Henry's Law :-

(1) In the production of Carbonated beverages:-

To increase the solubility of  $\text{CO}_2$  in Soda water, cold drinks, beer etc. Henry's Law can be used.

(2) In deep sea diving :- Deep sea divers depends upon compressed air for breathing at High pressure under water. The compressed air contains  $\text{N}_2$  in addition to  $\text{O}_2$ , which are not very soluble in blood at normal pressure. However at great depth under high pressure, when divers breath in compressed air, more  $\text{N}_2$  dissolves, but when they come back, due to decrease in pressure over earth surface,  $\text{N}_2$  comes out forming bubbles through blood stream. These bubbles affect blood flow and transmission of nerve impulse. The bubbles may burst the capillaries. This



Condition is called 'the bends'

with the help of Henry's law the above problem can be controlled by using oxygen gas diluted with He which has low ~~so~~ solubility than  $N_2$ .

(3) At High Altitude :- At high altitude due to decrease in pressure level of  $O_2$  decreases. This results in low conc. of  $O_2$  in blood in the tissues of people living at high altitude or climbers the low blood oxygen conc. causes climbers to become weak and unable to think clearly, it is known as anoxia.

Vapour pressure of liquid :-

The pressure exerted by the vapours of a liquid over its surface in equilibrium with the liquid at a given temp. is called vapour pressure.



⇒ Factors affecting vapour pressure of a liquid :-

(i) Nature of the liquid :- The vapour pressure of a liquid is inversely proportional to the magnitude of intermolecular forces. weaker the intermolecular forces, more easily and fastly, the molecules of the liquid go into vapour phase and vice-versa.

(2) Temp. :- The vapour pressure of a liquid increases with increase in temp. i.e greater the temp, more is the vapour pressure of the liquid and vice-versa.

Vapour pressure of liquid-liquid soln

OR

Raoult's Law :-

At a given temp, for a solution of volatile liquids, the partial vapour pressure of each component in solution is equal to the product of vapour pressure of pure component and its mole fraction.



Consider a binary solution of two volatile liquids A and B.

$x_A$  = is the mole fraction of Component 'A'.

$x_B$  = " " " " " " B.

$P_A$  = Partial vapour pressure of Component A.

$P_B$  = " " " " " " B.

$P_A^\circ$  = vapour pressure of Component A in pure state.

$P_B^\circ$  = " " " " " " B " " "

Then according to Raoult's law :-

$$P_A = P_A^\circ \times x_A \quad \text{--- (1)}$$

$$P_B = P_B^\circ \times x_B \quad \text{--- (2)}$$

The total vapour pressure of the soln. will be (acc<sup>n</sup> to Dalton's law) :-

$$P_S = P_A + P_B$$

$$P \text{ OR } P_S = P_A^\circ \times x_A + P_B^\circ \times x_B \quad \text{--- (3)}$$

the above eqn can be rearranged as :-

$$x_A + x_B = 1$$

$$x_A = 1 - x_B$$

Put this value of  $x_A$  into eq. (3) we get.





$$P = P_A^{\circ} (1 - x_B) + P_B^{\circ} x_B$$

$$P = P_A^{\circ} - P_A^{\circ} x_B + P_B^{\circ} x_B$$

$$P = P_A^{\circ} + (P_B^{\circ} - P_A^{\circ}) x_B \quad \text{--- (4)}$$

The above equation (4) shows that vapour pressure ( $P$ ) is a linear function of the mole fraction ( $x_B$ ) because  $P_A^{\circ}$  and  $P_B^{\circ}$  are constant at a particular temp.

- In the graph, the dotted lines give the partial pressures of the two components versus composition and the dark line gives the total vapour pressure versus composition - it is clear from graph:-

(a) If  $x_A = 1$  i.e. liquid is pure A

$$P_A = P_A^{\circ} \times 1$$

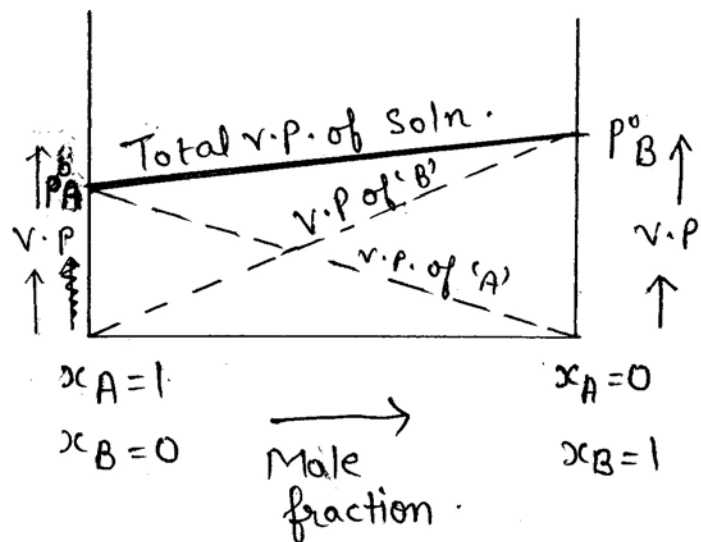
$$P_A = P_A^{\circ}$$

(b) when  $x_A = 0$

$$P_A = P_A^{\circ} \times 0$$

$$P_A = 0$$

Thus plot of  $P_A$  against  $x_A$  should give a straight line similarly for component B.





⇒ Vapour pressure of solution of solid in liquid:-

The vapour pressure of a solution containing non-volatile solute dissolved in volatile solvent is always less than that of the pure solvent. This can be explained as follows:-

We know that evaporation is a surface phenomenon. The vapour pressure depends on the escape of solvent molecules from the surface of the liquid. In case of soln containing non-volatile sugar, the sugar molecules also occupy surface area, As a result the surface area occupied by volatile solvent molecules decrease as compared to pure volatile solvent. Thus in soln lesser no. of molecule of solvent go. to vapour phase. Hence vapour pressure of the solvent in soln decreases than pure solvent.

Raoult's law for liquid solutions containing non-volatile solutes:-

In a solution containing non-volatile solute dissolved in volatile solvent the vapour pressure of the soln is only due to solvent. Thus:-



Vapour pressure of the soln = vapour pressure of solvent in soln.

if  $P_A$  = vapour pressure of solvent over the soln.

$x_A$  = mole fraction of solvent in soln.

then according to Raoult's law:

$$P_A = P_A^\circ \times x_A$$

or

$$P \text{ or } P_s = P_A^\circ \times x_A \text{ (because v.p. of soln is only due to solvent)}$$

rearranging the above

$$\frac{P}{P_A^\circ} = x_A$$

Subtracting each side of equation from one we get:

$$1 - \frac{P}{P_A^\circ} = 1 - x_A$$

$$\frac{P_A^\circ - P}{P_A^\circ} = x_B$$

$$\therefore 1 - x_A = x_B$$

or

$$\frac{P^\circ_{\text{solvent}} - P_{\text{soln}}}{P^\circ_{\text{solvent}}} = x_{\text{solute}}$$

Here  $P_A^\circ - P$  = diff. in the vapour pressure of pure solvent and the solution

It is also called as lowering in v.p.



$$\frac{P_A^\circ - P}{P_A^\circ} = \text{relative lowering in vapour pressure.}$$

Thus Raoult's law may be stated as:-

The relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temp.

Raoult's law as a special case of Henry's Law:-

Acc<sup>n</sup> to Raoult's law, the vapour pressure of a volatile component in given sol<sup>n</sup> is given by:-

$$P_A = P_A^\circ x_A \quad \text{--- (1)}$$

Here  $P_A^\circ$  = vap. p. of pure solvent

$P_A$  = Partial v.p. of Comp. A in Soln.

$x_A$  = mole fraction of component A.

But acc<sup>n</sup> to Henry's law 'the solubility of Component A in soln is given by relation:-

$$P_A = K_H \cdot x_A \quad \text{--- (2)}$$

$P$  = Pressure of the gas above the soln.

$K_H$  = Henry's constant.

$x$  = mole fraction of Comp. A.



If we compare equation (1) with equation (2), it is clear that partial pressure of a component is directly proportional to its mole fraction in the soln.

⇒ the only diff. in eq (1) and (2) is the proportionality constant.  $P^{\circ}_A$  and  $K_H$ . Therefore Raoult's law becomes a special case of Henry's law, in which  $K_H$  becomes equal to vapour pressure of pure component ( $P^{\circ}_A$ )

⇒ Diff. and similarity between Raoult's law and Henry's Law

⇒ (1) Both the laws apply to volatile components in soln.

⇒ (2) Both laws state that the v.p. of a component is proportional to its mole fraction.

⇒ (3) Raoult's Law defines proportionality constant as the v.p. of pure component - while Henry's law defines the proportionality constant as some experimentally determined value.



## Ideal and Non-Ideal soln:-

Ideal soln:- An ideal soln may be defined as the soln which obeys Raoult's law at all concentrations.

- ⇒ In the ideal soln. the intermolecular interactions bet<sup>n</sup> the components (A-B interactions) are of the same magnitude as the intermolecular interactions, in the pure components (i.e. A-A and B-B interactions)
- ⇒  $\Delta H_{\text{mixing}}$  for ideal soln is equal to zero.  
i.e.  $\Delta H_{\text{mixing}} = 0$
- ⇒  $\Delta V_{\text{mixing}}$  for an ideal soln is always equal to zero. i.e.  $\Delta V_{\text{mixing}} = 0$ .

### Examples of ideal soln:-

- Soln. of:
- (1) Benzene and Toluene
  - (2) n-Hexane and n-Heptane.
  - (3) Bromoethane and iodoethane
  - (4) chlorobenzene and Bromobenzene.



Non-ideal Solutions :- The solns which do not obey Raoult's Law at all concentrations are called non-ideal solns.

⇒ Therefore, for a soln. made up of components A and B.

$$P_A \neq P_A^\circ \times x_A \quad ; \quad P_B \neq P_B^\circ \times x_B.$$

⇒ In Non-ideal soln, the intermolecular interactions bet<sup>n</sup> the components (A-B interactions) are not of the same magnitude as the intermolecular interactions in the pure components i.e (A-A, B-B interactions).

⇒  $\Delta H_{\text{mixing}}$  for Non-ideal soln are not equal to zero i.e  $\Delta H_{\text{mixing}} \neq 0$ .

⇒  $\Delta V_{\text{mixing}} \neq 0$

Examples :- (1) Benzene and acetone  
(2) Ethyl alcohol and water.

Types of Non-ideal Solutions :-

(i) Non-ideal solutions showing positive deviations from Raoult's law :-

Consider a binary solution of two components A and B. If the A-B interactions in the soln. are weaker than A-A and B-B interactions in two liquids forming the solution, then the



escaping tendency of Component A and B types of molecules from the solution becomes more than from pure liquids. As a result, each Component of the soln. has a partial vapour pressure greater than expected on the basis of Raoult's law. The total v.p. of the soln will be greater than v.p. calculated by using Raoult's law. This type of solns are called as Non-ideal solns with positive deviations from ideal behaviour.

Mathematically

$$P_A > P_A^0 x_A \quad \text{--- (1)}$$

$$P_B > P_B^0 x_B \quad \text{--- (2)}$$

$$P_T > P_A + P_B \quad \text{--- (3)}$$

$$P_T > P_A^0 x_A + P_B^0 x_B \quad \text{--- (4)}$$

eg: soln of (1) Ethyl alcohol and cyclohexane

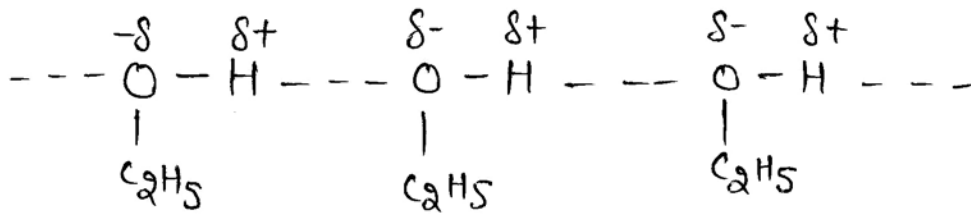
(2) Ethyl alcohol and water.

(3) Benzene and acetone.

Explanation for +ve deviations:

Consider the soln of ethyl alcohol and cyclohexane. In ethyl alcohol - the molecules are held together by H-bonding :-





When cyclohexane is added to ethyl alcohol, the molecules of cyclohexane tend to occupy the spaces between ethyl alcohol molecules. Due to this, some H-bonds between the alcohol molecules break and the attractive forces in alcohol decrease. Thus escaping tendencies of alcohol and cyclohexane molecules from the solution increase. Thus  $v.p.$  of the soln becomes greater than  $v.p.$  as expected on the basis of Raoult's law:-

$\Rightarrow$  In such solutions  $-\Delta H_{\text{mixing}}$  is positive because energy required to break A-A or B-B attractive forces, is greater than energy released during formation of A-B interaction. Thus dissolution process is endothermic.

$\Rightarrow$  Because of the decrease in magnitude of intermolecular forces in solution, the molecules will be loosely held and therefore there will be an increase in volume on mixing. Thus  $\Delta V_{\text{mixing}}$  will be +ve i.e. greater than zero.



⇒ Non-ideal Solns showing Negative deviations from ideal behaviour / Raoult's Law

Consider a solution made up of two Components A and B, If the A-B interactions are stronger than A-A and B-B interactions present in two liquids forming the solution, then the escaping tendencies of A and B type of molecules from the solution becomes less than pure liquids. As a result each Component of solution has less vapour pressure than expected on the basis of Raoult's law. The total vapour pressure of soln. will be less than calculated with the help of Raoult's law. Such a solution is called Non ideal Solns. with Negative deviations from Raoult's law.

Mathematically

$$P_A < P_A^\circ \times x_A \quad \text{--- (1)}$$

$$P_B < P_B^\circ \times x_B \quad \text{--- (2)}$$

$$P_T < P_A + P_B \quad \text{--- (3)}$$

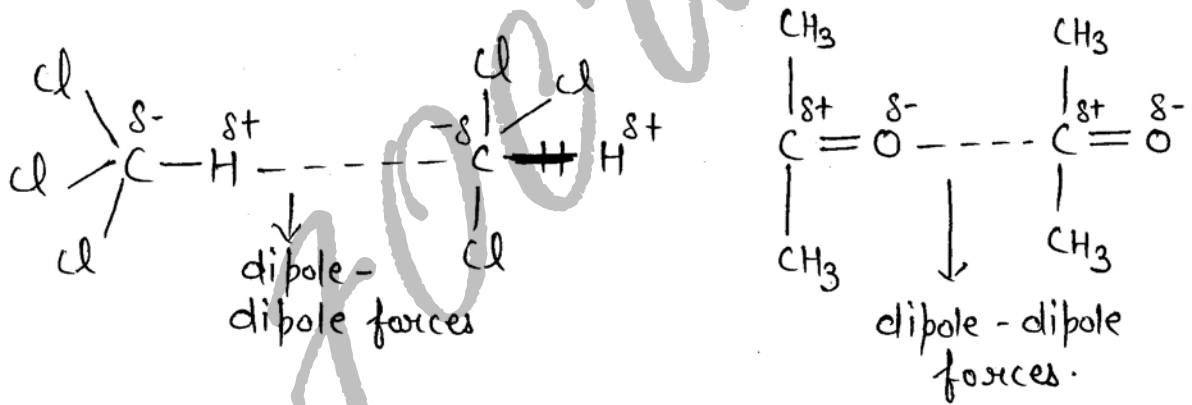
$$P_T < P_A^\circ \times x_A + P_B^\circ \times x_B \quad \text{--- (4)}$$



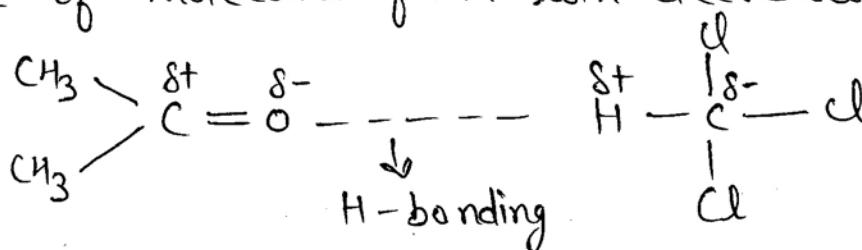
- eg :- Soln of (1) Acetone and chloroform  
 (2) chloroform and diethyl ether  
 (3) chloroform and HNO<sub>3</sub>.  
 (4) Acetone and Aniline  
 (5) water and Nitric acid.

Explanation for Negative deviations  $\frac{P}{P_0}$  we know

In pure chloroform and in acetone sol<sup>n</sup>, there are dipole-dipole interactions among the molecules i.e.



But when Acetone is mixed into chloroform, there develop new intermolecular force of attraction i.e. Hydrogen bonding, which more stronger. Due to this the escaping tendency of the each type of molecules from soln decreases.





⇒ For this soln  $\Delta H_{\text{mixing}} \neq 0$ ,  $\Delta H_{\text{mixing}} = -ve$

Thus dissolution process is exothermic

⇒  $\Delta V_{\text{mixing}} \neq 0$ ,  $\Delta V_{\text{mixing}} = -ve$ , The vol. of soln becomes less than the sum of the volumes of the two liquids mixed together to form soln.

⇒ Diff bet<sup>n</sup> ideal and Non-ideal solns.

Azeotropes :- The solutions which boils at a constant temp. like pure liquids and distill unchanged in composition are called as azeotropes or azeotropic mixtures.

Types of azeotropic mixtures :-

Minimum boiling

(1) Azeotropic mixtures :- The azeotropic mixtures which show positive deviation from Raoult's law are called as Minimum boiling azeotropic mixtures. eg :- soln of Ethanol and  $H_2O$  containing 95.6% Ethanol and 4.4%  $H_2O$ .

(2) Max. boiling azeotropic mixtures :-

The azeotropic mixtures which show Negative deviations from Raoult's law are called Max. boiling azeotropic mixtures.



eg: soln. of HCl and H<sub>2</sub>O containing 20.2% HCl and 79.8% H<sub>2</sub>O.

Colligative properties: The properties of the solution which depend only on the no. of solute particles but not on the nature of solute are called as colligative properties.

The four colligative properties are:-

- (i) Relative lowering in vapour pressure.
- (ii) Elevation in boiling point.
- (iii) Depression in fpt.
- (iv) Osmotic pressure.

(I) Relative Lowering in vapour pressure:-

We know, when non-volatile solute is added to a volatile solvent, the vapour pressure of solution decreases than pure solvent. This decrease in vapour pressure is called as Relative Lowering in vapour pressure.

Consider a soln. prepared by dissolving non-volatile solute B in volatile solvent A.

Let  $x_A$  = mole fraction of Solvent (A).



$x_B$  = Mole fraction of solute ('B').

$P_A$  = Vapour pressure of solvent.

$P$  = Vapour pressure of soln.

The vapour pressure of Soln = vap. p of solvent

i.e  $P = P_A$  — (1)

Accn to Raoult's law

$$P_A = P_A^\circ \times x_A$$

Put this value in eqn (1) we get

$$P = P_A^\circ \times x_A$$

On rearranging the above eqn.

$$\frac{P}{P_A^\circ} = x_A$$

Subtracting each side from one

$$1 - \frac{P}{P_A^\circ} = 1 - x_A$$

$$\boxed{\frac{P_A^\circ - P}{P_A^\circ} = x_B}$$

OR

$$\boxed{\frac{P_A^\circ - P_A}{P_A^\circ} = x_B}$$

bcoz  $P = P_A$

OR (Alternate way:)

from

$$P \text{ or } P_s = P_A^\circ \times x_A$$

We know v.p. of soln. i.e  $P$  is always less



than v.p. of pure solvent ( $P_A^\circ$ )

$$\text{Thus } \Delta P_A = P_A^\circ - P_A$$

$$\Delta P = P_A^\circ - P_A^\circ x_A$$

$$\Delta P = P_A^\circ (1 - x_A)$$

$$\Delta P_A = P_A^\circ x_B \quad \because x_B = 1 - x_A$$

$$\frac{\Delta P_A}{P_A^\circ} = x_B$$

$$\text{or } \boxed{\frac{P_A^\circ - P_A}{P_A^\circ} = x_B}$$

Here  $P_A^\circ - P_A =$  Lowering in v.p.

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \text{Relative lowering in v.p.}$$

Thus Relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute at a given temp.

Relative Lowering in v.p. as a colligative property:

we know Relative lowering in v.p. of a soln containing non-volatile solute dissolved in volatile solvent is given by:-



$$\frac{P^{\circ}_A - P_A}{P^{\circ}_A} = x_B$$

Thus Relative Lowering in v.p. depends upon mole fraction of solute, which depends upon no. of moles of solute in soln. Thus we can say that Relative lowering in v.p. of soln depends upon no. of moles of Non-volatile solute. Hence it is a colligative property.

Determination of Mol. wt. of solute from

Relative lowering in v.p. :-

from Relative lowering in v.p. of a soln containing non-volatile solute in volatile solvent we know

$$\frac{P^{\circ}_A - P_A}{P^{\circ}_A} = x_B \quad \text{--- (1)}$$

Let  $w_A$  = wt. of solute

$w_B$  = wt. of solvent used to prepare soln.

if  $M_A$  = mol. wt. of Solvent

$M_B$  = mol. wt. of Solute





$n_A$  = no. of moles of Solvent

$n_B$  = no. of moles of Solute

Thus

$$x_B = \frac{n_B}{n_A + n_B}$$

$$x_B = \frac{w_B/M_B}{\frac{w_A}{M_A} + \frac{w_B}{M_B}} \quad - (2)$$

Since the law is applicable to ideal soln, which is a very dilute soln. i.e containing lesser no. of moles of solute in larger amount of solvent.

Thus

$$\frac{w_B}{M_B} \ll \frac{w_A}{M_A}$$

Hence Neglecting  $w_B/M_B$  from eq (2) from denominator

$$x_B = \frac{w_B/M_B}{w_A/M_A} \quad - (3)$$

Put this value of  $x_B$  in eq (1) we get:-

$$\frac{P^{\circ}_A - P_A}{P^{\circ}_A} = \frac{w_B/M_B}{w_A/M_A}$$



$$\frac{P_A^\circ - P_A}{P_A^\circ} = \frac{w_B \times M_A}{w_A \times M_B}$$

$$M_B = \frac{w_B \times M_A}{w_A \times \left( \frac{P_A^\circ - P_A}{P_A^\circ} \right)}$$

## (II) Elevation in Boiling point :-

We know that v.p. of a soln containing non-volatile solute dissolved in volatile solvent is always less than solvent. As Bpt is Inversely proportional to v.p. Hence Bpt. of soln becomes greater than solvent. This diff in Bpt. of soln. and that of pure solvent is called as Elevation in Bpt.

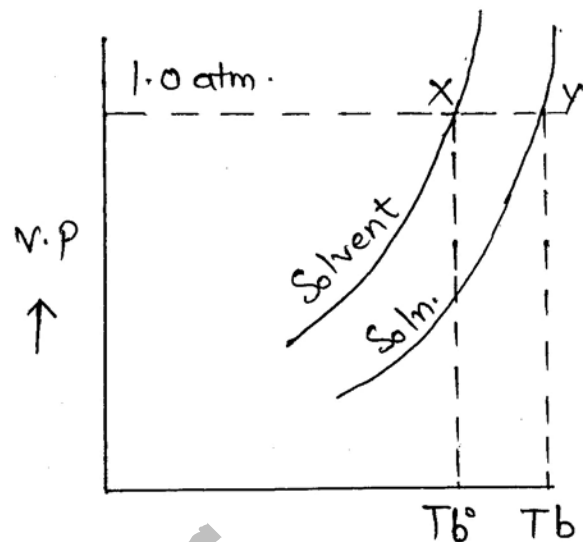
If we draw v.p. of soln as well as pure solvent versus temp the following curves are obtained for soln and pure solvent.

It is clear from the graph that as the v.p. of soln is lower than pure solvent, hence the curve for v.p. of soln lies below the curves for solvent.



Hence Soln has to be  
Heated more to make  
its v.p. equal to 1 atm.  
(atmospheric pressure)

Due to this soln boils  
at higher temp. than  
Solvent.



If the Bpoint of soln is  
represented by  $T_b$  and that  
of Solvent by  $T_b^0$ . The diff in boiling point  
of soln and solvent is called as Elevation  
in Bpt.

$$\text{i.e } \Delta T_b = T_b - T_b^0$$

Experimentally it is found that  $\Delta T_b$  i.e elevation  
in bpt. depends upon molal concentration  
of soln. i.e

$$\Delta T_b \propto m.$$

$$\Delta T_b = k_b \times m.$$

Here  $m$  = molality of the soln

$k_b$  = molal Bpt elevation constant

OR  
Molal Bpt constant



or  
ebulliscope Constant.

if  $m=1$  i.e. 1 mole of solute is dissolved  
per kg of the solvent

$$\text{Then } \Delta T_b = K_b \times 1$$

$$\Delta T_b = K_b.$$

Thus molal boiling point elevation constant, ( $K_b$ ) is defined as the elevation in bpt. for 1 molal soln. i.e. a soln containing 1 mole of solute dissolved per kg of the solvent.

$\Rightarrow$  Elevation in Bpt. as a Colligative property!

We know that elevation in Bpt. of a soln is directly proportional to molal conc. of the soln. i.e.

$$\Delta T_b \propto m.$$

molal conc. of the soln depends upon no. of moles of the solute dissolved per kg of the solvent. Hence  $\Delta T_b$  depends upon no. of moles of the solute present per kg of solvent.

Hence Elevation in bpt. is a Colligative property.



## Determination of Molar mass of solute from

### Elevation in Bpt :-

from Elevation in Bpt of a soln. containing non-volatile solute dissolved in volatile solvent, we know

$$\Delta T_b = K_b \times m \quad \text{--- (1)}$$

Let

$w_B$  gm of solute are dissolved in  $w_A$  gm. of solute.

$M_B$  = Mol. Mass of Solute

Thus molality of the soln is given by :-

$$m = \frac{\text{moles of Solute (n)}}{\text{wt. of Solvent in gm}} \times 1000$$

$$\text{No. of moles of Solute (n)} = \frac{w_B}{M_B}$$

$$m = \frac{w_B / M_B}{w_A} \times 1000$$

$$m = \frac{w_B}{M_B \times w_A} \times 1000 \quad \text{--- (2)}$$

Put this value of  $m$  in equation (1) :-

$$\Delta T_b = \frac{K_b \times w_B}{M_B \times w_A} \times 1000$$



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

### (III.) Depression in freezing point :-

We know freezing point is the temp. at which solid and liquid forms of a substance are in equilibrium. This is only possible if they have same vapour pressure. Thus a soln will freeze only when its vapour pressure becomes equal to pure solvent. But it is observed that the v.p. of a soln containing non-volatile solute in volatile solvent, is always lower than pure solvent. Hence f.p. of soln is always lower than solvent. This diff. in the f.p. of pure solvent and soln is called as depression in f.p.

This can also be explained by drawing a graph bet<sup>n</sup> vapour pressure and temp., for soln and pure solvent. It is clear from graph, that v.p. curve for soln lies below v.p. curve for solvent. In graph the curve BC is curve for v.p. of pure solvent. The temp.



Corresponding to point 'B' is the freezing point of solvent, while the temp. corresponding to point 'D' is the freezing point of soln. Since  $T_f$  (freezing pt. of soln) is less than  $T_f^\circ$  (fpt. of solvent)

The diff bet<sup>n</sup> the  $T_f$  and  $T_f^\circ$  is called as dep. in fpt. ( $\Delta T_f$ )

$$\Delta T_f = T_f^\circ - T_f$$

It is found experimen-  
-tly that  $\Delta T_f$  is  
directly proportional  
to molar conc. of the  
Soln - i.e.

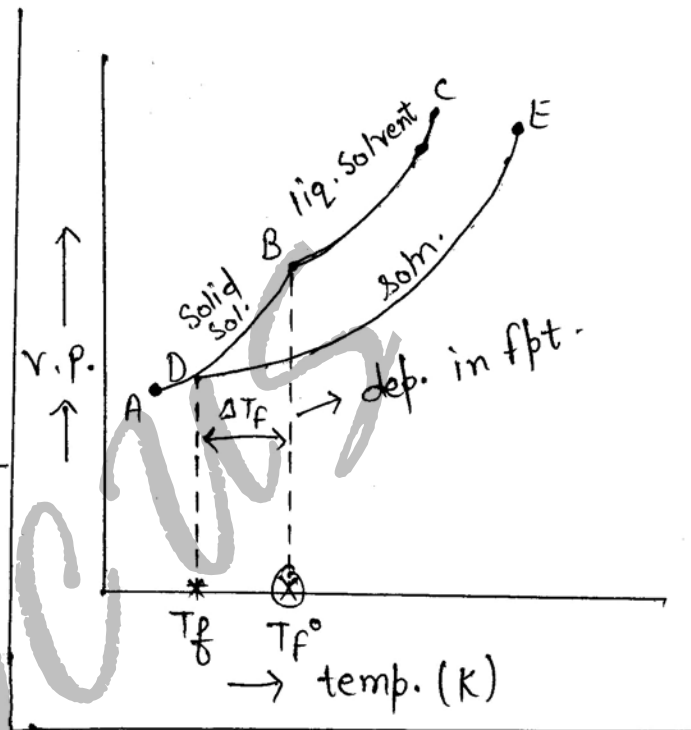
$$\Delta T_f \propto m.$$

$$\Delta T_f = K_f \times m \quad \text{--- (1)}$$

Here  $K_f$  = molal freezing point depression constant  
or  
molal cryoscopic constant.

if  $m = 1$  i.e Soln contains one mole of  
Solute per kg of Solvent.

The eq (1) becomes:





$$\Delta T_f = K_f \cdot$$

Thus molal fpt. depression constant is defined as the depression in fpt. for 1 molal soln.

Depression in fpt. - as a colligative property;

we know from dep. in fpt. of a soln that

$$\Delta T_f \propto m.$$

i.e. dep. in fpt. of a soln is directly proportional to molal conc. of soln. i.e. molality of soln.

As molality of soln depends upon no. of moles of the solute per kg of solvent.

Hence  $\Delta T_f$  depends upon no. of moles of solute present in the soln. Thus dep. in fpt is a colligative property.

Determination of Mol. Mass of Solute from

Depression in fpt. temp.

we know from dep. in fpt. of a soln that

$$\Delta T_f = K_f \times m \quad \text{---(1)}$$

Let  $w_B$  = wt. of solute used to prepare soln.

$M_B$  = Mol. mass of solute

$w_A$  = wt. of solvent used to prepare soln.





Therefore molality of Soln is :-

$$m = \frac{\text{no. of moles of solute (n)}}{\text{weight of Solvent in gm}} \times 1000.$$

$$\text{no. of moles of solute (n)} = \frac{W_B}{M_B}.$$

$$m = \frac{W_B/M_B \times 1000}{W_A}$$

Put the above value of 'm' in eq. (1) we get

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

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

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

#### IV Osmosis and Osmotic pressure :-

Osmosis :- The phenomenon of flow of solvent through a semipermeable membrane from pure solvent to solution is called osmosis

OR

Osmosis is defined as the flow of Solvent



molecules through semi-permeable membrane from the region of low solute conc. to that of higher solute conc.

⇒ Diff bet<sup>n</sup> osmosis and diffusion.

### Semipermeable membrane :- (SPM)

The membrane which allows only solvent molecules to pass through it and not the solute particles is called as semipermeable membrane.

It is of two types :-

(i) Natural Semipermeable membrane :-

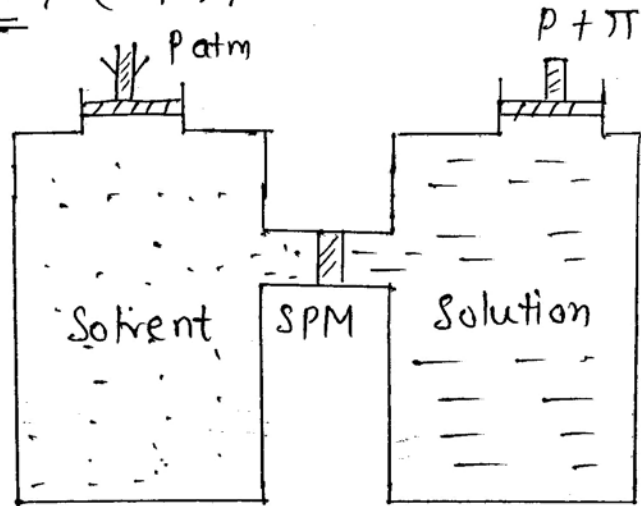
eg :- Animal membrane, egg membrane etc.

(2) Synthetic Semipermeable membrane :-

Synthetic SPM can be prepared from gelatinous ppt. of cupric ferrocyanide. cupric ferrocyanide form a film which contain submicroscopic holes or pores, through which only solvent molecules can pass but not solute particles.



Osmotic pressure :- (OP) :-



The excess pressure that must be applied over soln to prevent the passage of solvent into it through semipermeable membrane is called as Osmotic pressure. It is represented by  $(\pi)$ .

Osmotic pressure as a colligative property :-

Vant Hoff studied the osmotic pressure of ideal soln or dilute solns. and concluded that ideal or dilute soln. behave like ideal gases. Hence diff gas laws are applicable to dilute solutions.

vant Hoff observed that for dilute solutions the osmotic pressure  $(\pi)$  is given by :-

$$\pi = CRT .$$



where  $C =$  Conc. of soln i.e molarity of soln.

$T =$  Temp.

$R =$  gas constant.

for a soln at a given temp. both  $R$  and  $T$  are constant. Thus

$$\pi \propto C.$$

As osmotic pressure is directly proportional to conc. of the soln. i.e molarity of soln.

Hence osmotic pressure depends upon no. of moles of solute present per litre of soln. Thus it is a colligative property.

Det<sup>n</sup> of Molar mass from Osmotic Pressure:-

According to vant Hoff eqn :-

$$\pi = CRT$$

But  $C = \frac{n}{V}$

where  $n =$  No. of moles of solute  
 $V =$  volume of the soln.

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

But  $n = \frac{W_B}{M_B}$

Here  $W_B =$  wt. of solute used  
 $M_B =$  Mol. mass of solute

$$\pi = \frac{W_B / M_B}{V} \times RT$$



$$\pi = \frac{w_B \times R \times T}{v \times M_B}$$

$$M_B = \frac{w_B \times R \times T}{v \times \pi} \quad (1)$$

The results obtained from above eqn. will be accurate if (a) Solute is non-volatile.

(b) Soln must be dilute. i.e 5% Soln.

(c) Solute should not undergo association or dissociation in soln.

⇒ Isotonic Solns :- The Solns having same osmotic pressure are called as isotonic solutions. Such solns will have same conc. also.

⇒ Hypertonic Soln :- The Soln which has higher osmotic pressure than another soln is called as Hypertonic Soln.

⇒ Hypotonic Soln :- The Soln which has lower osmotic pressure than another Soln. is called as Hypotonic Soln.

⇒ Reverse osmosis :- The process of movement of solvent molecule through semi-permeable membrane from the soln to solvent,



by applying excess pressure on soln side, is called as Reverse osmosis.

### Abnormal Mol. Masses :-

The Molecular mass of the solute determined by using colligative properties, sometimes does not match with the actual mass of the solute. This molecular mass is called as abnormal molecular mass. The accurate molecular mass is obtained only if the following conditions are satisfied :-

(i) when the solution is dilute.

becoz if the soln is concentrated the solute particles interact with each other as well as with the solvent molecules. As a result, the soln becomes non-ideal. Hence Mol. masses obtained will be abnormal.

(2) (a) The solute must not associate or dissociate in soln. becoz due to association no. of particles of solute present per unit volume of soln will decrease. Hence value of colligative prop. will come out less. As colligative



prop. is inversely proportional to mol. wt. of solute. Thus in this case we will get mol. mass of solute which will be more than actual mass of solute.

(b) If the solute undergo dissociation, this will result in ↑ in No. of particles of solute per unit vol. of soln. Hence value of colligative properties will come out more. As colligative prop. is inversely proportional to mol. mass of solute. thus the value of Mol. mass obtained will be lesser than the actual mol. mass of solute.

Vant Hoff's factor :-

Vant Hoff's described the extent of association or dissociation of solute in the soln. by a factor 'i' called as Vant Hoff factor.

It is defined as the ratio of normal and observed molar mass of the solute i.e.

$$i = \frac{\text{Normal molar mass (M}_N\text{)}}{\text{Observed molar mass (M}_O\text{)}}$$



we know

value of colligative property  $\propto \frac{1}{\text{mol. mass of Solute}}$

Hence vant Hoff's factor may also be given as:-

$$\frac{\text{Observed value of Colligative prop.}}{\text{Normal value of Colligative prop.}}$$

$\Rightarrow$  In case of association of Solute, No. of particles of Solute in soln. decreases - Hence value of Colligative property comes out less, In this case Observed mol. mass comes out more than Normal value. Hence during association value of 'i' is less than one i.e.  $i < 1$ .

$\Rightarrow$  In case of dissociation - No. of particles of Solute in soln increases  $\rightarrow$  value of colligative prop. comes out more. Hence  $M_N > M_0$ . Due to which value of 'i' becomes greater than 1 i.e.  $i > 1$ .





## Calculation of degree of association and degree of association from vant Hoff's factor:-

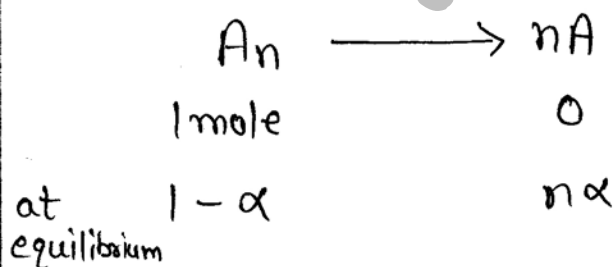
(a) Degree of dissociation ( $\alpha$ ) :-

It is defined as the fraction of the total salt that undergo dissociation into ions.

$$\text{Deg. of dissociation} = \frac{\text{No. of moles of sub. dissociated}}{\text{Total No. of moles of substance taken}}$$

Suppose one molecule of electrolyte gives ( $n$ ) ions upon dissociation. Then if we start with 1 mole of the solute and  $\alpha$  is the degree of dissociation.

Then at equilibrium-



$$\text{No. of moles of ions formed} = n\alpha$$

$$\text{Total no. of moles of particles} = 1 - \alpha + n\alpha$$

$$i = \frac{\text{observed no. of moles of solute}}{\text{Normal no. of moles of solute}}$$



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

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

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

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

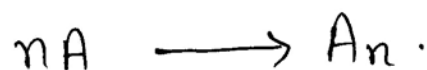
$$\alpha = \frac{(i-1)}{(n-1)}$$

### (b) Degree of Association :-

It is defined as the fraction of total no. of molecules which combine to form associated molecules.

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

Suppose 'n' simple molecules combines to form associated molecule.  $nA$ .

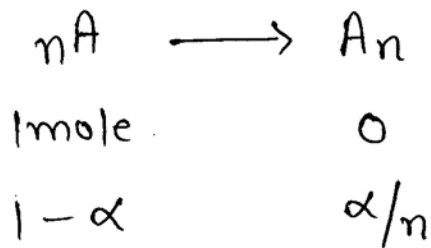


if we start with 1 mole of solute,

$\alpha$  = deg. of association.



then after association in soln.



Total no. of moles of ions observed =  $1 - \alpha + \alpha/n$

Vant Hoff factor (i) =  $\frac{1 - \alpha + \alpha/n}{1}$

$$i = 1 + \alpha/n - \alpha$$

$$i = 1 + \alpha \left( \frac{1}{n} - 1 \right)$$

$$i - 1 = \alpha \left( \frac{1}{n} - 1 \right)$$

$$\alpha = \frac{(i - 1)}{\left( \frac{1}{n} - 1 \right)}$$