1. SOLUTIONS

Synopsis :

- A **solution is a homogeneous mixture** of two or more substances at molecular or ionic levels.
- Formation of solution is a physical change single phase exists in solution.

  Individual molecules or ions will exist in solution.

  Components of true solution can not be separated by filtration, settling, centrifugation.
- Solute may lose it's physical state, but solvent retains it's physical state.
- Based on the number of components, solutions may be binary, ternary, quaternary etc,.
- A binary solution contains only two components known as solute and solvent.

  Solute + Solvent = Solution
- The substance present in smaller proportion in binary solution is known as the solute.

  The solute is called the dissolved component (or) dispersed component in the solution.
- The substance present in larger proportion is called as the solvent.

  The solvent is called the dissolving component (or) dispersion medium in the solution.
- In case of solid in liquid type solutions, irrespective of their amounts, solid is solute and liquid is solvent.
- Based on the physical state, solutions are of 3 types.

  Gaseous solution : Solvent is Gas

  The liquid solutions : Solvent is Liquid

  Solid solutions : Solvent is solid
- In any type of solution the solute may be gas or liquid or solid.
- Solutions are of 7 types based on the physical states of solute and solvent.

  1) Gas in gas : Mixture of any two gases

  2) Gas in liquid : Soda water

  3) Liquid in liquid : Alcohol in water

  4) Solid in liquid : Sugar in water

  5) Gas in solid : H_2 occluded in Pd

  6) Liquid in solid : Amalgams

  7) Solid in solid : Alloys
- Liquid in gas and solid in gas are not considered as true solutions as they are not homogenous.
- A solution in which water is used as a solvent is known as aqueous solution.
- A solution in which alcohol is used as a solvent is known as alcoholic solution.
- A solution in which an organic liquid is used as a solvent is known as non – aqueous solution.
- The commonly used solvents in non – aqueous solutions are CCl_4, CS_2, $CHCl_3$, C_6H_6 liquid SO_2, acetic acid , liquid NH_3 etc.
- Based on the amount of dissolved solute, solutions are of 3 types.

  I) *Saturated solutions :* which can not dissolve any more solute. Usually some amount of undissolved

solute is present in it. A dynamic equilibrium exists between dissolved solute and undissolved solute.

II *unsaturated solutions :* which can dissolve some more amount of solute.

No excess of undissolved solute exists.

No dynamic equilibrium exists.

III) *Super saturated solutions :* which contain excess of dissolved solute.

No equilibrium exists.These are unstable.

Concentration :

- The quantity of the solute present in a definite quantity of the solution relative to the solvent is known as the **concentration of the solution** (or) **strength of the solution .**

  Note: A solution whose concentration is known is called as standard solution. The container used to prepare a standard solution is known as standard flask.

- A solution which contains less quantity of the solute compared to the solvent is known as 'dilute solution' i.e., the strength of a dilute solution is 'very low'.

- A solution which contains excess solute, in a definite quantity of the solution is known as a 'concentrated solution' i.e., the strength of a concentrated solution is 'very high'.

- Weight of the solution

  = Volume of the solution $\times$ density of the solution

  $W = V \times d$

- The weight of one milli litre of a solution in grams is known as the density of the solution.

  The density of the solution depends on temperature of the solution.

  The units for the density of solution are gram/ml. The ratio between the density of solution and the density of water, both measured at the same temperature is known as relative density of the solution (or) specific gravity of the solution.

- The specific gravity of solution has no units.

  Various terms used in concentration:

  Weight percent:

  $$\text{Weight fraction} = \frac{\text{weight of solute}}{\text{weight of solution}}$$

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

  Volume percent :

  $$\text{Volume fraction} = \frac{\text{volume of solute}}{\text{volume of solution}}$$

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

- It is applicable for solution containing both solute and solvent as liquids.

  Solubility : It is the weight of solute dissolved in 100 grams of solvent to form saturated solution.

  $$\text{Solubility} = \frac{\text{weight of solute}}{\text{weight of solvent}} \times 100$$

Molarity : The number of gram moles of the dissolved solute per litre of solution is known as the molarity of the solution. It is represented by 'M'.

$$= \frac{\text{number of moles of the solute}}{\text{volume of the solution in litres}}$$

- Units for molarity are moles/litre.
- The molarity is the most convenient and commonly used method of expressing the concentration of solution.
- The molarity of a solution slightly decreases with increase in temperature of the solution, due to increase in volume.

$$M = \frac{n}{v};\ M = \frac{\text{no.of milli moles of solute}}{\text{volume of solution in m}\ell}$$

No.of moles of solute = $M \times V$ (lit)

No.of milli moles of solute = $M \times V$ (mℓ)

$$M = \frac{\text{weight of solute in grams}}{\text{G.M.W of solute}} \times \frac{1}{V_{(lit)}}$$

$$M = \frac{w}{M.W} \times \frac{1000}{V_{(ml)}}$$

$$w = M \times M.W. \times V_{(lit)}$$

$$M = \frac{\% \times 10}{G.M.W} \quad \left(\% \frac{W}{V}\right)$$

$$M = \frac{\text{density} \times 10 \times \%}{G.M.W} \quad \left(\% \frac{W}{W}\right)$$

- If a solution is diluted

$M_1V_1 = M_2V_2$

M_1 = Molarity before dilution

M_2 = Molarity after dilution

V_1 = Initial volume; V_2 = Final volume

$V_2 = V_1$ + volume of water added

- When two solutions having same solute are mixed.

The molarity of resultant mixture

$$= \frac{M_1V_1 + M_2V_2 + ...}{V}$$

- In case of complete neutralizations or complete reaction between two solutions, the molarity in the resultant mixture is

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

- In case of incomplete reaction or incomplete neutralisation , then the molarity in the resultant mixture,

$$M = \frac{M_aV_a - M_bV_b}{V}\ (M_aV_a > M_bV_b)$$

$$M = \frac{M_bV_b - M_aV_a}{V}\ (M_bV_b > M_aV_a)$$

Equivalent weight (E):

- The weight of the substance which combines with 1 gram of hydrogen or 8 grams of oxygen is called equivalent weight.
- Equivalent weight is the weight of the substance which loses or gains 1 mole of electrons

No.of equivalents = $\frac{\text{weight of the substance(g)}}{\text{equivalent weight}}$

No.of milli equivalents = $\frac{\text{weight of the substance(mg)}}{\text{equivalent weight}}$

$E_{element} = \frac{\text{Atomic weight}}{\text{valency}}$

$E_{acid} = \frac{\text{molecular weight}}{\text{number of replaceble hydrogens}}$

Ex: $E_{HCl} = \frac{\text{molecular weight}}{1}$

- $E_{HNO_3} = \frac{\text{molecular weight}}{1}$

$E_{H_2SO_4} = \frac{\text{molecular weight}}{2}$

$E_{H_3PO_4} = \frac{\text{molecular weight}}{3}$

$E_{H_3PO_3} = \frac{\text{molecular weight}}{2}$

$E_{H_3PO_2} = \frac{\text{molecular weight}}{1}$

$E_{H_2C_2O_4} = \frac{\text{molecular weight}}{2}$

Equivalent weight of base = $\frac{\text{molecular weight}}{\text{number of replaceble } OH^- \text{ ions}}$

Ex : $E_{NaOH} = \frac{\text{molecular weight}}{1}$

$E_{Ca(OH)_2} = \frac{\text{molecular weight}}{2}$

$E_{NH_3} = \frac{\text{molecular weight}}{1}$

- **Equivalent weight of salt:** = $\frac{\text{molecular weight}}{\text{total charge(postive or negative)}}$

Ex: $E_{NaCl} = \frac{\text{molecular weight}}{1}$

$E_{MgCl_2} = \frac{\text{molecular weight}}{2}$

$E_{AlCl_3} = \frac{\text{molecular weight}}{3}$

$E_{Al_2(SO_4)_3} = \frac{\text{molecular weight}}{6}$

- **Equivalent weight of oxidising or reducing agent**

$$= \frac{\text{molecular weight}}{\text{change in oxidation state}}$$

Ex: $E_{KMnO_4} = \frac{\text{molecular weight}}{5}$

($MnO_4^- \rightarrow Mn^{2+}$ in acid medium)

$$E_{KMnO_4} = \frac{\text{molecular weight}}{1}$$

($MnO_4^- \rightarrow MnO_4^{2-}$ in basic medium)

$$E_{KMnO_4} = \frac{\text{molecular weight}}{3}$$

($MnO_4^- \rightarrow MnO_2$ in neutral medium)

$$E_{K_2Cr_2O_7} = \frac{\text{molecular weight}}{6}$$

($Cr_2O_7^{2-} \rightarrow Cr^{3+}$ in acid and basic medium)

Normality (N):

- The number of gram equivalents of the solute dissolved in one litre of solution is known as its normality.
- Units for normality are gram equivalents/ litre.
- The normality of a solution decreases with increase in temperature of the solution.

$$N = \frac{\text{No.of gram equivalent of the solute}}{\text{volume of the solution in litres}}$$

$$N = \frac{\text{number of milli equivalents of solute}}{\text{volume of solution (m}\ell)}$$

- Number of equivalent weight of solute = $N \times V_{(lit)}$
- Number of milli equivalents of solute = $N \times V_{(ml)}$

$$N = \frac{\text{weight of solute in grams}}{\text{gram equivalent weight of solute}} \times \frac{1}{V_{(\text{litres})}}$$

$$N = \frac{W}{G.E.W} \times \frac{1000}{V_{(ml)}}$$

$W = N \times G.E.W \times V_{(lit)}$

$$N = \frac{10 \times \%}{G.E.W} \left(\% = \frac{w}{v}\right)$$

$$N = \frac{\text{density of solution} \times 10 \times \%}{G.E.W} \left(\% \frac{W}{W}\right)$$

- If a solution is diluted

$N_1V_1 = N_2V_2$

- If two solutions having same solute are mixed, normality of the resultant mixture

$$N = \frac{N_1V_1 + N_2V_2 + ...}{V}$$

- When two solutions react completely :

$N_1V_1 = N_2V_2$

- When a solid reacts with a solution :

$$\frac{W}{G.E.W} = NV_{(lit)}$$

- Normality × Equivalent weight
  = molarity × molecular weight

  For any given solute , Mol.weight ≥ equivalent weight.

  For any given solution . M ≤ N

Formality (F) :

- Fomality is the number of formula weights of solute per litre of solution.
- Ionic compounds and polymers do not contain molecules and molecular weights.

  Instead of molecular weight, the formula weight to be taken and instead of molarity the formality to be considered.
- For any given solution, molarity and formality are same.

  $$\text{Formality} = \frac{\text{weight of solute}}{\text{formula weight}} \times \frac{1000}{\text{volume of solution}(m\ell)}$$
- **Molality** : The number of gram moles of the solute dissolved in one kilogram of the solvent is known as the molality of the solution. It is represented by 'm'.
- The units for molality are mole / kg.
- Molality is independent of temperature.
- Molality is the most inconvenient method of expressing concentration of a solution because it involves determining the weights of liquids.

  $$m = \frac{\text{number of gram moles of the solute}}{\text{weight of solvent in kilograms}}$$

$$m = \frac{\text{weight of solute in grams}}{\text{G.M.W of solute}} \times \frac{1000}{\text{weight of solvent in grams}}$$

- The molality of a saturated solution is given by

  $$m = \frac{10 \times \text{solubility}}{\text{G.M.W.of solute}}$$

  If molarity is given :

  $$m = \frac{1000 \times M}{(1000 \times d) - (M \times \text{Mol.weight})}$$

Mole fraction :

- The ratio between the number of moles of solute and the total number of moles of solute and solvent in the solution is known as the mole fraction of the solute. It is represented by X_1.

  $X_1 = \frac{n}{n+N}$ n = No.of moles of solute

  N = No.of moles of solvent
- The ratio between the number of moles of solvent and the total number of solute and the solvent in the solution is known as the mole fraction of the solvent. It is represented by X_2.

  $X_2 = \frac{N}{n+N}$ N = No.of moles of solvent

  n = No.of moles of solute
- Mole fraction can be expressed with reference to any component of the solution.

- If molality of aqueous solutions is known, then

  $$X_1 = \frac{m}{m + 55.55}$$

- Mole fraction of solute has no units. The sum of mole fractions of all components in a solution = 1.
- Mole fraction is independent of temperature.

Mole percent :

- The number of moles of solute present in 100 moles of a homogenous mixture of solute and solvent is known as the mole percent of the solute.

  Mole percent of solute=Mole fraction of solute$\times$100

  Mole percent of solvent=Mole fraction of solvent$\times$100

Vapour pressure :

- Liquids having low boiling points are called volatile liquids.

  Ex: Ether, acetone, benzene, carbondisulphide, carbon tetrachloride are volatile liquids.
- Liquids having high boiling points are called non volatile liquids.

  Ex: Aniline, Nitrobenzene, Con.H_2SO_4, water are non volatile liquids.
- Volatile liquids have
  i) Weak intermolecular forces
  ii) High vapour pressure
  iii) Low boiling point
- Non – volatile liquids have
  i) Strong intermolecular forces
  ii) Low vapour pressure
  iii) High boiling point
- When a liquid is in equilibrium with its own vapour the pressure exerted by the vapour on the surface of the liquid is known as the vapour pressure of the liquid.
- The vapour pressure of the liquid must be called as saturated vapour pressure, because actually the atmosphere over the liquid, which is saturated with the vapour of the liquid, exerts the pressure on the liquid.
- The vapour pressure of the liquid is represented by P.
- The vapour pressure of water is known as aqueous tension.
- The vapour pressure of the liquid is directly proportional to the temperature of the liquid.
- The vapour pressure of a liquid is independent of shape of the vessel.
- Vapour pressure of liquid increases exponentially with increase in temperature.
- Log P Vs $\frac{1}{T}$ gives a straight line with – ve slope. This is called Clausius – clapeyoron curve.
- The temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure is known as the boiling point of the liquid.
- Boiling point of a liquid can be changed by changing the external pressure. If external pressure is

increased, the boiling point of a liquid is increased and vice- versa.

Lowering of vapour pressure :

- When a non – volatile solute is added to a solvent, the vapour pressure of pure solvent decreases. This is called lowering of vapour pressure.
- With increase in the concentration of solution, the lowering of vapour pressure further decrease.

$P_s < P°$ P_s = vapour pressure of solution

P°= vapour pressure of pure solvent

$P° - P_s$ = lowering of vapour pressure

- The ratio of lowering of vapour pressure to the vapour pressure of pure solvent is called relative lowering of vapour pressure.

$\frac{P^0 - P_s}{P^0}$ = Relative lowering of vapour pressure.

Raoult's law :

- **I)** For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B}$$

Simplified (or) reduced form of Raoult's law :

$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A}$ (for dilute solutions, n_B is very small and it can be neglected)

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W}$$

P°= Vapour pressure of pure solvent

P_s= Vapour pressure of solution

X_B = mole fraction of solute

m = molecular weight of solute

M = molecular weight of solvent

w = weight of solute W = weight of solvent

Relation between Raoult's law and molality :

$$\frac{P^0 - P_s}{P^0} = \frac{\text{molality} \times M}{1000}$$ (M=mol.wt.of solvent)

- II) Raoult's law for solution containing two or more miscible liquids is "the partial vapour pressure of a liquid component in the solution is directly proportional to it's mole fraction".
- If solution contains two miscible liquids A and B , then

$P_A \alpha x_A$ $P_B \alpha x_B$

$P_A = P_A^\circ . x_A \; P_B = P_B^\circ . x_B$

$P_{total} = P_A + P_B$

$P_{total} = P_A^\circ . x_A + P_B^\circ . x_B$

- **Ideal solutions:** The solutions which obey Raoult's law at all concentrations of temperatures are called ideal solutions.
- In case of ideal solutions,

  I) $\Delta V_{mixing} = 0$

  ii) $\Delta H_{mixing} = 0$

  iii) No change in interactions
- Solutions behave ideally at infinite dilution.
- Raoult's law is applicable to
  i) Ideal solutions
  ii) dilute solutions
  iii) solutions containing non volatile solute
  iv) no change in the interactions before and after mixing of liquid components in case of solution containing miscible liquids.
  v) Solute which neither dissociate nor associate.

COLLIGATIVE PROPERTIES:

- The properties of dilute solutions which depend on the number of particles (ions or molecules) of the solute dissolved in the solution are called colligative properties.
  They are
  i) Relative lowering of vapour pressure (RLVP) of solution
  ii) Elevation in the boiling point of the solution $\left(\Delta T_b\right)$
  iii) Depression in the freezing point of the solution $\left(\Delta T_f\right)$
  iv) Osmotic pressure of the solution $\left(\pi\right)$.

1. RELATIVE LOWERING OF VAPOUR PRESSURE

- Ostwald's dynamic method is based on the measurement of RLVP of a solution due to addition of a non volatile solute
- RLVP as per Raoult's law, is equal to the mole fraction of solute

$$\frac{P_o - P}{P_o} = x_s$$

- Where $x_s =$ mole fraction of solute

$$\frac{P_o - P}{P_o} = \frac{n_s}{n_o + n_s}$$

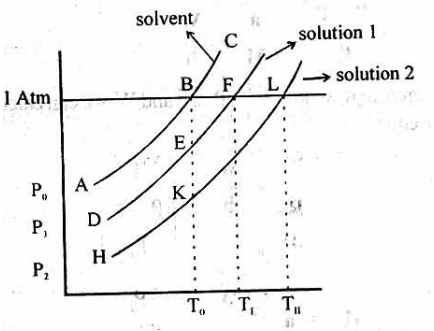
$$n_s = \frac{a}{M} : n_o = \frac{b}{W}$$

For dilute solutions $n_s < n_o$

$$\boxed{\frac{P_o - P}{P_o} = \frac{a}{M} \times \frac{W}{b}} \text{ or } \boxed{M = \frac{a \times W}{b} \times \frac{P_o}{\left(P_o - P\right)}}$$

2. ELEVATION IN BOILING POINT

- The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure (i.e., one atmosphere) is known as the boiling point of the liquid.
- The vapour pressure (P) of a dilute solution of the non-volatile solute is less than the vapour pressure of the pure $\left(P_o\right)$ solvent in which the non-volatile solute is dissolved.
- Boiling point of solution (T) is grater than the boiling point of solvent $\left(T_o\right)$.
- $\left(T - T_o\right) = \Delta T_b =$ elevation of Boiling point.



The principle of elevation of Boiling Point

- According to the principle of elevation in boiling point

$$\frac{\text{BE}}{\text{BK}} = \frac{\text{BF}}{\text{BL}}$$

Or

$$\frac{P_o - P_1}{P_o - P_{11}} = \frac{T_o - T_1}{T_o - T_{11}} \ (a)\ \Delta P \alpha\, \Delta T$$

- As per Raoults law $\Delta P \alpha X_s$, is $\Delta T_b \alpha X_s$

Or

$$\boxed{\Delta T_b = K_b X_s}$$

- $K_b =$ proportionality constant
- $X_s =$ Mole Fraction of solute.
- From thermodynamic laws
- $K_b = \dfrac{RT_o^2}{\Delta H_{vap}}$, $\Delta H_{vap} =$ molar heat of vapourisation of liquid
- $T_o =$ boiling point
- R = gas constant.

$$\boxed{\Delta T_b = \frac{RT_o^2}{\Delta H_{vap}} \times X_s}$$

- For dilute solutions, $X_s = \dfrac{n_s}{n_o} = \dfrac{a}{M} \times \dfrac{W}{b}$

$$\therefore \Delta T_b = \frac{RT_o^2}{\Delta H_{vap}} \left(\frac{a}{M} \times \frac{W}{b} \right)$$

- But ($\therefore \Delta H_{vap} = W \times l_v$ = latent heat of boiling point)

$$\therefore \Delta T_b = \frac{RT_o^2}{l_v} \times \frac{a}{M} \times \frac{1}{b}$$

- for 1 molal solution,

$$\therefore \Delta T_b = \frac{RT_o^2}{l_v} \times 1 \times \frac{1}{1000}$$

$$\left(\frac{a}{M} = 1, b = 1000 gr \right)$$

$$\boxed{K_b = \frac{RT_o^2}{l_v \times 1000}}$$

- ΔT_b and K_b are related by the equation
- $\boxed{\Delta T_b = K_b \times m}$ (m=molality)

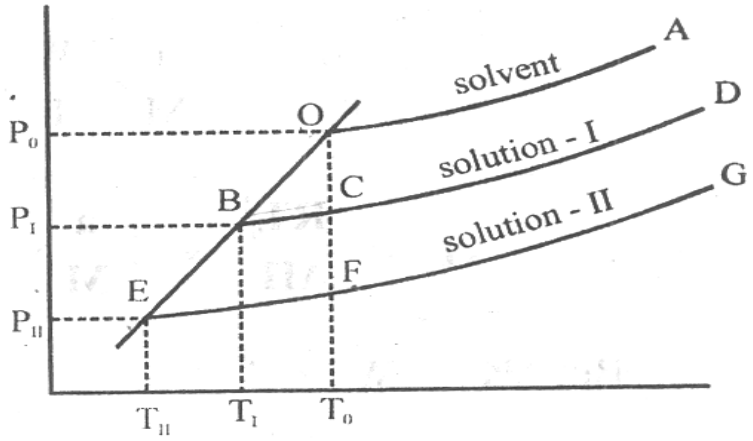
Or

$$\boxed{\Delta T_b = K_b \times \frac{a}{M} \times \frac{1000}{b}}$$

- The elevation in boiling point observed in one molal solution of a non-volatile solute is called molal elevation constant $\left(K_b\right)$ (or) Ebullioscopic constant.
- The molal elevation constant of a solvent does not change with the change in the nature of solute dissolved in it.
- Cottrell's method is used for determination of molar mass of solute using elevation of boiling point.

3. DEPRESSION OF FREEZING POINT

- Freezing point is the temperature at which the solid form of liquid begins to separate out from the liquid. At this temperature solid and liquid will be in equilibrium.
- When non volatile solute in dissolved in a solvent the freezing point decreases.
- For dilute solutions the curves are considered almost linear.



- From OBC, OEF,

$$\frac{OC}{OF} = \frac{BC}{EF}$$

Or

$$\frac{P_o - P_1}{P_o - P_{11}} = \frac{T_o - T_1}{T_o - T_{11}} \ (or)\ \Delta P \alpha \Delta T$$

- As per Raoults law, $\Delta P \alpha X_s$ is $\Delta T_f \alpha X_s$

  Or

  $\boxed{\Delta T_f = K_f X_s}$

- K_f = proportionality constant or molal depression constant or cryoscopic constant
- X_s = Mole Fraction of solute.
- From thermodynamic laws
- $K_f = \frac{RT_o^2}{\Delta H_f}$ molar heat of freezing $\Delta H_f =$
- T_o = freezing point
- R = gas constant.

  $\boxed{\Delta T_f = \frac{RT_o^2}{\Delta H_f} \times X_s}$

- For dilute solutions, $X_s = \frac{n_s}{n_o} = \frac{a}{M} \times \frac{W}{b}$

  $\therefore \Delta T_f = \frac{RT_o^2}{\Delta H_+}\left(\frac{a}{M} \times \frac{w}{b}\right)$

- But $\therefore \Delta H_f = W \times l_f$ (l_f = latent heat of freezing point)

  $\therefore \Delta T_f = \frac{RT_o^2}{l_f} \times \frac{a}{M} \times \frac{1}{b}$

- for 1 molal solution,

  $\therefore \Delta T_f = \frac{RT_o^2}{l_f} \times 1 \times \frac{1}{1000}$

  $\left(\frac{a}{M} = 1, b = 1000 gr\right)$

  $\boxed{K_f = \frac{RT_o^2}{l_f \times 1000}}$

- ΔT_f and K_f are related by the equation
- $\boxed{\Delta T_f = K_f \times m}$ (m=molality)

  Or

  $\boxed{\Delta T_f = K_f \times \frac{a}{M} \times \frac{1000}{b}}$

- The depression of freezing point observed in 1 molal solution of a non volatile solute is known as K_f

- K_f depends on chemical nature of solvent but not solute in the solution.
- Rast method is used for determination of molar mass of solute. Using depressing in freezing point.
- Rast method is used for solid solutions.

4. OSMOSIS:

- The spontaneous flow of the solvent through semipermeable membrane from pure solvent to solution (or) from a dilute solution to concentrated solution is known as osmosis.
- The membranes which allow to pass only solvent molecules through it but not solute molecules is called semipermeable membrane.
- Ex. Animal membranes like pig's bladder, membrane round the red blood corpuscle, cell membrane, parchment paper, cellophane paper, inorganic precipitate membranes like cupric ferro cyanide
- $Cu_2\left[Fe(CN)_6\right]$
- Calcium phosphate $Ca_3\left(PO_4\right)_2$

OSMOTIC PRESSURE

- The hydrostatic pressure developed on the aqueous dilute solution at equilibrium state due to inflow of water when the solution is separated from the water by a semipermeable membrane.
  (or)
- The pressure required to be applied on the solution to just stop the inflow of solvent into the solution, when the solution is separated from the solvent by a semipermeable membrane.
- **VANT HOFF'S THEORY OF DILUTE SOLUTIONS**
- According to vant Hoff's, dilute solutions behave as gases. Hence the laws that applicable to gases are also applicable to dilute solutions.
- **VANT HOFF'S BOYLES LAW**
- At constant temperature the osmotic pressure (π) of a dilute solution is directly proportional to its concentration (C)
- C = mole / litre

$$\pi\alpha\frac{1}{V} \qquad \left(\because C\propto\frac{1}{V}\right)$$

- $\pi V = K$ .....(1)
- **VANT HOFF'S CHARLE'S LAW**
- The osmotic pressure (π) of a solution of constant concentration (C) is directly proportional to the temperature in Kelvin Scale (T)

$$\pi\alpha T$$

- $\pi = KT$ ..... (2)
- from (1) and (2) $\pi\propto\frac{T}{V}$

$$\pi = S\frac{T}{V}$$

$$\therefore \pi = CST \qquad \left(\because \frac{1}{V}=C\right)$$

- here S = solution constant

- The value of 'S' is similar to the value of 'R'
- (gas constant)
- Hence $\pi V = RT$ for 1 mole
- for 'n' mole $\boxed{\pi V = nRT}$
- If 'a' is weight of the solute and 'm' is its molecular weight then

  $n = \frac{a}{M}$
- for 'n' moles $\pi V = \frac{a}{M} RT$

  (a) $M = \frac{aRT}{\pi V}$ (b) $M = \frac{aRTC}{\pi}$
- osmotic pressure is determined by Berkely - Hartely method

REVERSE OSMOSIS

- When a pressure greater than that of osmotic pressure (π) is applied on solution side, then the solvent from the solution flows into pure solvent this process is called reverse osmosis.
- It used in desalination of sea water

ISOTONIC SOLUTIONS:

- At a given temperature solutions of same osmotic pressure are called isotonic solutions:
- eg: Blood is isotonic with saline (0.9% w/v NaCl solution)

HYPOTONIC SOLUTIONS

- Solutions having lower osmotic pressure

HYPER TONIC SOLUTIONS

- Solutions having higher osmotic pressure

PLASMOLYSIS

- The flow of the liquid from the plant cell when placed in a hypertonic solution is called plasmolysis. The plant cell undergoes shrinkage. It is an example to exo-osmosis

HAEMOLYSIS:

- When a plant cell is placed in hypotonic solution then the solvent flows into plant cell. This is known as Haemolysis. The plant cell finally bursts. It is an example to endo-osmosis.
- Plants taken up water from soil through the phenomenon of osmosis through root hairs
- A raw mango placed in salt solution loses water via osmosis. This is a pickle.
- Osmotic pressure of solutions have high values and are of the order of about 20-200 atm.
- Ordinary membranes can't with stand pressure. Hence Berkely - Hartley measured osmotic pressure using cupric ferrocyanide as semipermeable membrane.
  The osmotic pressure of a solution containing 1 mole of solute particles per litre (1M) at is 22.4 atm.

FORMULAE:

1. $\pi V = nST$ Hence $\pi =$ Osmotic pressure

   $\pi V = \frac{w}{m} ST \left(\therefore n = \frac{w}{m} \right)$ S = Solution constant

$m = \frac{wST}{\pi V}$ T = absolute temperature

2. $\pi V = nST$ W=Weight of solute

$\pi = \frac{n}{v} ST = MST$ m = molecular wt of solute

V = volume of the solution
N = no. moles of solute
M=Molarity of the solution

3. Consider two solutions I and II having n_1 and n_2 moles of the solute in V_1 and V_2 litres of the solution respectively let P_1 and P_2 be their osmotic pressures at the same temperature (T)

If $P_1 = P_2$ i.e., isotonic solutions

then $\frac{n_1}{V_1} = \frac{n_2}{V_2}$

(a) $\frac{W_1}{M_1 V_1} = \frac{W_2}{M_2 V_2}$

OSMOTIC PRESSURE OF MIXTURE OF TWO SOLUTIONS

Case(I) Let two solutions of same substance having different osmotic pressures π_1 and π_2 are mixed then osmotic pressure of the resultant solution can be calculated as $\pi_1 V_1 + \pi_2 V_2 = {}_r\left(V_1 + V_2\right)$

Here π_r =osmotic pressure of resulting solution

Case (II) Let n_1 and n_2 are the number of moles of two different solutes present in V_1 and V_2 volumes respectively. Osmotic pressure of the mixture can be calculated as

$$\pi = \pi_1 + \pi_2 = \frac{n_1 i_1 ST}{\left(V_1 + V_2\right)} + \frac{n_2 i_2 ST}{\left(V_1 + V_2\right)}$$

$$= \frac{\left(n_1 i_1 + n_2 i_2\right)}{\left(V_1 + V_2\right)} ST$$

here i_1 and i_2 are vant Hoff's factors for the two solutes.

OSTWLAD'S -DYNAMIC METHOD :-

- This method is used to measure the molar mass of a solute based on the measurement of relative lowering of vapour pressure of a solution.
- solution is taken in first two bulbs(A - bulbs) and solvent is taken in the other two bulbs [B]. $CaCl_2$ is present in 'U' tube [C- bulb]
- Above 3- bulbs weights are determined before and after experiment.
- dry air in passed through the bulbs
- x= loss of weight solution bulbs α P.
- y = loss of weight of solvent bulbs α $P^0 - P$
- Total loss = gain (Z) in weight of U- tube [C]

$$\therefore Z = \left(x + y\right) = P_0$$

$$x + y = P + \left(P^0 - P\right) = P^0$$

$$\frac{P^0 - P}{P^0} = \frac{y}{x + y}$$

$$\frac{y}{x+y} = \frac{a}{M} \times \frac{W}{b}$$

$$M = \frac{aW}{b} \times \frac{(x+y)}{y}$$

COTTRELL'S METHOD :-

- This method is used to measure the molar mass of a solute using elevation of boiling point.
- Beckman thermometer is used to measure the elevation or depression in temperature.
- This thermometer does not measure absolute values of B.pt and F.pt.
- This thermometer contains Hg-reservoir at one end mercury bulb at the another end. these two are connected by capillary.
- It measures the elevation or depression temperature level of - 6^0 C to 300^0 C

$$\therefore \Delta T_b = K_b \times \frac{a}{M} \times \frac{1000}{b}$$

K_b = molal elevation constant of solvent

$$\therefore M = K_b \times \frac{a}{\Delta T_b} \times \frac{1000}{b}$$

RAST'S METHOD :-

- This method is used to measure the molar mass of a solute using depression in freezing point.
- In this method Camphor is used as a solvent.
- This method is generally used for solid solutions i.e. a sold solute in a solid solvent.
- Wt of Camphor = b gm
- Wt of solute = a gm
- mol.wt of solute = M.

$$\Delta T_f = K_f \times \frac{a}{M} \times \frac{1000}{b}$$

$$M = K_f \times \frac{a}{\Delta T_f} \times \frac{1000}{b}$$

BERKELY- HARTLEY METHOD :-

- This method is used to determine the Osmotic pressure which is used to measure the molar mass of a solute.
- A porous tube whose both ends are open is taken and its pores are precipitated with copper ferrocyanide.
- Copper ferro cyanide can act as semi permiable membrane
- Porous tube is fixed in an outer cylendrical tube made from gun metal.
- As Osmosis strarts the level in the capillary decreases due to flow of water from inner tube in to outer tube.
- Now pressure is applied extermally on the piston and the level of liquid in the capillary is brought to initial position, called as Osmotic pressure .

$$\pi V = nRT$$

$$\pi V = \frac{a}{M} RT$$

$$\therefore M = \frac{aRT}{\pi V}$$

a = wt of solute M = mol. wt of solute

- **ABNORMAL MOLAR MASS**
- Colligative properties are shown by dilute solutions.
- solutions which obey Raoult's law are called ideal solutions.
- Deviations in Raoult's law are observed due to increase in concentration of solutions.
- Solutions which deviate from Raoult's law are known as non-ideal solutions.
- In ideal solutions intermolecular forces in the solvent are negligible.
- But in non ideal solutions intermolecular forces are considerable.
- Non ideal solutions show deviations in colligative properties.
- Electrolytes undergo ionisation in aqueous solutions as a result number of particle in the solution increases hence magnitude of colligative properties increases.
- Colligative property and molar mass of solute are inversely proportional.
- So molar mass of electrolytic solutes determined experimentally is less than true value.
- Some solutes when dissolved in solvents may undergo association i.e, solute molecules combine to form dimers or trimers etc.
- Due to association number particles in the solution decreases, as a result magnitude of colligative property decreases. So molar mass of such solute will be higher than true value.
- Van't Hoff introduced a factor 'i' in the equations to equalise the experimental value and calculated value.
- For example, osmotic pressure (π) equation is
- $\pi V = RT$ (calculated)
- $\pi V = iRT$ (experimental)

$$\therefore \frac{\pi_{expt}}{\pi_{cal}} = i$$

- $$i = \frac{\text{experimental value of colligative property}}{\text{Calculated value of colligative property}}$$

example $$i = \frac{\text{observed osmotic pressure}}{\text{Calculated osmotic pressure}}$$

- For solutes which undergo dissociation and ionisation of a solute on ionisation gives 'n' ions (particles) and $'\alpha'$ is degree of ionisation at the given concentration, we will have $\left[1+(n-1)\alpha\right]$ particles (ions)

$$A_n \rightarrow nA$$

$$1 \qquad 0$$

$$1-\alpha \qquad n\alpha$$

- Total no of particles after dissociation = $1-\alpha+n\alpha=\left[1+(n-1)\alpha\right]$

$$i = \frac{\text{no.of particles after dissociation}}{\text{no.of particles before dissociation}}$$

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

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

- 'α' is degree of dissociation or ionisation.

Salt	Van't Hoff Factor i for complete dissociation of solute
NaC1	2.0
KC1	2.0
$MgSO_4$	2.0
K_2SO_4	3.0

- For solutes which undergo association
- If 'n' 'A' molecules combine to give A_n, we have

$nA \rightleftharpoons A_n$

- 1 O (α =degree of association at the given concentrate)

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

- $\therefore$ Total particle after association

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

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

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

$$\boxed{\alpha_{association}=\frac{i-1}{\frac{1}{n}-1}} \text{ or } \boxed{\alpha_{association}=\frac{1-i}{1-\frac{1}{n}}}$$