Solubility of Gases in liquids

A saturated solution of gas is prepared when any gas passes through a definite volume of liquid. This is actually solubility of gas in liquid.

Henry described the pressure dependence on solubility by a law. According to this law, at constant temperature, the amount of gas dissolved in a fixed volume of liquid (w) is directly proportional to the pressure (p) of the gas.

i.e., $w \propto p$ when T const.

$w = K_H \cdot p$ $(K_H = \text{const})$

$\therefore \frac{w}{p} = K_H$ K_H is called Henry's Constat.

or, at constant temperature, partial pressure (p) of any gas at vapour phase is directly proportional to the mole fraction (x) of the gas dissolved in the liquid. i.e.,

$p \propto x$

* or, $p = K_H x$.

Limitations:

i) If the pressure of the gas is very high, then the law is not valid.

ii) The gas should not undergoes association or dissociation in the solution.

iii) This law is applicable only when temperature is not too low.

iv). This law is not applicable if the gas is too much soluble in liquid.

* Alternate Representation :

From ideal gas equation, $PV = nRT$

n = no. of moles $= \frac{W}{M}$

$$\therefore \quad V = \frac{nRT}{P} = \frac{W}{M} \times \frac{RT}{P} = \frac{W}{P} \times \frac{RT}{M}.$$

At constant temperature for a definite amount of gas, T, M = constant

$$\therefore \quad \frac{RT}{M} = \text{Const. } (K') \quad \therefore \quad V = \frac{W}{P} \times \frac{RT}{M} = K \times K' = \text{constant}$$

$\therefore$ At constant ~~ten~~ temperature, ~~&~~ volume (V) of dissolved gas at a fixed amount of liquid does not depend on pressure (P).

Solution of liquid in liquid (Partially miscible liquids) :

When a liquid is miscible in another liquid, then their relative solubility depends on temperature. When two partially miscible liquids mix to form a homogeneous mixture ~~at~~ a above and below of a particular temperature, that ~~the~~ temperature is known as Critical solution temp (CST).

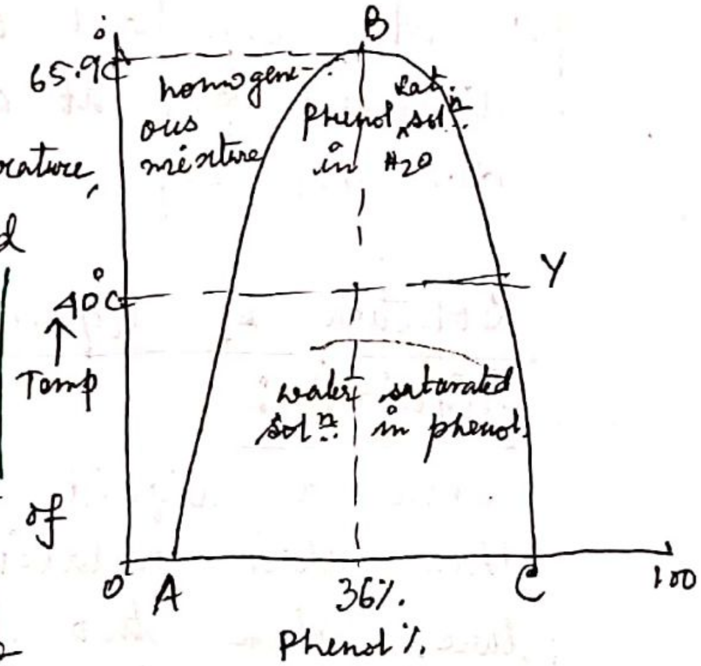
Temperature - dependence on solubility is not same for every ~~at~~ liquid. We can classify them on 3 different groups. i.e., —

i) MST → As the temperature rises, both liquids become more soluble in each other. They reach a 'mutual solubility temperature' (MST). Above that temperature, the mixture becomes homogeneous. Eg — The phenol - water system. (MST ~ 67°c)

(ii) As the temperature increases, both liquids become less soluble and ~~at~~ below a particular temperature, they form a homogeneous mixture. Eg: Tri ethyl ammine – water system.

(iii) Solubility increases both in higher and lower temperature, but decreases in the intermediate temperature. In the intermediate temperature, two liquids form a homogeneous mixture. Eg- nicotine – water system.

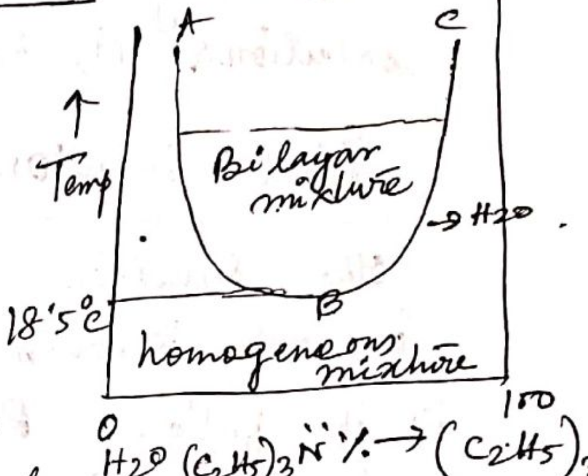
- **Phenol – water system:**



From the figure, we see that with increase in temperature, solubility of ~~sol~~ water and phenol increases. Line AB indicates solubility of phenol in water and line CB indicates solubility of water in phenol. Line AB and CB meet at B point and it looks like a parabola and there are two different layers of this parabola. and there is only one layer outside the parabola. Phenol and water forms a single phase by any ratio above 65.9°c. This temperature is known as <u>Upper critical solution temperature (UCST)</u> and composition of B point is known as <u>critical composition.</u>

~~At 40°c~~,

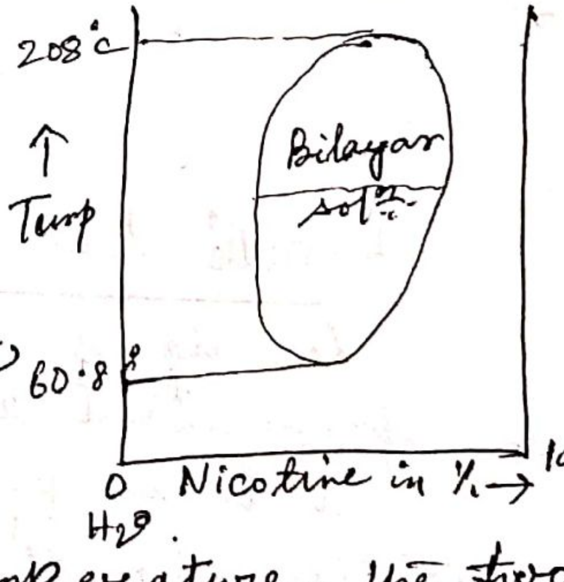
- Triethyl amine - water system :



from figure, it is clear that the solubility of triethyl amine and H_2O decrease with increase in temperature. Below 18.5 °c, these two liquids form a homogeneous mixture at any ratio. This temperature is known as lower critical solution temperature (LCST).

AB indicates solubility of triethylammine in H_2O and BC indicates solubility of H_2O in $(C_2H_5)_3\ddot{N}$. Outside the ABC line, it is ~~so~~ homogeneous mixture and inside the ABC line, it is bilayer solution.

It is a closed in nature.



It is shown from the figure that greater than 208 °c and below than 60.8 °c, ~~tho~~ these two liquids form a homogenous mixture.

In between these two temperature, the two liquids are partially soluble. So, two different critical temperatures are present here.

⑤

Ideal and non-ideal solution

Normally solution can be classified into 2 different solutions. (i) ideal (ii) Non-ideal.

Ideal Solution :

The solution which follows the following condition is ~~soto~~ known as ideal solution.

i) it follows Raoult's law at any concentration and at any temperature.

ii) when solution is prepared, it follows

$\Delta V_{mix} = 0$ — ΔV_{mix} = volume change during preparation of solⁿ.

$\Delta H_{mix} = 0$ — ΔH_{mix} = heat change during preparation of solⁿ.

Example – i) n-Heptane and n-Hexane
ii) Benzene and Toluene
iii) Chlorobenzene and Bromobenzene.
etc.

Raoult's law for relative lowering of vapour pressure

Lowering of vapour pressure of a solvent is directly proportional to the number of moles of solute only and is independent of the nature of the solute.

Relative lowering of vapour pressure is a colligative property.

Non-volatile dilute solution follows Raoult's law.

According to this law

vapour pressure of solvent in solution (p) = mol. fraction of solvent in solution (x) × vapour pressure of pure ~~solute~~ solvent (p°)

★ Mathematical Form:

~~Vapo f~~ If Vapour pressure of pure solvent and solution are p° and p respectively, then lowering of v.p. is given by $p^\circ - p$, then relative lowering of v.p. is $\frac{p^\circ - p}{p^\circ}$.

If n_2 moles of solute is ~~dissovled~~ dissolved in n_1 moles of solvent, then mol fraction of solute $x_2 = \frac{n_2}{n_1+n_2}$ and mol fraction of solvent $x_1 = \frac{n_1}{n_1+n_2}$

According to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{n_2}{n_1+n_2} = x_2$$

$p = x_1 p_0.$

$\therefore \frac{p}{p_0} = x_1 = 1 - x_2$

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1+n_2}$$

$$1 - \frac{p^\circ - p}{p^\circ} = 1 - \frac{n_2}{n_1+n_2} = \frac{n_1 + \cancel{n_2} - \cancel{n_2}}{n_1+n_2}$$

$$\frac{\cancel{p^\circ} - \cancel{p^\circ} + p}{p^\circ} = \frac{n_1}{n_2+n_2} = x_1$$

$$\therefore \quad p = x_1 p^\circ$$

$$\therefore \quad p \propto x_1 \quad (\text{as } p^\circ = \text{const})$$

★ For 2 volatile solutions:

If a solution is prepared by 2 volatile liquids, A + B, then partial pressure of A,

$p_A = x_A \times p_A^\circ$ and partial pressure of B,

$p_B = x_B \times p_B^\circ$

where x_A, x_B are the mole fraction of A + B in solution, p_A°, p_B° are ~~A + B~~ v.p. of A + B in pure state respectively.

∴ Total v.p. of solution $P = p_A + p_B$

Again, $x_A = \frac{n_A}{n_A + n_B}$, $x_B = \frac{n_B}{n_A + n_B}$

∴ $P = x_A p_A^\circ + x_B p_B^\circ$.

∵ $x_A + x_B = 1$.

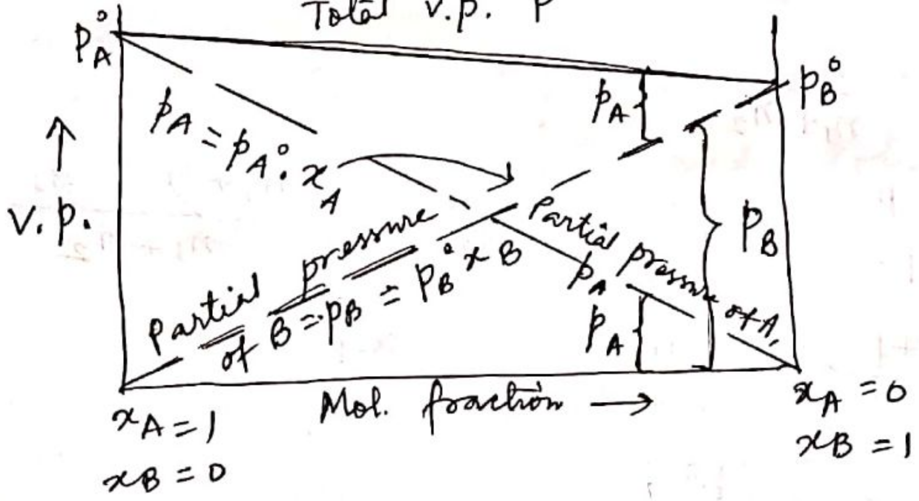
∴ $x_A = 1 - x_B$.

∴ $P = p_A^\circ (1 - x_B) + x_B p_B^\circ$

$P = p_A^\circ - p_A^\circ x_B + p_B^\circ x_B$

$= p_A^\circ - x_B (p_B^\circ - p_A^\circ)$

V.p. vs mole fraction graph for ideal solⁿ is given below :



Graph for Mole fraction vs v.p. of solution

★ **Non-ideal solution :**

If the total vapour pressure of the solution is not equal to the the sum of partial vapour pressure of the constituents, then this solution is known as non-ideal solution.

Characteristics :

(i) Does not obey Raults' law.

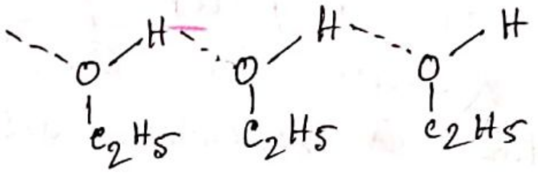
(ii) $\Delta H_{mix} \neq 0$, (iii) $\Delta V_{mix} \neq 0$.

classification :

(i) Positive deviation of non-ideal solⁿ :

For this type of solution, partial vapour pressure of each constituents is greater than that of v.p. calculated from Raoult's law.

Eg – Ethanol and n – Hexane mixture.



We can see H-bonding in ethanol. But in the mixture, n-hexane molecules enter between ethanol molecule and thats why intermolecular H-bonding become weaker. So vapour pressure of the solution increases. Since the intermolecular force becomes weaker, so the binding becomes weaker, and hence, volume of the solution increases. So,

$\Delta V_{mixing} = +ve$

Beside this, also, $\Delta H_{mixing} = +ve$ (heat absorbed)

∴ We can write, for this type of solⁿ,

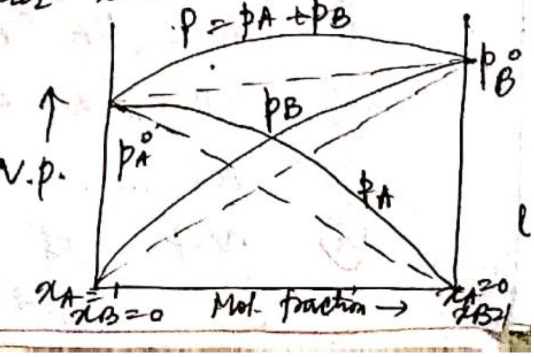
① $p_A > p_A^0 x_A$; $p_B > p_B^0 x_B$

②. $\Delta H_{mix} > 0$ (+ve)

③. $\Delta V_{mix} > 0$ (+ve)

④. Intermolecular attraction force between solvent-solvent and solute-solute are greater than solvent-solute interaction.

⑤ V.p. of the solution is greater than that obtained from Raoult's law.



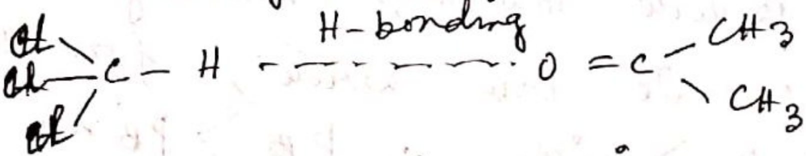
(ii) Negative deviation ~~from~~ of non-ideal solution:

~~For this type of solution, the partial vapour pressure of the solution is lower than that of~~

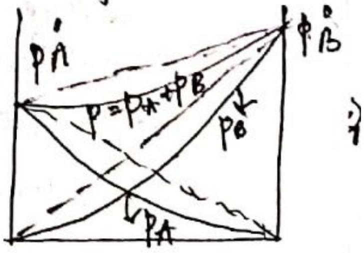
For this type of solution, the partial vapour pressure of each constituents is lower than that of vapour pressure calculated from Raoults' law. Generally, the intermolecular attraction between solvent-solvent and solute-solute are lower than solvent-solute attraction. Since intermolecular attraction in solution is stronger, so the molecule cannot leave the solution. So, the partial pressure decreases.

* Eg— mixture of chloroform and acetone.

There are no intermolecular H-bonding in acetone and chloroform. But when both mix, there is H-bonding.



Since strong attraction force is generated between two different molecules, so heat evolves, i.e., $\Delta H_{mix} = -ve$ and the molecules are coming closer due to strong H-bonding, so $\Delta V_{mix} = -ve$. So, for this type of solⁿ—



① $p_A < p_A^\circ x_A$; $p_B < p_B^\circ x_B$.

② $\Delta H_{mix} < 0$ (−ve)

③ $\Delta V_{mix} < 0$ (−ve)

④ v.p. of solⁿ is lower than that of v.p. calculated from Raoults' law.

⑤. Intermolecular attraction force between solvent-solute is higher than solvent-solvent and solute-solute interaction.

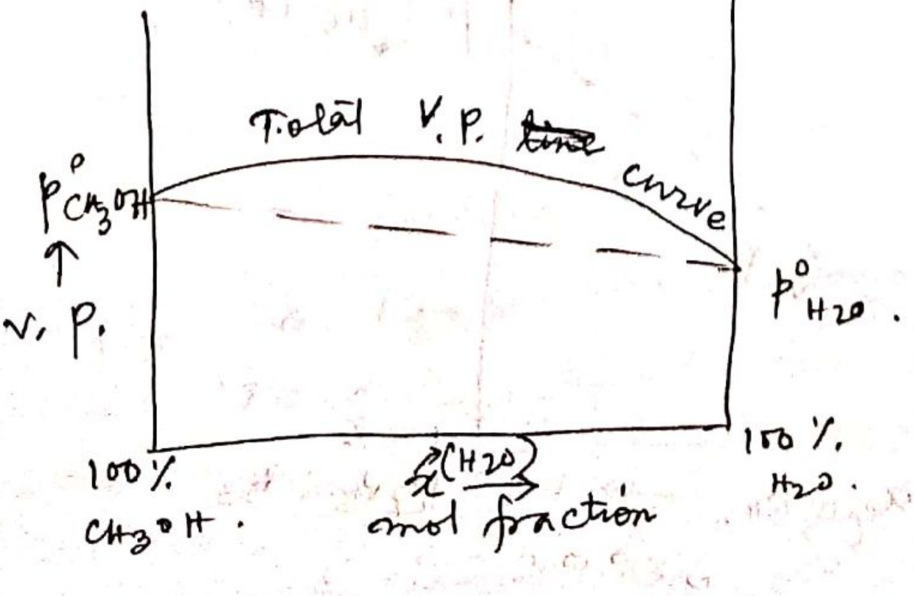
Difference between ideal and non-ideal sol^n:

Ideal sol^n	Nonideal sol^n with (+)ve deviation	Nonideal sol^n with (-) ve deviation
1. $P_A = P_A^\circ x_A;\ P_B = P_B^\circ x_B$	1. $P_A > P_A^\circ x_A;\ P_B > P_B^\circ x_B$	1. $P_A < P_A^\circ x_A;\ P_B < P_B^\circ x_B$
2. $\Delta H_{mix} = 0$	2. $\Delta H_{mix} > 0$	2. $\Delta H_{mix} < 0$
3. $\Delta V_{mix} = 0$	3. $\Delta V_{mix} > 0$	3. $\Delta V_{mix} < 0$
4. Does not form azeotrop.	4. form ~~of~~ azeotrop mixture with lowest boiling temperature.	4. Form azeotrop mixture with highest boiling temp.

We can classify the non-ideal sol^n's vapour pressure-curve into 3 different group.

1. Intermediate Boiling Point solution:

The vapour pressure curve ~~looks like~~ looks like convex nature i.e., we can see (+)ve deviation for these solutions. Eg - mixture of CH_3OH and H_2O.



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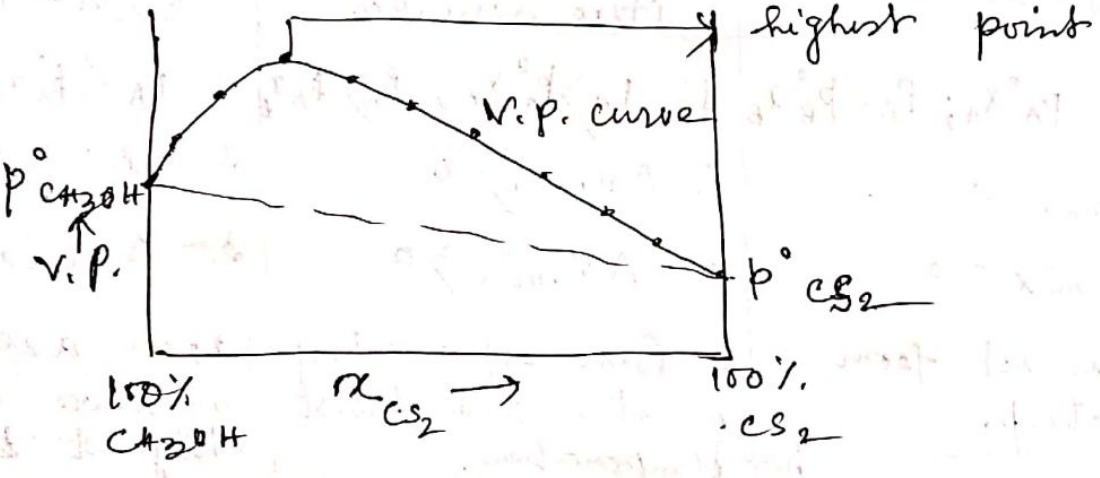
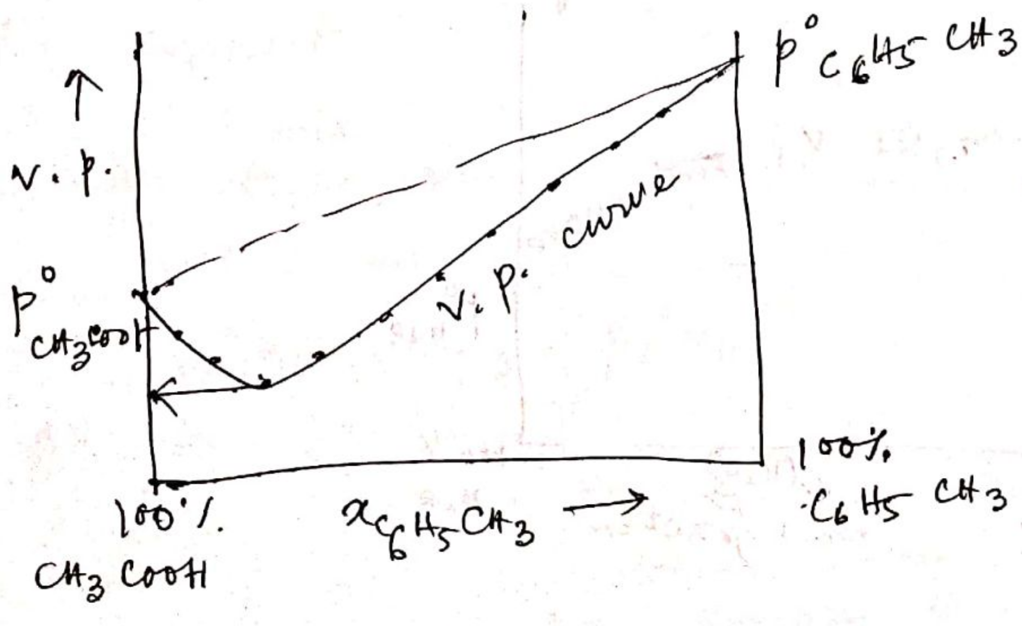
2. Lowest Boiling Point Solution :

Vapour pressure curves are more convex nature. i.e, we can see large (+) ve deviation and there is a highest point. Eg – CH_3OH and CS_2 mixture.



3. Highest Boiling Point Solution :

Vapour pressure curves are more concave nature. i.e, we can see large (−) ve deviation for these type solutions. There is a lowest point. Eg – mixture of CH_3COOH and $C_6H_5CH_3$.



Steam Distillation :

The distillation made in presence of steam is known as steam distillation. *

Principal : A and B are two partially miscible liquids. At equilibrium, both molecules of two liquids are present in the vapour state. At constant temperature, total vapour pressure(P) is equal to the sum of the partial vapour pressure (P_A) and (P_B) of respectiv gases. The total vapour pressure of the mixture does not depend on the amount of the individual gases.

∴ $p = p_A + p_B$.

Again, $p_A = \frac{n_1}{n_1+n_2}$ and $p_B = \frac{n_2}{n_1+n_2}$

or, $\frac{p_A}{p_B} = \frac{n_1}{n_2}$ where n_1 and n_2 be no. of gm-moles of the gas A and B respectively.

Since, $\frac{n_1}{n_2}$ = constant as $\frac{p_A}{p_B}$ = Const. at const temperature

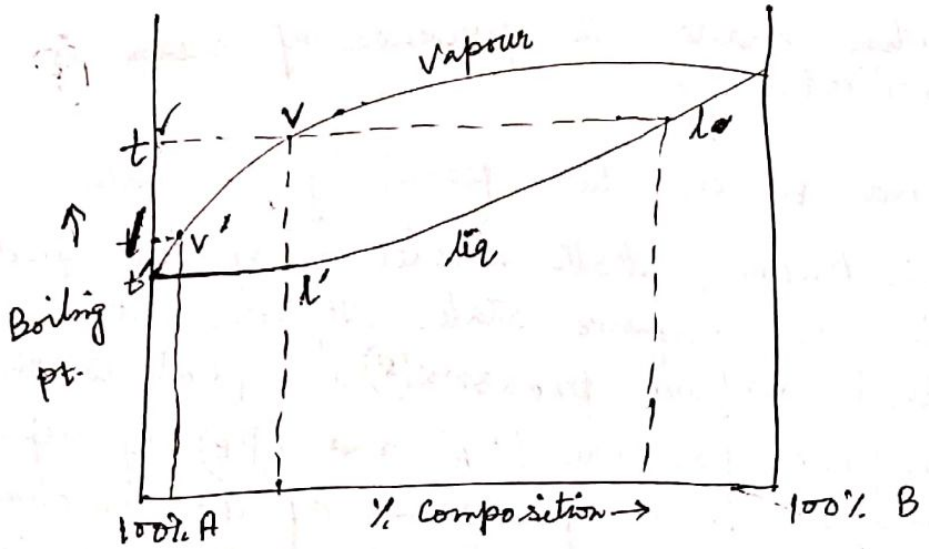
In vapour phase, w_A and w_B be the amount of A and B respectively.

∴ $\frac{p_A}{p_B} = \frac{n_1}{n_2} = \frac{w_A/M_A}{w_B/M_B} = \frac{w_A M_B}{w_B M_A}$ [M_A & M_B are the ~~[illegible]~~ molecular weight respectively.]

∴ $\boxed{\frac{w_A}{w_B} = \frac{p_A M_A}{p_B M_B}}$

Fractional Distillation :

When two liquids of different boiling points heated, then the liquid having low boiling point evaporate firstly and the vapour is ~~collected~~ cooled and then collected. But this method is not correct. Actually two vapours are present over the solution. So, when we condense the vapour, two liquids present.



It is clear from the figure the liquid having composition 'l' can boil at t temperature and composition of vapour formed is v. If this vapour converted to liquid separately, its composition will be l'.

If we heat the liquid of l', it boils at t' temperature and the composition of vapour produced is v'. In this way, if fractional distillation is carried out several times, amount of A increases (having lower b.pt) and in the remaining liquid, amount of B increases (higher b.pt). In this way, by using this method, we can separate the two liquids.

Nernsts' Distribution Law :

At a constant temperature, when a solute is taken up with two immiscible liquids, in both of which the solute is soluble, the solute distributes itself between the two liquids in such a way that the ratio of its concentration in the two liquids phases is constant.

Eg – Suppose, iodine is taken up two immiscible liquids, water and carbon tetrachloride, I_2 distributes itself between the two liquids in such a way, ~~such~~ sothat its' concentration ratio becomes a constant.

Let us consider, the concentrations are c_1 and c_2.
According to this law, $\frac{c_1}{c_2} = K_d$ = partition co-efficient.
= Const. value

This partition co-eff. depends on the nature of solute and solvent and temperature. It does not depend on the amount of solute and solvent.

Use :

1. If K_d is known, then we can evaluate the ratio of c_1 and c_2. If c_1 is known, then c_2 can be calculated.
2. Between two liquids, A and B, if dissociation occures in only one liquids, say B, and if degree of dissociation is α, then

$$\frac{C_A}{C_B(1-\alpha)} = K_d \text{ (const)}.$$

3. For few materials purification partially done by this law.

Limitations :

i) Solution should be very dilute, i.e., ideal solution.
ii) There should be no reaction between solute and solvent.
iii) Temperature should be constant throughout.
iv) This ~~so~~ law is not applicable if there is any dissociation or association between solute and solvent. Eg– if Benzoic $\bar{a}$ is mixed with H_2O

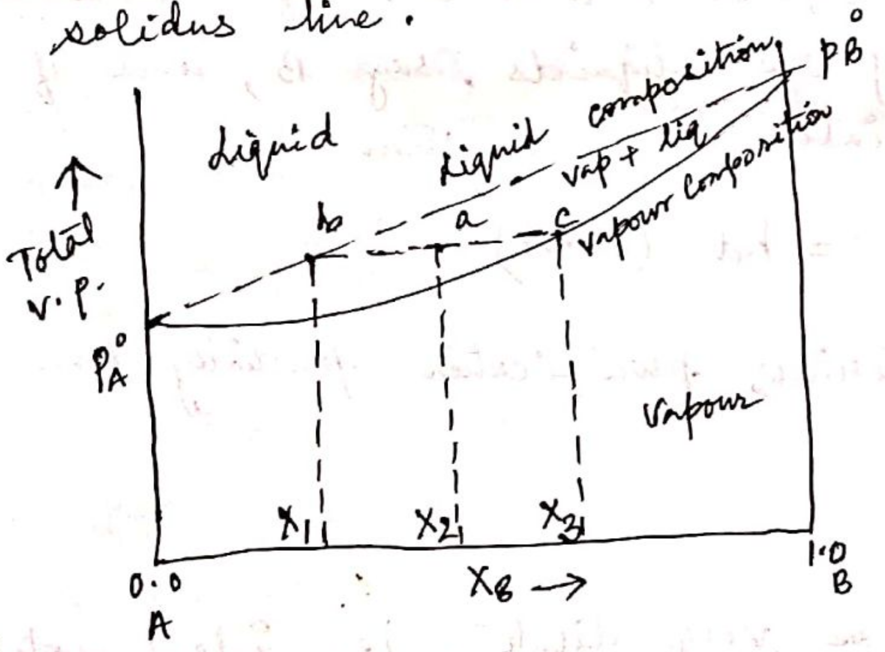
and Benzene, $\frac{C_A}{C_B} \neq$ const, but

$$\frac{C_A}{\sqrt[n]{C_B}} = \text{const}$$

$$\left[\, 2\, C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2 \,\right]$$

Lever Rule :

The lever rule is a tool used to determine the mol fraction (x_i) or the mass fraction (W_i) of each phase of a binary equilibrium phase diagram. It can be used to determine the fraction of liquid and solid phases for a given binary composition and temperature that is between the liquidus and solidus line.



Graph for liquid and vapour of ideal solution.

From the graph, it is clear that the composition at point a, b & c are X_2 (overall), X_1 (liquid) & X_3 (vapour) respectively.

Therefore, overall yield at 'a' can be calculated by the following way :

Let n_l and n_v be the mol fraction at liquid and vapour phase resp. ly.

Therefore, according to conservation of mass law, we can write,

$$X_2(n_L + n_V) = X_1 n_L + X_3 n_V \quad \text{---(1)}$$

$$\text{or, } (X_2 - X_1) n_L = (X_3 - X_2) n_V \quad \text{---(2)}$$

$$\text{or, } \frac{n_L}{n_V} = \frac{X_3 - X_2}{X_2 - X_1} = \frac{ac}{ab} \quad \text{---(3)}$$

Eqn. (3) is known as "Lever law". If $n_L \ll n_V$, then mainly vapour is presents. If $n_V \ll n_L$, mainly liquide is present.

Azeotropic Mixture :

An 'azeotrope' or a 'constant boiling point mixture' is a mixture of two or more liquids whose proportions cannot be altered or changed by simple distillation. This happens because when an azeotrope is boiled, the vapour has the same proportions of constituents as the unboiled mixture. Because their composition is unchanged by distillation, azeotropes are also called 'constant boiling point' mixtures.

For azeotrope mixture, it is not possible to seperate the components by fractional distillation. There is 2 types of azeotropes: minimum boiling azeotrope and maximum boiling azeotrope.

Let us consider, at equilibrium, no of components, $c = 2$, no of phases $= 2$, degrees of freedom $=$

$F = C - P + 2 = 2 - 2 + 2 = 2$

Since pressure is constant and boiling point is fixed, $\therefore$ $F = 2 - 2 = 0$, $\therefore$ structure of liquid is unchangable.

- Minimum Boiling Azeotrope :

A solution that shows greater positive deviation from Raoult's law forms a minimum boiling azeotrope at a specific composition. For example, an ethanol-water mixture (obtd from fermentation of sugars) on fractional distillation yields a sol^{n} containing approx. 95% by volume of ethanol. Once this composition has been achieved, the liquid and vapour have the same composition, and no further separation occurs. ~~A solution~~

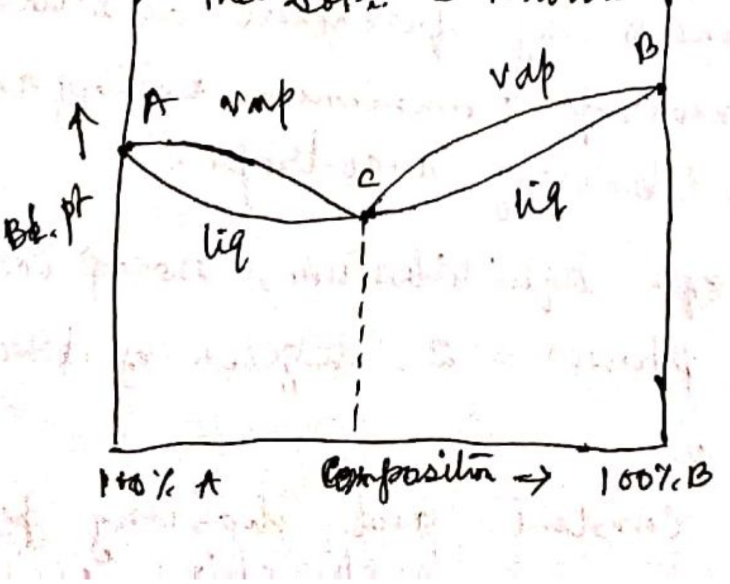
eg→95.6% C_2H_5OH and 4.4% H_2O mixture. At pt. 'c', the sol^{n} is known as minimum Boiling Azeotrope.

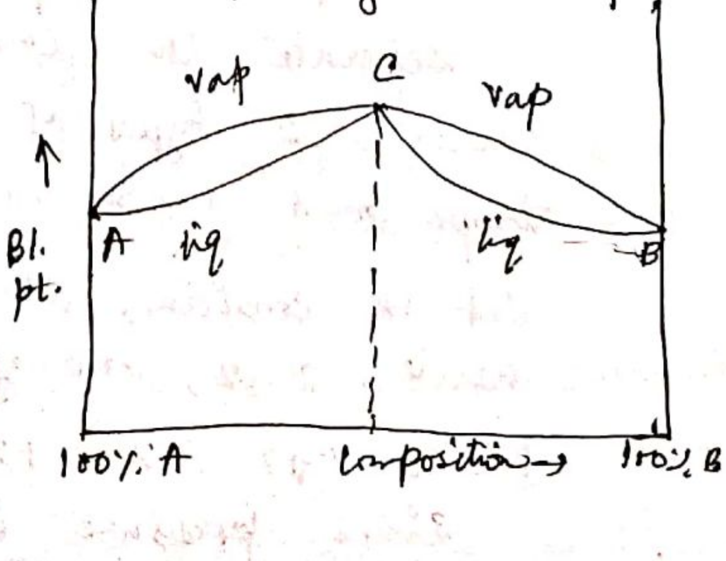
Maximum Boiling Azeotrope :

A solution that shows large (-)ve deviation from Raoult's law forms a maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrop has an approximate composition of 68% nitric a and 32% water by mass, with a boiling point of 393.5K (120.4°c).

eg → 68.2% HNO_3 and 31.8% H_2O mixture.

At 'c' pt, the composition of liq and vap. are same. The sol^{n} is known as Maximum Boiling Azeotrope.





Solvent Extraction Technique:

To separate a solid from a liquid, best method is evaporation. In this method, if one cool the vapour, then pure solvent can be found out and also solid present in the flask. But for some solute, it breaks at higher temperature. For ~~the~~ these solute, the best way is to collect the ~~solute~~ ~~solvent~~ solute in a solvent where the solubility of the solute is much higher and it does not mixed with solvent. This method is known as "Solvent Extraction Technique."

Let us consider, 'L' volume any organic solvent is required in one-step to seperate ~~V volume~~ the solvent from 'V' volume aquous solution.

The amount of solute in solution = x.

x_1 = Unextracted amount after 1st time extraction

K = degree of distribution.

$$\therefore\ C_{org} = \frac{x - x_1}{L} \quad \text{and} \quad C_{aq} = \frac{x_1}{V}$$

~~Or,~~

$$\therefore \frac{\frac{x-x_1}{L}}{\frac{x_1}{V}} = \frac{C_{org}}{C_{aq}} = K$$

$$\therefore\ K = \frac{(x-x_1)V}{x_1 L}$$

$$\therefore\ K x_1 L = (x - x_1)V = xV - x_1 V.$$

$$\therefore\ x_1 = \frac{V}{(KL+V)}x$$

Let us consider, after 2nd time distilation, x_2 be the remaining part.

$$\therefore \quad x_2 = x_1 \frac{V}{(KL+V)}$$

Putting the value of x_1,

$$x_2 = \frac{x_0 V^2}{(KL+V)^2}$$

∴ After 'n' times extractions, remaining portion is

$$\boxed{x_n = x\left(\frac{V}{KL+V}\right)^n}$$