

CHAPTER -

Solution and colligative Property

UNIT - I

SOLUTION, DILUTE SOLUTION

AND COLLIGATIVE PROPERTY

Solutions:- The homogeneous mixture of two or more than two components. Each component may be solid, liquid or gaseous.

Homogeneous mixture:- The mixture which have same composition throughout the mixture.

Concetrated Dilute Solution:- A sol' in which solute is present in very small quantity.

Concentrated solution & A sol' in which solute is present in large quantity.

concentration can be expressed in many ways. the most commonly expressed conc' terms are-

1. Mass Percentage
2. Volume
3. Mass by Volume Percentage
4. ppm (Parts per million)
5. mole fraction
6. Molarity (M)
7. molality (m)
8. normality (N)
9. formality (F)

Concentration:- The amount of solute which is dissolved in definite amount of solvent its known as concentration.

1. Mass Percentage :- It is denoted with ($\text{S}/\text{S}\%$). The amount of solute in grams percent in 100 grams of the solution is called Mass Percentage.

$$\text{Mass \% of Component} = \frac{\text{Mass of solute (gm)}}{\text{Mass of solution}} \times 100$$

2. Volume Percentage :- It is denoted with ($\text{V}/\text{V}\%$). The volume of solute in ml present in 100 ml of the solⁿ. It is called Volume Percentage.

$$\text{Volume Percentage of a component} = \frac{\text{Volume of solute (ml)}}{\text{Volume of Sol}^n (\text{ml})} \times 100$$

3. → It is denoted with ($\text{W}/\text{V}\%$).
The mass of solute in grams present in 100 ml solution or it is the mass of solute dissolved in 100 ml of solution.

$$\text{mass by Volume \%} = \frac{\text{Mass of Solute}}{\text{Volume of Solution (ml)}} \times 100$$

4. → when a solute is present in very small (trace) quantities then it is convenient to express the conc" in Ppm.

Definition: Amount of solute in grams present in 10^6 gm of solution is known as P.P.M.

$$\text{Ppm} = \frac{\text{Amount of Solute in gm}}{\text{Mass of Solution in gm}} \times 10^6$$

Eg) Conc' of dissolved oxygen in sea water can be expressed in P.P.M.

→ Conc' of pollutants in water or atmosphere can be expressed in P.P.M.

5. → It is denoted with χ .

The ratio of no. of moles of one component to the total no. of moles of all the components present in a solution.

Eg) In a binary mix if the no. of moles of A & B are n_A & n_B respectively, the mole fraction of A will be

$$\chi_A = \frac{n_A}{n_A + n_B} \quad \chi_B = \frac{n_B}{n_A + n_B}$$

$$\chi_A + \chi_B = 1$$

It has no units (becoz it is a ratio of no. of moles)

It is independent of temperature

6. → It is denoted by M

The no. of moles of solute dissolved in 1 litre of a solution.

$$M = \frac{n}{V} = \frac{\text{no. of moles of the Solute}}{\text{Volume of soln in litre}}$$

Unit = Moles/litre

$$n = \frac{\text{Amount of solute in gm}}{\text{Molecular weight of solute}}$$

$$M = \frac{\text{Amount of solute in gm}}{\text{molecular weight of solute} \times \text{Volume of sol (ml)}} \times 100$$

$$\begin{aligned} \text{No of moles} \\ \text{of Solute} \end{aligned} = \text{Molarity} \times \text{Volume of Solution} \\ \text{in liters}$$

$$n = M \times V$$

$$\begin{aligned} \text{No of milli} \\ \text{moles of Solute} \end{aligned} = \text{Molarity} \times \text{Volume of Solution (ml)}$$

→ Molarity is inversely proportional to volume

$$M \propto \frac{n}{V}$$

Molarity changes with temp., because volume depends on temp.

- with rise in temp. volume ↑ ses
- ↓ fall ↓ ses
- increases in temp. molarity ↑ ses
- decreases " " ↓ ses

Important Points :-

$$\text{Decimolar} = 0.1 \text{ molar} = M/10$$

$$\text{Centimolar} = 0.01 \text{ molar} = M/100$$

$$\text{Millimolar} = 0.001 \text{ molar} = \frac{M}{1000}$$

$$\text{Semi molar} - 0.5 \text{ molar} = \frac{M}{2}$$

$$\text{Deca molar} - 10 \text{ molar} = 10M$$

7. It is denoted by N

The no. of gram equivalents of solute present in 1 liter of solution.

$$\text{Mole} = \frac{\text{Amount of Solute in gm}}{\text{Gram molecular weight}}$$

$$\text{Gram Equivalent} = \frac{\text{Amount of Solute in gm}}{\text{Equivalent mass}}$$

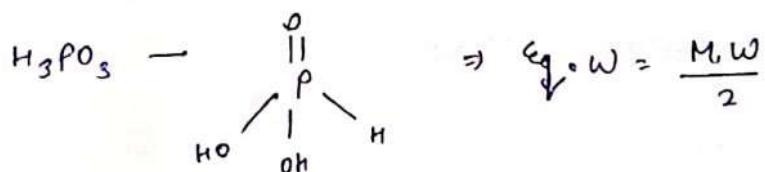
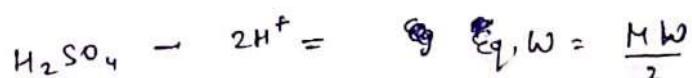
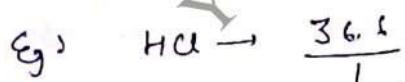
→ A normal Sol" contains one gram equivalent of solute.

$$\text{Normality} = \frac{\text{Weight of Solute in gram}}{\text{GEW} \times V(\text{in ml})} \times 1000$$

$$N_1 V_1 = N_2 V_2$$

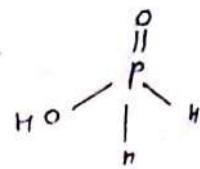
$$\boxed{\text{Equivalent weight of Acid} = \frac{\text{Formula weight / Molecular weight}}{\text{Basicity}}}$$

Basicity = no. of H^+ denoted / no. of $-OH$ linkage



$$\text{H}_3\text{PO}_4 = \text{Eq. W} = \frac{\text{M.W}}{3} = \frac{98}{3} = 32.6$$

H_3PO_4 (Hydro Phosphorus acid) -



$$\text{Eq. W} = \frac{\text{M.W}}{3}$$

$$\text{HCl} \rightarrow \frac{\text{M}}{1} = \frac{36.5}{1} = 36.5$$

$$\text{HNO}_3 = \frac{\text{M}}{1}$$

$$\text{Equivalent weight of Base} = \frac{\text{Formula weight of Base}}{\text{Acidity of Base}}$$

No. of replaceable hydroxyl grp of base is called Acidity.

$$\text{Eg. } \text{E}_{\text{Ba}(\text{OH})_2} = \frac{\text{M}}{2} = \frac{171.33}{2} = 85.67$$

$$\text{E}_{\text{Fe}(\text{OH})_3} = \frac{\text{M}}{3} = \frac{107}{3} = 35.7$$

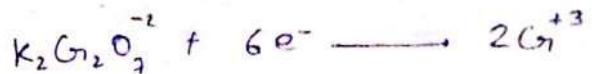
$$\text{E}_{\text{NaOH}} = \frac{\text{M}}{1}, \quad \text{E}_{\text{Ca}(\text{OH})_2} = \frac{\text{M}}{2}$$

$$\text{E}_{\text{Al}(\text{OH})_3} = \frac{\text{M}}{3}$$

Equivalent weight of salt :-

$$\text{E}_{\text{salt}} = \frac{\text{Formula weight of the salt}}{\text{Total charge of the cation or anion of the salt}}$$

Eg: $K_2Cr_2O_7$



Change in oxidation no.

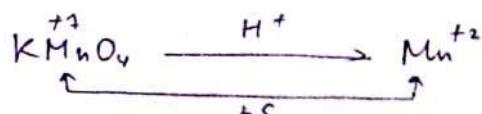
For one 'Cr' atom = 3

Change in oxidation no

For two 'Cr' atom = 6

No. of e^- s gained = 6

$$K_2Cr_2O_7 = \frac{F}{6} = \frac{204}{6} = 49$$



$$E_{KMnO_4} = \frac{M.W}{S}$$

Equivalent weight of Reducing agent:

$$E_{\text{reductant}} = \frac{\text{formula weight of reductant}}{\text{electrons lost by reductant}}$$

Eg: Mord's salt (Ferrous Ammonium sulphate)

$$\text{formula} = FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$$

Formula weight = 392

$$E_{\text{Mord's salt}} = \frac{392}{1} = 392$$



∴ It is denoted by m.

8.

The no. of moles of the solute present in 1 kg of the solvent or 100 gm of the solvent is called Molality.

$$\text{Molarity (m)} = \frac{\text{No. of moles of the Solute}}{\text{Mass of Solvent in kg}}$$

Units = Moles/kg

- ⇒ Molarity is independent on temper because the mass does not change with temper.
- So it is the most common & convenient method to express the concentration of the Solutions.

Q)

$$m = \frac{\text{weight of the Solute in gm}}{\text{GMW of Solute}} \times \frac{100}{\text{weight of solvent in gm}}$$

Q) A solⁿ of glucose in water is labelled as 10% w/w%. What would be the molality of the Solution?

Solⁿ) 10% means 10 gm solute dissolve in 100 gm solution

$$\text{mass of glucose (w)} = 10 \text{ gm}$$

$$\text{solution (w)} = 100 \text{ gm}$$

$$\text{water} = 100 - 10$$

$$= 90 \text{ gm} = 0.09 \text{ Kg}$$

$$\text{Molecular mass of glucose } [C_6H_{12}O_6] = 180 \text{ g mol}^{-1}$$

Molarity of a solⁿ

$$m = \frac{\text{mass of glucose}}{\text{GMW of glucose}} \times \frac{1}{\text{mass of solvent (kg)}}$$

$$m = \frac{10}{180} \times \frac{1}{0.09} = 0.617 \text{ mol kg}^{-1}$$

$$= 0.617 \text{ m}$$

Q] calculate the molality of a sol⁻ containing 5g of NaOH in 450 ml of sol⁻.

$$\text{Ans Moles of NaOH} = \frac{5}{40 \text{ g/mol}} = 0.125 \text{ mol}$$

$$\text{Volume of sol}^{-} \text{ in litres} = \frac{450 \text{ ml} \times 1 \text{ l}}{1000 \text{ ml}} \\ = 0.45 \text{ l}$$

$$\text{Molarity (M)} = \frac{\text{no. of moles of the solute}}{\text{Volume of sol}^{-} \text{ in litres}} \\ = \frac{0.125}{0.45} = 0.278 \text{ M}$$

NOTE :- Mass Percentage, Parts per million, mole fraction & molality do not change with temper. Only molality changes with temper.

Activity and Activity Coefficient :



$$K = \frac{[A^+][B^-]}{[AB]}$$

Dissociation constant

$[s]$ = Active mass

$$K = \frac{C_A^+ \cdot C_B^-}{C_{AB}}$$

It has been observed that value of K is not constant. It varies with the change in concentration. It is due to inter ionic forces b/w ions.

Due to INF all ions are not free to carry current. The fraction of ions which are absolute free to carry current are known as effective ions.

The terms used to express amount of effective ion is known as activity.

$$K = \frac{a_A^+ \cdot a_B^-}{a_{AB}}$$

$$a \propto c$$

$$a = f c$$

f = activity coefficient

$$K = \left(\frac{c_A^+ c_B^-}{c_{AB}} \right) \left(\frac{f_A^+ f_B^-}{f_{AB}} \right)$$

for non ideal sol⁻ value of f is less than 1 while in the case of ideal sol⁻ value of f is equal to 1

as the sol⁻ is diluted interionic attraction (\downarrow) goes and f approaches to unity ($f \rightarrow 1$), at ∞ dilution f is almost equal then $a = c$

(Q) Calculate the effective conc["] of ~~0.098 M~~ 0.098 M NaCl at 25°C

If activity coefficient of sol["] is 0.780?

Now $a = f c$ ← theoretical conc["]

actual effective conc["] $a = 0.098 \times 0.780$

$a = 0.07644 \text{ M}$

HENRY'S LAW :- This law is used to explain effect of pressure on solubility of gases.

This law states that at a const. temper. the solubility of a gas in a liquid or solⁿ is directly proportional to the partial pressure of gas present above the surface of liq or solⁿ.

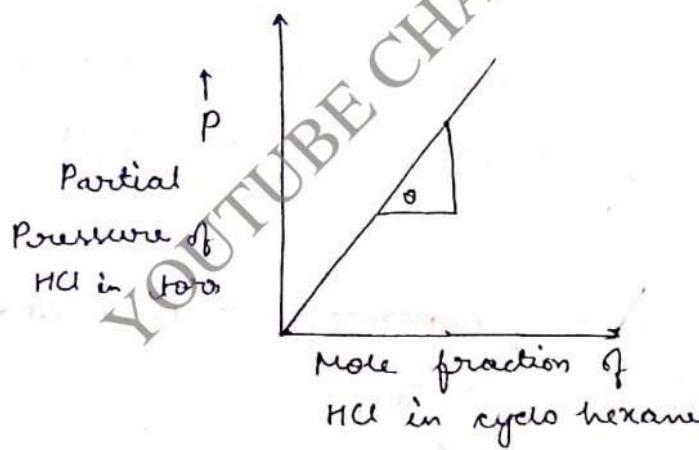
- mole fraction of a gas in a solⁿ is proportional to the partial pressure of the gas over the solution.
- the partial Pressure of the gas in vapour phase (P) is proportional to the mole fraction (X) of the gas in the solution

Henry's law is expressed as

$$P \propto X$$

$$P = K_H X$$

K_H = Henry's law const.



$$\text{Slope (tan} \theta\text{)} = K_H$$

Gas	Temperature / K	K_H / bar
He	293	144.97
H ₂	293	69.48
N ₂	293	76.48

N ₂	303	88.84
O ₂	293	34.86
O ₂	303	46.82
Ar	298	40.3
CO ₂	298	1.87
HCHO	298	1.83×10^{-5}
CH ₄	298	0.413
C ₂ H ₃ Cl	298	0.611

T ↑, K_H ↑ solubility ↓

1. In soft drinks & soda water, CO₂ is passed under high pressure and sealed why?
→ increase the solubility of CO₂ based on Henry's law
2. Scuba divers have high concentration of dissolved atmospheric gases in blood why?
→ Scuba divers go deep into sea which results in high pressure under activity water, which causes more solubility of gases inhaled based on Henry's law.
3. When scuba divers comes to surface experiences a medical condition known as bends, which are painful & dangerous to life why?
→ When divers come to step surface pressure (0) sea, this releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries & creates condition called bends.

4. What is the scuba divers air tank composition?
- Air diluted with helium He = 11.7% + 56% N₂ + 32.1% O₂
5. Why do people living at hill tops or at higher altitude experience a condition known as anoxia?
- At high altitudes the partial pressure oxygen is less than that on ground. This leads to low concentration of oxygen in the blood & tissues of the people. This leads to weakness & inability to think properly for climbers.
6. B/w ammonium chloride & sodium chloride which is more soluble with rise in temp?
- Ammonium chloride as its enthalpy of dissolution is endothermic.

RAULT'S LAW (PART - II)

Acc to Rault's law "vapour pressure of the sol" is directly proportional to the mole fraction of the solvent.

$$P_s \propto X_{\text{solvent}}$$

$$P_s = P_0 X_{\text{solvent}}$$

$$P_s = \text{V.P of solution}$$

$$P_0 = \text{V.P of pure solvent}$$

$$\frac{P_s}{P_0} = X_{\text{solvent}}$$

$$1 - \frac{P_s}{P_0} = 1 - X_{\text{solvent}}$$

Solution, Dilute Solution and Colligative Properties :-

Raoult's law :-

According to Raoult's law " V.P of soln is directly proportional to the mole fraction of solvent.

$$P_s \propto \chi_{\text{solvent}}$$

$$P_s = P_0 \chi_{\text{solvent}}$$

$$P_s = \text{V.P of solution}$$

$$P_0 = \text{V.P of pure solvent}$$

$$\frac{P_s}{P_0} = \chi_{\text{solvent}}$$

$$1 - \frac{P_s}{P_0} = 1 - \chi_{\text{solvent}}$$

* $\left[\frac{P_0 - P_s}{P_0} = \chi_{\text{solute}} \right] \quad \left\{ \chi_{\text{solute}} + \chi_{\text{solvent}} = 1 \right\}$

RLVP = Relative lowering in vapour press

$$\text{RLVP} = \frac{P_0 - P_s}{P_0} = \chi_{\text{solute}}$$

i.e RLVP is equal to mole fraction of solute

$$\frac{P_0 - P_s}{P_0} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

if solⁿ is very dilute $n_{\text{solute}} \ll n_{\text{solvent}}$

$$\frac{P_0 - P_s}{P_0} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$n_{\text{solute}} = \frac{w_1}{M_1} \quad n_{\text{solvent}} = \frac{w_0}{M_0}$$

$$\left. \begin{array}{l} \frac{P_0 - P_s}{P_0} = \frac{w_1 \times M_0}{M_1 w_0} \end{array} \right\} *$$

Raoult's law for a volatile liquid's solution :-

According to this law for solⁿ of 2 non-volatile liquids, partial vapour pressure of each component is directly proportional to its mole fraction present in solⁿ.

$$P_A \propto x_A$$

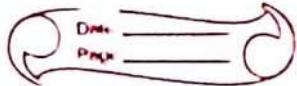
$$P_A = P_A^{\circ} x_A \quad \text{--- (1)}$$

$$P_A^{\circ} = \text{V.P of pure liquid A}$$

$$P_B \propto x_B$$

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

$$P_B^{\circ} = \text{V.P of pure liquid B.}$$



Acc to Dalton's law

$$P_T = P_A + P_B$$

$$P_T = P_A^\circ x_A + P_B^\circ x_B$$

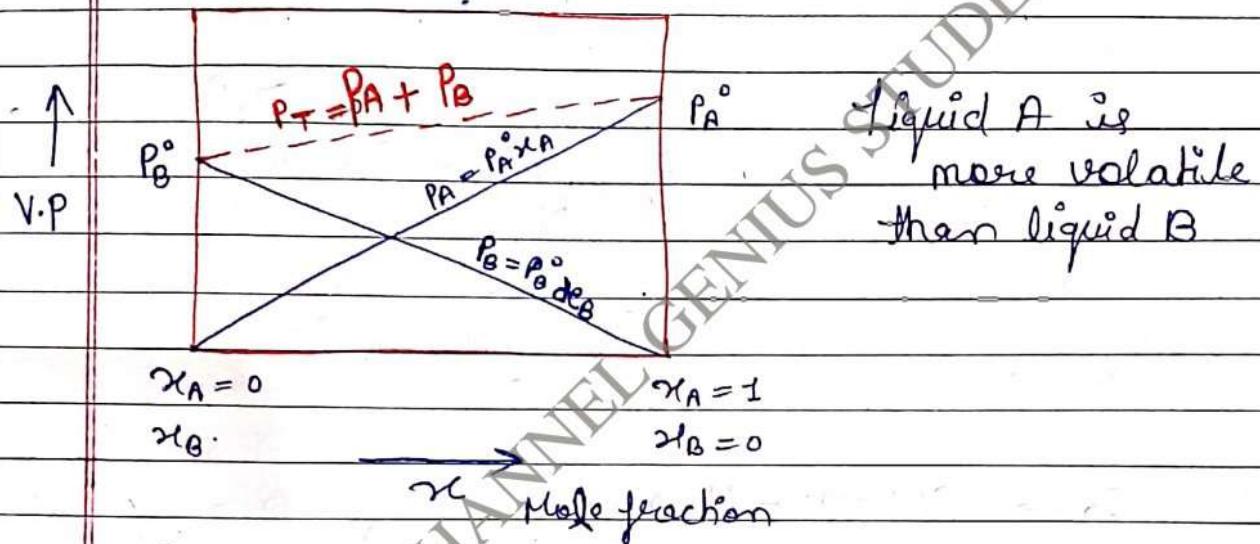
$$P_T = P_A^\circ x_A + P_B^\circ (1 - x_A)$$

$$P_T = P_B^\circ + P_A^\circ x_A - P_B^\circ x_A$$

$$P_T = P_B^\circ + x_A (P_A^\circ - P_B^\circ)$$

$$\text{similar } P_T = P_A^\circ + x_B (P_B^\circ - P_A^\circ)$$

:



Ideal solution \rightarrow The sol'n which obey Raoult's law at all value of concn and temp.

Characteristic of Ideal solution :-

$$\textcircled{1} \quad P_T(\text{observed}) = P_T(\text{Raoult's law})$$

$$\textcircled{2} \quad f_{A-B} = f_{A-A} = f_{B-B}$$

$$\textcircled{3} \quad \Delta H_{\text{mixing}} = 0$$

$$\textcircled{4} \quad \Delta N_{\text{mixing}} = 0$$

Eg \rightarrow $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$, Benzene + Toluene

Chlorobenzene + Bromobenzene, n-Pentane + n-hexane

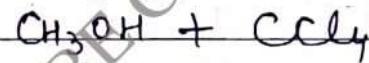
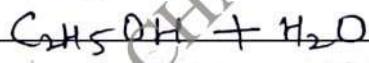
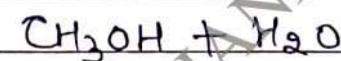
Non-Ideal solⁿ → The solⁿ which don't obey Raoult's law on every value of concn and temp.

They are of 2 types

① Non ideal solⁿ which show +ve deviatⁿ from Raoult's law :-

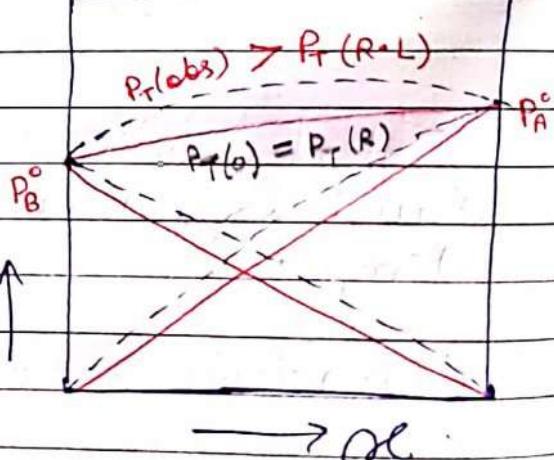
- Characteristic
- (i) $P_T(\text{observed}) > P_T(\text{Raoult's law})$
 - (ii) $F_{A-B} < F_{A-A} \text{ or } F_{B-B}$
 - (iii) $\Delta H_{\text{mixing}} > 0$
(Endothermic)
 - (iv) $\Delta V_{\text{mixing}} > 0$
(Expansion of volume)

Eg →



--- final
— initial

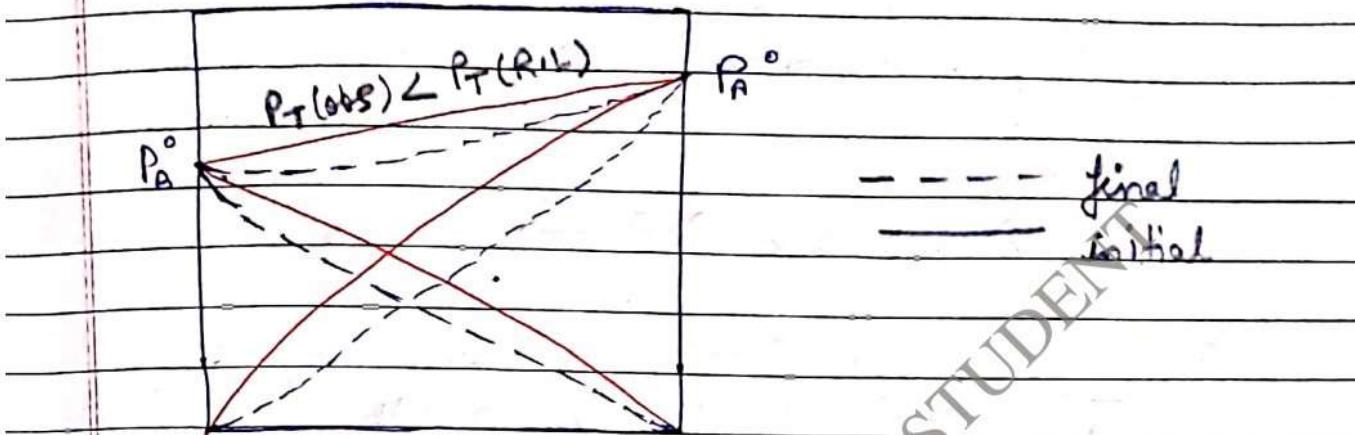
V.P ↑



② Non-ideal solⁿ which show -ve deviation from Raoult's law :-

- Characteristics
- (i) $P_T(\text{observed}) < P_T(\text{Raoult's law})$
 - (ii) $F_{A-B} > F_{A-A} \text{ or } F_{B-B}$

- (iii) $\Delta H_{\text{mixing}} < 0$ Exothermic.
 (iv) $\Delta V_{\text{mixing}} < 0$ Contraction of volume.



Azeotropic Mixture

The mixtures which have same compnⁿ in liquid phase and vapour phase and boils at a definite temp^r is known as Azeotropic mixtr.

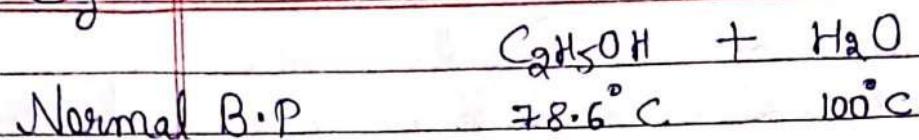
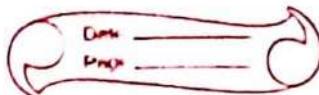
Components of Azeotropic mixtr can't be separated by fractional distillation bcz they boils at same temp^r.

Types of Azeotropic mixture

① Minimum boiling Azeotrop :-

The solⁿ which shows the deviation from Raoult's law forms minimum boiling Azeotrop.

Eg →



Azeotropic compns \rightarrow 96% $\text{C}_2\text{H}_5\text{OH}$ (by mass)
4% H_2O (by mass)

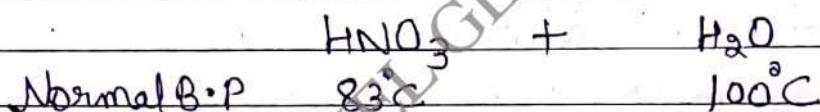
Azeotropic B.P. $\rightarrow 78.15^\circ\text{C}$

②

Maximum Boiling Azeotrop.

The soln which shows -ve deviation from Raoult's law form maximum boiling Azeotrop.

Eg →



Azeotropic compns \rightarrow 68% HNO_3 (by mass)
32% H_2O (by mass)

Azeotropic B.P. $\rightarrow 121^\circ\text{C}$

Colligative property

The physical property of the soln which depends upon the no. of solute particle but not on the nature of solute are k/a colligative property.

They are following 4 types

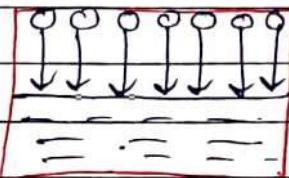
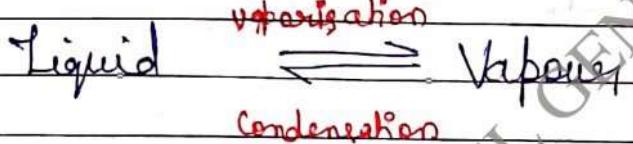


- (ii) R.L.V.P (Relative lowering in Vapour press^r)
- (iii) Elevation in B.P
- (iv) Depression in F.P
- (v) Osmotic pressure

(i) R.L.V.P :-

- Vapour pressure →

The pressure exerted by the vapours on the surface of liquid in eq^m state is K.I.g.s vapour pressure of that liquid.



At Eq^m Rate of V.P = Rate of condensⁿ

- ~~↑~~ Lowering in vapour pressure.

When non-volatile solute (urea, sugar, glucose) are added in pure solvent then they occupy the surface of liquid due to which less vapours are formed and V.P of solⁿ decreases.

i.e. V.P of non-volatile solute containing solution is always lower than V.P of pure solvent. This is K.I.g.s lowering in vapour pressure.

V.P of pure solvent = P_0

V.P of non volatile solute containing solution = P_s

Lowering in vapour pressure (ΔP) = $P_0 - P_s$

- Relative lowering in Vapour pressure

The ratio of lowering in V.P. and V.P. of pure solvent is $K_{\text{a}} \text{ or RLVP}$

$$\text{RLVP} = \frac{\Delta P}{P_0} = \frac{P_0 - P_s}{P_0}$$

- Calculation of molar mass of solute from RLVP :-

from Raoult's law

$$\frac{P_0 - P_s}{P_0} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} \quad (\text{if solution is very dilute})$$

$$\frac{\Delta P}{P_0} = \frac{w_1 \times M_0}{M_1 \times w_0}$$

$$M_1 = \frac{w_1 \times M_0 \times P_0}{\Delta P \times w_0}$$

Ques. 13 gm of compound A was dissolved in 100 gm of H_2O . V.P of this sol'n was found ~~to~~ 27.371 mm of Hg at

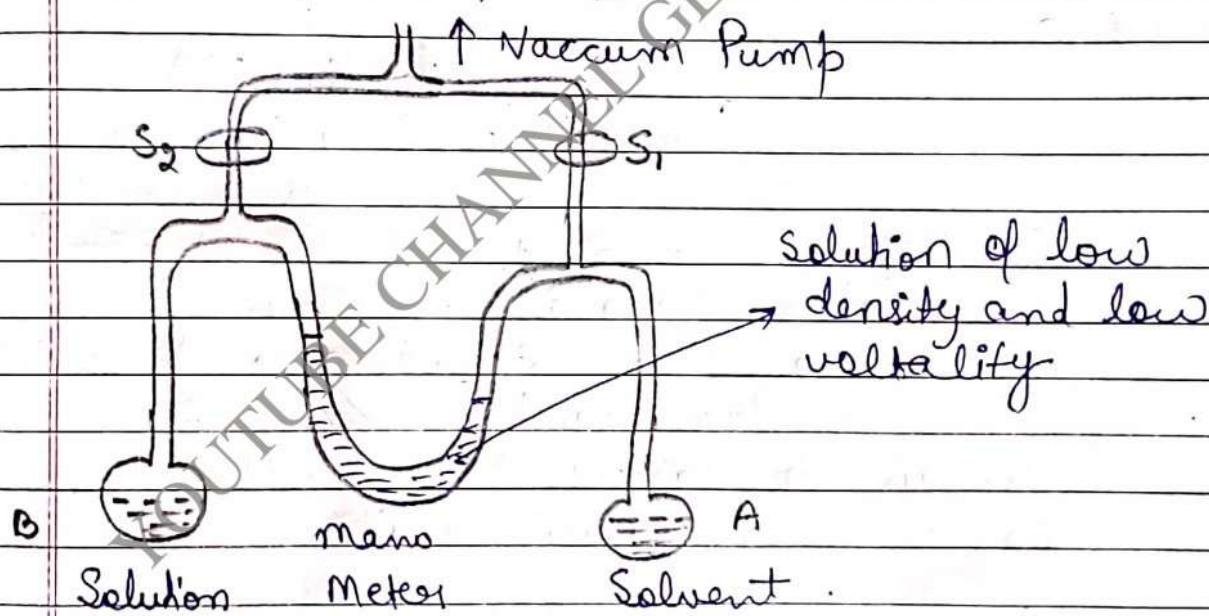
25°C. Calculate molecular weight of comp'd A if V.P of pure water is 28.06 mm of Hg.

$$\Delta P = 28.06 - 27.371 \\ = 0.689$$

$$M_1 = \frac{13 \times 18 \times 28.06}{0.689 \times 100} = \frac{6566.04}{68.9} = 95.29 \text{ gm/mole}$$

Measurement of RLVP

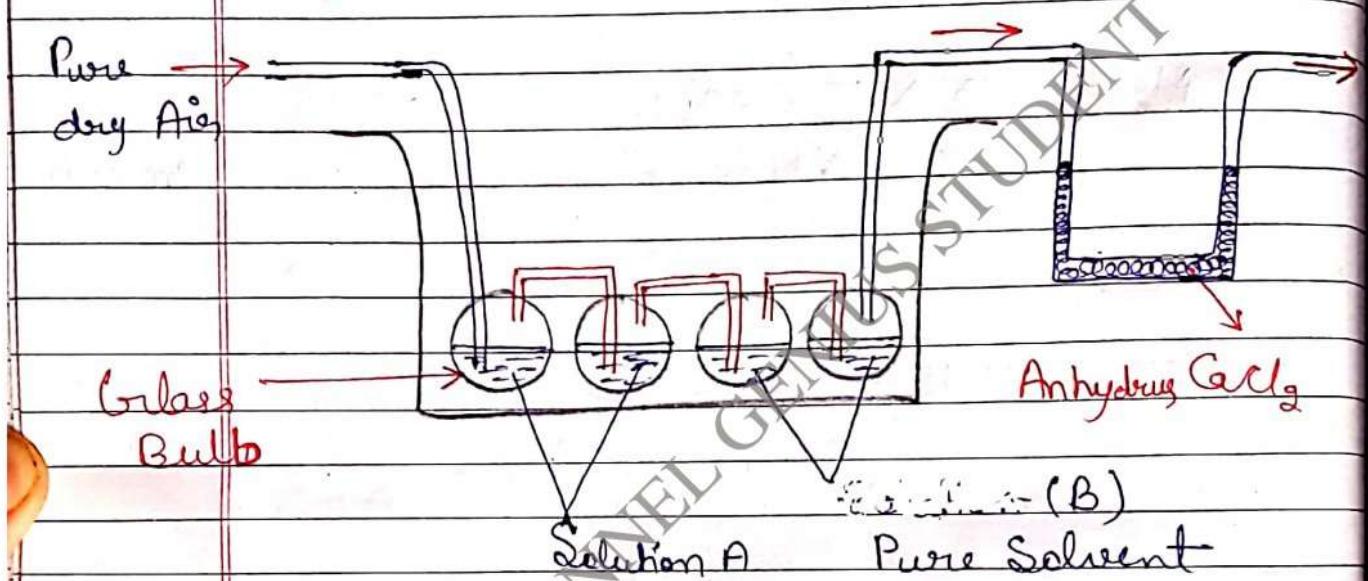
(a) Static Method / Differential manometric method



The stop cork S_1 and S_2 are opened and air inside the apparatus is removed by connecting it to a vacuum pump, so that air and other gas are removed and only the vapour of solvent remain in tubes. Now the stop cork S_1 and S_2 are closed. The difference in the

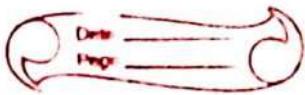
levels of the liquid in the two limbs of the manometer is read off with the help of a moving telescope. This is the measurement of the difference b/w v.p of pure solvent and solution ($P - P_s$).

(b) Dynamic Method / Ostwald-Walker Method



In this method a strip of dry air is passed through a series of bulbs containing the solution and then through the pure solvent finally the air is passed through U tubes containing Anhydrous CaH_2 .

- (i) Loss in weight of Bulb A containing soln $\propto P_s$
- (ii) Loss in weight of Bulb B containing Solvent $\propto P_o - P_s$



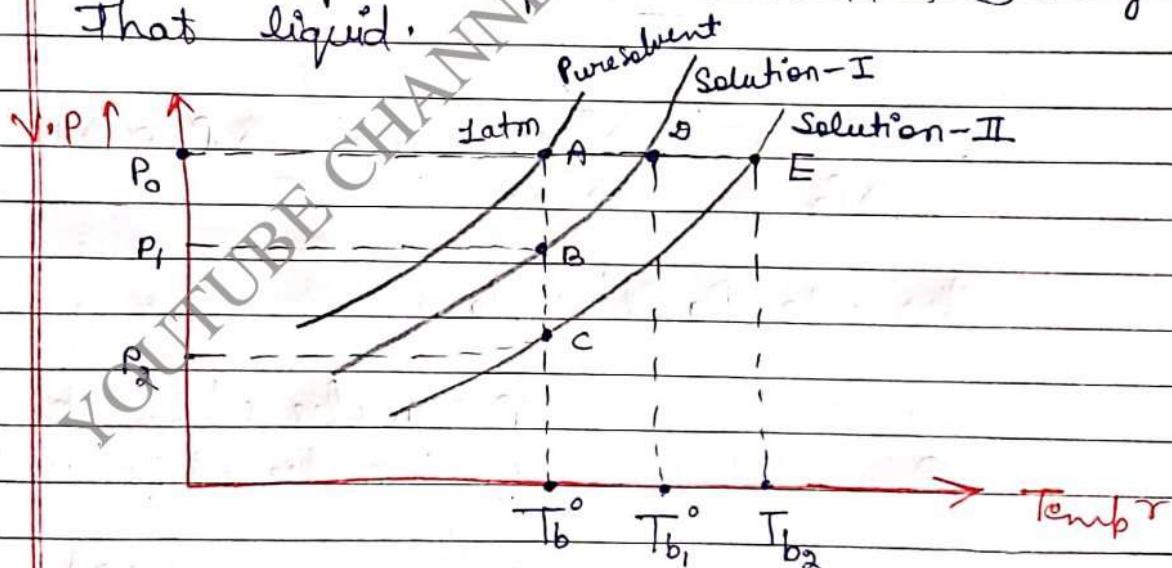
Total loss in weight of both bulb $\propto P_s + (P_0 - P_s)$
 $\propto P_0$

$$\frac{\text{Loss in weight of Bulb B containing solvent}}{\text{Total weight gain by Call}_2} = \frac{P_0 - P_s}{P_0}$$

$$\text{(iii) Total loss in weight of both bulb} = \text{Total weight gain by Call}_2$$

(ii) Elevation in Boiling Point :-

Boiling Point \rightarrow The temp at which v.p of any liquid becomes equal to atmospheric pressure. i.e K/as B.P of That liquid.



$P_0 \rightarrow$ V.P of pure solvent

$P_1 \rightarrow$ V.P of Soln I

$P_2 \rightarrow$ V.P of Soln II

$T_b \rightarrow$ B.P of pure solvent

$T_{b_2} \rightarrow$ B.P of Soln I

When a non-volatile solute is added to a solvent its V.P. decreases so that more heat is required to raise its V.P. upto atmospheric pressure and thereby its B.P. increases.

The difference b/w B.P. of solⁿ & that of pure solvent is known as Elevation in B.P.

from Δ_{ABD} & Δ_{ACE} are similar

$$\frac{AB}{AC} = \frac{AD}{AE}$$

$$\frac{P_0 - P_1}{P_0 - P_2} = \frac{T_{b_1} - T_{b_0}}{T_{b_2} - T_{b_0}}$$

$$\frac{\Delta P_1}{\Delta P_2} = \frac{\Delta T_{b_1}}{\Delta T_{b_2}} \quad \text{So } \boxed{\Delta P \propto \Delta T_b} \quad (i)$$

Acc. to Raoult's law

$$\frac{\Delta P}{P_0} = \frac{n}{n+N} \quad n = \text{moles of solute} \\ N = \text{moles of solvent}$$

If solⁿ is very diluted $n \ll N$

$$\frac{\Delta P}{P_0} = \frac{n}{N} \Rightarrow \boxed{\Delta P = \left(\frac{n}{N}\right) P_0} \quad (ii)$$



From Eq. ii) and iii)

$$\Delta T_b \propto \left(\frac{n}{N} \right) P_0$$

$$\Delta T_b \propto \left(\frac{w_1}{M_1} \frac{M_0}{w_0} \right) P_0$$

$$So \quad \Delta T_b = K' \frac{w_1}{M_1} \frac{M_0}{w_0} P_0 \quad K' M_0 P_0 = \text{constant}$$

$$= K$$

(Elevation constant)

$$\Delta T_b = K w_1 \frac{1}{M_1 w_0}$$

If $w_1 = 1 \text{ mole}$ & $w_0 = 1 \text{ gm}$

$$\text{Then } \boxed{\Delta T_b = K} *$$

$$* \left\{ \Delta T_b = K_b \cdot \frac{w_1 \times 1000}{M_1 w_0} \right\}$$

Molarity

$K_b = \text{molal elevation constant}$
 $= \text{Ebulliscopy}$

The elevation constant is the elevation in B.P when 1 mole of solute is dissolved in 1gm of solvent. But practically it is not possible to dissolve 1 mole of solute in 1gm solvent hence instead of 1gm, '1 Kg' solvent is taken.

$$\Delta T_b = K_b \frac{w_1 \times 1000}{M_1 w_0} = K_b \times \text{Molarity}$$



R_b : if molality = 1 $w_1 = 1$
 and $w_0 = 1000 \text{ gm}$ M_1

$$\text{then } \Delta T_b = K_b$$

when 1 mole of solute is dissolve in
 1 kg of solvent then elevation in B.P
 is equal to the molal elevation constant

* Unit of K_b = $\frac{\text{K} \cdot \text{kg}}{\text{mole}}$ / Kelvin X gm
 mole

Relationship b/w latent heat of vaporization and Molal elevation constant :-

according to Van't Hoff

$$K_b = \frac{R(T_b^o)^2}{L_v \times 1000} \quad R = \text{gas const.}$$

T_b^o = B.P of pure solvent

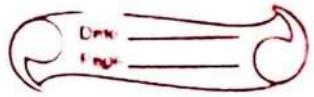
L_v = Latent heat of
 vaporisation per
 gram = H_v

$$\left\{ K_b = \frac{R(T_b^o)^2 M_0}{H_v \times 1000} \right\}$$

where H_v = molar heat
 of vapourisation

Ques 4.18 gm of a comp x was dissolved in
 240 gm water, the B.P of soln was found
 100.06°C calculate the molecular
 weight of compound X.

$$K_b \text{ for water} = 0.513$$



$$w_1 = 4.18 \text{ gm}, w_0 = 240 \text{ gm}$$

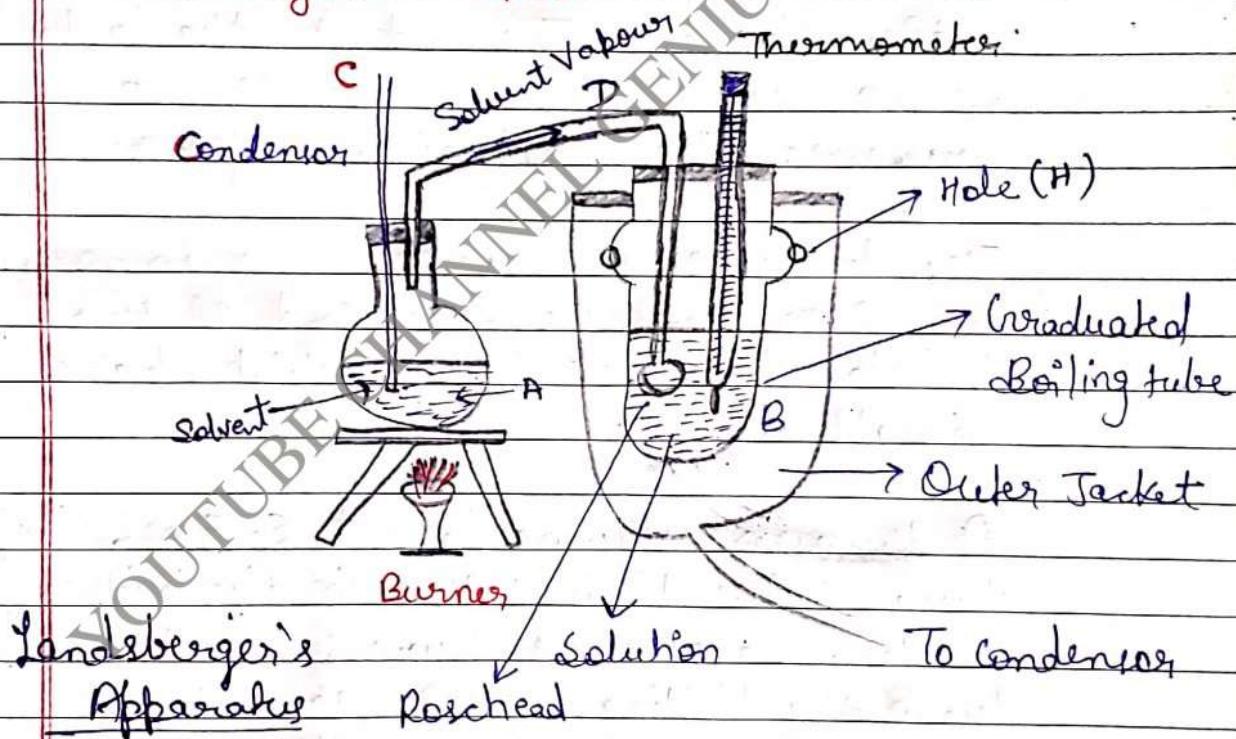
$$T_{b1} = 100.06^\circ\text{C}, T_{b0} = 100^\circ\text{C}$$

$$\Delta T_b = 0.06, K_b = 0.513$$

$$\Delta T_b = K_b \times \frac{w_1 \times 1000}{M_1 \times w_0} \quad \text{so } M_1 = 137.4 \text{ gm/mole}$$

Experimental determination of Elevation of B.P

Landsberger's Method



In this method the Sol^m is heated by the vapours of Solvent through it, to avoid over heating of Sol^m . It consist of Boiling flask A in which pure Solvent is boiled. The flask A is

connected by a delivery tube D to a graduated boiling tube B which also contains a small amount of solvent. The tube B is fitted with a Beckmann thermometer T which can read off with an accuracy of 0.01°C.

The middle portion of B is blown into bulb with a hole H through which the solute can be added to the solvent. The tube is surrounded by outer jacket. The end of the jacket is connected to a condenser to condense the outgoing vapour.

The lower end of tube D is in form of Rose head i.e. the end of tube is in form of bulb which has many small holes.

A known volume (about 5-7 ml) of pure solvent is taken in the boiling tube. Vapours of pure solvent from the boiling flask A are passed through tube D until the liquid starts boiling.

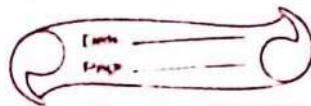
When the temp^r reaches to max^m in the thermometer, it is recorded. This is the B.P of pure solvent.



Now a known quantity of solute under investigation is inserted into the Boiling tube. Again the vapours of solvent are passed and temp^r of thermometer is recorded until it reaches to maximum. This is the boiling point of solution.

The difference of 2 boiling point gives the elevation of Boiling point.

The volume of solⁿ is noted and this on multiplication with the density of solvent gives the weight (W) of solvent.



Thermodynamic derivation of ΔT_b

according to Clapeyron - Clapeyron Eqⁿ

$$\begin{aligned}\ln \frac{P_0}{P_1} &= \frac{\Delta H_v}{R} \left(\frac{1}{T_b^\circ} - \frac{1}{T_1} \right) \\ &= \frac{\Delta H_v}{R} \left(\frac{T_1 - T_b^\circ}{T_b^\circ T_1} \right) = \frac{\Delta H_v (\Delta T_b)}{R (T_b^\circ T_1)}\end{aligned}$$

if solⁿ is very dilute then

$$T_b^\circ T_1 \approx (T_b^\circ)^2$$

$$\ln \frac{P_0}{P_1} = \frac{\Delta H_v}{R} \frac{\Delta T_b}{(T_b^\circ)^2} \quad \text{--- (1)}$$

ΔH_v = molar heat of vapourisation of solvent

$\ln \frac{P_0}{P_1}$ can be written as

$$\ln \frac{P_0}{P_1} = -\ln \frac{P_1}{P_0} = -\ln \left(1 - \frac{(P_0 - P_1)}{P_0} \right)$$

$$\ln \frac{P_0}{P_1} = -\left(-\frac{(P_0 - P_1)}{P_0} \right) = \frac{P_0 - P_1}{P_0} \quad \text{--- (2)}$$

$$\therefore \ln(1-x) = -x$$

if x is very small

from Raoult's law $\frac{P_0 - P_1}{P_0} = \frac{n}{n + N}$

$$\frac{P_0 - P_1}{P_0} = \frac{n}{N} \quad \text{--- (3)}$$

if soln is very dilute

from Eq (1) (2) (3)

$$\ln \frac{P_0}{P_1} = \frac{P_0 - P_1}{P_0} = \frac{n}{N} = \frac{\Delta H_v \cdot \Delta T_b}{R (T_b^\circ)^2}$$

$$\frac{n}{N} = \frac{\Delta H_v \cdot \Delta T_b}{R (T_b^\circ)^2} \quad \text{So} \quad \Delta T_b = \frac{n}{N} \frac{R (T_b^\circ)^2}{\Delta H_v}$$

$$\left\{ \Delta T_b = \frac{R (T_b^\circ)^2}{\Delta H_v} \frac{w_1 M_0}{M_1 w_0} \right\} * \quad \text{--- (4)}$$

as we know that $L_v = \frac{\Delta H_v}{M_0}$ = latent heat
of vapour
of solvent
per gram

$$\Delta H_v = L_v M_0$$

$$\text{So} \quad \Delta T_b = \frac{R (T_b^\circ)^2 M_0 w_1}{L_v M_0 M_1 w_0}$$

$$\Delta T_b = \frac{R (T_b^\circ)^2 w_1}{L_v M_1 w_0} \quad \text{--- (5)}$$

if 1 mole of solute is dissolved in 1000gm
of solvent then eq (5) becomes

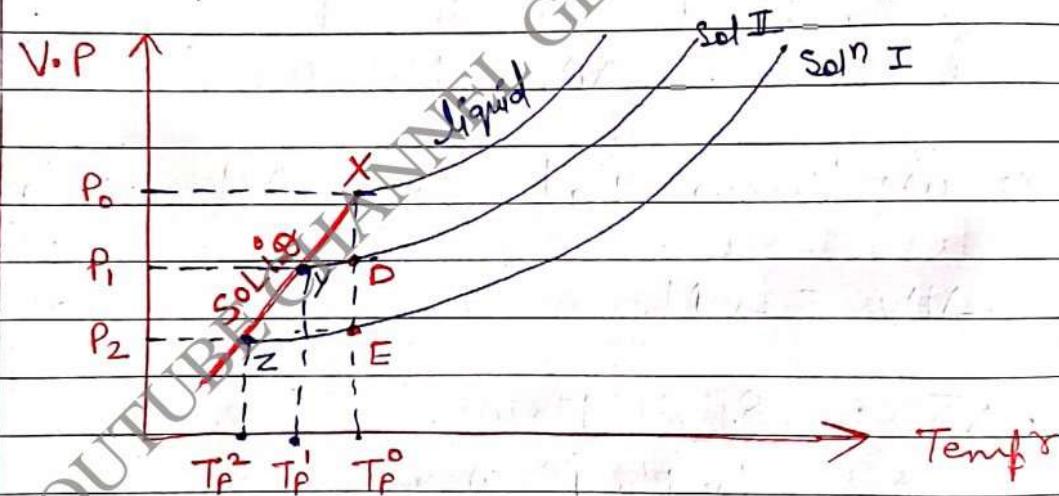
$$\Delta T_b = \frac{R (T_b^\circ)^2}{L_v \times 1000}$$

as we know that when 1 mole of solute is dissolved in 1 kg Solvent
then $\Delta T_b = K_b$

$$\Delta T_b = \frac{R(T_b^\circ)^2}{L_v \times 1000} = K_b$$

(iii) Depression in Freezing point :-

Freezing point \rightarrow The F.P of a liquid is the temp^r at which the solid phase and liquid phase are in eqm and have equal v.p



$$\Delta T_f = T_f^\circ - T_f^1 \quad \text{for solution I}$$

$$\Delta T_f = T_f^\circ - T_f^2 \quad \text{for soln II}$$

when non-volatile solute is added into pure solvent then v.p of soln become lower and at lower temp^r, its v.p



become to equal V.P of solid phase. This difference of F.P of the pure solvent & that of soln is K as depression of F.P.

In $\Delta X^y D$ and $\Delta X Z E$

$$yD = xD$$

$$ZE = XE$$

$$\frac{T_{f_1} - T_{f_0}}{T_{f_2} - T_{f_0}} = \frac{P_0 - P_1}{P_0 - P_2}$$

$$\frac{\Delta P_1}{\Delta P_2} = \frac{\Delta T_{f_1}}{\Delta T_{f_2}} \quad \text{So } \Delta P \propto \Delta T_f \quad \text{--- (1)}$$

According to Raoult's law $\frac{\Delta P}{P_0} = \frac{n}{n+N}$

$$\frac{\Delta P}{P_0} = \frac{n}{N} \quad \text{when } n \ll N$$

$$\text{So } \Delta P = \left(\frac{n}{N}\right) P_0 \quad \text{--- (2)}$$

From eqn (1) and (2)

$$\Delta T_f \propto \frac{n}{N} (P_0)$$

$$\Delta T_f \propto \frac{w_1 M_0}{m_1 w_0} P_0 \Rightarrow \Delta T_f = \frac{k' w_1 M_0 P_0}{m_1 w_0}$$

$$\Delta T_f = \frac{k \cdot w_1}{M_1 w_0} \quad \text{--- (3)} \quad k' M_0 P_0 = k$$

If $\frac{w_1}{m_1} = 1 \text{ mole}$ & $w_0 = 1 \text{ gm.}$ Then $\Delta T_f = k$
 $k = \text{depression constant}$

But practically it is not possible to dissolve 1 mole solute in 1gm solvent. So instead of taking 1gm solvent we take 1 kg solvent.

$$\Delta T_f = K_f \frac{w_1 \times 1000}{M_1 w_0}$$

K_f = molal depression const.
= Cryoscopic const.

$$\Delta T_f = K_f \times \text{molarity}$$

$$\Delta T_f = K_f \quad \text{if molarity} = 1$$

~~$$That K_f = \frac{K \cdot M_g}{\text{mole}}$$~~

Relationship b/w latent heat of fusion and molal depression constant :-

$$K_f = \frac{R(T_f^\circ)^2}{1000 L_f} \quad L_f = \text{latent heat of fusion of solvent per gm}$$

$$K_f = \frac{R(T_f^\circ)^2 M_0}{1000 \cdot \Delta H_f} \quad \Delta H_f = \frac{\Delta H_f}{M_0}$$

ΔH_f = molar heat of fusion

Ques. When 0.2 gm of solute A is dissolved in 100 gm of solvent. Solution freezes at $160.4^\circ C$ when 2.24 gm of another solute B is dissolved in same 100 gm solvent this sol' freezes at $16^\circ C$. If molecular weight of A is 74 then



Calculate M. mass of Solute B. (F.P of pure Solvent is 16.5°C)

Solve for Solute A

$$\Delta T_f = \frac{k_f \times w_1 \times 1000}{M_1 \times w_0}$$

$$\Delta T_f = T_f^{\circ} - T_f' = 16.5 - 16.4 = 0.1^{\circ}\text{C}$$

$$0.1 = \frac{k_f \times 0.2 \times 1000}{74 \times 100} \quad \text{So } k_f = 3.7$$

for Solute B

$$\Delta T_f = \frac{k_f \times w_1 \times 1000}{M_1 \times w_0}$$

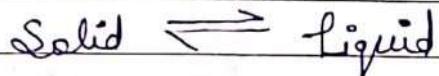
$$\begin{aligned} \Delta T_f &= T_f^{\circ} - T_f' \\ &= 16.5 - 16.0 \\ &= 0.5^{\circ}\text{C} \end{aligned}$$

$$0.5 = \frac{3.7 \times 2.24 \times 1000}{M_1 \times 100}$$

$$\text{So } M_1 = 165.75 \text{ gm/mole}$$

Thermodynamic derivation of ΔT_f

In eqⁿ of freezing solid and liquid state are in equilibrium.



And in eqⁿ of freezing, chemical potential of both solid and liquid will be equal

$$\mu_{\text{liquid}}(T, P, x_0) = \mu_{\text{solid}}(T, P) \quad \text{chemical Potential}$$

(1)



But for dilute solⁿ

$$\mu_{\text{liq}}(T, P, x_0) = \mu_{\text{liq}}^{\circ}(T, P) + RT \ln x_0 \quad \text{--- (2)}$$

$$\mu_{\text{liq}}^{\circ}(T, P) + RT \ln x_0 = \mu_{\text{solid}}(T, P)$$

$$RT \ln x_0 = \mu_{\text{solid}}(T, P) - \mu_{\text{liq}}^{\circ}(T, P)$$

$$\ln x_0 = \frac{\mu_{\text{solid}}(T, P) - \mu_{\text{liq}}^{\circ}(T, P)}{RT} \quad \text{--- (3)}$$

for solvent molar gibbs free energy for fusion will be

$$\Delta G_f = \mu_{\text{liq}}^{\circ}(T, P) - \mu_{\text{solid}}(T, P) \quad \text{--- (4)}$$

from eqⁿ (3) and (4)

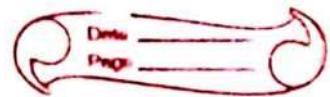
$$\ln x_0 = -\frac{\Delta G_f}{RT}$$

$$\left(\frac{\partial \ln x_0}{\partial T}\right)_P = -\frac{1}{R} \left(\frac{\partial \left(\frac{\Delta G_f}{T}\right)}{\partial T}\right)_P$$

where x_0 = mole fracⁿ of pure solvent

By using Gibbs-Helmholtz eqⁿ the above eqⁿ become as

$$\left(\frac{\partial \ln x_0}{\partial T}\right)_P = \frac{\Delta H_f}{RT^2}$$



On integration of above Eqⁿ

$$\int_{\frac{x_0}{x_0}}^1 \frac{dx_0}{x_0} = \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_f}{T^2} dT$$

lower limit
 $x_0 = 1$ pure solvent

$$\ln x_0 = \frac{\Delta H_f}{R} \left(\frac{1}{T_f} - \frac{1}{T_0} \right)$$

which have F.P. \rightarrow
To higher limit
 $x_0 \rightarrow$ soln \rightarrow sol'n

$$\ln x_0 = - \frac{\Delta H_f}{R} \left(\frac{T_0 - T_f}{T_f T_0} \right)$$

which have F.P. \rightarrow T_f

if solⁿ is very dilute then $T_f \cdot T_0 = (T_0)^2$

$$\ln x_0 = - \frac{\Delta H_f}{R T_0^2} \Delta T_f$$

for very dilute solⁿ $\ln x_0 = \ln(1-x_1) \approx -x_1$

x_0 = M.F of solvent

x_1 = M.F of solute

$$-x_1 = - \frac{\Delta H_f}{R T_0^2} \cdot \Delta T_f \Rightarrow \Delta T_f = \frac{RT_0^2}{\Delta H_f} \cdot x_1$$

we know $x_1 = \frac{n}{n+N}$ for very dilute solⁿ

$$x_1 = \frac{n}{N} = \frac{w_1 \times M_0}{M_1 \times w_0}$$

$$\text{So } \Delta T_f = \frac{RT_0^2}{\Delta H_f} \cdot \frac{w_1 \times M_0}{M_1 \times w_0}$$

$$\Delta T_f = RT_0^2 \frac{w_1}{M_1 \times w_0} \quad \therefore L_f = \frac{\Delta H_f}{M_0}$$

$$\text{molality} = m = \frac{w_1 \times 1000}{M_1 \times w_0}$$

$$\Delta T_f = \left(\frac{RT_0^2}{1000 \cdot L_f} \right) m = K_f \times m$$

Ques) Calculate the F.P of 1% soln of Glucose in water. Calculate the molar depression constant of water is $1.84 \text{ K kg-mole}^{-1}$.

Solve $\Delta T_f = K_f \times w_1 \times 1000$

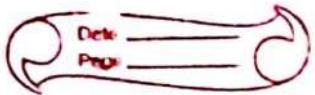
$$\Delta T_f = \frac{1.84 \times 1 \times 1000}{180 \times 100} = 0.102 \text{ K}$$

$$\Delta T_f = T_f^\circ - T_f = 273 - 0.102 = 272.89$$

T_f° = water freezing point = 0°C

or $\Delta T_f = 0^\circ - 0.102 = -0.102^\circ\text{C}$

Ques An aqueous soln of a non-volatile solute boils at 100.21°C . Calculate the freezing point of same solution K_b and K_f for water = 0.51 and $1.86^\circ\text{C kg mole}^{-1}$



Solve $\Delta T_b = K_b \times m \Rightarrow \Delta T_b = K_b$
 $\Delta T_f = K_b \times m \quad \Delta T_f = K_f$

$$\frac{T_b - T_b^{\circ}}{\Delta T_f} = \frac{100.21^{\circ}\text{C} - 100^{\circ}\text{C}}{\Delta T_f} \Rightarrow \frac{0.21}{\Delta T_f} = \frac{0.51}{1.86}$$

$$\Delta T_f = 0.765^{\circ}\text{C}$$

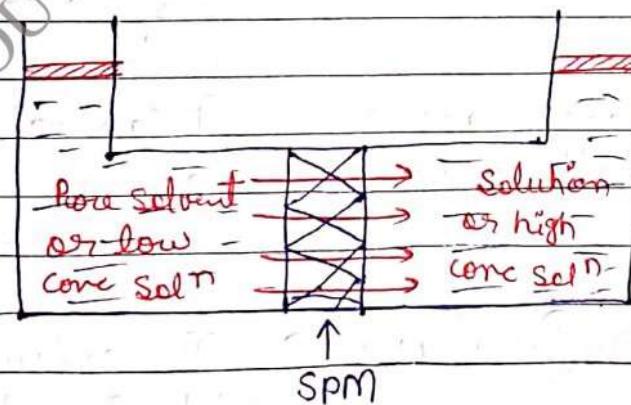
$$T_f^{\circ} - T_f = 0.765^{\circ}\text{C}$$

$$T_f = 0^{\circ} - 0.765^{\circ} = -0.765^{\circ}\text{C}$$

(iv) Osmotic Pressure :-

Diffusion \rightarrow The movement of particles of any substance from higher conc' region to lower conc' region until the conc' become uniform throughout.

Osmosis \rightarrow The movement of solvent molecule through semi-permeable membrane from pure solvent to sol'n or low conc' sol'n to higher conc' sol'n.



Semi permeable membrane \rightarrow The membrane



which allowed to pass solvent molecule through it but not allowed solute molecule is K/as semi permeable Membr.

Difference b/w Diffusion and Osmosis

Diffusion

Osmosis

- | | |
|---|---|
| ① In diffusion particles move from high conc' region to low conc' region. | In osmosis solvent molecule moves from lower conc' to high conc'. |
| ② In diffusion, solute and solvent both molecule can move. | In osmosis only solvent molecule moves. |
| ③ No SPM is required. | SPM is required. |
| ④ This can't be stopped. | This can be stopped by applying external / opposite pressure. |
| ⑤ It can take place in sol ⁿ as well as in gaseous. | It can take place only in solutions. |

Osmotic Pressure → The external pr^r which is applied on solution to stopped process of osmosis. is K/as osmotic pressure.

Osmosis (movement of solvent molecule through SPM from pure solvent to solution)

Law of Osmotic Pressure

① Von't Hoff Boyle's Law

According to this law at const. temp^r osmotic pressure of soln is directly proportional to its conc.

$$\textcircled{1} \quad \Pi \propto c \quad \text{where } c = \frac{1}{V}$$
$$\frac{\Pi}{c} = \text{constant}$$

So $\Pi V = \text{constant}$ in which \pm mole of solute is dissolved

② Von't Hoff Charles Law

According to this law, at const. volume osmotic press^r of a dilute soln is directly proportional to the temp^r

$$\Pi \propto T \quad \textcircled{2}$$

from eqⁿ ① and ② $\Pi \propto \frac{T}{V}$

$$\Pi V = \text{const} \times T$$

$$\Pi V = s \times T \quad (s = \text{soln constant})$$

$$\Pi V = RT$$

$$\Pi = \frac{RT}{V}$$

If n mole of solute is dissolved in V ltr solⁿ

$$\left\{ \frac{\pi}{V} = \frac{nRT}{V} = CRT \right\} *$$

Ques Calculation of mol wt. Solute from osmotic pressure

$$\pi = CRT$$

$$\pi = \frac{n}{V} RT \quad n = \text{mole of Solute}$$

$$n = \frac{w_1}{M_1} \quad \text{So } \pi = \frac{w_1 RT}{M_1 \times V}$$

$$\left\{ M_1 = \frac{w_1 \times R \times T}{\pi \times V} \right\} *$$

Ques Calculate osmotic pressure of 3% (w/v) urea solⁿ at 0°C

Solⁿ 3% w/v urea

3 gm urea is dissolved in 100 ml solⁿ

$$\text{mass of solute} = 3 \text{ gm}$$

$$\text{Vol of solute} = 100 \text{ ml}$$

$$\text{Molar mass of solute} = 60 \text{ gm/mol}$$

$$T = 0^\circ\text{C} + 273 = 273 \text{ K}$$

$$R = 0.0821 \text{ atm litr mol}^{-1} \text{ K}^{-1}$$

$$= 1/2$$

$$\Pi = \frac{w_1 RT}{M_1 V} = \frac{0.1 \times 1 \times 273 \times 1000}{12 \times 60 \times 100}$$

$$\Pi = 11.21 \text{ atm}$$

Relation b/w Osmotic Pressure & RLVP :-

$$\Pi = \frac{n}{V} \cdot RT \quad \text{--- (1)}$$

Suppose n mole of solute is dissolved in w_0 gm of solvent of molar mass M_0 .

Since sol^n is diluted hence its volume is considered as the volume of pure solvent density of sol^n is ρ

$$V = \frac{w_0}{\rho}$$

$$\text{mole of solvent } N = \frac{w_0}{M_0} \Rightarrow w_0 = M_0 N$$

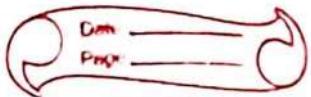
$$\left\{ V = \frac{M_0 N}{\rho} \right\} \text{ on putting value of } V \text{ in eq^n (1)}$$

$$\Pi = \frac{n \cdot RT \rho}{M_0 N} = \frac{n}{N} \frac{RT \rho}{M_0} \quad \text{--- (2)}$$

According to Raoult's law

$$\frac{P_0 - P_s}{P_0} = \frac{n}{n + N}$$

for very dilute $\text{sol}^n \quad N \gg n$



$$\frac{P_0 - P_s}{P_0} = n \quad \text{--- (3)}$$

from Eqn ② & ③

$$\Pi = \frac{P_0 - P_s}{P_0} \left(\frac{RTP}{M_0} \right)$$

$$\Pi = P_0 - P_s \left(\frac{RTP}{M_0 P_0} \right) \rightarrow \text{constant}$$

$$\Pi \propto (P_0 - P_s) \quad \text{So} \quad \boxed{\Pi \propto \Delta P}$$

i.e. at const Osmotic press^r of dilute solⁿ is directly proportional to lowering in vap. press^r.

* Abnormal value of colligative property & molar mass :-

When there is no assocⁿ or dissociⁿ of the solute in the solvent then such colligative properties are k/_{as} normal colligative property and molar mass of solute is k/_{as} normal molar mass.

But if dissociⁿ or association of solute particle take place then values of colligative properties are k/_{as}

Abnormal value of C.P & molar mass of solute is known as Abnormal molar mass.

Von't Hoff factor (i)

$$i = \frac{\text{observed value of C.P}}{\text{Theoretical value of C.P}} = \frac{(RLVP)_{\text{obs}}}{(RLVP)_{\text{theo.}}}$$

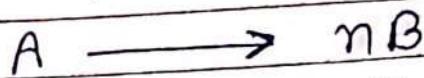
$$i = \frac{(\Delta T_b)_{\text{obs}}}{(\Delta T_b)_{\text{theo.}}} = \frac{(\Delta T_f)_{\text{obs}}}{(\Delta T_f)_{\text{theo.}}} = \frac{T_{\text{obs.}}}{T_{\text{theo.}}}$$

$$i = \frac{\text{observed no. of solute particle}}{\text{theoretical no. of solute particle}}$$

$$i = \frac{\text{theoretical molecular mass of solute}}{\text{observed molecular mass of solute}}$$

(i)

Relationship b/w Van't Hoff factor and degree of dissociation (α) :-



no. of moles before dissociation

$1-\alpha$

0

No. of moles after dissociation

$n\alpha$

$$\text{Total moles after dissociation} = 1 + n\alpha - \alpha \\ = 1 + \alpha(n-1)$$

$i = \frac{\text{observed No. of particle}}{\text{theoretical no. of particle}}$

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

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

$$i = \frac{M_{\text{theor}}}{M_{\text{actual}}} = \frac{M_t}{M_o}$$

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

Relationship b/w i and degree of associaⁿ :-



moles before associaⁿ

1

0

" After Assocⁿ

$1-\alpha$

α

n



$$\text{Total moles after assoc'n} = \frac{1 + \alpha}{n}$$

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

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

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

* Some formulas

$$(i) \frac{P_o - P_s}{P_o} = i \times \frac{n}{N}$$

$$(ii) \Delta T_b = i K_b \cdot m$$

$$(iii) \Delta T_f = i K_f \cdot m$$

$$(iv) \Pi = i c \cdot R \cdot T$$

Case 1 → when no assoc'n or dissoci'n of solute
 $i = 1$

Case 2 → when dissociation take place $i > 1$

Case 3 → if assoc'n take place $i < 1$