

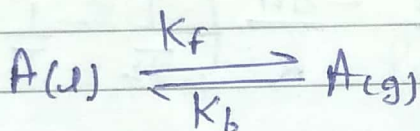
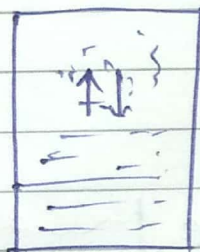
SBG STUDY

23/09/17

* Liquid Solution *

* Vapour pressure of ^{Pure} Liquid

if a liquid present in a close container it hold eq^b with its vapour at eq^b. Pressure exerted by vapour called vapour pressure of liquid



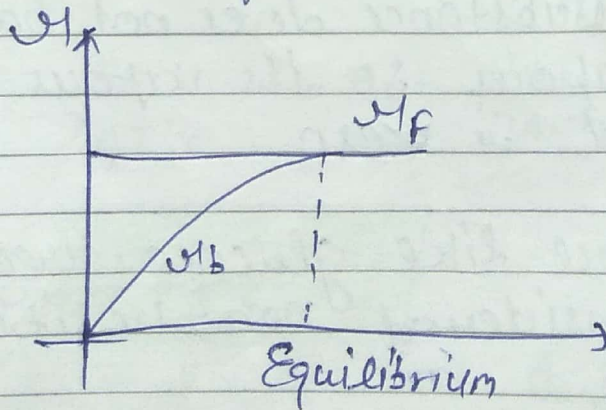
$$K_p = \frac{P_{A(g)}}{1}$$

$$r_f = k_f [A(l)] = k_f'$$

$$r_b = k_b [A(g)]$$

r_f = rate of evaporation

r_b = rate of condensation



* Important point :-

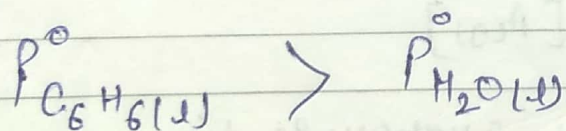
(1) Vapour pressure of pure liquid depend only on temp. it does not depend on ~~the~~ shape and size of container.

$$P^{\circ} = K_{eq} = A \cdot e^{-\Delta H/RT}$$

$$\ln \left(\frac{P_2^{\circ}}{P_1^{\circ}} \right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

2. Intermolecular Bonding in liquid state ↓

v.p of liquid ↑



3) Non-volatile substance does not have a tendency to form vapour, so its vapour pressure is considered as zero

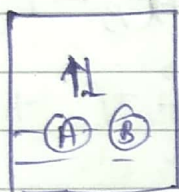
4) Solid substance like glucose, urea, sucrose, NaCl etc all considered non-volatile substance.

$$P_{\text{glucose}}^{\circ} = 0$$

'Raoult's law'

* Vapour pressure of liquid solution!

According to Raoult Law partial pressure of a liquid in ^{vapour} it will be proportional to its mole fraction in liquid solution



for A

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

for B

$$P_B \propto x_B$$
$$P_B = x_B P_B^{\circ}$$

$$P_T = P_A + P_B$$

$$P_T = x_A P_A^{\circ} + x_B P_B^{\circ} \quad \text{Important}$$

P_T or $P_s \Rightarrow$ v.p. of solution

x_A & $x_B =$ mol fraction of A & B in liquid phase

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

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

$$x_A + x_B = 1$$

P_A° & $P_B^{\circ} \Rightarrow$ v.p. of pure A & pure B respectively

* Vapour pressure of liquid solution depend on Temp. and composition of liquid solution

Graph: (T = const.)

$$P_T = n_A P_A^0 + n_B P_B^0$$

$$= n_A P_A^0 + (1 - n_A) P_B^0$$

$$\begin{aligned} & n_A P_A^0 + P_B^0 - P_B^0 n_A \\ & n_A (P_A^0 - P_B^0) + P_B^0 \end{aligned}$$

$$P_T = n_A (P_A^0 - P_B^0) + P_B^0$$

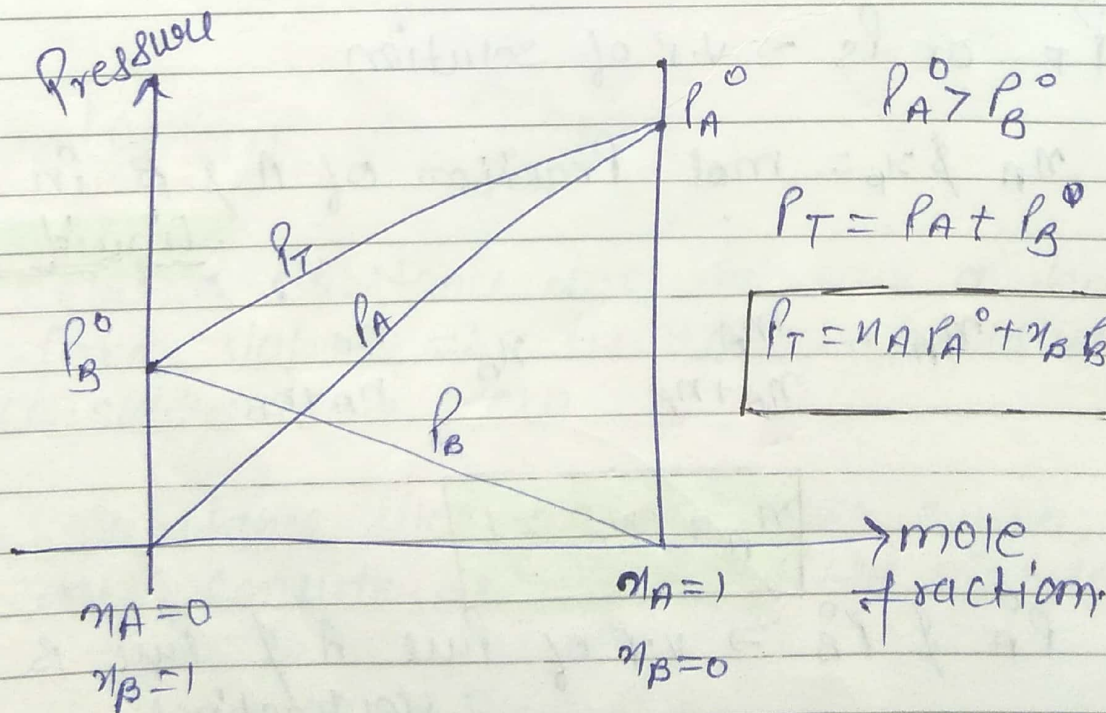
$$y = mx + c$$

$$P_A = n_A P_A^0$$

$$P_B = n_B P_B^0$$

$$P_B = (1 - n_A) P_B^0$$

$$P_B = -n_A P_B^0 + P_B^0$$



Note: At boiling point Vapour pressure of liquid will be equal to external pressure and liquid hold eq^b. with its vapour.

$$P_A^\circ > P_B^\circ$$

$$T_A^\circ < T_B^\circ$$

Que: Calculate Vapour pressure of 1 molar aq. glucose solution if vapour pressure of pure H₂O is 600 Torr.

$$P_T = \chi_{H_2O} P_{H_2O}^\circ + \chi_{\text{glucose}} P_{\text{glucose}}^\circ$$

$$\Rightarrow \frac{\text{mole of solute}}{\text{mass of solvent in kg}} = 1$$

$$= P_T = \text{mass}$$

Let mass of solvent = 1 kg.

$$\text{mol of solute} = 1$$

(glucose)

$$= \frac{\chi_{H_2O}}{\chi_{H_2O} + \chi_{\text{glucose}}} \cdot (600)$$

$$P_T = \frac{\left(\frac{1000}{18}\right)}{\left(\frac{1000}{18}\right) + 1} (600)$$

Q. Vapour pressure of 30% weight/volume aq. solution of sucrose is 400 torr if density of solution is 1.2 g/ml then calculate vapour pressure of pure H_2O

Molar mass = ~~342~~ molar mass = 342

gm \rightarrow

Weight of Solute $\times 100 = 30$

ml \rightarrow V_{solution}

Let volume of solution is 100 ml

$$\frac{W_{\text{solute}}}{V_{\text{soln}}} \times 100 = 30$$

$$V_{\text{soln}} = 100$$

$$W_{\text{solute}} = 30$$

then weight of solute = 30 g

$$P_T = n_{H_2O} P_{H_2O}^{\circ} + n_{\text{sucrose}} P_{\text{sucrose}}^{\circ}$$

$$P_T = n_{H_2O} P_{H_2O}^{\circ}$$

$$V = 100$$

$$D = \frac{m}{V}$$

$$m = D \times V$$

$$m \text{ of Solution} = 120 \text{ g}$$

$$400 = \frac{n_{H_2O}}{n_{H_2O} + n_{\text{sucrose}}} \times P_{H_2O}^{\circ}$$

$$400 = \frac{(90/18)}{(90/18) + \frac{30}{342}} \times P_{H_2O}^{\circ}$$

* Relation b/w y_A, y_B & P_T :

(1) Partial Pressure of A and B can be calculated from Raoult's Law from mol fraction of A and B present in liquid phase

$$P_A = n_A P_A^{\circ} \quad P_B = n_B P_B^{\circ}$$

(2) From Dalton's law of partial pressure, partial pressure of A and B can be calculated with the help of mole fraction of A and B present in vapour phase

$$P_V = n'RT$$

$$P_T V = n'_T RT$$

$$\frac{P_A}{P_T} = \frac{n'_A}{n'_T}$$

$$P_A = y_A P_T$$

$$P_B = y_B P_T$$

$$P_A = y_A P_T$$

Here, y_A and y_B are mol fraction of A & B in vapour phase

* By Comparing Raoult's Law with Dalton's law

$$n_A P_A^{\circ} = y_A P_T$$

$$n_B P_B^{\circ} = y_B P_T$$

$$y_A = \frac{n_A P_A^{\circ}}{P_T}$$

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

$$n_A + n_B = 1$$

$$\frac{y_A P_T}{P_A^{\circ}} + \frac{y_B P_T}{P_B^{\circ}} = 1$$

$$\frac{1}{P_T} = \frac{y_A}{P_A^{\circ}} + \frac{y_B}{P_B^{\circ}}$$

If A is more volatile than B

$$\text{Let } P_A^\circ > P_T > P_B^\circ$$

$$y_A = \frac{n_A P_A^\circ}{P_T}$$

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

$$y_A > n_A$$

$$y_B < n_B$$

* mol fraction of more volatile substance will be more in vapour phase as compared to liquid phase

* mol fraction of less volatile substance will be more in liquid phase as compared to vapour phase

$$\frac{1}{P_T} = \frac{y_A}{P_A^\circ} + \frac{y_B}{P_B^\circ}$$

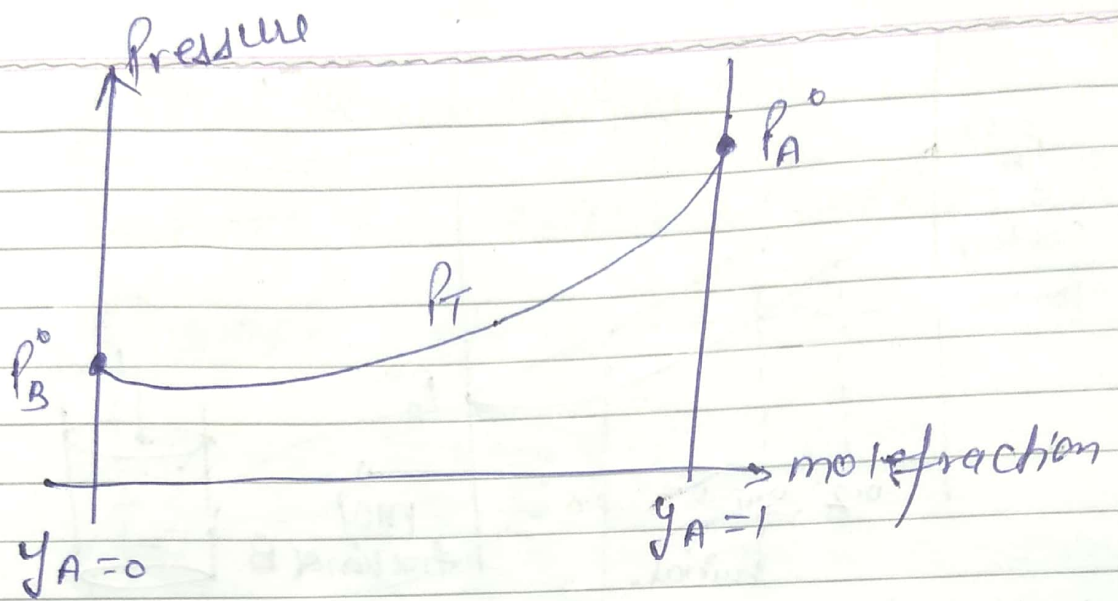
$$\{y_A + y_B = 1\}$$

$$\frac{1}{P_T} = \frac{y_A}{P_A^\circ} + \frac{1 - y_A}{P_B^\circ}$$

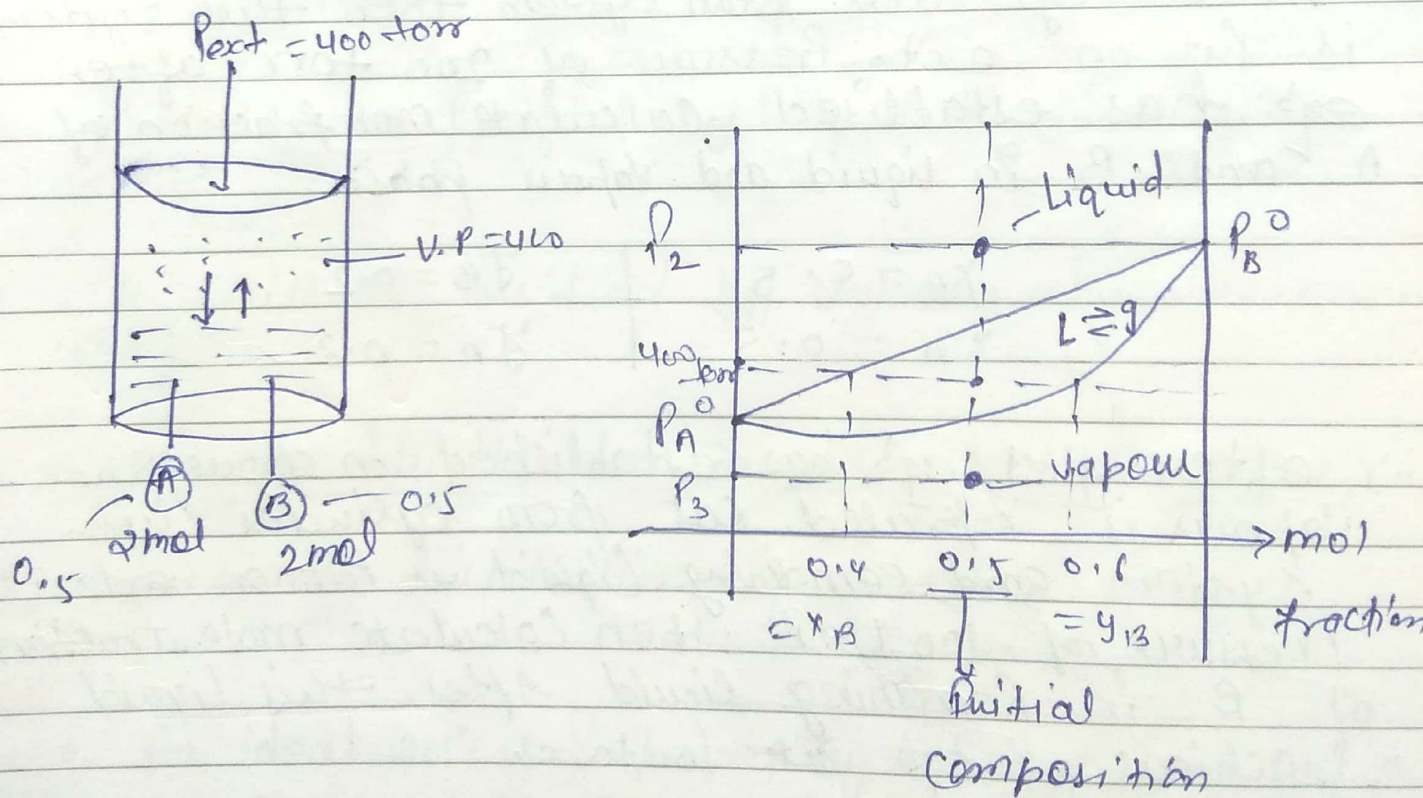
$$\frac{1}{P_T} = y_A \left(\frac{1}{P_A^\circ} - \frac{1}{P_B^\circ} \right) + \frac{1}{P_B^\circ}$$

$$P_T = \frac{1}{y_A \left(\frac{1}{P_A^\circ} - \frac{1}{P_B^\circ} \right) + \frac{1}{P_B^\circ}}$$

$$y = \frac{1}{m_1 n + c}$$



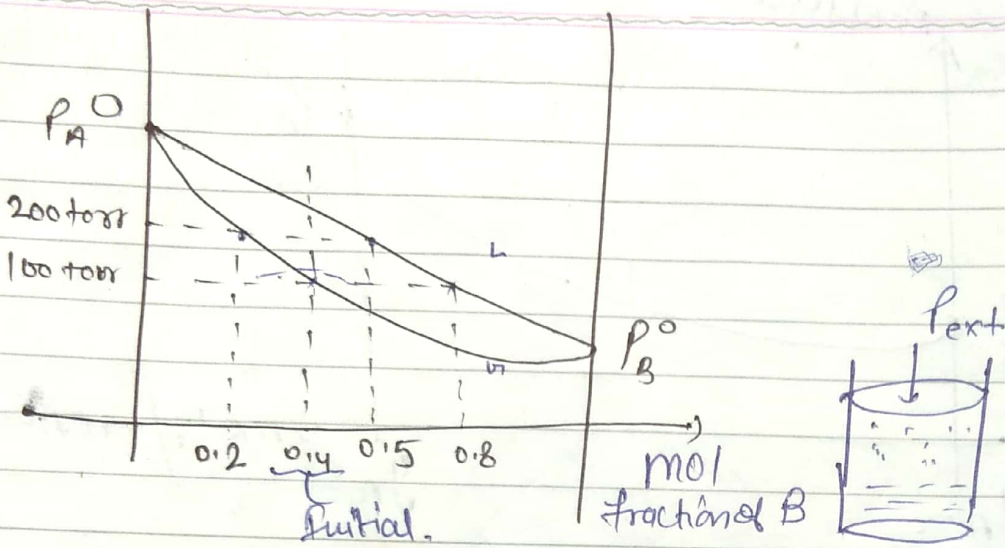
* fractional distillation:



Que!

mol

Ques

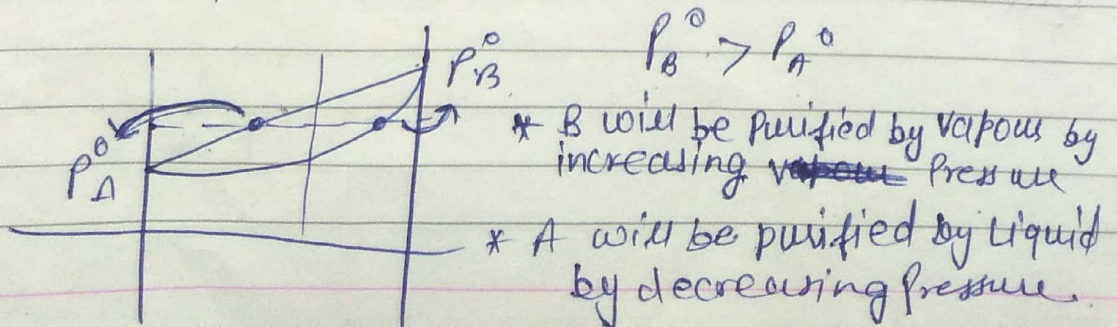


Initial mole fraction of B is mixed with 6 mol of A in a cylinder piston system then this system is put on ext. pressure of 200 torr after eq^b has established calculate mol fraction of A and B in liquid and vapour phase.

$x_B = 0.5$		$y_B = 0.2$
$x_A = 0.5$		$y_A = 0.8$

iii) after first eq^b has established in above que vapour is separated out from cylinder piston system and remaining liquid is put on ext. pressure of 100 torr then calculate mole fraction of B in remaining liquid after this liquid achieve eq^b at 100 torr.

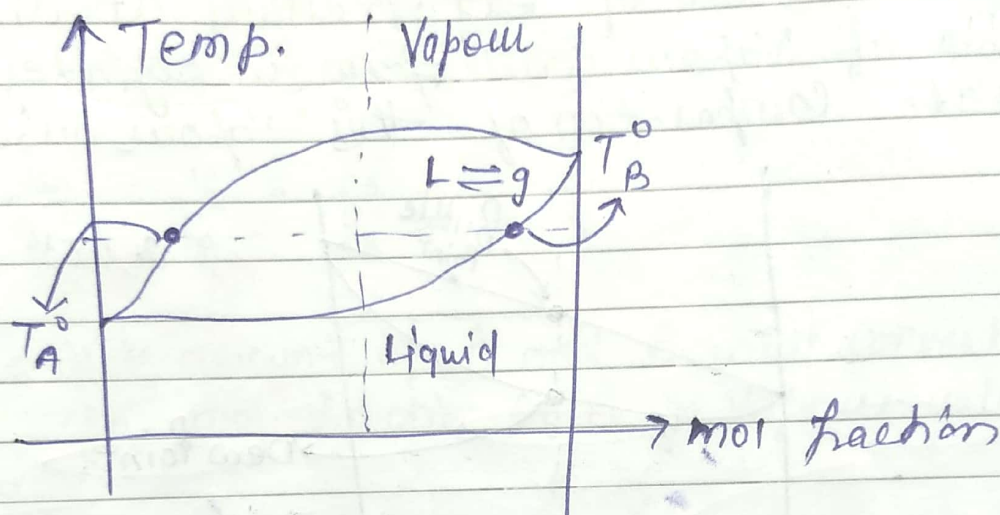
$$x_B' = 0.8.$$



$P_B^0 > P_A^0$
 * B will be purified by vapour by increasing pressure
 * A will be purified by liquid by decreasing pressure.

Temp. v/s mol fraction curve:

T_A° and T_B° are Boiling point of A and B



- * B will be purified by liquid by increasing temp.
- * A will be purified by vapour by decreasing temp.
- * Fractional distillation can be of two type.

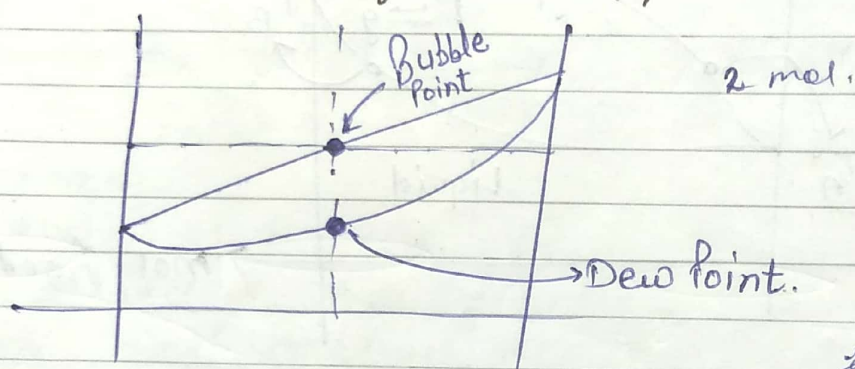
- (i) fractional distillation by pressure.
- (ii) " " " Temp.

Que: An ideal solⁿ is prepared by mixing 2 mol of A and 3 mol of B. This solⁿ is put on under a very high pressure. In a cylinder piston system. Now pressure over the piston released very slowly then answer the following questions

$$P_A^\circ = 400 \text{ torr.}$$

$$P_B^\circ = 600 \text{ Torr}$$

- (i) Calculate value of ext. pressure at which first bubble of vapour will form in cylinder. also Calculate composition of this vapour bubble.



$$x_A = \frac{2}{5}$$

$$x_B = \frac{3}{5}$$

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

$$P_T = \frac{2}{5}(400) + \frac{3}{5}(600)$$

$$P_T = \underline{\underline{520}} \text{ torr.}$$

$$y_A = \frac{x_A P_A^\circ}{P_T} = \frac{(0.4) \times 400}{520}$$

(ii) Calculate Value of ext. Pressure at which almost complete solⁿ will convert in vapour and last drop of solⁿ remain in liquid form
(Dew Point)

$$x_A = \frac{2}{5} \quad y_B = \frac{3}{5}$$

$$P_T = x_A P_A^0 + x_B P_B^0$$

$$P = P$$

$$\frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0}$$

Now,

Almost complete amount of A and B will convert in vapour so, mol fraction of A in vapour will be $\frac{2}{5} = 0.4$.

$$y_A = \frac{2}{5} \quad y_B = \frac{3}{5}$$

$$\frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0}$$

$$\frac{1}{P_T} = \frac{0.4}{400} + \frac{0.6}{600}$$

$$P_T = 500$$

⇒ Composition of last drop of liquid at Dew Point.

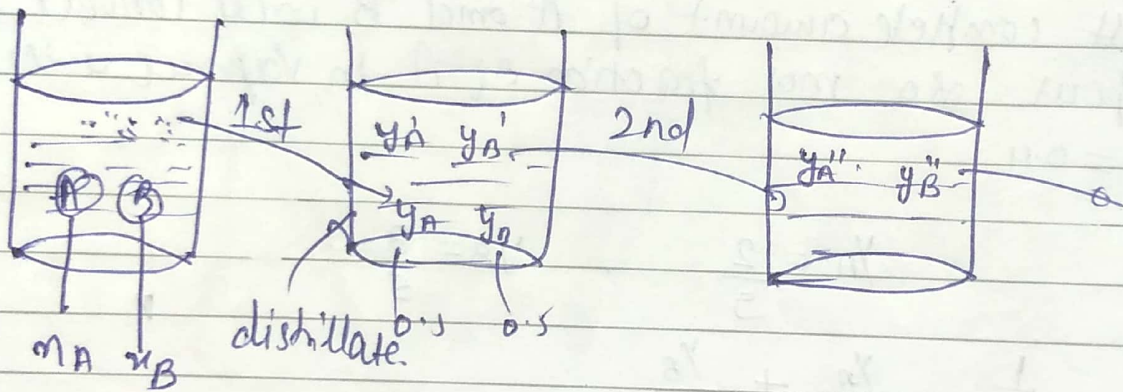
$$y_A = \frac{x_A P_A^0}{P_T}$$

$$0.4 = \frac{x_A (400)}{500}$$

* Composition of distillate after an n-step of fractional distillation?

* Condense vapour is called distillate

* During the solving due in liquid solⁿ it is assume that vapour is formed in very negligible amount so, Initial composition of liquid can be taken equal to eq^b composition of liquid.



1st step.

$$y_A = \frac{n_A P_A^0}{P_T}$$

$$y_B = \frac{n_B P_B^0}{P_T}$$

$$\frac{y_A}{y_B} = \frac{n_A}{n_B} \left(\frac{P_A^0}{P_B^0} \right)$$

2nd step

$$\frac{y'_A}{y'_B} = \frac{y_A}{y_B} \cdot \frac{P_A^0}{P_B^0}$$

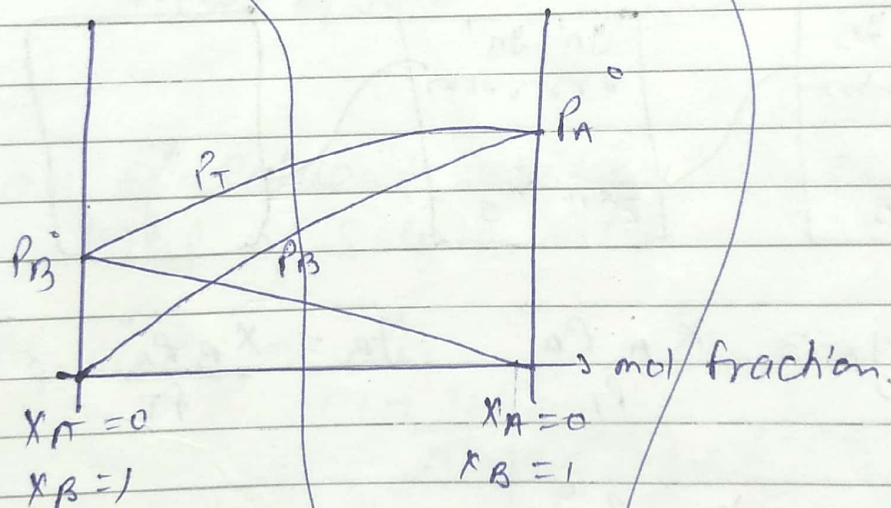
$$\frac{y'_A}{y'_B} = \frac{n_A}{n_B} \left(\frac{P_A^0}{P_B^0} \right)^2$$

after n-step of distillation

$$\left(\frac{y_A}{y_B} \right)_{n \text{ step}} = \frac{x_A}{x_B} \left(\frac{P_A^{\circ}}{P_B^{\circ}} \right)^n$$

Vapour pressure of liquid solⁿ depends on temp. & composition of liquid solⁿ.

Graph: {T-constant}



$$P_A^{\circ} > P_B^{\circ}$$

$$P_T = P_A + P_B$$

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

Note: At Boiling Point vapour pressure of liquid will be equal to external pressure & liquid hold eq^b with its vapour

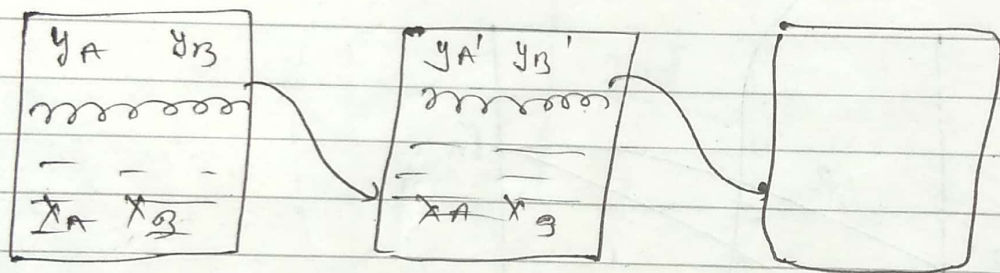
$$P_A^{\circ} > P_B^{\circ}$$

$$T_A^{\circ} > T_B^{\circ}$$

Q. Calculate vapour pressure of 1 molal aq glucose solution if vapour pressure of pure H_2O is 60 torr

$$P_t = X_{H_2O} P_{H_2O}^{\circ} + X_{glucose}$$

Q. A solution is prepared by mixing 2 mol. of A & 3 mol of B then calculate vapour pressure of its distillate where $P_A = 400$ torr
 $P_B = 200$ torr



$$y_A = \frac{X_A P_A^{\circ}}{P_t} \quad y_B = \frac{X_B P_B^{\circ}}{P_t}$$

$$\frac{y_A}{y_B} = \frac{X_A P_A^{\circ}}{X_B P_B^{\circ}}$$

$$\frac{y_A}{1-y_A} = \frac{2/5 (400)}{3/5 (200)}$$

$$\frac{y_A}{1-y_A} = \frac{4}{3}$$

$$3y_A = 4 - 4y_A$$

$$7y_A = 4$$

$$y_A = 4/7$$

$$y_B = 3/7$$

80

$$P_T' = X_A' P_A^\circ + X_B' P_B^\circ$$

$$P_T' = \frac{4}{7} \times 4000 + \frac{3}{7} \times 2000$$

$$P_T' = \frac{22000}{7}$$

* Relation b/w Mole fraction & Molality!

$$m = \frac{\text{mol of solute}}{\text{mass of solvent in kg}}$$

Let,

$$\begin{aligned} \text{mass of solvent} &= 1 \text{ kg} = 1000 \text{ gm} \\ \text{mol of solute} &= m \end{aligned}$$

$$X_{\text{solute}} = \frac{m}{m + 1000}$$

mol (solute)

for a dilute solution:

$$X_{\text{solute}} = \frac{m}{1000}$$

mol (solvent)

* Relation b/w Molarity & molality:

$$m = \frac{\text{mol of solute}}{\text{mass of solvent in kg.}}$$

$$\begin{aligned} \text{Let, mass of solvent in 1 kg} &= 1000 \text{ gm} \\ \text{mol solute} &= m \text{ mol.} \end{aligned}$$

$$M = \frac{m}{\frac{1000 + m(\text{mwt solute})}{1000 d_{\text{sol}}}} \quad \text{when } d_{\text{sol}} = \text{gm/ml.}$$

For dilute solution:

$$M = \frac{m}{\frac{1000 + m(\text{mwt})}{1000 d_{\text{sol}}}}$$

$$M = m d_{\text{sol}}$$

For dilute aq solution: $d_{\text{sol}} \approx \text{gm/ml}$

$$M \approx m$$

Dmp

★ ★ Colligative Properties:

for the definite amount of a definite solvent properties that depend on No. of solute particles called colligative properties

Colligative property do not depend on nature of solute because during the study of colligative properties always use a non-volatile solute.

* Colligative Properties can be of 4 types:

- (1) Lowering in v.p or relative lowering in v.p
- (2) Elevation in boiling point
- (3) Depression in freezing point.
- (4) Osmotic Pressure

(1) Lowering Or Relative lowering in v.p:

If a non-volatile solute is mixed in a solvent than vapour pressure of resulting solⁿ will be less than vapour pressure of pure solvent. This is called lowering in vapour pressure. solvent + solute = solⁿ

P_T Non-volatile P^0

$$P_T < P^0$$

$$P_T = X_{\text{solvent}} \cdot P^0_{\text{solvent}} + X_{\text{solute}} \cdot P^0_{\text{solute}}$$

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

$$P_T < P^0 \Rightarrow \Delta P = P^0 - P_T$$

$$\Delta P = P^0 - P_T$$

$$\Delta P = P^0 (1 - X_{\text{solvent}})$$

$$\Rightarrow \Delta P = X_{\text{solute}} P^0$$

Relative lowering in v.p.

$$\frac{\Delta P}{P^0} = \chi_{\text{solute}}$$

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

For dilute solution: $N \gg n$.

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

$$\chi_{\text{solute}} = \frac{n}{n+N} \quad \text{where } n = \text{mol of solute}$$
$$N = \text{mol of solvent}$$

For any solution:

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

$$\frac{a}{b} = \frac{x}{y}$$

$$\frac{a}{b-a} = \frac{x}{y-x}$$

Q. A 373°K (100°C) Relative lowering in v.p. of aq. glucose solⁿ is 10%. Then Calculate Molality of glucose in solⁿ & also Calculate v.p. of solⁿ.

Sol: Boiling point of $\text{H}_2\text{O} = 373^\circ\text{K}$

$$\text{So, } P_{\text{H}_2\text{O}} = 1 \text{ atm} = 768 \text{ Torr}$$

$$\frac{\Delta P}{P^0} \times 100 = 10 \quad \text{So } \frac{\Delta P}{P^0} = \frac{1}{10}$$

$$P_0 \cdot X_{\text{solute}} = 0.1 = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$n_{\text{solute}} + n_{\text{solvent}} = 1$$

$$\Rightarrow n_{\text{solute}} = 0.1$$

$$P_0, m = \frac{0.1}{0.9 \times 18} = \frac{1000}{9 \times 18}$$

we know that: $\Delta P/P_0 = 0.1$

$$\text{So } \frac{P_0 - P_T}{P_0} = 0.1 \quad \frac{760 - P_T}{760} = 0.1$$

$$P_T = 684$$

2) elevation in Boiling point: (ΔT_b)

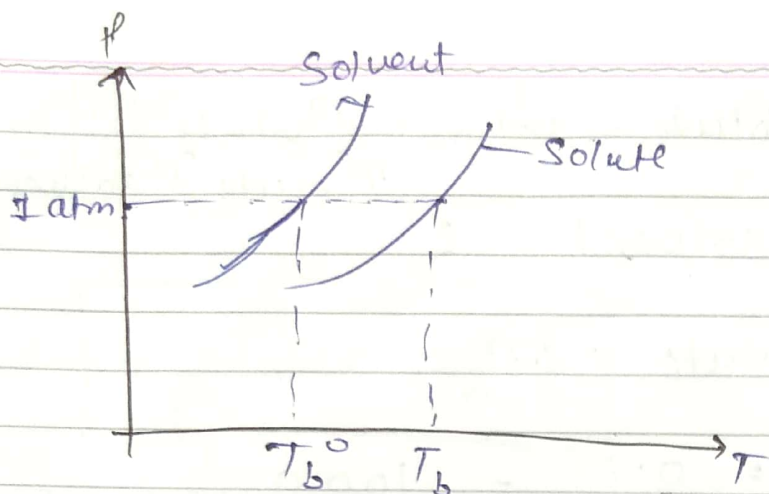
On mixing Non-volatile solute in solvent B.P of resulting solⁿ will be more as compared as compared to pure solvent it is called elevation in Boiling point

Solvent + non-volatile solute = Solⁿ
 T_b

$$T_b^0 < T_b$$

$$\Delta T_b = T_b - T_b^0$$

Elevation in B.P.



$$\Delta T_b \propto \Delta P \propto X_{atm} \propto m$$

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

Here K_b called Mole elevation constant or ebullioscopic const.

$$K_b = \frac{R(T_b^0)^2 \cdot M_w(\text{solvent})}{1000 \times \Delta H_{\text{vap}}}$$

K_b depend on solvent

* Important Point

- * Value of K_b depend on Nature of solvent
- * At Boiling point in such a soln in which Non-volatile solute is present liquid solvent will be in eqb. with vapour solvent.

(3) Depression in Freezing point:

on mixing non-volatile solute in solvent the freezing point of resultant solⁿ will be less than freezing point of pure solvent. This is called depression in freezing point.

Solvent + non-volatile solute = Solution
 T_f° T_f

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

$$\Delta T_f \propto \Delta T_b \propto \Delta P \propto X_{\text{dilute}} \propto m$$

$$\Delta T_f \propto m$$

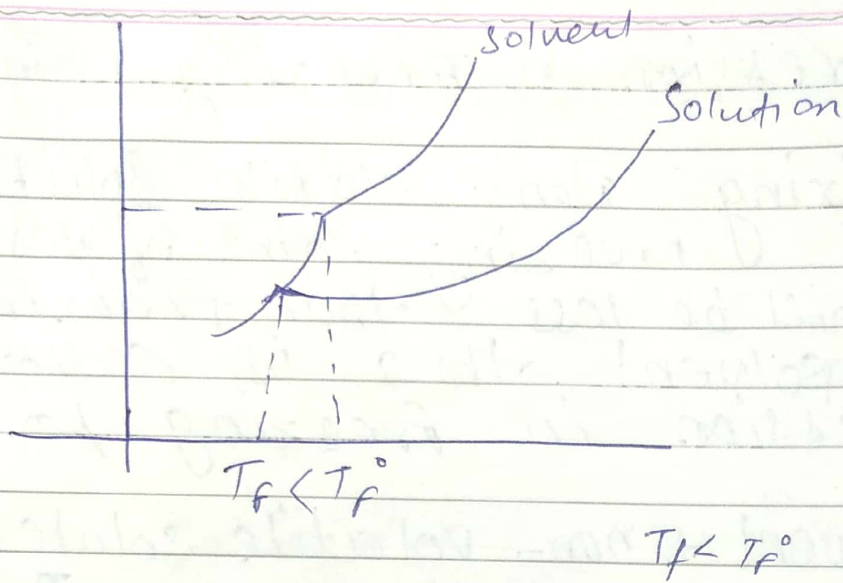
$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

Here, K_f is called molar depression constant or cryoscopic constant.

$$K_f = \frac{R(T_f^\circ)^2 \text{ M.Wt. (Solvent)}}{1000 \times \Delta H_{\text{fusion}}}$$

K_f depend on solvent



⇒ In Colligative property depression in freezing point -
Liquid solvent will be in eq^b. with solid solvent

Q. % lowering in vapour pressure of aq NH2CONH2 is 1%. then calculate freezing point of this solⁿ.

$$K_f \text{ for } H_2O = 1.8 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

$$\left(\frac{\Delta P}{P_0} \right) \times 100 = 1 \quad \text{NH}_2\text{CONH}_2$$

Molar mass = 60 gm/mol

$$\frac{K_f \cdot m}{100}$$

ΔP in
atm.

$$X_{\text{urea}} = \frac{1}{100}$$

Solute =
NH2CONH2

$$\Delta T_f = K_f m$$

$$X_{\text{urea}} = \frac{1}{100} = \frac{n_{\text{urea}}}{n_{\text{urea}} + n_{\text{H}_2\text{O}}}$$

$$n_{\text{urea}} + n_{\text{H}_2\text{O}} = 1 \text{ mol.}$$

$$n_{\text{urea}} = 0.01 \text{ mol.}$$

$$n_{\text{H}_2\text{O}} \approx 1 \text{ mol}$$

$$m = \frac{0.01}{1 \times 18} = \frac{10}{1000}$$

$$\Delta T_f = k_f m$$

$$\Delta T_f = (1.8) \left(\frac{10}{18} \right) = 1$$

$$T_f = -1^\circ\text{C} \text{ or } 272 \text{ Kelvin.}$$

Q. 8 gram urea is mixed in 100 ml of pure H_2O resulting solution is put at -9°C then calculate amount of ice that can be separated out.

$$K_f = 1.8 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$$

$$K_f = 1.8 \text{ K} \cdot \text{kg}$$

$$= -9^\circ\text{C}$$

$$= -8$$

$$K_f = 1 = 9$$

$$q = \frac{0.2}{1.8} \cdot \frac{18/60}{\text{mass of solvent in kg}}$$

$$\text{mass of solvent in kg} = \frac{1.6}{60} \text{ kg}$$

$$= \frac{1600}{60} = \frac{160}{6} = 26.67 \text{ gm}$$

$$= 100 - 26.67 = 73.23$$

(ii) In above case if initial solution is put on ext. temp. of 105°C then calculate mass of H_2O that can be separated as vapour.

\Rightarrow

$$K_b = 0.5 \text{ K kg mol}^{-1}$$

100

$$m = \frac{m}{m_{\text{sol}}}$$

$$\Delta T_b = K_b \frac{\text{mol of solute}}{\text{mass of solvent in kg}}$$

105 -

$$5 = 0.5 \text{ K} \frac{(\frac{8}{60})}{\text{mass of solvent in kg}}$$

$$\begin{aligned} \text{mass of solvent} &= \frac{0.8 \text{ kg}}{60} \\ &= \frac{800}{60} \end{aligned}$$

$$= 100 - \frac{80}{6}$$

Boiling point, freezing pt. is automatically equal to surrounding temp.

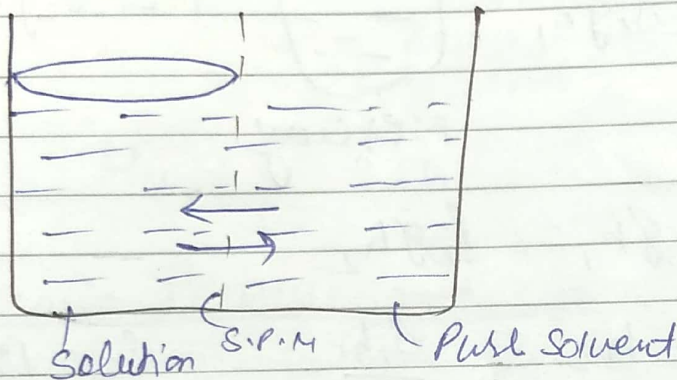
↳ for a solⁿ during a colligative property

* Osmotic Pressure (π) ?

* Osmotic: flow of solvent particles from pure solvent to solution through S.P.M (semi-permeable membrane). Called osmotic.

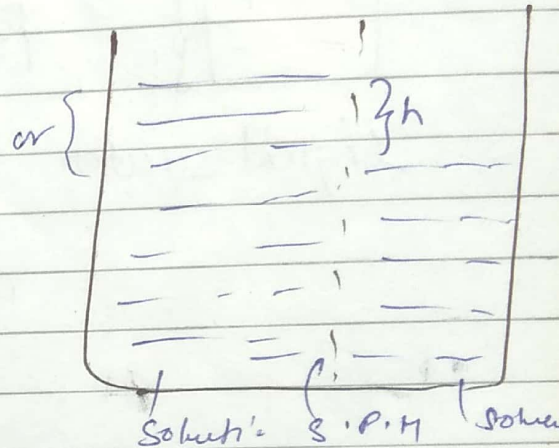
* Osmotic Pressure :

Ext. Pressure applied over solⁿ or hydrostatic pressure develop over the solution to stop osmotic called osmotic pressure.



$$\pi = CST$$

$$\pi = CST = \rho gh$$



$$\pi = \rho gh$$

$$S = 0.0821$$

S = Solution Constant = $0.0821 \frac{\text{atm} \cdot \text{lit}}{\text{mol} \cdot \text{lc}}$

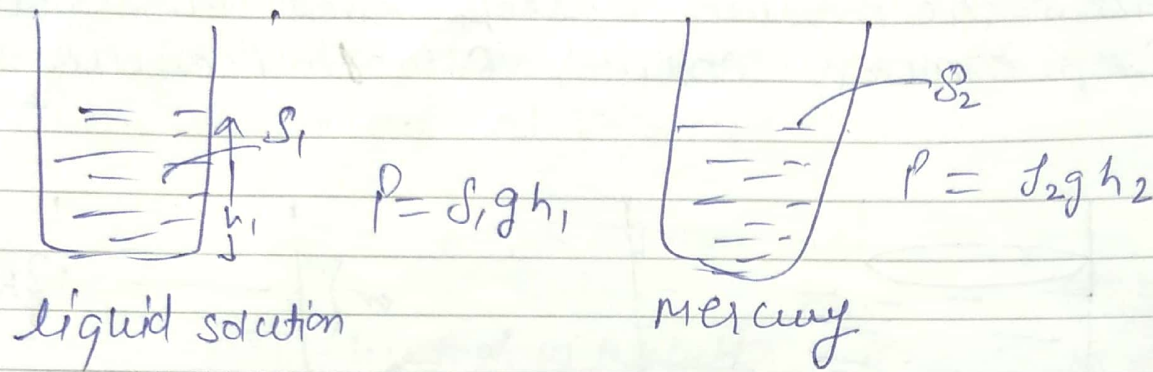
* Reverse osmotic :

Applied ext. pressure over solution is more than osmotic pressure then flow of solvent particles is start from solution to pure solvent this is called reverse osmotic.

Reverse osmotic can be used for desalination of impure water.

$[760 \text{ mm of Hg} = 1 \text{ atm}]$

* Calculation of Sgh by mercury scale calibration:



$\rho_1 g h_1 = \rho_2 g h_2$

$h_2 = \frac{\rho_1 h_1}{\rho_2}$

$\rho_2 = 13.6 \text{ gm/ml}$
 ↓
 Density of mercury.

$\Rightarrow \pi_1 = \pi_2$ (Isotonic solution)

$\pi_1 > \pi_2$ π_1 is hypertonic then π_2

$\pi_1 < \pi_2$ π_1 is hypotonic then π_2

Ques: 0.2 Molar glucose solution is isotonic with 5% w/v soln of a non-volatile substance at same temp. then calculate molecular wt. of non-volatile substance.

$\frac{W_{\text{solute}}}{V_{\text{solution}}} \times 100 = 5$

me. let, $V_{\text{solution}} = 100 \text{ ml}$.

$W_{\text{solute}} = 5 \text{ gm}$.

$$M = \frac{(\% w/v / \text{m.wt (solute)})}{(100/1000)}$$

$$\text{Molarity} = \frac{\% w/v \times 10}{\text{M.wt (solute)}}$$

$$C_1RT = C_2RT$$

$$\frac{n_2}{\text{m.wt (solute)}}$$

$$0.2 = \frac{5 / \text{m.wt (solute)}}{\left(\frac{100}{1000}\right)}$$

$$\text{M.wt} = 250.$$

Q. Osmotic pressure ^{↑ height} rise in 0.001 the % w/v solⁿ of a non-volatile substance is 13.6 mm. They calculate m.wt of non-volatile substance
 Temp = 300K.
 density of solution = 0.76 gm/ml.

extra height 13.6 mm.

$$\pi = cRT$$

$$\pi = \rho gh$$

$$\frac{\% w}{v}$$

$$= \frac{w_{\text{solute}} \times 100}{V_{\text{solution}}} = 0.001$$

$$\text{Let } V_{\text{solution}} = 100$$

$$w_{\text{solute}} = 0.001$$

$$\rho_1 h_1 = \rho_2 h_2$$

$$h_2 = \frac{\rho_1 h_1}{\rho_2}$$

mol.
0.001

$$\text{Molarity} = \frac{\% w/v \times 10}{\text{m.wt (solute)}}$$

$$= \frac{(0.76)(13.6)}{13.6} = 0.76 \text{ mm of Hg.}$$

$$\text{Osmotic Pressure} = \frac{0.76}{760} = 10^{-3} \text{ atm.}$$

$$\pi = cRT$$

$$10^{-3} = \frac{0.501 \times 10}{M \cdot w +} \times 0.0821 \times 300$$

★ ★ ★ ~~Imp~~
★ ★ ★ ~~Ab~~
★ ~~based~~

AbNormal Colligative Property and
Van't Hoff factor (i):

If solute particles associate or dissociate then actual value of (Practical value or observed value) of colligative property will be different from theoretical value (expected value) of colligative property.

This is called abnormal colligative property and can be represented by van't Hoff factor i .

$$i = \frac{\text{final mol. of solute in solution}}{\text{Initial mol. of solute in sol}^n} = \frac{\text{observed value of c.p.}}{\text{theoretical value of c.p.}}$$

$$= \frac{\text{Theoretical molar mass of solute}}{\text{Observed molar mass of solute}}$$

$$\Delta T_b = K_b (im)$$

$$\Delta T_f = K_f (im)$$

$$\pi = icRT$$

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

For dilute solution $N \gg \gg n$

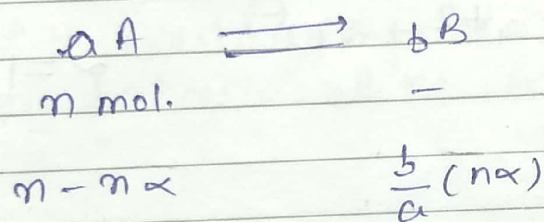
$$\frac{\Delta P}{P^0} = \frac{i n}{N}$$

If more than one type of solute are present in solution then

$$\pi = (i_1 c_1 + i_2 c_2 + i_3 c_3 \dots) RT$$

$$\Delta T_b = K_b (i_1 m_1 + i_2 m_2 + i_3 m_3 \dots)$$

* Relation b/w Van't Hoff factor i and α (degree of dissociation)



$$n_{\text{initial}} = n$$

$$n_{\text{observe}} = n - n\alpha + \frac{b}{a} (n\alpha)$$

$$i = \frac{n_{\text{observe}}}{n_{\text{initial}}} = \frac{n - n\alpha + b/a (n\alpha)}{n}$$

$$= \frac{M_{\text{theoretical}}}{M_{\text{observe}}}$$

$$i = 1 - \alpha + \frac{b}{a} \alpha$$

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

$$n = \frac{\text{s.c of Product}}{\text{s.c of Reactant}}$$

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

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

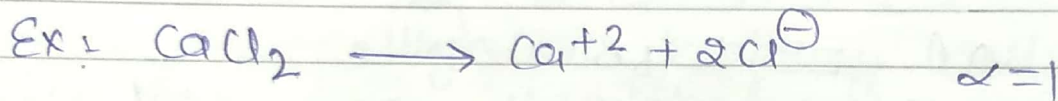
Calculation of i° for different type of substance:

i) for non-electrolyte:

for ex: urea, glucose, fructose etc.

$$\alpha = 0 \quad i^{\circ} = 1$$

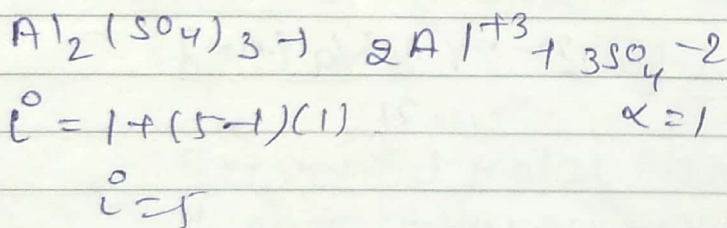
ii) for strong electrolytes:



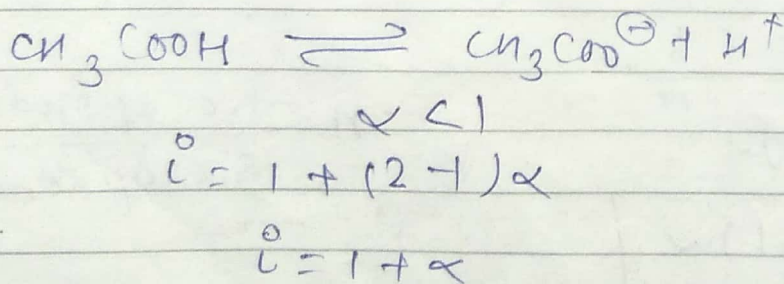
$$i^{\circ} = 1 + \left(\frac{3}{1} - 1\right)(1)$$

$$i^{\circ} = 3$$

for strong electrolytes value of van't Hoff factor will be equal to no. of mol. of ions provided by one mol. electrolyte.



iii) In partial dissociate - or weak electrolyte:



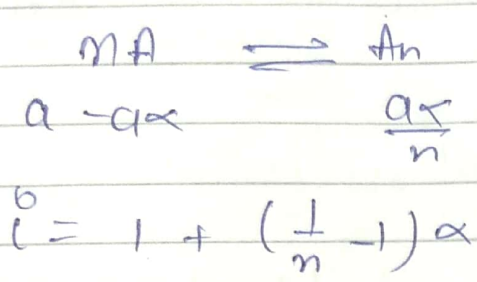
$$A_n = nA$$

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

L.S. 51 11 to 25 +

E.C JA = 26 to 30

* In a association R_n 1

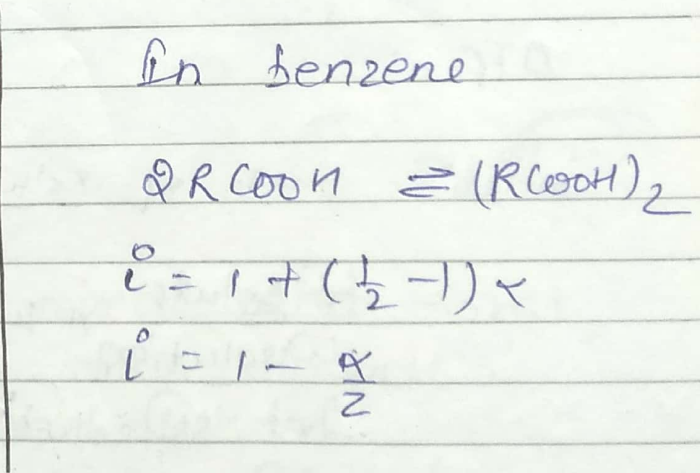
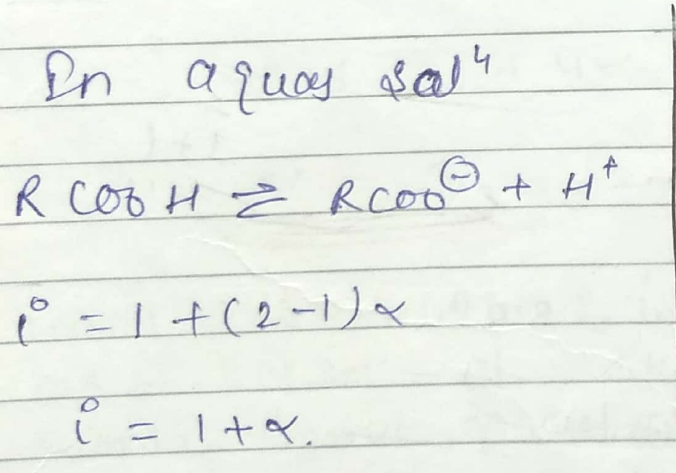


$$i = 1 - \alpha + \frac{\alpha}{n}$$

Here α will be degree of association.

Note: for Carboxylic acids in their aq. solⁿ they behave like weak electrolyte.

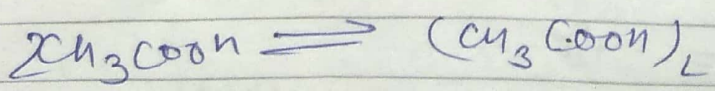
in e



* Unknown solutes are considered non-electrolytes.

Ques: degree of association of acetic acid in Benzene is 40%. then calculate observed molar mass of acetic acid in Benzene.

Ans:



= 140 g/mol

$$i = 1 + \left(\frac{1}{2} - 1\right) \alpha = \frac{n_{\text{observed}}}{n_{\text{theoretical}}} \cdot \frac{M_{\text{theoretical}}}{M_{\text{obs.}}}$$

$$= 1 + \left(\frac{1}{2} - 1\right) (0.4) = \frac{60}{M_{\text{obs.}}}$$

Que! Calculate Normal freezing point of 3.68% w/w aq. solⁿ of $K_4[Fe(CN)_6]$ $M_{wt} = (368)$.
 $K_f(H_2O) = 1.9284 \text{ K} \cdot \text{kg/mol}$

$$\frac{1.9284}{0.9632} = 2.$$

$$i = 5.$$

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

$$\Delta T_f =$$

Molality = mole of solute

$$\frac{w_{\text{solute}}}{w_{\text{solution}}} \times 100 = 3.68$$

Let $w_{\text{solution}} = 100$

$$w_{\text{solute}} = 3.68.$$

$$\Delta T_f = (1.9284)(5) \frac{\left(\frac{3.68}{368}\right)}{\left(\frac{96.32}{1000}\right)}$$

$$\Delta T_f = 1$$

$$T_f = -1^\circ\text{C}.$$

$$\frac{w_{\text{solute}}}{w_{\text{solution}}} \times 100 = 3.68.$$

Let $w_{\text{solute}} = 100$

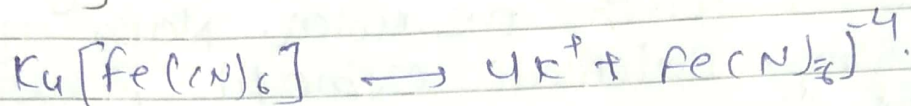
$$w_{\text{solution}} = 3.68.$$

$$m = \frac{\text{mole}}{\text{kg}} =$$

$$= \frac{1}{1+1}$$

Ques: In above Ques, if observed value of freezing point is -0.5°C then calculate degree of dissociation of $\text{K}_4[\text{Fe}(\text{CN})_6]$.

$$\Delta T_f = -0.5^\circ\text{C}$$



$$0.5$$

~~0.5~~

$$0.5 = (1.4284) i \left(\frac{3.68/368}{\frac{96.32}{1000}} \right)$$

$$i = 2.5$$

$$i = 1 + (v - 1)\alpha$$

$$2.5 = 1 + 4\alpha$$

$$\alpha = \frac{3}{8} = 0.375$$

$$= 1 + (2)$$

Q. 100ml 1Molar NaCl is mixed with 50ml, 0.5M KCl solⁿ. at 300K. then calculate osmotic pressure of resultant solⁿ

(27)

$$\pi = CRT$$

$$\pi = (i_1 C_1 + i_2 C_2) RT$$

$$= (2 \times 1 + 2 \times 1) (0.0821) (300) \times \alpha$$

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

$$\Rightarrow [\text{NaCl}]_{\text{resultant}} = \frac{1 \times 100}{150} = \frac{10}{15}$$

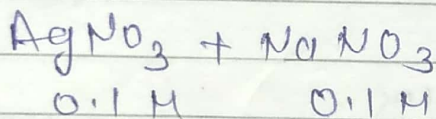
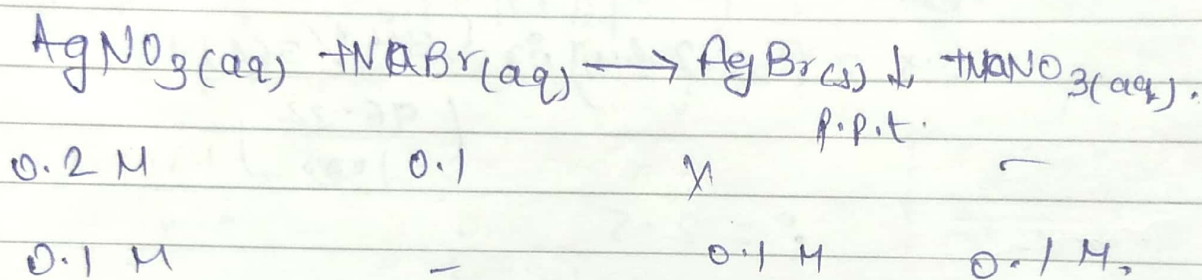
$$[\text{KCl}]_{\text{res.}} = \frac{0.5 \times 50}{150} = \frac{1}{6}$$

$$\pi = \left(2 \times \frac{10}{15} * 2 \times \frac{1}{6} \right) (0.0821) (300)$$

Q. Equal Volume of 0.4 Molar AgNO_3 (aq) is mixed with 0.2 Molar NaBr (aq) at 300 K temp. Calculate osmotic pressure of resultant solⁿ.

$$\pi = CRT$$

$$= \frac{0.2}{3}$$



$$\pi = (i_1 C_1 + i_2 C_2) RT$$

$$= (2 \times 0.1 + 2 \times 0.1) (0.0821) (300)$$

* Solubility of gas in liquid solutions

1) Factors Affecting Solubility of gas in Liquid solⁿ:

ii) Nature of gas:

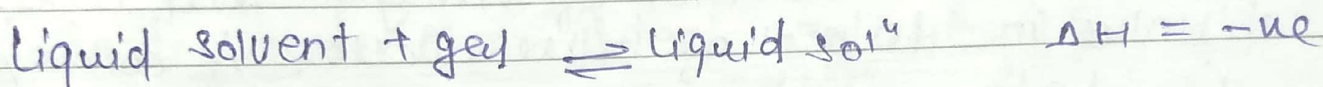
Polar gases dissolve more in polar solvent and non-polar dissolve more in non-polar solvent.

ii) Pressure :-

on increasing Pressure solubility of gases increases

iii) Temperature :-

on increasing temp. solubility of gases decrease.



* Henry's law for solubility of gases :-

Mol. fraction of gas in liquid solution will be proportional to partial pressure of gas over the solution

$$P_A \propto x_A$$

$$P_A = K_H x_A$$

$K_H \uparrow \text{ sol}^n \downarrow$

$K_H \Rightarrow$ Henry's constant.

if value of K_H is high then solubility of gas in solution will be less.

Q. Compare the value of K_H for N_2 and NH_3 in

H_2O

$$K_H(NH_3) < K_H(N_2)$$

* Value of Henry const. K_H depend on nature of gas, nature of solvent and temperature.

on increasing temp. ~~value~~ value of K_H increase.

Ques: In atmosphere mol. fraction of Nitrogen is 0.8 then calculate mol. of Nitrogen that will dissolve in 10 mol of pure water if atmospheric is 1 atm.

$$K_H(N_2) = 10^5 \text{ atm.}$$

$$P_{N_2} = 0.8 \times 1 = 0.8 \text{ atm.}$$

$$P_{N_2} = K_H \times N_2$$

$$0.8 = 10^5 \times \left(\frac{n_{N_2}}{n_{H_2} + 10} \right)$$

$$8 \times 10^{-6} = \frac{n_{N_2}}{n_{H_2} + 10}$$

$$8 \times 10^{-5} + (8 \times 10^{-6}) n_{N_2} = n_{N_2}$$

$$8 \times 10^{-5} = n_{N_2} (1 - 8 \times 10^{-6})$$

$$n_{N_2} = 8 \times 10^{-5}$$

$$= 10 \text{ mol}$$

$$n_{N_2} = 0.8$$

$$P_0 = K_H \times x_2$$

gas mol
atm. pressure

Ques: In a closed cylinder piston system. Over benzene two gases are present in 3:4 mol ratio if total gaseous pressure over the benzene is 5 atm. then calculate solubility of gas A in benzene in mol/litre.

$$d_{\text{benzene}} = 0.89 \text{ g/ml}$$

$$K_H \text{ for A in benzene} = 10^4 \text{ atm}$$

Suppose B is insoluble

$$P_A = \frac{5}{7} \times 3.$$

$$P_A = K_H \cdot X_A$$

$$\frac{5}{7} \times 3 = 10^4 \left(\frac{n_A}{n_A + \left(\frac{800}{78}\right)} \right)$$

$$P_A = K_H \cdot X_A$$

$$\frac{5 \times 3}{7} =$$

$$= \frac{15}{7} = 10^4 \left(\right)$$

beaker = 1 L.

Mass of $C_6H_6 = 800 \text{ g.}$

* Ideal and non-Ideal solutions

Ideal solution	+ve deviated ideal solution	-ve deviated ideal solution
<p>1] follow Raoult's law</p> $P_A = X_A P_A^0$ $P_B = X_B P_B^0$	<p>⇒ Do not follow Raoult's law actual V.P of solⁿ will be more than calculated from Raoult's law</p> $P_A > X_A P_A^0$ $P_B > X_B P_B^0$	<p>⇒ Do not follow Raoult's law actual V.P of solⁿ will be less than calculated from Raoult's law.</p> $P_A < X_A P_A^0$ $P_B < X_B P_B^0$
<p>2] Bond strength b/w solute and solvent will be almost equal to bond strength in pure solvent and in pure solute.</p> $\Delta H_{mix} = 0$ $\Delta V_{mix} = 0$	<p>⇒ In solⁿ Bond st. b/w solute and solvent will be less as compared to bond st. in solute and solvent when they are separated.</p> $\Delta H_{mix} > 0$ $\Delta V_{mix} > 0$	<p>⇒ Bond strength b/w solute and solvent will be more as compared to bond strength when they are separately as a solvent and solute.</p> $\Delta H_{mix} < 0$ $\Delta V_{mix} < 0$

} Bond strength

Solid state
thermochemistry.
Liquid soln.

(i) kinetics
acid-base

(ii) chemical equilibria
Redox.

(iii) Ionic Equilibrium, (conductance),
Electrochemistry.

(-ve
+ve

$A-A < AB > B-B$
 $A-A > A-B < B-B$
Solute Solvent.

$$\Delta S_{\text{unimix}} = \frac{-q_{\text{sys}}}{T}$$

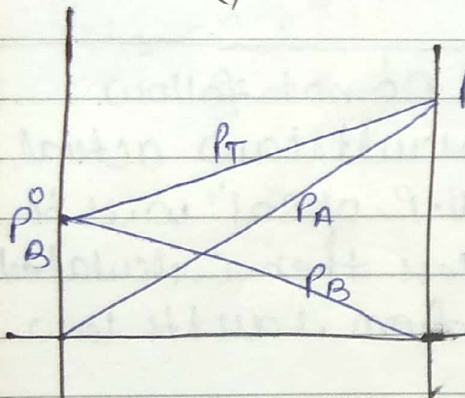
Deleat.

$$\Delta S_{\text{mix}} > 0$$

$$\Delta b_{\text{mix}} < 0$$

$$\Delta S_{\text{sur}} = \frac{-q_{\text{sys}}}{T} = 0$$

⇓



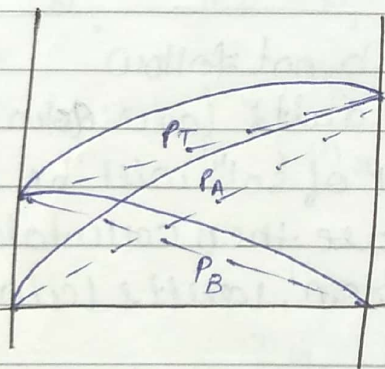
+ve

$$\Delta S_{\text{mix}} > 0$$

$$\Delta b_{\text{mix}} < 0$$

$$\Delta S_{\text{sur}} = \frac{-q_{\text{sys}}}{T} < 0$$

⇓



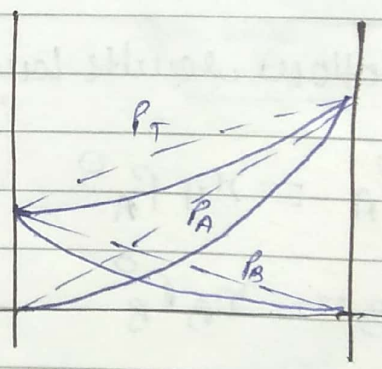
-ve

$$\Delta S_{\text{mix}} > 0$$

$$\Delta b_{\text{mix}} < 0$$

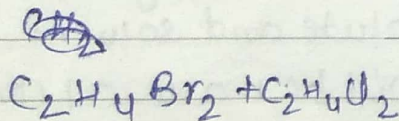
$$\Delta S_{\text{sur}} = \frac{-q_{\text{sys}}}{T} > 0$$

⇓



⇒ Similar structure

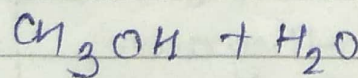
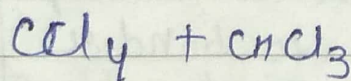
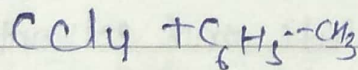
Ex:



★ benzene + toluene

i) CCl4
ii) -OH

Ex:

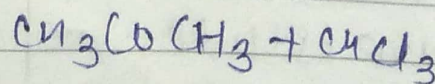
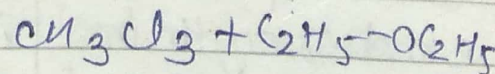
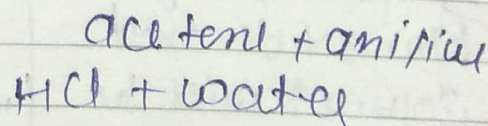


★ acetone + CS2

(i) acid/base

(ii) CH2Cl2

Ex:



Chlorotic \Rightarrow 1 gm $\frac{4}{100}$
 Per gram
 80 gm

$$\frac{20}{50} = \frac{4}{100}$$

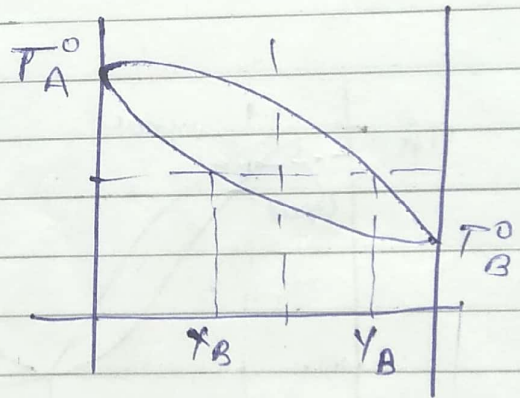
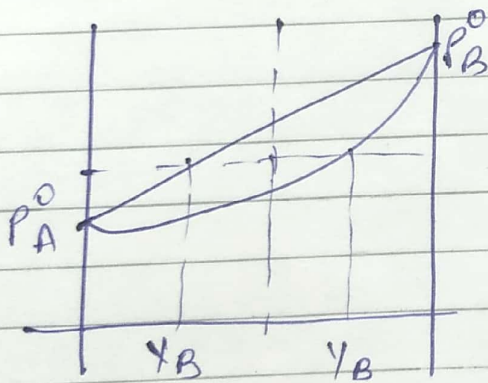
L.S. \Rightarrow 1 to 17
 \Rightarrow 31 to 35

* Azeotrope solution:

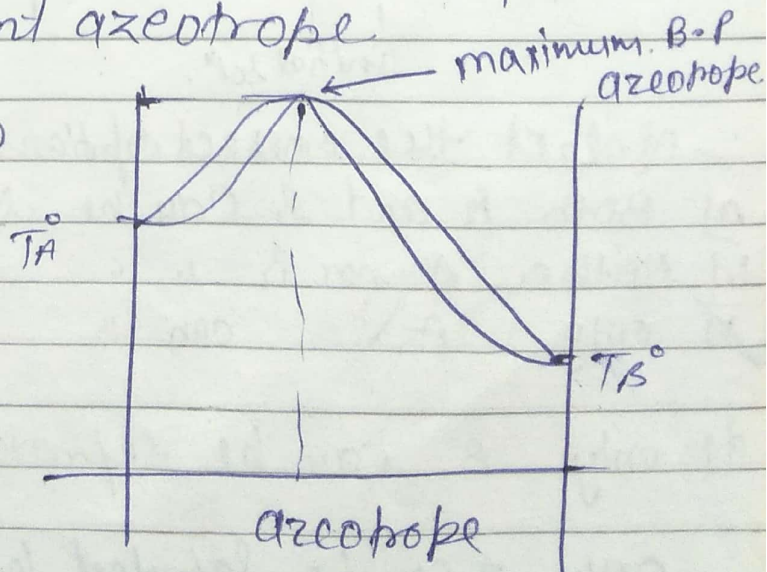
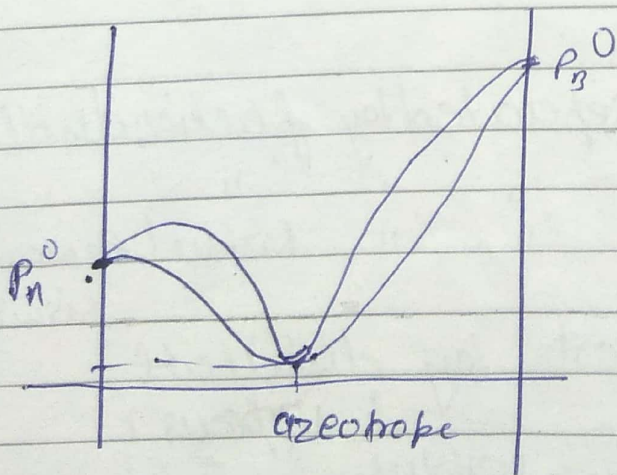
Azeotrope solution which have equal mol fraction in liquid phase and vapour phase called azeotrope solution

* Azeotrope sol^y can not be purified with the help of fractional distillation.

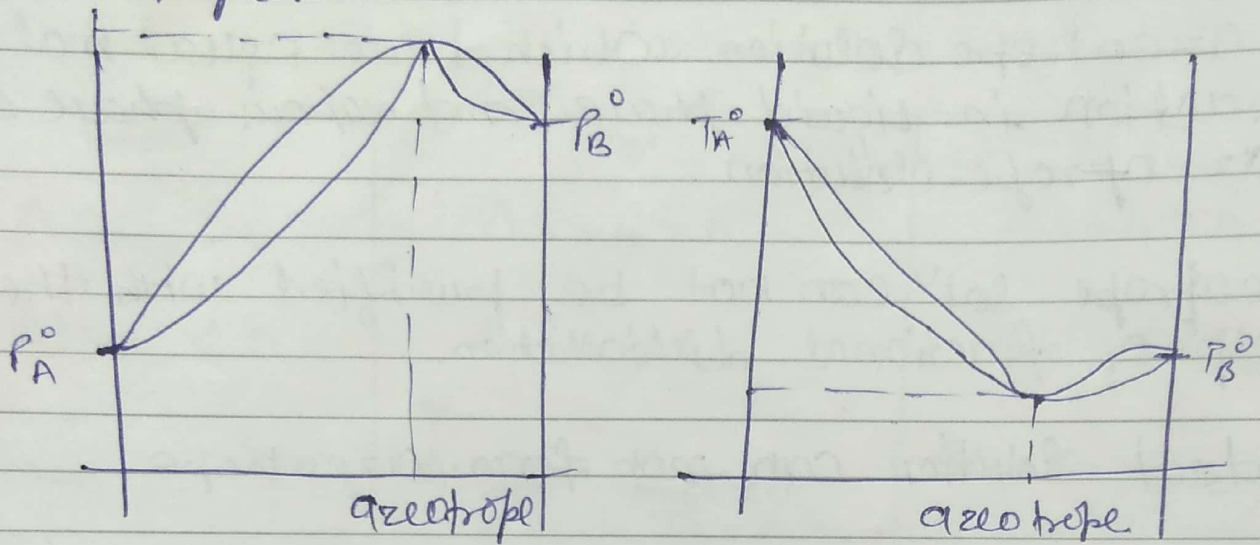
* Ideal solution can not form azeotrope



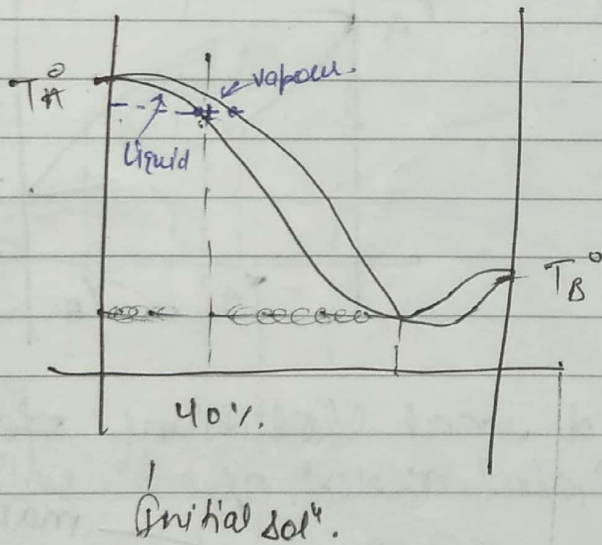
* Negatively deviated real solutions form maximum boiling point azeotrope



* Positively deviated real solution form minimum azeotrope.



Ques!



Select the correct options

- a) Both A and B can be separated by fraction distillation.
- b) Neither A nor B " " " " " " " " " " " "
- c) only A can " " " " " " Residue (Remaining liquid)
- d) only B can be separated by distillation (vapour)
- e) only A can be separated by residue.