

# Solutions

Solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied with certain limits.

A solution containing only one solute dissolved in a solvent is called binary solution.

A Solvent is the component of the solution which is present in larger amount by mass than the other component, termed as solute.

☞ Solvent determines the physical state in which solution exist.

## Types of solution :

Depending upon the physical state of solvent various types of solution are :-

1). Solid Solution is a solution in which the solvent is solid and solid, liquid or gas can be solute.

e.g. Solid in solid  $\rightarrow$  Alloys

Liquid in Solid  $\rightarrow$  Amalgam of Hg with Na.

Gas in solid  $\rightarrow$  H<sub>2</sub> in Pd, Cu in Au.

2). Liquid Solution is a solution in which the solvent is liquid and solid, liquid or gas component can be solute.

- eg. Solid in liquid → Glucose dissolved in H<sub>2</sub>O  
 Liquid in liquid → Ethanol dissolved in H<sub>2</sub>O  
 Gas in liquid → Oxygen dissolved in H<sub>2</sub>O

3. Gasous Solutions is solution in which the solvent is gas and solid, liquid or gas can be solute.

- eg. Solid in gas → Camphor in N<sub>2</sub>  
 Liquid in gas → CHCl<sub>3</sub> in N<sub>2</sub>  
 Gas in gas → Mixture of O<sub>2</sub> and N<sub>2</sub>

### Concentration Terms :-

↓  
volume related  
(temperature dependent)

- % by volume
- wt by volume
- Molarity
- Normality

↓  
Mass related  
(T independent)

- wt/wt %
- Mole fraction
- Molality
- PPM or PPB

#### ① wt by wt %

$$\text{wt/wt \%} = \frac{\text{mass of solute (g)}}{\text{mass of solution g}} \times 100$$

- A solution of NaCl in water 5% (wt/wt).
- 5 g of NaCl present in 100 g solution.

### ② Volume by volume %

$$V/V \% = \frac{\text{volume of solute (mL)}}{\text{volume of solution (mL)}} \times 100$$

► A HCl solution is 7 %. (V/V%)

→ 7 mL of HCl is present in 100 mL of solution.

### ③ wt by volume %

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

► A sugar solution is 3% (wt/v)

→ 3 g of sugar dissolved in 100 mL water.

### ④ Mole fraction :-

(X) Moles of a particular component divided by total moles of all components.

$$X_A = \frac{n_A}{n_A + n_B} \quad A + B \rightarrow \text{solution.}$$

Note:-  $X_A + X_B = 1$

### 5. Parts per Million (PPM)

$$\text{No. of PPM} = \frac{\text{mass of solute (g)} \times 10^6}{\text{mass of solution (g)}}$$

► Sugar 2 PPM in a solution.

2 g sugar in  $10^6$  g of solution.

### 6. Parts per Billion (PPB)

$$\text{No. of PPB} = \frac{\text{mass of solute(g)} \times 10^9}{\text{mass of solution(g)}}$$

7. Molarity : Number of moles of solute present in 1 L solution.

$$\text{Molarity} = \frac{\text{no. of moles of solute}}{\text{volume of solution (L)}}$$

On dilution :

$$[n = MV] \quad [M_1 V_1 = M_2 V_2]$$

Molarity of Mixture :

$$M = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$$

8. Molality (m) : Number of moles of solute present in 1 kg solvent.

$$m = \frac{\text{no. of moles of solute}}{\text{mass of solvent in kg}}$$

9. Equivalent Mass :

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{valency factor} \times}$$

Valency factor for

Acid  $\rightarrow$  basicity

Base  $\rightarrow$  acidity

Salt  $\rightarrow$  total +ve charge on cation.

Note: Number of gram equivalent =  $\frac{\text{mass}}{\text{Equivalent mass}}$

also,

Number of gram equivalent = no. of moles  $\times \text{X}$

10.  $(N)$  Normality : Number of gram equivalent of solute which are present in 1 L solution.

$$N = \frac{\text{no. of gram equivalent of solute}}{\text{volume of solution}}$$

also,  $N_1 V_1 = N_2 V_2$

11. Mass fraction : Mass of given component per unit mass of solution.

$$x_A = \frac{m_A}{m_A + m_B}$$

Solubility :-

The maximum amount of solute that can be dissolve in a specified amount of solvent at a particular temperature.

Dissolution :-

When solute is added continuously in solvent (liquid) ; the concentration of solution keeps on increasing. This process is known as dissolution.

Crystallisation :- When solute particles starts collecting and get separated out of solution. This is known as crystallisation.

### Saturated Solution :

When no more solute dissolves in solution at a given temperature because the rate of dissolution becomes equal to rate of crystallisation and dynamic equilibrium is achieved it's called Saturated Solution.

An Unsaturated Solution is one in which more solute can be dissolved at same temperature.

### Solubility of a solid in a liquid :-

The Solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid (solute) in grams which can dissolve in 100g of liquid (solvent) to form saturated solution at a specific temperature.

#### factors affecting solubility :

- 1). Nature of solute and solvent.
- 2). Temperature.

Note: Pressure has very little effect on solubility of solid in a liquid solid and liquids are highly incompressible.

#### 1) Nature of solute and solvent :

'Like dissolves like' this implies that solid solute dissolves in solvent which is chemically similar. Polar (ionic) solute dissolve in polar solvent and Non-Polar solute dissolve in non-polar solvent.

## 11) Effect of temperature on solubility :

The substance in which the process of dissolution is exothermic, the solubility decreases with increase in temperature.

The substance in which process of dissolution is endothermic, the solubility increases with increase in temperature.

## Solubility of Gas in a liquid :-

The solubility of any gas in a particular liquid is the volume of gas that can be dissolved in unit volume of liquid to form saturated at particular temperature and pressure of 1 atm.

### factors affecting solubility :

- 1). Nature of gas and solvent
- 2). Effect of temperature
- 3). Effect of Pressure.

### 1) Nature of gas and solvent :

The greater solubility of gases in solvent is due to their chemical similarity with solvent.

Gases like  $N_2$ ,  $H_2$ ,  $O_2$  etc. dissolve in water only to a small extent and  $CO_2$ ,  $HCl$ ,  $NH_3$  are highly soluble.

II) Effect of temperature :-

The solubility of gases decreases with increase in temperature. Temperature ↑ ; solubility ↓. Because on heating, kinetic energy cause more motion in gas molecules which break intermolecular bonds and escape from solution.

III) Effect of Pressure (Henry's Law) :-

The solubility of gases increases with increase in pressure.

Henry's law :-

This law states that, at a constant temperature, solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

Or

The partial pressure of a gas in vapour phase ( $P$ ) is directly proportional to the mole fraction ( $x$ ) of the gas in solution.

$$\therefore P \propto x$$

$$P = k_H x$$

$k_H$  is Henry's constant.

Different gases have different values of  $k_H$  at same temperature and in same solvent.

•  $k_H$  is function of nature of gases.

- Greater value of  $K_H$  ; lower the solubility.

$$P = X \downarrow ; \text{ solubility} \downarrow ; X \downarrow$$

$\uparrow K_H$

- Value of  $K_H$  increases with increase of temperature implying that the solubility decreases with increase in temperature.

$$\begin{aligned} K_H &\uparrow ; \text{ temperature} \uparrow \\ X &\downarrow ; \text{ solubility} \downarrow \\ \therefore \text{temperature} \uparrow : \text{solubility} &\downarrow \end{aligned}$$

That's why aquatic life prefer cold water.

#### Applications of Henry's Law:

- 1). In production of carbonated beverages .

To increase the solubility of  $CO_2$  , the bottles are sealed under high pressure .

When sealed open  $CO_2$  bubbles come out because partial pressure of  $CO_2$  decreases .

- 2). Scuba divers depends on compressed air for their  $O_2$  supply .

At depth , Pressure  $\uparrow$  , solubility  $\uparrow$

As come upper side of sea ,  $O_2$  dissolved into blood will used up in metabolic process , but  $N_2$  form bubbles as divers comes to atm pressure . This cause Bends or decompression sickness . To avoid this , cylinders are filled with air diluted with Helium .

(iv) Mountain Climbers :-

At high altitude, the partial pressure of O<sub>2</sub> is less than ground level. Thus, low O<sub>2</sub> concentration in blood and tissue, resulting anoxia, in which they feel weak and unable to think properly.

Vapour Pressure :-

Vapour Pressure of a liquid or solution is the pressure exerted by the vapours in equilibrium with liquid or solution at a particular temperature.

factors affecting Vapour Pressure :-

- 1). Nature of liquid.  
weaker the intermolecular forces, greater the amount of vapour pressure.

$$\text{vapour pressure} = \frac{1}{\text{force of attraction between molecule}}$$

2) Temperature

Higher the temperature, greater the vapour pressure.

Vapour Pressure of Liquid-Liquid solution :-

for a solution of liquid-liquid, as both the component of solution are volatile, each component form vapour pressure above the liquid.

This is governed by Raoult's law :-

In a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

According to Raoult's law,

$$P_A \propto X_A$$

$P_A = P^\circ A X_A$ , where  $P^\circ$  is vapour pressure of pure component one, at same temperature.

Similarly, for other

$$P_B = P^\circ B X_B$$

By Dalton's law of partial pressure,

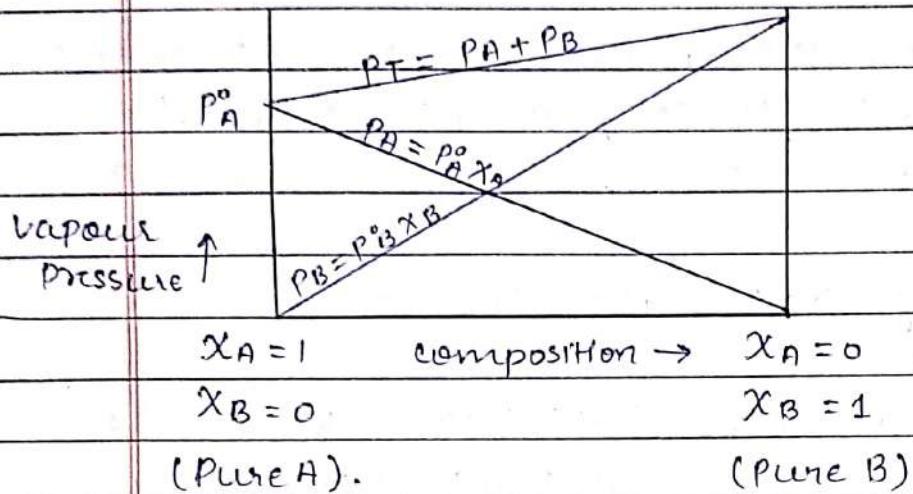
$$\begin{aligned} P_{\text{Total}} &= P_A + P_B \\ &= P^\circ A X_A + P^\circ B X_B \\ &= P^\circ A (1 - X_B) + P^\circ B X_B \\ &= P^\circ A - P^\circ A X_B + P^\circ B X_B \\ &= P^\circ A + X_B (P^\circ A - P^\circ B) \end{aligned}$$

$$P_{\text{Total}} = P^\circ A + X_B (P^\circ A - P^\circ B)$$

If  $y_A$  and  $y_B$  represent the mole fraction of the component A and B respectively in vapour phase, then

$y_A = \frac{P_A}{P_{\text{Total}}}$	,	$y_B = \frac{P_B}{P_{\text{Total}}}$
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Graph:



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

According to Raoult's law,

$$P_i = P_i^{\circ} X_i$$

and, Henry's Law

$$P = K_H X$$

On comparing both equations we can say that Raoult's law becomes a special case of Henry's law in which  $K_H$  becomes equal to  $P_i^{\circ}$ . Only constant differs.

Vapour Pressure of solution of solid in liquid :-

On adding non-volatile solute in a solution it is observed that presence of non-volatile solute reduces the escaping tendency of solvent molecule into vapour phase and thus lower the vapour pressure of the solvent.

According to Raoult's law

Vapour pressure of solvent in solution ( $P_s$ )

$$= \text{Mole fraction of solvent in solution} \times \frac{\text{Vapour pressure of pure solvent}}{\text{at } P^o}$$

Non volatile solute do not contribute in total vapour pressure of the solution.

so, vapour pressure = vapour pressure of the solvent in solution.

$$\therefore \frac{P_s}{P^o} = x_1 \quad (P_s \propto x_1) \quad \text{eqn 1}$$

$$\text{Mole fraction of solvent} = x_1 = \frac{n_1}{n_1 + n_2}$$

Substituting value of  $x_1$  in equation 1.

$$\frac{P_s}{P^o} = \frac{n_1}{n_1 + n_2}$$

$\frac{P^o - P_s}{P^o}$	$= \frac{n_2}{n_1 + n_2}$
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$P^o - P_s$  expresses lowering of vapour pressure.

and  $\frac{P^o - P_s}{P^o}$  is called relative lowering of vapour pressure.

Hence, we can define that,

'The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to mole fraction of solute in the solution'

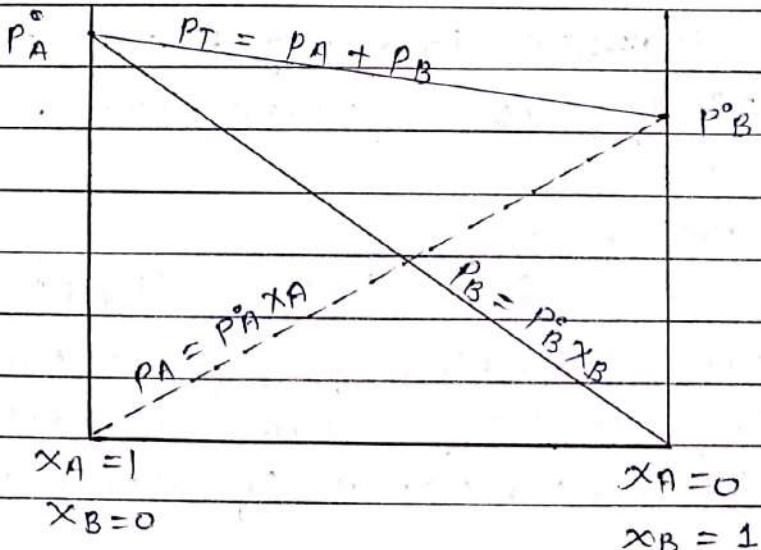
## IDEAL AND NON - IDEAL SOLUTIONS :-

### 1. IDEAL Solution

- Obey's Raoult's law under all condition of temperature and concentration.
- no change in volume on mixing.  $\Delta V_{mix} = 0$
- no change in enthalpy.  $\Delta H_{mix} = 0$   
[no heat absorbed or evolved]
- Intermolecular interaction between the components are of same magnitude as the pure component.

Example:

- Benzene + Toluene
- n*-Hexane + *n*-Heptane
- Ethyl bromide + Ethyl chloride
- Chlorobenzene + Bromobenzene.



2. NON-IDEAL Solution (do not obeys Raoult's law).

↓  
Showing positive Deviation

- the interaction between the components are less than in the pure component.

- $\Delta V_{mix} = +ve$

- $\Delta H_{mix} = +ve$

- $P_A > x_A P_A^{\circ}$ ,  $P_B > x_B P_B^{\circ}$

- form minimum boiling azeotropes.

↓  
Showing negative Deviation

- the interaction between the components are greater than the pure pure component.

- $\Delta V_{mix} = -ve$

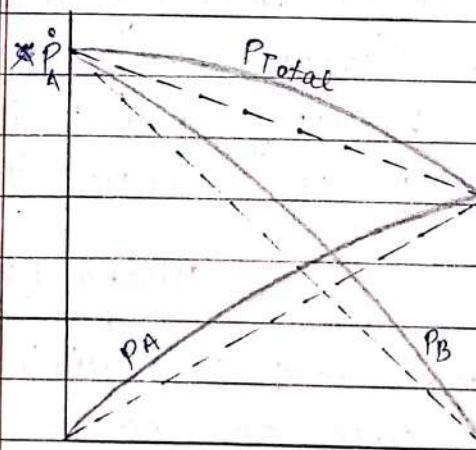
- $\Delta H_{mix} = -ve$

- $P_A < x_A P_A^{\circ}$ ,  $P_B < x_B P_B^{\circ}$

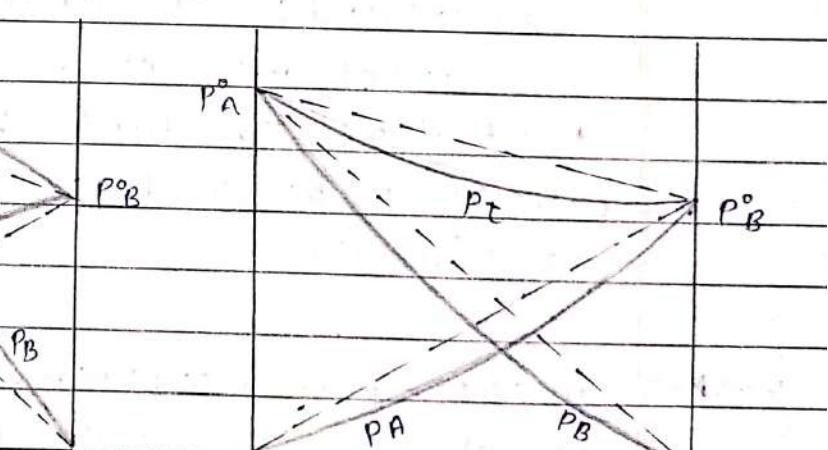
- form maximum boiling azeotropes.

Graphs :

→ +ve deviation



→ negative deviation



## Non Ideal Solution examples -

### ① Positive Deviation.

- Acetone + Carbon disulphide
- Methyl alcohol + H<sub>2</sub>O
- Acetone + Ethyl alcohol
- Acetone + Benzene
- Ethyl alcohol + H<sub>2</sub>O
- ~~CHCl<sub>3</sub>~~ Carbon tetrachloride + Chloroform
- CCl<sub>4</sub> + Benzene
- CCl<sub>4</sub> + Toluene.

### ② Negative Deviation -

- CHCl<sub>3</sub> + Benzene
- CHCl<sub>3</sub> + Diethyl ether
- Acetone + Aniline
- HCl + H<sub>2</sub>O
- HNO<sub>3</sub> + H<sub>2</sub>O
- Acetic acid + Pyridine
- HI + H<sub>2</sub>O

## Azeotropic or constant Boiling Mixture -

An azeotropic is a liquid mixture that has constant boiling point and whose vapour has same composition as liquid.

(ethanol + water)

In case of +ve deviation, we get minimum azeotropes and in case of negative deviation we get maximum boiling azeotropes (e.g. Nitric acid + water).

## Colligative Properties :

The properties depend on the number of solute particles relative to total number of particles present in solution irrespective of their nature. Such properties are called colligative properties.

These are -

1. Relative lowering of vapour pressure
2. Elevation in boiling point
3. Depression in freezing point
4. Osmotic pressure of solution

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1. Relative lowering of vapour pressure :

when a non-volatile solute is dissolved in a solvent, the vapour pressure of the solution is lower than that of pure solvent.

It was derived earlier:

$$\frac{P^{\circ} - P_s}{P^{\circ}} = \frac{n_2}{n_1 + n_2} \quad \text{or} \quad \frac{P_i^{\circ} - P_i}{P_i^{\circ}} = x_2$$

or

$$\frac{P^{\circ} - P_s}{P_s} = \frac{n_2}{n_1}$$

→ this formula can be used for dilute as well as concentrated solutions.

## 2. Elevation in Boiling point :

When a non-volatile solute is added to a solvent the resulting solution has a higher boiling point than that of pure solvent.

→ Boiling point is the temperature at which the vapour pressure of solution become equal to atmospheric pressure.

The increase in B.P.  $\Delta T_b = T_b - T_b^{\circ}$  is known as elevation in boiling point.

$$\Delta T_b = T_b - T_b^{\circ}$$

From experiments,

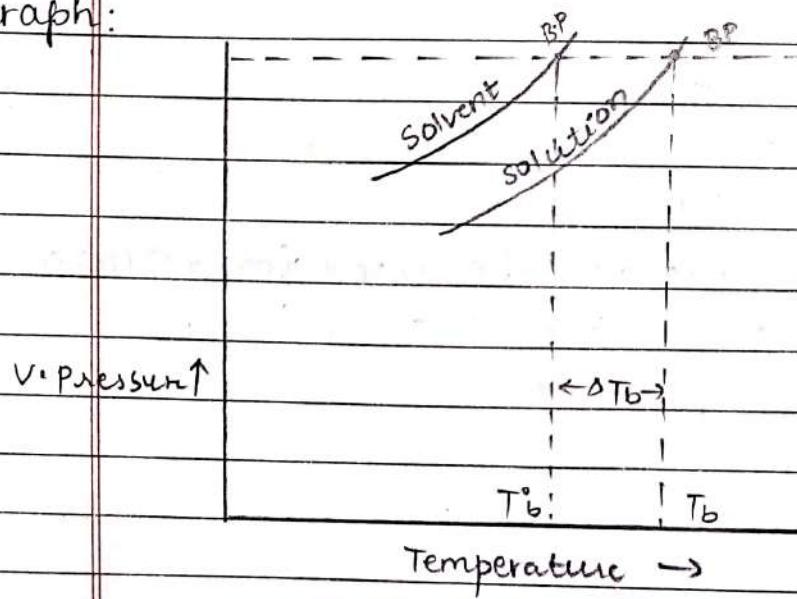
$$\Delta T_b \propto m \text{ (molal conc. of soln).}$$

$$\Delta T_b = K_b m$$

where  $K_b$  is molal elevation constant and depends upon nature of solvent.

$$\Delta T_b = \frac{K_b \times w_2 \times 1000}{M_2 \times w_1}$$

Graph:



### 3. Depression in freezing Point :

when a non-volatile solid is added to the solvent its vapour pressure decreases and become equal to that of solid solvent at lower temperature . Thus , freezing point of solvent decreases.

Freezing point is the temperature at which vapour pressure of liquid state becomes equal to vapour pressure of solid state .

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

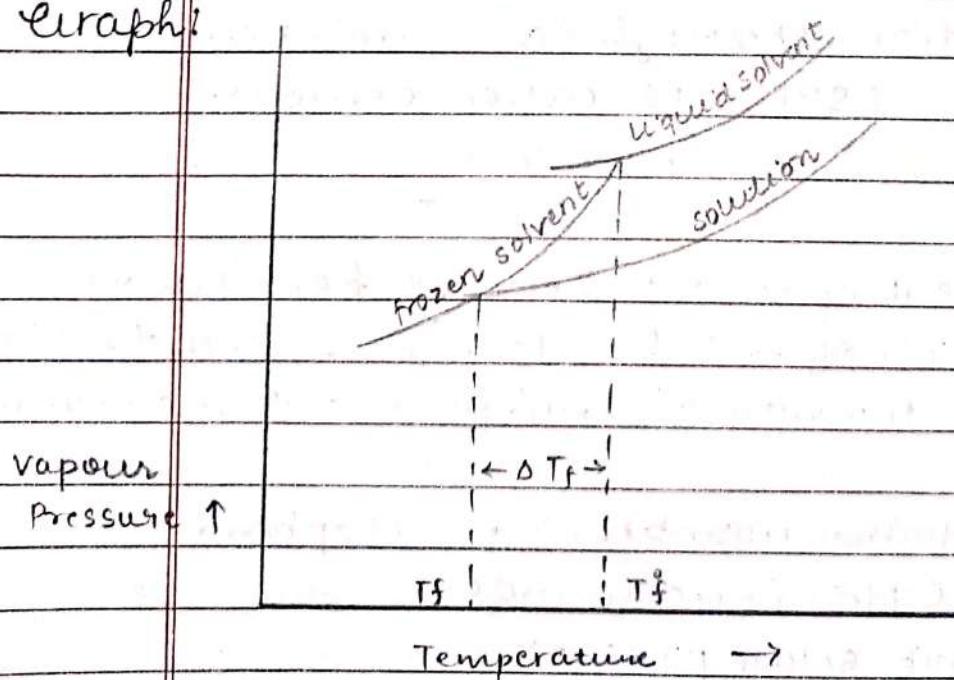
$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

where  $K_f$  is molal depression constant and depends on solvent .

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{w_1 \times M_2}$$

Graph:



### Constant $K_f$ and $K_b$

The values of  $K_f$  and  $K_b$  can be ascertained from the following relations,

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{\text{fus.}} H}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{\text{vap.}} H}$$

$R$  is gas constant.

$M_1$  is Molar mass of solvent.

$T_f$  is freezing point of pure solvent in K

$T_b$  " boiling " " " " " "

$\Delta_{\text{fus.}} H$  represent enthalpy for fusion of solvent.

$\Delta_{\text{vap.}} H$  " " vapourisation " "

### 4. Osmotic Pressure :

Osmosis : The movement of solvent molecule from their higher concentration to their lower concentration through a semi-permeable membrane (SPM) is called osmosis.

or

The movement of solvent molecules from lower concentration of solution to higher concentration of solution through a semi-permeable membrane.

SPM  $\rightarrow$  Animal membrane, cellophane,

$\downarrow$  copper ferrocyanide.

(do not permit solute particle)

### Osmotic Pressure : ( $\Pi$ )

The net movement of solvent molecule from solvent to solution can be stopped by applying some extra pressure over solution and that extra pressure over solution side which stops osmosis is called osmotic pressure.

$\Pi \propto C/M$  ( molarity of solution )

$\Pi \propto T$  ( Temperature in K ).

$$\Pi = MRT \text{ or } CRT$$

$$\boxed{\Pi = CRT} \quad \text{where, R is solution constant.}$$

$$R = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

→ Diffusion: Resultant movement of any substance from region of higher concentration to lower concentration.

- ▷ Isotonic: Solution with equal osmotic pressures are called isotonic.
- ▷ Hypotonic: Solution have lower osmotic pressure than normal solution.
- ▷ Hypertonic: Solution have higher osmotic pressure than normal solution.

Reverse Osmosis : Reverse osmosis is a special type of filtration that uses a semi-permeable membrane that allows only pure water to pass through it, filtering the larger molecules or impurities.

→ Applied pressure should be more than osmotic pressure ( $\Pi$ ).

### Abnormal molar Mass -

A molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

Weak electrolyte dissociate in water to form ions.

Van't Hoff factor : (i)

It can be defined as -

ratio of concentration of particles formed when a substance is dissolved to a concentration of substance by mass.

- The extent to which a substance associates or dissociate in a solution is described by Van't Hoff factor.

$$i = \frac{\text{total number of moles of solute after dissociation}}{\text{total number of moles of solute before dissociation or association}}$$

$$i' = \frac{\text{observed (actual) colligative Property}}{\text{calculated colligative property.}}$$

$$i = \frac{\text{normal molar mass}}{\text{observed molar mass}}$$

for example :



initial	1	0	0
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equilibrium	$1 - \alpha$	$4\alpha$	$\alpha$
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$$i = \frac{1 - \alpha + 4\alpha + \alpha}{1}$$

$$i = \frac{1 + 4\alpha}{1}$$

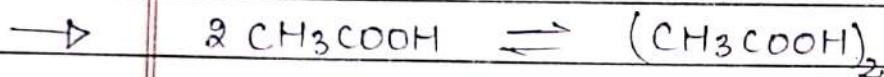
in case of dissociation

if dissociation 100%

$i$ 's greater than 1.

$$i = \frac{1 + 4 \times 1}{1} = 5$$

$i' = 5$



initial	1	0
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equilibrium	$1 - \alpha$	$\alpha/2$
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$$i = \frac{1 - \alpha + \alpha}{1 \times 2}$$

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

in case of association  
 value of  $i$  is less than  
 unity.

$$1. \frac{P_1^\circ - P_1}{P_1^\circ} = i \times \frac{n_2}{n_1}$$

$$2. \Delta T_b = i k_b m$$

$$3. \Delta T_f = i k_f m$$

$$4. \pi = i CRT$$