

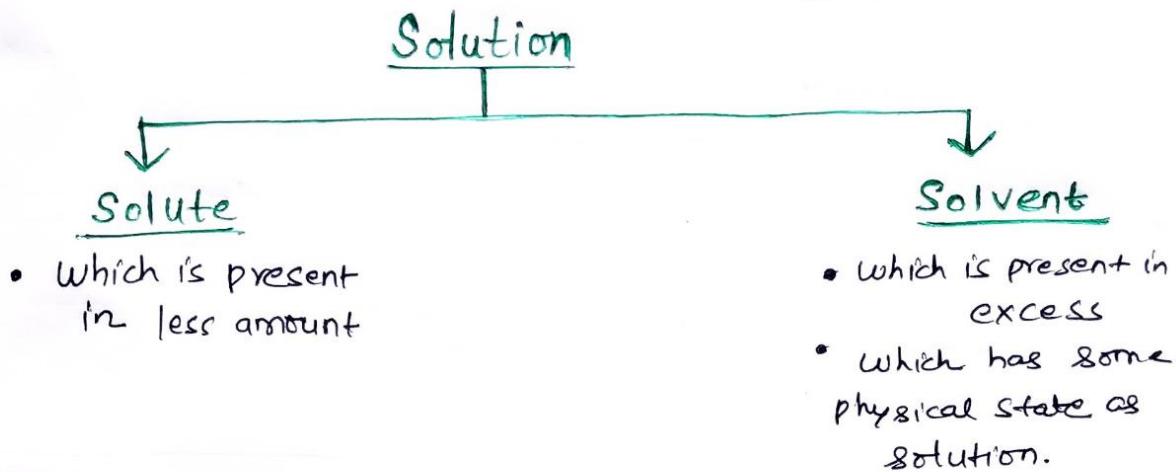
Handwritten Notes

SOLUTION Colligative Properties

JEE → NEET

Solution & Colligative Properties

- Homogeneous mixture of two or more than two components is known as Solution



Types of Solution

Solute	Solvent	Example
Solid	Solid	[Alloys Cu, in Au] Brass.
Liquid	Solid	[Amalgam (Mg in solid metal)] [H ₂ in palladium]
Gas	Solid	
Solid	Liquid	NaCl in H ₂ O
Liquid	Liquid	Alcohol + water
Gas	Liquid	O ₂ in water
Solid	Gas	Camphor in air
Liquid	Gas	Chloroform in air
Gas	Gas	Air

• Concentration Units :

① % w/w

$$\% \text{ w/w} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 100$$

② % w/v

$$\% \text{ w/v} = \frac{\text{weight of solute}}{\text{volume of solution}} \times 100$$

③ PPM (parts per million)

$$\text{PPM} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 10^6$$

④ PPb (parts per billion),

$$\text{PPb} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 10^9$$

⑤ Molarity (M) : Number of moles of solute dissolved in 1 Litre solution is known as Molarity.

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in litre)}} = \frac{n}{V_L}$$

$$M = \frac{\text{Weight}}{\text{Molecular weight}} \times \frac{1000}{\text{volume (ml)}} \quad \text{**}$$

$$\frac{M_1 V_1 + M_2 V_2 + M_3 V_3}{V_1 + V_2 + V_3} = M_F \quad \text{**}$$

⑥ Molality (m) : Number of moles of solute dissolved in 1 kg of solvent.

$$m = \frac{\text{no. of moles of solute}}{\text{weight of solvent (kg)}}$$

★ Relation between molarity & molality :-

$$d = M \left[\frac{1}{m} + \frac{\text{molar mass}}{1000} \right]$$

→ density

M = molarity

m = molality.

★ Normality (N),

$$N = \frac{\text{No. of equivalents}}{\text{Volume of solution}}$$

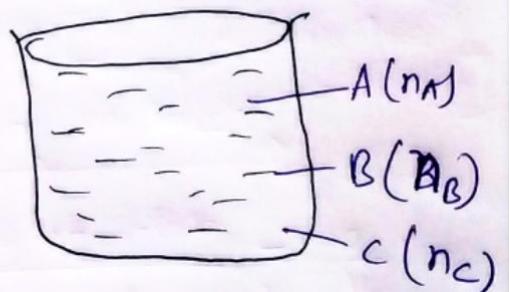
$$\text{No. of equivalents} = \frac{\text{weight}}{\text{Mole weight}} \times n \text{ factor}$$

★ Mole fraction :-

$$X_A = \frac{n_A}{n_T}$$

$$X_B = \frac{n_B}{n_T}$$

$$X_C = \frac{n_C}{n_T}$$



n_T = Total moles

$$X_A + X_B + X_C = 1$$

★ Formality :-

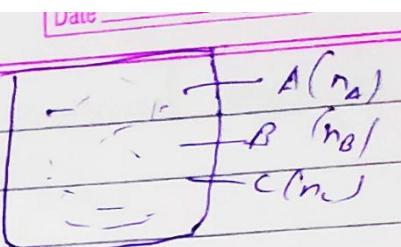
$$M_{\text{ionic}} = \text{Formality}$$

$$F = \frac{\text{No. of moles of ionic compound}}{\text{Volume of solution (L)}}$$

Dalton's Law of Partial Pressure

For non-reacting gaseous mixture

$$P_T = P_A + P_B + P_C$$



$$P_A = \frac{n_A RT}{V}$$

$$P_T = \frac{n_T RT}{V}$$

$$\frac{P_A}{P_T} = \frac{n_A}{n_T} = \gamma_A$$

Mole fraction of A in gas phase

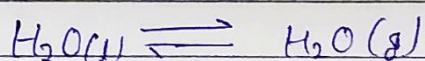
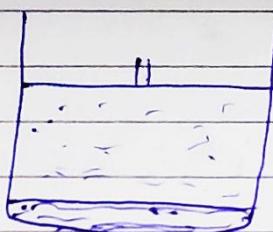
$$P_A = \gamma_A \cdot P_T$$

P_A = mole fraction in gas phase \times total pressure

Vapour pressure.

When a liquid is present in equilibrium with its vapour then pressure exerted by vapour on the surface of liquid is known as vapour pressure.

Vapour pressure is actually equilibrium constant that is why for same liquid it only depend on temperature



$$K_p = P_{H_2O}$$

V.P of liquid
(Saturated V.P.)

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303} \frac{(T_2 - T_1)}{(T_1 T_2)}$$

P_1 = V.P of liquid at Temp.

ΔH_{vap} = Enthalpy of vaporization

$$\textcircled{B} \quad P_T = P_{\text{air}} + P_{\text{H}_2\text{O}}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{700}{300} \neq \frac{P_2}{330} \Rightarrow P_2 = 770$$

$$P'_T = 770 + P'_{\text{H}_2\text{O}}$$

$$P'_T = 770 + 80 = 850 \text{ mm}$$

Solubility.

Maximum amount of solute that can be dissolve in fixed amount of solution or solvent at particular temperature.

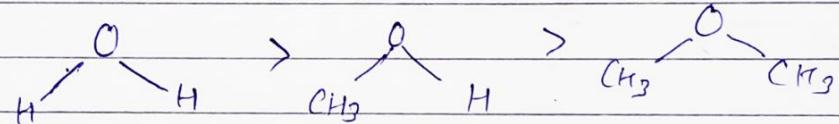
Factors affecting solubility.

① Nature of solute and solvent \rightarrow Like dissolve like means polar solute more soluble in polar solvent and Non-polar solute dissolve more in Non-polar Solvent.

efficiency.

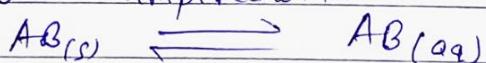
of dissolution
for NaCl.

(ionic)



Polarity \propto O.E.N.

② Temperature \rightarrow if dissolution of solid is exothermic then in saturated solⁿ solubility decrease with increase in temperature.



T ↑ Solubility ↓

* Dissolution of gas is always exothermic that is why solubility of gas decrease on increasing temperature.

Effect of pressure on dissolution of gas (Henry's law)
On increasing pressure solubility of gas increases.

According to Henry's law mole fraction of gas in dissolved form is directly proportional to partial pressure of gas.

Partial pressure $\propto X_{\text{gas}}$
(mole fraction of gas in liquid)

$$P = k_H X_{\text{gas}}$$

$$P = k_H \frac{n}{n+N}$$

k_H = Henry's const (Atm)

n = no. of moles of gas

N = No. of moles of solvent.

For Dilute solution $n \ll N$

$$\therefore n+N \approx N$$

$$P_{\text{gas}} = k_H \frac{n}{N}$$

$$P_{\text{gas}} = k_H \times \frac{\omega}{m} \times \frac{M}{W}$$

Important point

① k_H is Henry's constant which on nature of gas.
if k_H is higher then solubility of gas is lower.

② k_H also depend on temperature and it increase with increase in temperature.

Application of Henry's law.

① Bottling of cold drink is done at very high pressure so that more CO_2 is dissolved in cold drink.

② ANOXIA → At mountains atmospheric pressure is less that is why less O₂ is soluble in blood and less O₂ is available for brain. and due to these decision making power of a person decreases. This is known as ANOXIA.

③ BEND FORMATION → When a scuba diver dives deep in depth of sea then more N₂ is soluble in blood when scuba divers come back at surface N₂ comes out of blood vessel leaving air bubble in it this is known as Bend formation and to avoid this some part of N₂ is replaced by Helium (He) gas less soluble.

Q. Calculate weight of N₂ dissolved in 10 moles of H₂O in an open container.

$$\begin{array}{l} \text{Atmospheric pressure} = 1 \text{ atm} \\ K_H = 4 \times 10^5 \text{ atm.} \end{array} \quad \begin{array}{l} 80\% \text{ N}_2 \quad 20\% \text{ O}_2 \\ \text{mole fraction} = 0.8 \\ P_{N_2} = 0.8 \times 1. \end{array}$$

$$P_{N_2} = K_H \times \frac{n_{N_2}}{n_{H_2O}}$$

$$0.8 = 4 \times 10^5 \times \frac{n_{H_2O}}{10}$$

$$n_{H_2O} = 2 \times 10^{-5}$$

$$wt = 28 \times 2 \times 10^{-5} = 5.6 \times 10^{-4} \text{ g.}$$

Note: ① Henry's law is applicable for dilute solution only
 ② Henry's law is not applicable to highly soluble gas such as NH₃, NH₄, HCl, CO₂ etc.

RAUOLT'S LAW

According to Raoult's Law partial pressure of any component is directly proportional to mole fraction of component in solution.

$$P_A \propto X_A$$

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

Mole fraction of A in solution
 Vapour pressure of pure liquid.
 Partial pressure of A.

Raoult's law in case of two volatile liquid solution

Assume, two liquid A & B are mixed with X_A & X_B mole fraction respectively. Their v.p are P_A° & P_B° [$P_B^{\circ} > P_A^{\circ}$]

According to Raoult's law

$$P_A \propto X_A ; P_B \propto X_B$$

$$P_A = P_A^{\circ} X_A \quad ; \quad P_B = P_B^{\circ} X_B \quad \text{--- (1)}$$

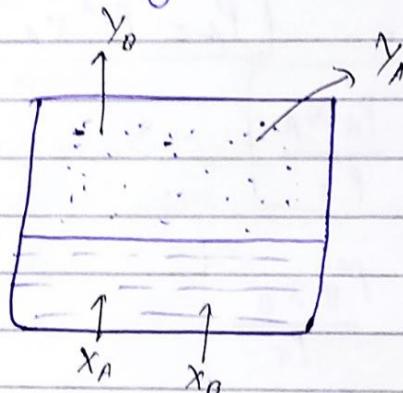
$$\text{Total pressure} = P_T = P_A + P_B$$

$$P_T = P_A^{\circ} X_A + P_B^{\circ} X_B \quad \text{--- (2)}$$

$$\text{We know, } X_A = 1 - X_B$$

$$P_T = P_A^{\circ} (1 - X_B) + P_B^{\circ} X_B$$

$$= P_A^{\circ} - P_A^{\circ} X_B + P_B^{\circ} X_B$$



$$P_T = P_A^{\circ} + (P_B^{\circ} - P_A^{\circ}) X_B$$

$$P_T = P_B^{\circ} + (P_A^{\circ} - P_B^{\circ}) X_A$$

This gives relation between total P & mole fraction of one component.

P_T will remain same between P_A° to P_B°

$$P_T = P_B^{\circ} \quad \text{then} \quad X_B = 1$$

$$P_T = P_A^{\circ} \quad \text{L.H} \quad X_B = 0, X_A = 1$$

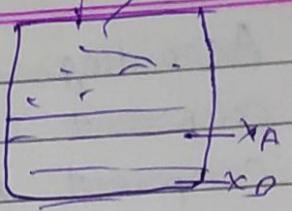
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Determination Vapour Phase Composition

In the liquid mixture of A & B their vapour phase mole fraction are y_A and y_B .

Acc. to Raoult's law

$$P_A = P_A^{\circ} x_A; \quad P_B = P_B^{\circ} x_B$$



Acc to Dalton's law

$$\text{Partial pressure} = \frac{\text{mole fraction} \times \text{total pressure}}{\text{in gas phase}}$$

$$P_A = y_A \cdot P_T \quad \& \quad P_B = y_B \cdot P_T$$

on combining both laws

$$P_A = P_A^{\circ} x_A = y_A \cdot P_T \quad \left\{ P_B = P_B^{\circ} = y_B \cdot P_T \right\}$$

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

$$y_B = \frac{P_B^{\circ} x_B}{P_A^{\circ} (P_A^{\circ} - P_B^{\circ}) x_A} \quad \text{--- (2)}$$

$$y_B = \frac{P_B^{\circ} x_B}{P_T}$$

$$y_B = \frac{P_B^{\circ} x_B}{P_A + (P_B^{\circ} - P_A^{\circ}) / x_A}$$

This formula gives relation between liquid phase mole fraction with vapour pressure phase mole fraction

Q. Benzene and Toluene obey Raoult's law by following formula $P_T = 180 + 30 x_B$ mm (x_B = mole fraction of Benzene).

Sol. P_{Benzene} and P_{Toluene}

$$P_T = P_f^{\circ} = P_f^{\circ} + (P_B^{\circ} - P_f^{\circ}) / x_B$$

$$P_T = 180 + 30 x_B$$

$$P_B^{\circ} = 270 \text{ mm}$$

$$P_f^{\circ} = 180 \text{ mm}$$

$$P_f^{\circ} = P_f^{\circ} + (P_B^{\circ} - P_f^{\circ}) B$$

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Q) In above mix. if we mixed 936 g of Benzene and 736 g Toluene (C_7H_8) then calculate pressure of mixture A \rightarrow Toluene B \rightarrow Benzene.

$$\begin{aligned} P_T &= P_f + (P^o_A - P^o_f) \times B \\ P_T &= 180 + 90 \times B \\ &= 180 + 90 \times 0.6 \\ &= 234 \end{aligned} \quad \begin{aligned} n_{Benzene} &= \frac{wt}{molar\ weight} = \frac{936}{78} = 12 \\ n_{Toluene} &= \frac{wt}{molar\ weight} = \frac{736}{92} = 8 \\ X_B &= \frac{n_B}{n_T} = \frac{12}{20} = 0.6 \end{aligned}$$

In above mixture calculate vapour phase mole fraction

$$\begin{aligned} Y_A &= \frac{P_A^o \times X_B}{P_T} = \frac{P_A}{P_{Total}} \\ &= \frac{270 \times 0.6}{180 + 90 \times 234} = 0.7. \end{aligned}$$

$$Y_A = 1 - 0.7 = 0.3.$$

\rightarrow liquid phase

Q. Calculate mole fraction of methanol in a mixture of methanol and ethanol if total pressure of mixture is 55 mm. Also calculate vapour phase mole fraction of methanol. $P_{CH_3OH} = 60 \text{ mm}$. $P_{C_2H_5OH} = 90 \text{ mm}$.

Sol:

$$P_A = P_A^o X_A \Rightarrow 58 \text{ mm}$$

$$X_{CH_3OH} = 0.75$$

$$X_{C_2H_5OH} = 0.25$$

$$Y_{CH_3OH} = 0.825$$

$$Y_{C_2H_5OH} = 0.175$$

Q. Calculate Partial pressure of methanol and ethanol.

$$P_{CH_3OH} = 60 \times 0.75 = 45$$

$$P_{C_2H_5OH} = 10.$$

Q. Calculate mole fraction of Benzene in mixture Benzene and Toluene at Boiling point. $P_{\text{Benzene}}^{\circ} = 800 \text{ mm}$, $P_{\text{Toluene}}^{\circ} = 600 \text{ mm}$

Sol At Boiling pt $P_T = 1 \text{ atm} = 760 \text{ mm}$

$$P_T = P_{\text{Toluene}}^{\circ} + (P_{\text{Benzene}}^{\circ} - P_{\text{Toluene}}^{\circ}) X_B$$

$$760 = 600 + (200) X_B$$

$$X_B = 0.8 \quad X_A = 0.2$$

Also calculate vapour phase mole fraction of Benzene.

$$Y_B = \frac{P_B X_B}{P_T} = \frac{800 \times 0.8}{760} = \frac{640}{760} = \frac{16}{19}$$

Also calculate partial pressure of toluene.

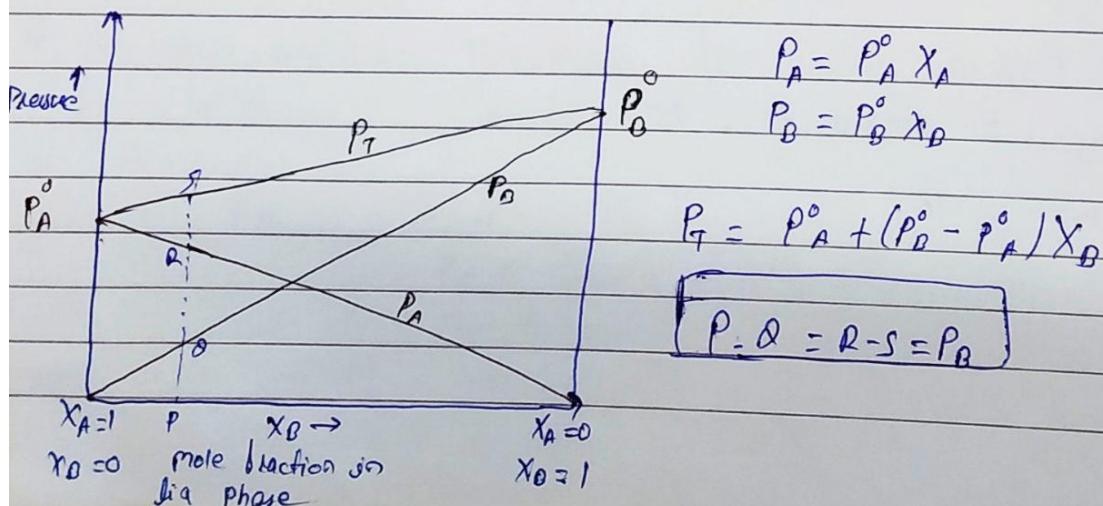
$$P_T = P_t X_t = 600 \times 0.2 = 120 \text{ mm}$$

$$P_{\text{Benzene}} = 760 - 120 = 640 \text{ mm}$$

Ideal solution

Those liquid solution which obey Raoult's Law are known as ideal solution. Their experimental vapour pressure is equal to theoretical vapour pressure ($P_T = P_A^{\circ} (P_A^{\circ} - P_A) X_A$)

Vapour Pressure Curve (liq phase).



③ In ideal solution average attraction force between solute and solvent is almost equal to average attraction force solute-solute and solvent-solvent.

$$\frac{\text{solute}}{\overbrace{A-A}^2} + \frac{\text{solvent}}{\overbrace{B-B}^2} = \overbrace{A-B}^{\text{Soln.}}$$

④ $\Delta H_{\text{solution}} = 0$ that means neither energy absorb or release due to formation of solution.

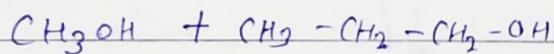
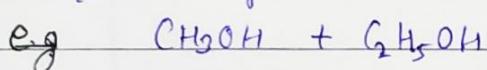
⑤ $(V \cdot P)_{\text{experimental}} = (V \cdot P)_{\text{theoretical}}$.

⑥ $\Delta V_{\text{soln}} = 0$ means no volume change due to mixing.

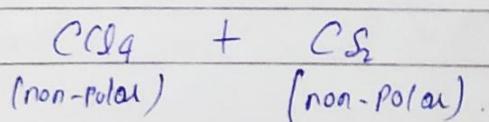
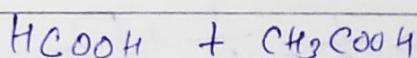
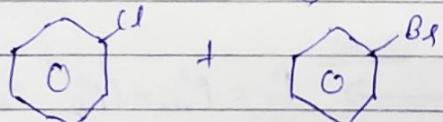
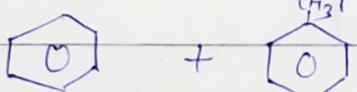
⑦ $\Delta S_{\text{mixing}} = +ve$.

⑧ $\Delta G_{\text{mixing}} = -ve$.

* Nearly ideal solution can prepare by mixing liquids of similar nature or Homologues members.



n-heptane + n-heptene.



Phase

Date _____

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Relation between total Pressure & vapour mole fraction (γ_A , γ_B)

$$\gamma_A = \frac{P_A^o X_A}{P_T} ; \quad \gamma_B = \frac{P_B^o X_B}{P_T}$$

$$X_A = \frac{\gamma_A P_T}{P_A^o}$$

$$X_B = \frac{\gamma_B P_T}{P_B^o}$$

$$\text{we know } X_A + X_B = 1$$

$$\frac{\gamma_A P_T}{P_A^o} + \frac{\gamma_B P_T}{P_B^o} = 1$$

$$\frac{1}{P_T} = \frac{\gamma_A}{P_A^o} + \frac{\gamma_B}{P_B^o}$$

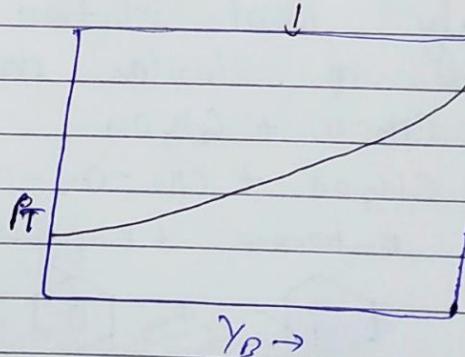
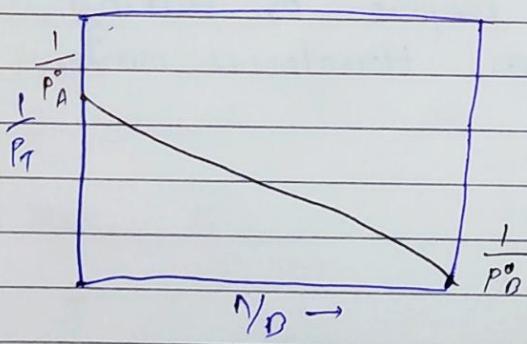
$$\text{we know } Y_A = 1 - \gamma_B$$

$$\frac{1}{P_T} = \frac{1}{P_A^o} - \frac{\gamma_B}{P_A^o} + \frac{\gamma_B}{P_B^o}$$

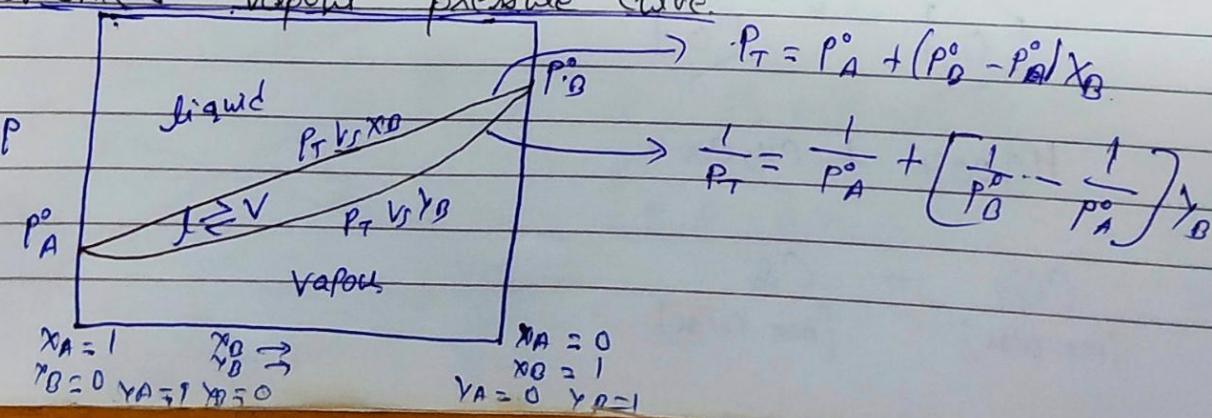
$$\boxed{\frac{1}{P_T} = \frac{1}{P_A^o} + \left[\frac{1}{P_B^o} - \frac{1}{P_A^o} \right] \gamma_B}$$

$$\boxed{\frac{1}{P_T} = \frac{1}{P_A^o} + \left[\frac{P_A^o - P_B^o}{P_B^o \times P_A^o} \right] \gamma_B}$$

Rectangular hyperbola

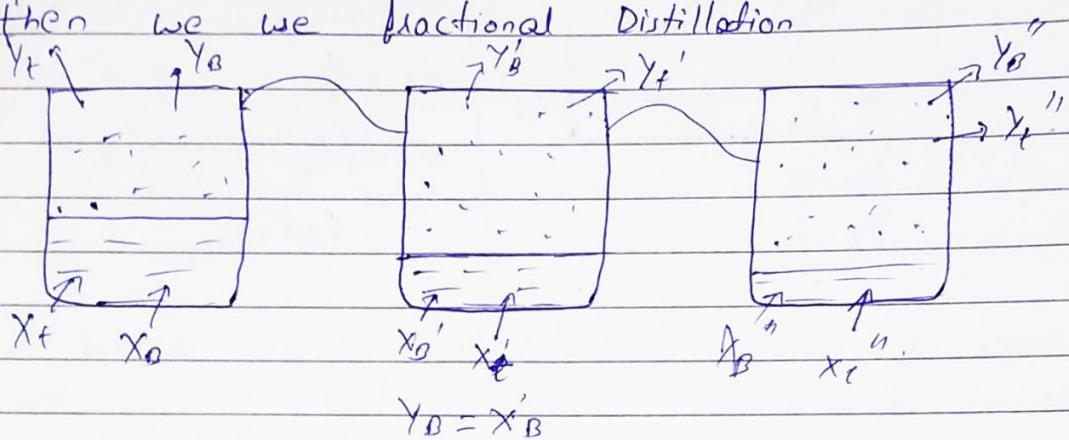


Combined vapour pressure curve.



Fractional Distillation

Distillation is the method by which we separate two liquids on the basis of Boiling point. difference. if B.P difference is less than 10°C then we use fractional Distillation.

Ex-1

$$\text{Q.20} \quad P_T = 180 X_B + 30$$

$$P_B^{\circ} = 270$$

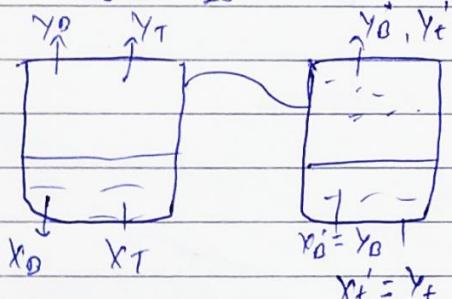
$$P_T^{\circ} = 90$$

$$n_{C_6H_6} = \frac{936}{70} = 12$$

$$n_{C_2H_6} = \frac{736}{32} = 8$$

$$X_B = \frac{12}{20} = 0.6$$

$$X_T = \frac{8}{20} = 0.4$$



In 1st chamber

$$Y_B = \frac{P_B^{\circ} X_B}{180 X_B + 30} = \frac{270 \times 0.6}{180 \times 0.6 + 30} = \frac{9}{11}$$

$$Y_T = \frac{2}{11}$$

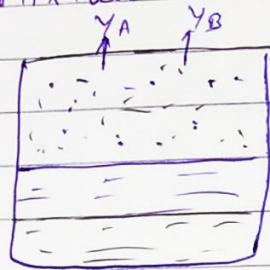
$$\text{In Second chamber} \quad Y_B' = X_0' = \frac{9}{11} \quad Y_T' = X_T' = \frac{2}{11}$$

$$Y_B' = \frac{P_B^{\circ} X_B'}{180 X_B' + 30} = \frac{270 \times \frac{9}{11}}{180 \times \frac{9}{11} + 30} = \frac{27}{29} = 0.932$$

$$Y_T' = \frac{2}{29}$$

STEAM DISTILLATION

This is used to separate immiscible (not mixed) liquid mixture. In this case only Dalton's law is applicable



$$P_A^o = P_A = \frac{n_A R T}{V}$$

$$P_B^o = P_B = \frac{n_B R T}{V}$$

$$\frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{w_A}{M_A} \times \frac{M_B}{w_B}$$

Non-Ideal solution

Those liquid mixture which do not obey Raoult's law are known as non-ideal solution.

These are of two types.

- ① +ve Deviation non-ideal solution
- ② -ve Deviation non-ideal soln

+ve Deviation

$$\textcircled{1} \quad (V \cdot P)_{\text{exp}} > (V \cdot P)_{\text{Theo.}}$$

Raoult law.

$$\textcircled{2} \quad \frac{A-A + B-B}{2} > A-B$$

Due to formation of solution
average attraction force decrease

$$\textcircled{3} \quad \Delta H_{\text{mix}} = +ve \quad (\text{endothermic})$$

$$\textcircled{4} \quad \Delta V_{\text{mix}} = +ve$$

$$\textcircled{5} \quad \Delta S_{\text{mix}} = +ve$$

$$\textcircled{6} \quad \Delta G = \Delta H - T \Delta S -$$

At High Temp $\Delta G = +ve$
At low Temp $\Delta G = +ve$

-ve Deviation

$$\textcircled{1} \quad (V \cdot P)_{\text{exp}} < (V \cdot P)_{\text{Theo.}}$$

$$\textcircled{2} \quad \frac{A-A + B-B}{2} < A-B$$

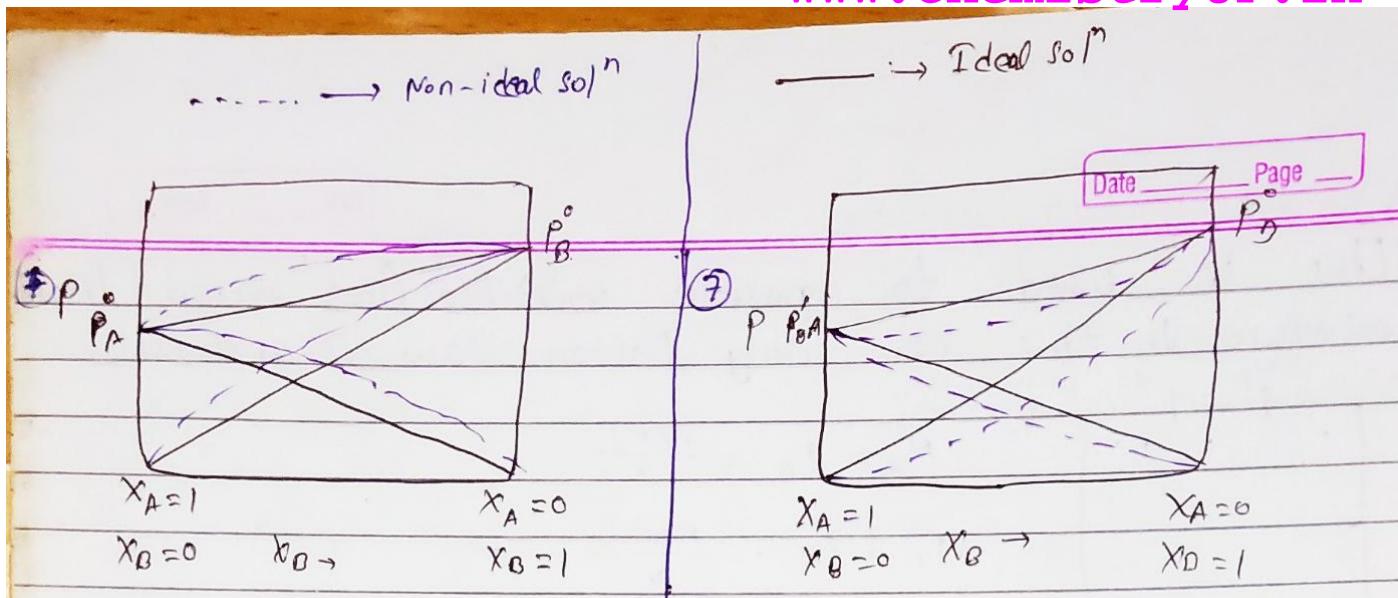
$$\textcircled{3} \quad \Delta H_{\text{mix}} = -ve. \quad (\text{exothermic})$$

$$\textcircled{4} \quad \Delta V_{\text{mix}} = -ve.$$

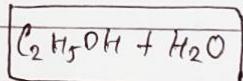
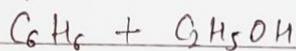
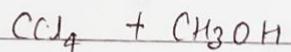
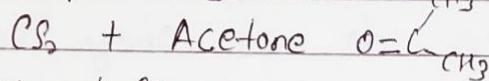
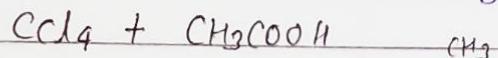
$$\textcircled{5} \quad \Delta S_{\text{mix}} = +ve$$

$$\textcircled{6} \quad \Delta G = \Delta H - T \Delta S -$$

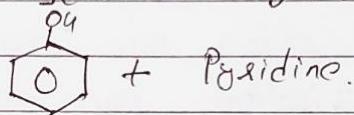
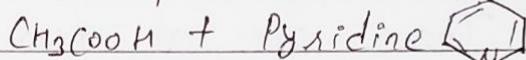
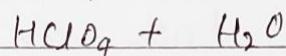
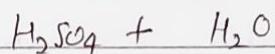
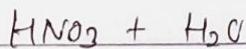
At High Temp $\Delta G = -ve$
At low Temp $\Delta G = -ve.$



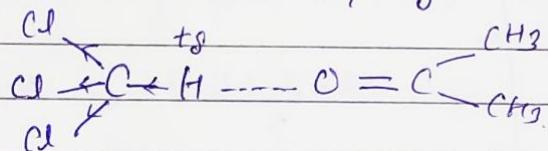
⑧ Non polar + Polar + H bonding.



⑧ Acid + Base or Amphoteric.



Note: chloroform and acetone will form Negative Deviation due to Hydrogen Bonding.



AZEOTROPEs

It is also known as constant Boiling mixture Because at this point mixture behave as one pure liquid.

It is formed by non-ideal solution. At this point on Boiling their composition do not change and these can only be separated by azeotropic distillation.

In azeotropes mole fraction of liquid become equal

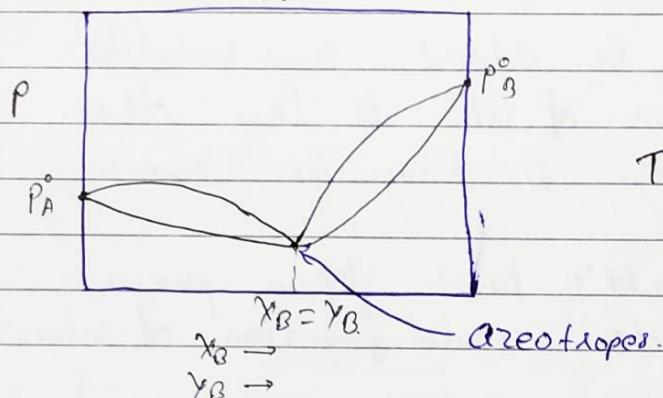
to mole fraction of vapors.

Azeotropes are of two types.

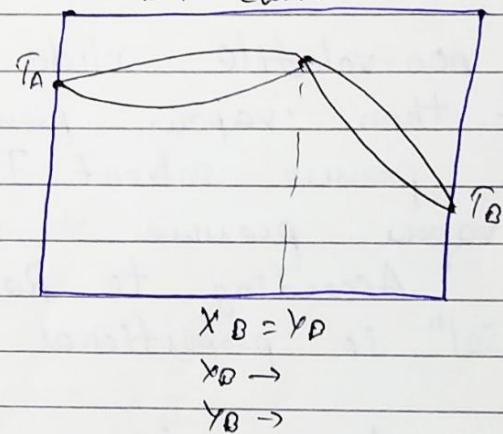
- Maximum boiling azeotropes.
- This is formed by -ve deviation non-ideal solution. e.g. $\text{HNO}_3 + \text{H}_2\text{O}$

- In these there is maxima in boiling point curve and minima in vapor pressure curve.

V.P. Curve.



B.P. Curve.

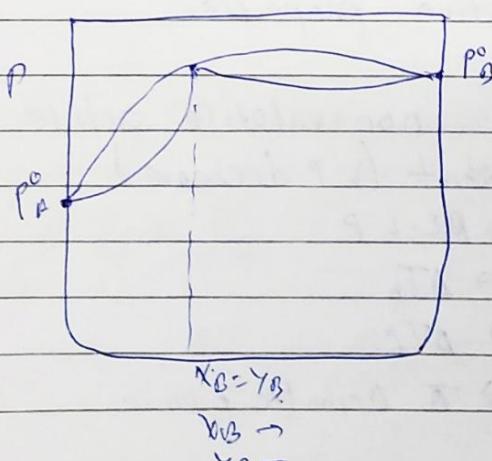


- Minimum Boiling azeotropes.

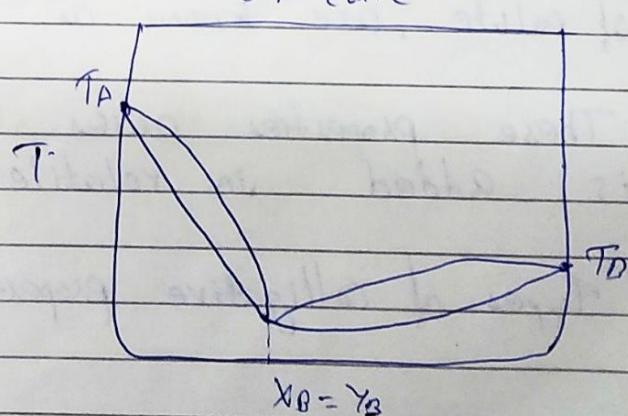
- This is formed by +ve deviation non-ideal solution e.g. $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$

- In these there is maxima in V.P. curve and minima in B.P. curve.

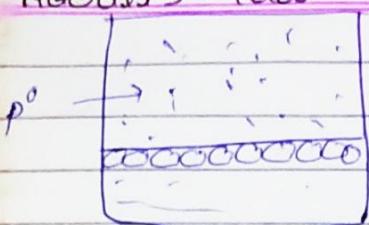
V.P. Curve



B.P. Curve

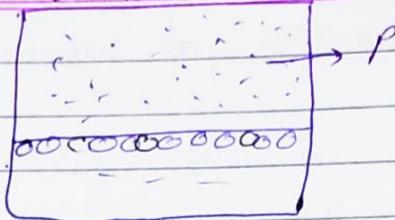


Raoult's law when solvent is volatile and solute is Non-volatile.



Pure solvent

$$P^o = v.p \text{ of pure liquid}$$



Solution

$$P = v.p \text{ of soln}$$

$$P_{soln} \propto X_{solvent}$$

$$P_{soln} = P^o X_{solvent}$$

When non-volatile solute is added in volatile solvent, then vapour pressure of soln is less than vapour pressure of solvent. This is known as lowering in vapour pressure.

According to Raoult's law vapour pressure of soln is proportional to mole fraction of solvent.

Relative lowering in vapour pressure is equal to mole fraction of solute.

Colligative properties.

(i) Those properties which do not depend on nature of solute but on the No. of particles (no. of moles) of solute, are known as colligative properties.

(ii) These properties arises when non-volatile solute is added in volatile solvent (v.p decrease)

(iii) Types of colligative properties

- R.L. v.p
- ΔT_b
- ΔT_f
- π Osmotic pressure.

Relative lowering in vapour pressure [R.L.V.P]

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- (i) when non-volatile solute is added in volatile solvent then vapour pressure is decrease. and the ratio of lowering in vapour pressure and V.P of solvent is known as R.L.V.P. $P \rightarrow V.P \text{ of soln}$
 $P^0 \rightarrow V.P \text{ of pure solvent}$

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

$$P = P^0 X_{\text{solvent}}$$

$$P = P^0 / (1 - X_{\text{solute}})$$

$$P = P^0 - P^0 X_{\text{solute}}$$

$$P^0 - P = P^0 X_{\text{solute}}$$

$$\frac{P^0 - P}{P^0} = \frac{X_{\text{solute}}}{n+1}$$

$$\text{R.S.V.C. } P = P^0 - P^0 X_{\text{solute}}$$

$$P^0 - P = P^0 X_{\text{solute}}$$

$$\left[\frac{P^0 - P}{P^0} = X_{\text{solute}} \right] \xrightarrow{\text{partial density}}$$

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

For dilute soln ($n \ll N$)

$$\frac{P^0 - P}{P^0} = \frac{m}{M} \cdot \frac{n}{N} \Rightarrow \frac{P^0 - P}{P^0} = \frac{m}{M} \times \frac{1}{n} \rightarrow \frac{P^0 - P}{P^0} = \frac{m}{M}$$

$$\therefore \left[\frac{P^0 - P}{P^0} = \frac{m}{M} \times \frac{n}{n} \right] \rightarrow (3)$$

Formula (3) gives approximate result so we can write another most formula.

$$\frac{P^0 - P}{P^0} = \frac{N}{n+N} \quad \frac{P^0 - P}{P^0} = \frac{n}{N+n}$$

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

$$1 - \frac{P}{P^{\circ}} = \frac{n}{n+N} \Rightarrow \frac{P}{P^{\circ}} = 1 - \frac{n}{n+N}$$

$$\frac{P}{P^{\circ}} = \frac{n \times N - n}{n + N}$$

$$\frac{P}{P^{\circ}} = \frac{n}{N} + 1$$

$$\Rightarrow \frac{P^{\circ}}{P} - 1 = \frac{n}{N}$$

$$\boxed{\frac{P^{\circ} - P}{P} = \frac{n}{N}} \quad \text{--- (iv)}$$

$$\boxed{\frac{P^{\circ} - P}{P} = \frac{n}{N}} \quad \text{--- (v)}$$

$$\boxed{\frac{P^{\circ} - P}{P} = \frac{w}{m} \times \frac{M}{W}} \quad \text{--- (vi)}$$

$$\frac{P^{\circ} - P}{P} = \frac{w}{m} \times \frac{1000}{W} \times \frac{M}{1000}$$

$$\frac{P^{\circ} - P}{P} = \text{molarity} \times \frac{M}{1000}$$

Q. On adding 10 g of solute in 360 gm of water vapor pressure of water decrease 10%. Calculate molar weight of solute.

$$M_w = 20 \quad P^{\circ} = 100 \quad P = 90.$$

$$\frac{10}{90} = \frac{10}{m} \times \frac{10}{360}, \quad \frac{10}{90} = \frac{1}{m} \Rightarrow m = \frac{90}{10} = 9 \text{ g.}$$

Q. What is the Boiling pt. v.p at B.P of SO_3 in which 18 g. $\text{C}_6\text{H}_5\text{OH}$ is dissolved in 360 g water

$$\frac{1 - P}{P} = \frac{1/10}{360/18} \Rightarrow \frac{1 - P}{P} = \frac{1}{200}$$

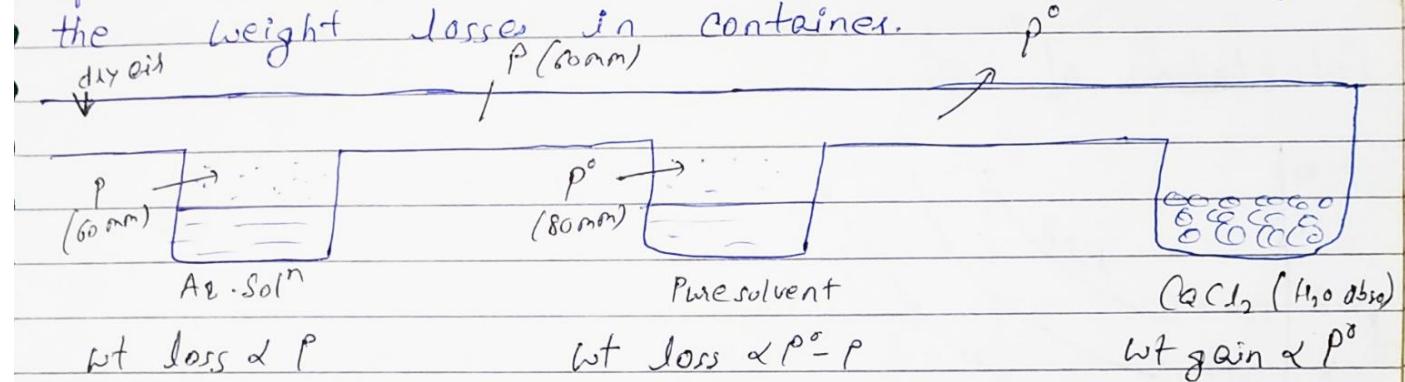
$$\Rightarrow 200 - 200P = P.$$

$$P = \frac{200}{201} = 0.995 \text{ atm.}$$

Ostwald-Walker Method

(i) This is the experimental method to determine R.L.V.P through which we can determine molecular weight of unknown solute.

(ii) In this method dry air passed through container of solⁿ and solvent and R.L.V.P is measured by the weight losses in container.



$$\frac{\text{wt loss in solvent}}{\text{wt loss in sol}^n} = \frac{P^{\circ} - P}{P} = \frac{n}{N}$$

Elevation in Boiling point (ΔT_B)

① Boiling point is temperature at which vapour pressure of liquid becomes equal to atmospheric pressure. and at this temperature liquid starts boiling.

② When non-volatile solute is added in solvent then vapour pressure of solvent decrease that is why more heat is required to increase its vapour pressure upto atmospheric pressure.

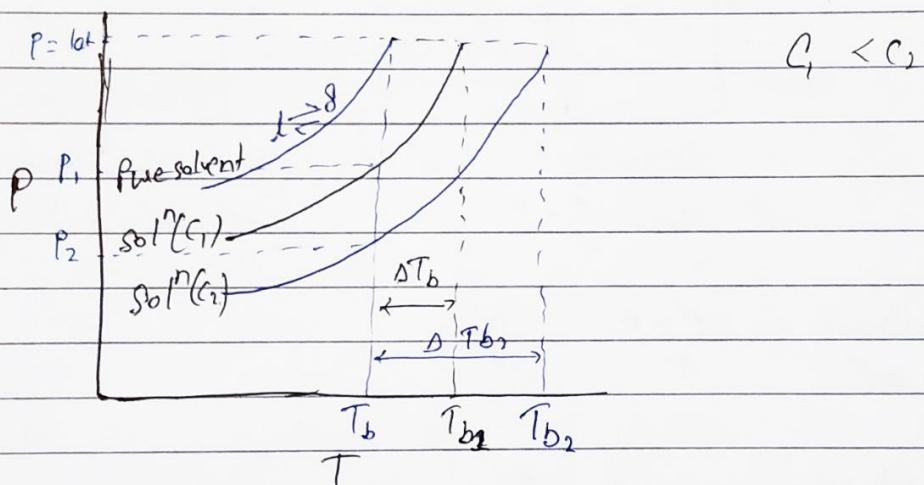
So, boiling point is increase. This is known as elevation in Boiling point (ΔT_B)

③ At mountains food preparation is difficult becoz due to less atmospheric pressure boiling point of

water decrease and wastage of energy occurs in evaporation of water.

④ Use of pressure cookers reduce the time for cooking becoz in pressure cookers boiling point of water increase due to increase atmospheric pressure.

Calculation of ΔT_b



$$\text{elevation in B.P} \quad \Delta T_b \propto R \cdot L \cdot V \cdot P = X_{\text{solute}}$$

$$\Delta T_b \propto X_{\text{solute}}$$

$$\Delta T_b \propto \frac{n}{n+N}$$

For dilute soln $n \ll N$.

$$\therefore \Delta T_b \propto \frac{n}{N}$$

$$\Delta T_b \propto \frac{w}{m} \times \frac{M}{w}$$

$$\Delta T_b \propto \frac{w}{m} \times \frac{1000}{w} \times \frac{M}{1000} \quad \text{constant}$$

$\Delta T_b \propto$ molality.

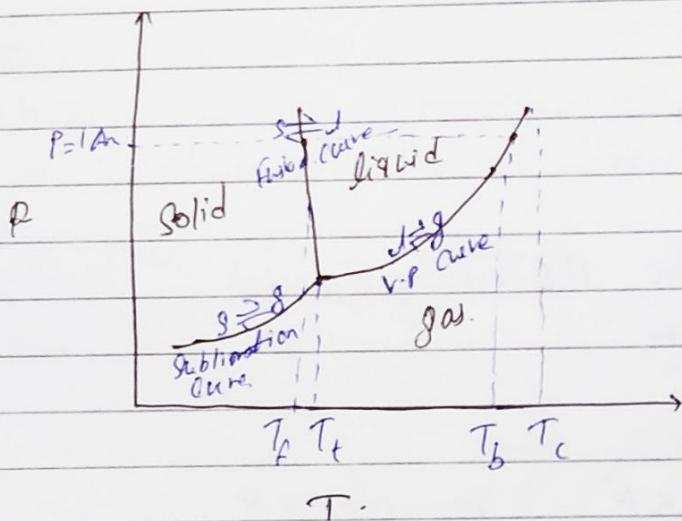
$$\Delta T_b \propto \boxed{\Delta T_b = k_b \text{ molality} = k_b m} \quad \text{--- (1)}$$

$$\Delta T_b = k_b \frac{w}{m} \times \frac{1000}{w}$$

k_b = molal elevation constt = Ebullioscopic constt

Phase Diagram of water

Variation of different phases with pressure and temperature can be explain in phase diagram.



Triplet point(T_f) → It is the temp. at which all 3 phases of substance exists in equilibrium

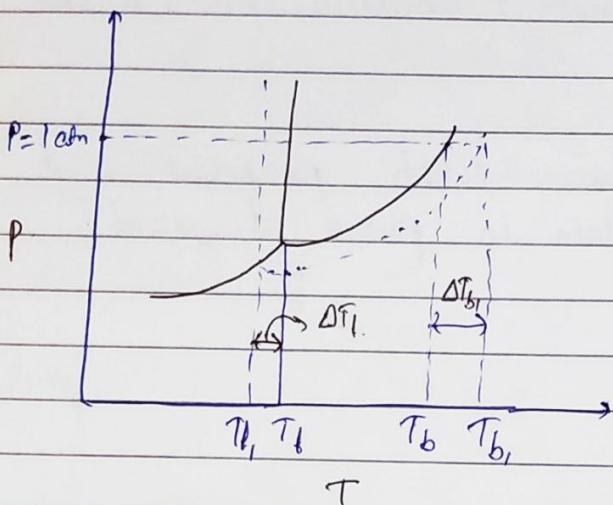
Depression in Freezing Point (ΔT_f)

(1) The temperature at which solid and liquid exists in equilibrium is known as freezing point.

(2) T_f is the temperature at which vapour pressure of solid becomes equal to vapour pressure of liquid. And at this temperature liquid solvent starts freezing.

(3) On adding non-volatile solute vapour pressure of solvent decrease that is why equilibrium

both solid and liquid shift to lower temp.
These is known as depression in freezing point.



Depression in F.Pt. $\Delta T_f \propto R \cdot E \cdot V \cdot P = X_{\text{solute}}$
 $\Rightarrow \Delta T_f \propto X_{\text{solute}}$

$$\Delta T_f \propto \frac{n}{n+N}$$

For dilute sol'n $n \ll N$. so $n+N=N$

$$\Delta T_f \propto \frac{n}{N}$$

$$\Delta T_f \propto \frac{\omega}{m} \times \frac{M}{\omega}$$

$$\Delta T_f \propto \frac{\omega}{m} \times \frac{1000}{\omega} \times \frac{M}{1000}$$

$\Delta T_f \propto$ molality

$$[\Delta T_f = k_f \text{ molality} = k_f m]$$

$$\boxed{\Delta T_f = k_f \times \frac{\omega}{m} \times \frac{1000}{\omega}}$$

k_f = molal depression const = cryoscopic const

Q. 30g of NH_2CONH_2 (60g) $\frac{1}{2}$ is dissolved in 180g H_2O 1° . Determine following. [$k_b = 0.52$, $k_f = 1.86$]

(a) V.P of solⁿ at 100° $P^{\circ} = 760$

$$\frac{P^{\circ} - P}{P} = \frac{n}{N} = \frac{\frac{1}{2}}{10}$$

$$\Rightarrow \frac{760 - P}{P} = \frac{1}{20} \Rightarrow 20(760 - P) = P$$

$$\Rightarrow 15200 - 20P = P$$

$$\Rightarrow 15200 = 21P \Rightarrow P = 723.80.$$

(b) B.P of solⁿ

$$\Delta T_b = 0.52 \times \frac{\frac{1}{2}}{\frac{180}{1000}}$$

$$\Delta T_b = 0.52 \times \frac{1}{2} \times \frac{\frac{50}{100}}{\frac{180}{1000}} = 1.44.$$

$$\therefore \text{B.P} = 100 + 1.44 = 101.44$$

(c) F.P of solⁿ

$$\Delta T_f = 1.86 \times \frac{1}{2} \times \frac{\frac{100}{180}}{\frac{50}{100}} = 5.166$$

$$\therefore \text{F.P} = -5.166$$

$$\begin{array}{r} 1 \\ 126 \\ 194 \\ \hline 292 \\ 16 \\ \hline 11 \\ 11 \\ \hline 170 \end{array}$$

Q. What is the wt of sucrose ($\text{C}_12\text{H}_{22}\text{O}_{11}$) is required to add in 500g of H_2O so that difference between B.P & F.P becomes 105°C

~~$$\Delta T_b = 0.52 \times \frac{n}{342} \times \frac{1000^2}{5000} = \frac{0.52n}{171}$$~~

~~$$\therefore \Delta \text{B.P.} = 100 + \frac{0.52n}{171}$$~~

~~$$\Delta T_f = 1.86 \times \frac{n}{171}$$~~

~~$$\text{F.P.} = 0 - \frac{1.86n}{171} = -\frac{1.86n}{171}$$~~

~~$$100 + \frac{0.52n}{171} + \frac{1.86n}{171} = 105$$~~

$$100 \cdot 003x + 0 \cdot 010x = 105$$

$$100 \cdot 0138x = 105 \Rightarrow$$

$$\Delta T_b = 100^\circ \quad T_f = 0^\circ \quad \Delta T_f = 100^\circ$$

$$\Delta T_b + \Delta T_f = 5 = k_b m + k_f m$$

$$5 = m(k_b + k_f)$$

$$5 = \frac{w}{342} \times \frac{1000}{500} \times 2 \cdot 38$$

$$w = 359 \cdot 2$$

Q. If 30 g of NH_4CONH_2 is add in 500 g H_2O and if soln is cooled to -6°C then calculate wt of ice separated.

Given Mole of $\text{NH}_4\text{CONH}_2 = \frac{1}{2}$ wt of $\text{H}_2\text{O} = 500 \text{ g}$
 $\Delta T_f = 1.86 \times \frac{\frac{1}{2} \times 1000}{500} = 1.86 \cdot 2$

$$\text{F.P. of } \text{H}_2\text{O} = -2^\circ\text{C}$$

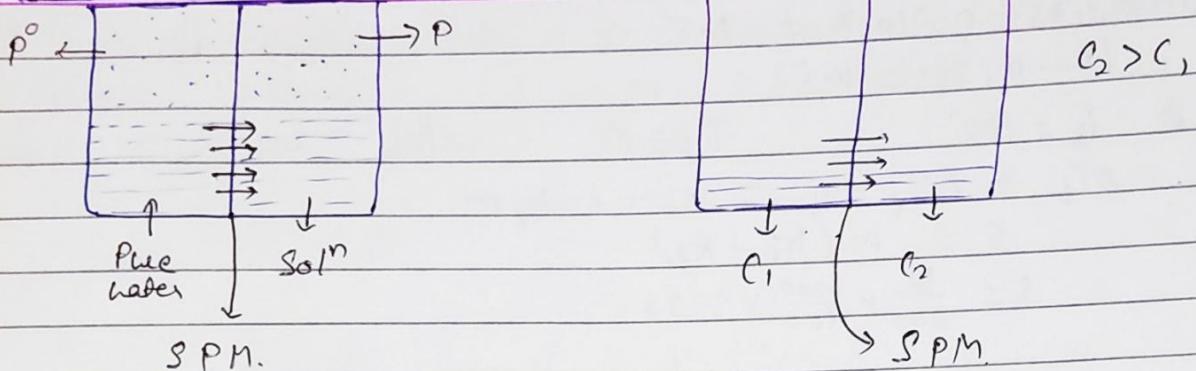
$$f = 2 \times \frac{1}{2} \times \frac{1000}{w} \Rightarrow w = \frac{1000}{f} = 166.6 \text{ g}$$

$$\therefore \text{ice separan.} = 500 - 166.6 = 333.4 \text{ g}$$

Hint. On cooling of the soln ice separated as crystals and molality of increase continuously Hence freezing point is lowered.

(v) Osmotic Pressure & Osmosis.

Date _____



Semi Permeable membrane

When a pure solvent and its solution is separated by SPM. then net flow of solvent occurs from solvent side to solution side. This is known as osmosis. (NET solvent of H₂O solvent at d²⁴)

The main reason for osmosis difference in vapour pressure of solvent and solution.

SPM → It is selective membrane which only allow transfer of solvent molecule only.

Natural SPM → Animal membrane, egg membrane, cell membrane

Synthetic SPM → $Cu_2[Fe(CN)_6]$ OR Copper ferro cyanide.

Osmosis.

Exo osmosis

Movement of solvent toward outside

Endo-osmosis

Movement of solvent toward inside.

e.g. (i) when grape is kept in conc. sugar solution it shrink.

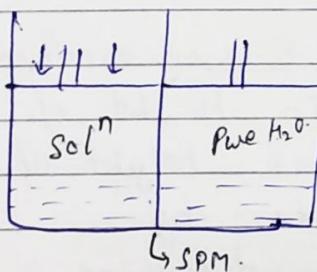
(ii) if dry raisin is kept in pure water it swell up.

(iii) if Blood cell is kept in pure water it swell and finally it can burst (Haemolysis).

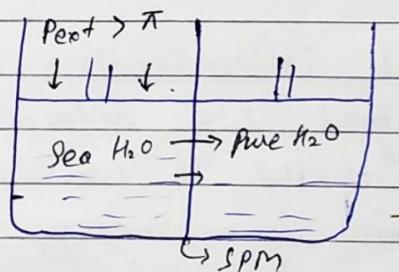
(iv) when Blood cell is kept in conc NaCl solution it shrink. (Plasmolysis)

Osmotic Pressure (π)

It is the extra pressure required in solution side so that transfer of solvent stop. (when solvent & solⁿ is separated by (SPM))



Osmosis



Reverse Osmosis

When Higher pressure than osmotic pressure is applied in solⁿ side then movement of solvent take place from solⁿ side to solvent side. This is know as Reverse Osmosis.

Calculation of Π

Osmotic pressure is directly proportional to concentration and temp¹.

$$\Pi \propto c$$

$$\Pi \propto T$$

$$\Pi = C S T$$

$$\Pi = C R T$$

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

$$S = \text{Van't Hoff const.}$$

$$S = R$$

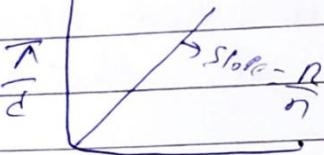
$$\boxed{\Pi = \frac{n}{V} RT}$$

$$\boxed{\Pi = \frac{w}{M \times V} RT}$$

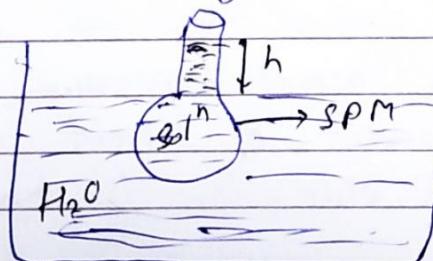
If we mix two same compound solⁿ or two different compound solⁿ then final concentration and final osmotic pressure can be determine by following formula:

$$C_F = \frac{C_1 V_1 + C_2 V_2}{V_1 + V_2}$$

$$\Pi_F = \frac{\Pi_1 V_1 + \Pi_2 V_2}{V_1 + V_2}$$

Experimeted Determination of Π [Barkly Heanty method]

In this method we determine increase in Height of liquid solⁿ- due to osmosis. We can convert height of liquid column in mecury column height by $h_{Hg} = h_{H2O}$ and then determine pressure in atm by dividing 76.



$$(1) \Pi = h d g$$

Here, $h = m$ $d = \text{kg/m}^3$

$g = \text{m/sec}^2$ $\Pi = \text{N/m}^2$

$$1 \text{ Atm} = 1.01325 \times 10^5 \text{ N/m}^2$$

$$\textcircled{2} \quad h_1 d_1 = h_2 d_2$$

$$\frac{\pi}{(\text{atm})} = \frac{h_2 \text{ cm.}}{76}$$

Isotonic, Hypotonic, Hypertonic

(1) Isotonic \rightarrow Those solⁿ which has same osmotic pressure are known as Isotonic solⁿ

$$\pi_1 = \pi_2$$

$$C_1 T_1 = C_2 T_2$$

$$\text{at same temp} \quad C_1 = C_2$$

$$\textcircled{2} \quad \pi_1 > \pi_2$$

Hypertonic \hookrightarrow Hypotonic

(3) If Hypertonic & Hypotonic solution are attached through SPM then solvent transfers from Hypotonic to Hypertonic solution.

$$\frac{50}{60} \times 5 - 100$$

Q. Calculate π of 5% NH_2CONH_2 solⁿ (w/v) at 27°C.

$$\pi = \frac{1/12}{1/10} \times 0.0821 \times 300$$

$$= \frac{1}{12} \times \frac{10}{1} \times 0.0821 \times 300 = 20.525 \text{ N/m}^2$$

Q. 5% Glucose solⁿ at 27°C is isotonic to 10% solutio-

of unknown solute at 47°C. Calc. Molecular mass

$$C_1 T_1 = C_2 T_2$$

$$\frac{5}{180 \times 1} \times 300 = \frac{10^2}{M_2 \times 1} \times 320$$

$$M_2 = \frac{6400}{320} = 384$$

C.P. → Colligative Prop.

Date _____ Page _____

Application of Osmotic Pressure

- (1) Peoples who intake Higher amount of salt their cells have High water retaining capacity This problem is known as EDEMA.
- (2) Wilting of plants on addition of excess fertilizers
- (3) Higher amount sugar and salt is added in jams and pickles to preserve them.
- (4) Upward movement of water in plants.

Abnormal colligative properties [Vant Hoff coefficient]

If solute do not dissociate or associate then colligative properties are known as Normal colligative properties and if solute dissociate or associate then colligative properties are known as Abnormal colligative properties (experimental colligative property).

Vant Hoff coefficient gives relation between theoretical C.P and experimental C.P.

$$i = \frac{\text{Exp C.P}}{\text{Theo. C.P}} = \frac{\text{Exp No. of moles}}{\text{Theo. No. of moles}} = \frac{\text{Theo. Mole wt of solute}}{\text{Exp Mole wt of solute}}$$

$$\text{Exp C.P} = i \times \text{Theo. C.P.}$$

$$\text{Exp R.L.V.P} = i \times \frac{n}{n+n}$$

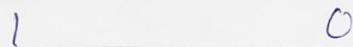
$$\text{Exp. } \Delta T_b = i \times k_b m$$

$$\text{Exp. } \Delta k_f = i \times k_f m$$

$$\text{Exp. } \Pi = i \cdot C \cdot T$$

if solute is non-electrolyte and non-associative then value of $i = 1$. e.g. glucose, sucrose, urea.

Calculation of i in dissociation



$$\text{total moles of eq} = 1 - \alpha + n\alpha$$

(Actual mole).

$$i = \frac{\text{Actual moles (exp)}}{\text{Theoretical moles}} = \frac{1 - \alpha + n\alpha}{1}$$

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

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

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

$$i = 1 + n\alpha - \alpha = \frac{M_{\text{The}}}{M_{\text{exp}}}$$

IMP Points

① In Dissociation no. of moles increase **in that** is why experimental colligative properties are greater than theoretical C.P. and following comparison can be done.



$$n > 1$$

$$i > 1$$

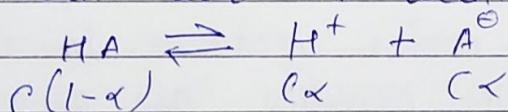
$$\begin{aligned} M_{\text{The}} &> M_{\text{exp}} \\ (C.P)_{\text{exp}} &> (C.P)_{\text{Th}} \\ (V.P)_{\text{exp}} &< (V.P)_{\text{Th}} \\ (T_b)_{\text{exp}} &> (B.P)_{\text{Th}} \\ (T_f)_{\text{exp}} &< (T_f)_{\text{Th}} \end{aligned}$$

In association these properties will reverse.

② For strong electrolyte if α is not given then it can be consider as 1 (100% dissociation) in that case $i = n = \text{No. of ions.}$

	α	i	$M_{\text{exp}} = \frac{M_{\text{the}}}{i}$
# NaCl $n=2$	-	2	$M_{\text{exp}} = \frac{58.5}{2}$
NaCl	$\alpha = 0.6$	$1 - 0.6 + 2 \times 0.6 = 1.6$	$M_{\text{exp}} = \frac{58.5}{1.6}$
K_2SO_4 $n=3$	-	3	$M_{\text{exp}} = \frac{174}{3}$
K_2SO_4	$\alpha = 0.8$	$1 - 0.8 + 3 \times 0.8 = 2.6$	$M_{\text{exp}} = \frac{174}{2.6}$
$\text{K}_4[\text{Fe}(\text{CN})_6]$ $n=5$	-	1 - α + 5	
$\text{K}[\text{Co}(\text{C}_5\text{O})_6]\text{Cl}_3$ $n=4$		4	

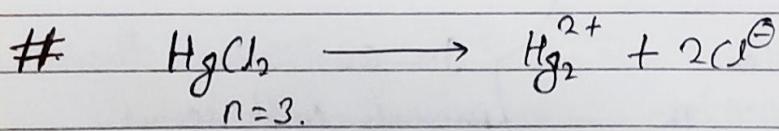
③ For weak acid or weak base.



$$1 - \alpha = 1.$$

$$K_a = c\alpha^2$$

$$[\text{H}^+] = c\alpha = 10^{-\text{pH}}$$



Calculation of vant-Hoff coefficient in association

Date _____ Page _____

$$nA \longrightarrow An$$

$$t=0 \quad 1 \quad O$$

$$t=\text{eq} \quad 1-\beta \quad P/n$$

$$\text{At eq. total mole} = 1 - \beta + \frac{\beta}{n}$$

$$i = \frac{\text{Actual. mol}}{\text{The. mol}} = \frac{1 - \beta + \frac{\beta}{n}}{1}$$

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

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

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

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

IMP. Points

(1) If value to β is not given then it can be considered as 1 and in that case

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

$$\text{Dimer / Dimerisation} = \frac{1}{2}$$

(2) In non aqueous solvent like Benzene dimerisation of Carboxylic acid occurs due to Hydrogen Bonding that is why their theoretical mole experimental molecular mass is twice of the theoretical mass.

(3) For To Determine molecular weight of polymer by colligative property best method is osmotic pressure measurement.

e.g. Which of the following have. Highest O.P.

- (A) 0.1 molal urea. (B) 0.2 molal Glucose (C) 0.08 molal $Al_2(SO_4)_3$
 (D) 0.05 molal NaCl.

$$\Delta T_b = i K_f m$$

- (A) $1 \times 0.1 = 0.1$ (B) $0.2 \times 1 = 0.2$ (C) $5 \times 0.08 = 0.4$
 (D) $0.05 \times 2 = 0.1$

$$C > B > A = D.$$

Osmotic Pressure. $C > B > A = D$

F.P.

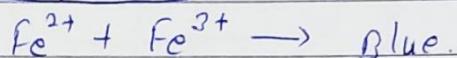
$A = D < B < C$

V.P.

$A = D > B > C$

e.g. In which side Blue colour solⁿ will form

A	B
$\pi = iC$ $= 5 \times 0.09$ $= 0.45$	$\pi = 0.4$
$K_4(Fe^{2+})$ $0.09M$	$0.1M$ Fe^{3+}



No. colour develop

water will flow from B to A

e.g. if experimental Molal conc. of NaCl is 30
then calculate % α of NaCl.

$$i = \frac{58.5}{30} \rightarrow$$

$$i = 1 - \alpha + 2\alpha \rightarrow i = 1 + \alpha \quad \alpha = \frac{58.5}{30} - 1 = \frac{58.5 - 30}{30}$$

$$\therefore \frac{28.5}{30} \times 100 = \frac{28.5}{3} \% = 95\%$$

e.g. Which of the following have freezing point

- (A) 0.02 molal K_2SO_4 $3 \times 0.02 = 0.06$
- (B) 0.05 m NaCl $2 \times 0.05 = 0.1$
- (C) 0.08 m $MgCl_2$ $1 \times 0.08 = 0.08$
- (D) 0.01 n $CuSO_4$ $- 1 \times 0.01 = 0.01$

$$B < C < A < D$$

Q

A	B
0.04	0.06
\sim	\sim

$A \rightarrow B$.

e.g. 0.004 M Na_2SO_4 is isotonic with 0.01 M $\text{NH}_4\text{COONH}_4$ soln. What is % dis of Na_2SO_4

$$\Pi_1 = \Pi_2$$

$$C_1 = C_2$$

$$i_1 C_1 = i_2 C_2$$

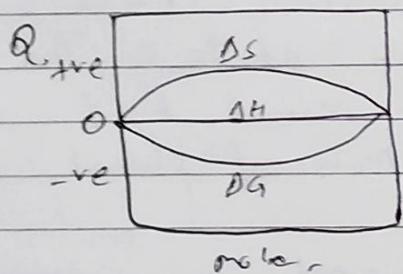
$$i_1 0.004 = i_2 0.01$$

$$i_1 = \frac{0.01}{0.004} = 2.5$$

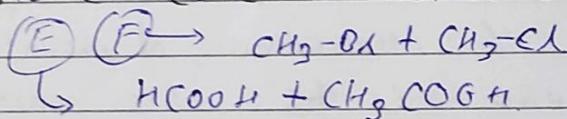
$$\frac{0.004}{0.01} = 1 - \alpha + 3\alpha = 1 + 2\alpha$$

$$\alpha = \frac{0.01}{0.004} - 1 = \cancel{-} \frac{1}{4} - 1 = \frac{10 - 4}{4}$$

$$\alpha = \frac{6}{4} \times \frac{6}{8} \times 100\% = \frac{150}{2} = 75\%$$



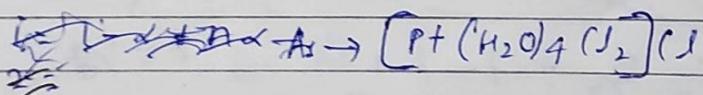
Above curve is suitable for



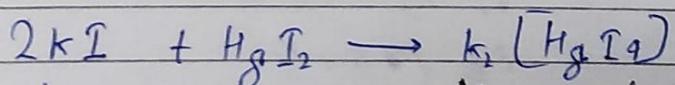
Q. 0.1 molal soln of $\text{Pt}(\text{H}_2\text{O})_6\text{Cl}_2$ freezes at -0.96°C

What is formula of complex. $K_f = 1.8$

$$i = \frac{0.36}{1.8 \times 0.1} = \frac{0.36}{0.18} = 2.$$



Q. What is the effect on freezing point of K.T soln when HgI_2



\downarrow
+ ion

Nesler's reagent

Used in detection of NH_4^+

\downarrow
ion.