Solution

Solution : A 'solution' is a homogeneous mixture of two or more non-reacting components.

Types of solution :

Depending on physical state or phase of solute and solvent solutions can be classified into nine types:

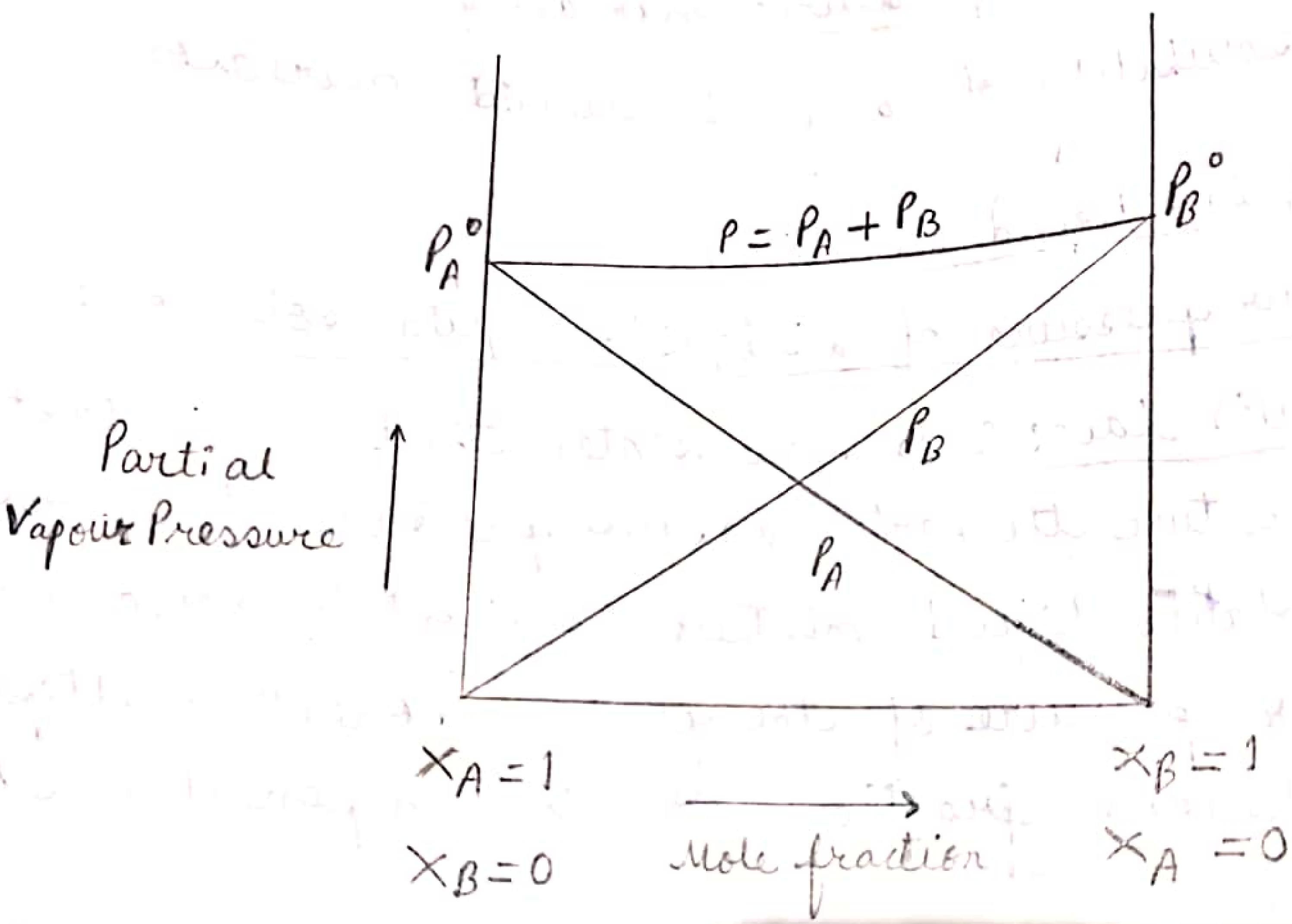
Types of solution	Solvent	Solute	Example
1) Solution of gas in gas.	gas	gas	Air
2) Solution of gas in liquid	Liquid	gas	O_2 in H_2O
3) Solution of gas in solid	solid	gas	H_2O in Pd. (Palladium)
4) Solution of liquid in gas	gas	Liquid	Moisture in air
5) Solution of Liquid in Liquid	Liquid	Liquid	H_2O in ethanol
6) Solution of liquid in solid	solid	Liquid	Hg in Au (Mercury in gold)
7) Solution of solid in gas	gas	solid	Camphore in air
8) Solution of solid in Liquid	Liquid	solid	Sugar in H_2O
9) Solution of solid in solid	solid	solid	Alloys

Roult's law: This law states that at Constant temperature the partial vapour pressure of a component of a volatite liquid mixture/solution is equal to the vapour pressure of the pure component multiplied by the mole fraction of the component in the solution.

For a binary solution of two components A & B,

$$P_A = P_A^0 X_A .$$

$$P_B = P_B^0 \cancel{\times} X_B$$, where P_A^0 and P_B^0 are the vapour pressure of pure component A and B respectively.


$P = P_A + P_B$
P_A°
P_B°
P_B
P_A
Partial Vapour Pressure
$x_A = 1$
$x_B = 0$
Mole fraction
$x_B = 1$
$x_A = 0$

Deviations from Roult's Law (Non-Ideal Solutions):

A solution which does not obey Roult's law over a entire range of concentration is called non-ideal solution. For non-ideal solution,

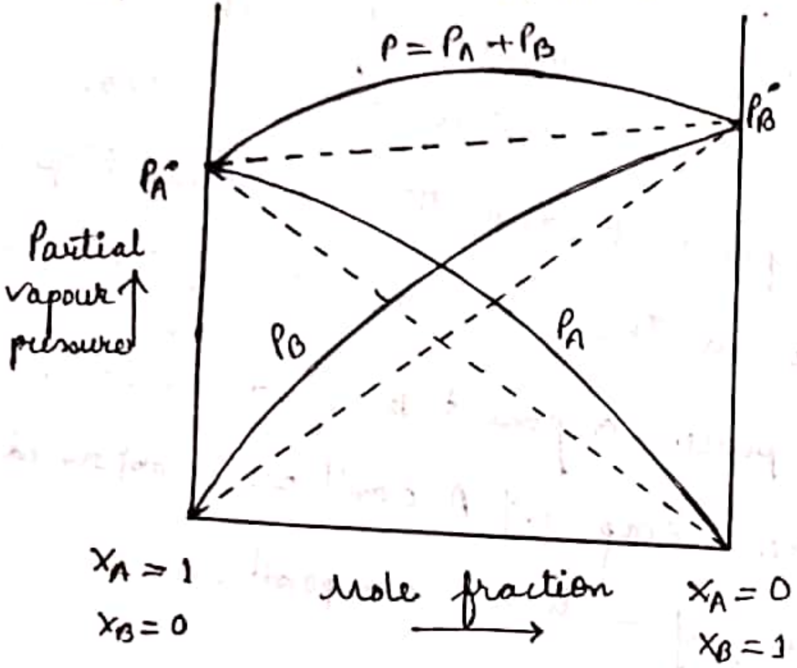
$\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$. and,

$P_A \neq P_A^\circ \cdot X_A$, $P_B \neq P_B^\circ \cdot X_B$.

Non-ideal solutions show two types of deviations from Roult's law.

① Positive Deviation: Here, the total vapour pressure of the solutions is greater than that would be expected for ideal liquids. This is due to the weaker attractive forces which operate between the molecules in soln, due to which there is increase in volume and an absorption of heat on mixing. The process is endothermic. Here, $\Delta V_{mix} > 0$, $\Delta H_{mix} > 0$

$P_A > P_A^\circ X_A$ and $P_B > P_B^\circ \cdot X_B$.

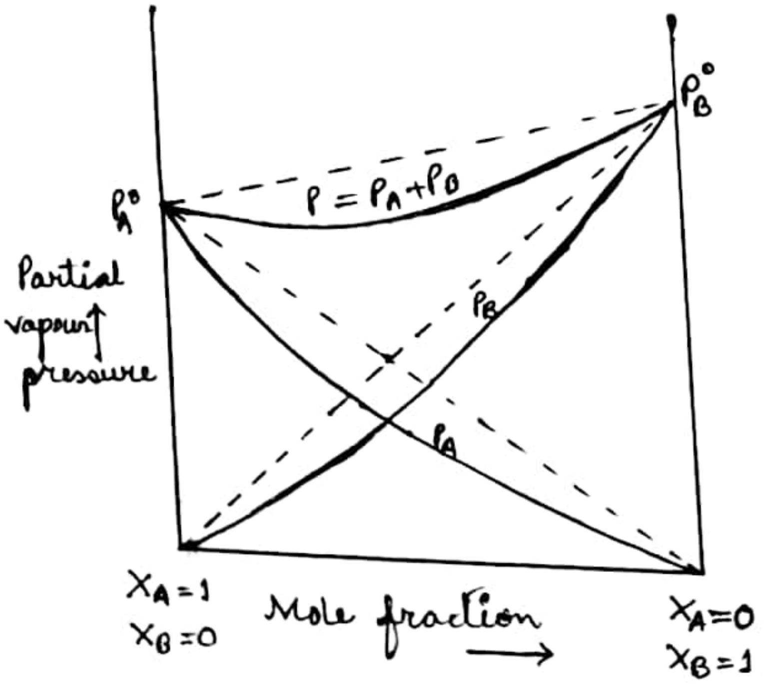


e.g ① ethyl alcohol and cyclohexane

② acetone and carbon disulphide

③ carbon tetrachloride and chloroform.

② **Negative Deviation:** There is less tendency for molecules in such solutions to escape from the solution than from pure liquids. Also, the total vapour pressure above the liquid mixture is less than that it would be if liquids were pure. It is due to the association of one or both of the ~~composite~~ components in the solution. Here, $\Delta V_{mix} < 0$, $\Delta H_{mix} < 0$, $P_A < P_A^\circ \cdot X_A$ and $P_B < P_B^\circ \cdot X_B$.



e.g. ① Water - HCl solution

② Acetone - diethyl ether solution

③ H_2O - HNO_3 solution.

④ Acetone - aniline solution.

Azeotropes:

Mixtures of liquids which boil at constant temperature like a pure liquid such that the distillate has the same composition as that of the liquid mixture are called constant boiling mixtures or azeotropic mixtures or azeotropes.

Azeotropes are of two types —

(a) **Minimum boiling azeotropes:** These are formed from liquid pairs which show positive deviations from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the highest and thus the boiling point is the lowest. Such azeotropes have boiling point lower than either of the pure components.

e.g. Mixture of 95.57% ethanol and 4.43% H_2O have boiling point 351.15 K.

ⓑ Maximum boiling azeotropes:

These are formed by liquid pairs which show negative deviations from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is lowest and thus boiling point is the highest. Such azeotropes have boiling point higher than either of the pure components. e.g. Mixture of 20.23 % HCl and 79.77 % H_2O have boiling point 385.54 K.

Distillation of Ideal Solutions (Temperature - Composition Diagram)

The components of only ideal solution can be separated by fractional distillation. The boiling tempr - composition curves for liquid and vapour phases of the liquid components A and B is shown in the following figure. Let a solution of composition X be heated. The boiling takes place at temperature T and vapours having composition X_1 will come off. As X_1 is richer ~~the~~ in component B than X, the composition (Y) of the residual liquid will become rich in A. This liquid having different composition will boil at a higher temperature (T_1). The vapours which come off at this tempr will still be richer in B. The residual liquid will become more richer in liquid A and it boils at T_1. If this process is continued, the boiling point of the solution will go on rising towards T_A (maximum) ~~&~~ which is the boiling point of the pure liquid A. It means

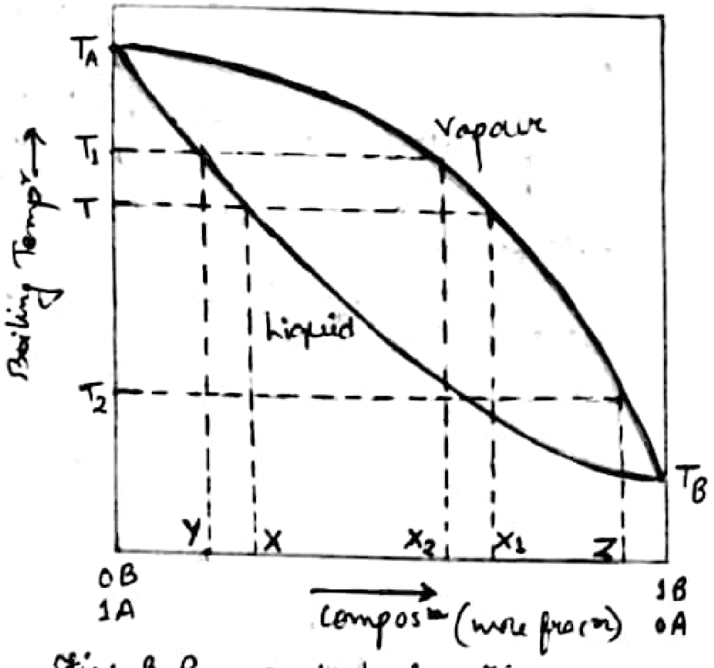


Fig: B.P. vs Mole fraction.

that the residual liquid will become more and more rich in A and finally only liquid A remains in the liquid phase.

Again, the vapours coming out at the temperature T of the original solution have composition X_1. If these vapours are condensed and the liquid is again distilled, then the new boiling point will be T_2. Also the composition of the vapours now distilling over will be given by z, and the distillate obtained will be richer in B than before. If this process of condensing the vapours and the redistillation of the liquid is continued, the distillate will be finally the pure component B.

Thus, the process of separating mixtures of two or more liquids having close boiling points by repeated distillation and condensation is called fractional distillation.

Distillation of Non-Ideal Solutions (Temp^r - Composition Diagram)

① Minimum boiling azeotropic solutions:

Let us consider the distillation of a mixture having composition x. The first fraction collected (composition x_1) will be richer in the constant boiling mixture. Thus, the residual liquid will be richer in the component A. As the distillation progresses, the distillate will be richer in the constant boiling mixture and the residual mixture will be richer in component A. Thus by repeated fractional distillation, the mixture of the minimum boiling point of composition C will be collected as distillate and pure component A will be left as residue in the distillation flask. Hence pure component B can't be collected and vice versa.

e.g. Mixture of 95.6% ethanol & 4.4% water boils at 78.13°C.

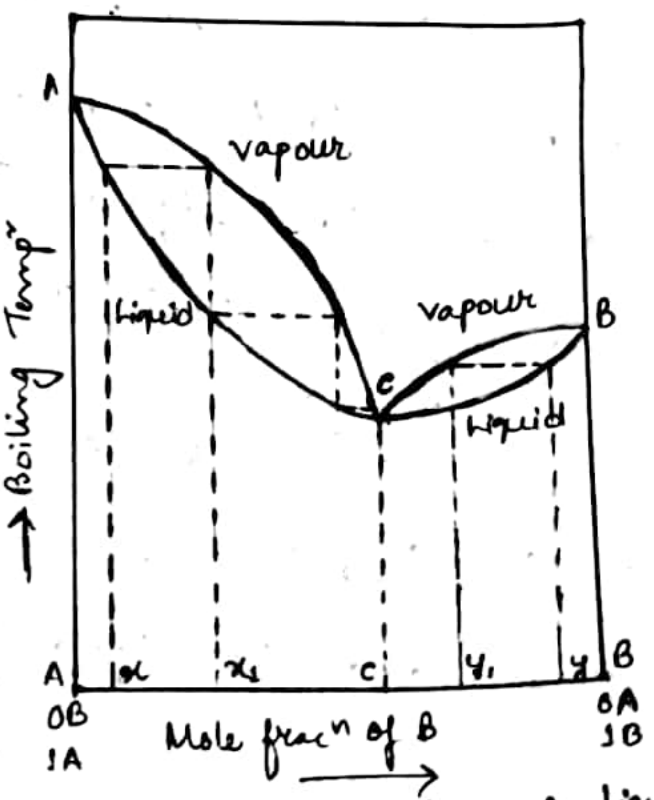


Fig: Temp^r – Compo^n curves for liquid and vapour phases in binary sol^{ns}

② Maximum boiling Azeotropic Solutions :

Let us consider a mixture of any composition represented by a point lying between A and D. When such a mixture is distilled, the distillate will be richer in ~~com~~ component A and the residual liquid will be richer in constant boiling mixture (D). As the distillation progresses, the distillate will become richer in component A & residual mixture will be richer in constant boiling mixture. Finally, pure component A and residual liquid will be obtained. Pure component B can not be obtained by the distillation of the sol^{n} of such a composition.

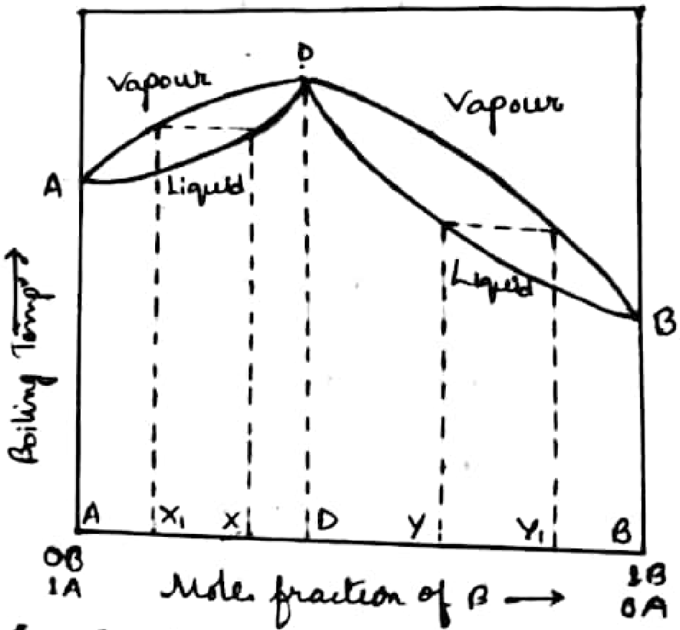


Fig: Temp^{r}-Compos^{n} curves for Liquid & vapour phases in binary sol^{n}.

Similarly, let us consider a mixture of any composition lying between B and D. When a mixture of such a composition is distilled, then the distillate will become richer and richer in component B and the residual liquid will be richer and richer in the constant boiling mixture represented by D. Finally, pure component B and residual liquid will be obtained. Pure component A can't be obtained by the distillation of the solution of such a composition.

e.g. HCl - H_2O mixture (80% by mass H_2O). Boiling point is 108·5°C.

The Lever Rule :

Let us consider a two-component temp^r-composition diagram of two components A and B where ~~can be~~ it is assumed that B is more volatile than A, ie. the boiling point of pure B, T_B° is less than that of pure ~~solvent~~ A, T_A°.

In this system, the composition of the liquid and vapour phases can be determined with the help of Lever rule as :

$$\boxed{\frac{n_{\text{Liquid}}}{n_{\text{vapour}}} = \frac{\text{length } av}{\text{length } al}}$$

where n_{liquid} ⇒ no. of moles of liquid phase.

n_{vapour} ⇒ no. of moles of vapour phase.

This rule can be used to illustrate fractional distillation.

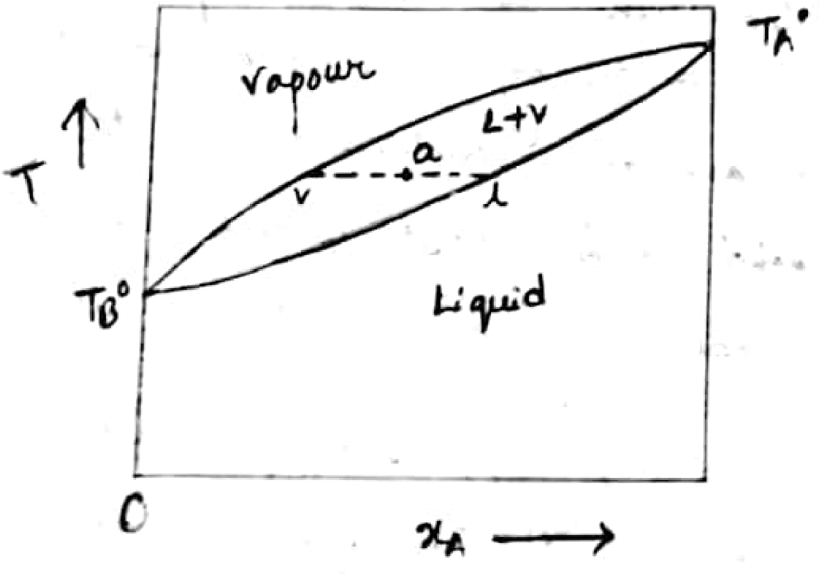


Fig: Lever rule in liquid ⇌ vapour equilibrium

CST :

The temperature above or below which a pair of partially miscible liquids becomes miscible in all proportions, is called critical solution temp^r (CST) or consolute temp^r for the pair.

The liquid pairs, ~~attain~~ which attain complete miscibility above a certain temp^r ~~in which~~ are said to have the upper critical solution temp^r (UCST). e.g. water – phenol.

The liquid pairs which attain complete miscibility below a certain temp^r are said to have lower critical solution temp^r (LCST). e.g. water – ~~nicotine~~ Triethylamine.

Solubility of partially miscible liquids:

Four types of partially miscible liquid-liquid systems have been observed. These are —

① Those in which the partial miscibility increases with increase in temp^r. e.g. phenol-water, aniline-H_2O, aniline - hexane, etc.

② Those in which partial miscibility increases on lowering the temp^r. e.g. $(C_2H_5)_3N - H_2O$. and $(C_2H_5)_2NH - H_2O$.

③ Those in which partial miscibility increases ~~both~~ on both raising as well as lowering the tempr in certain ranges. e.g. H_2O - nicotine and H_2O-β-picoline systems.

④ Those in which complete miscibility tempr can't be obtained. e.g. ether-water system.

① Phenol - water System (UCST) :

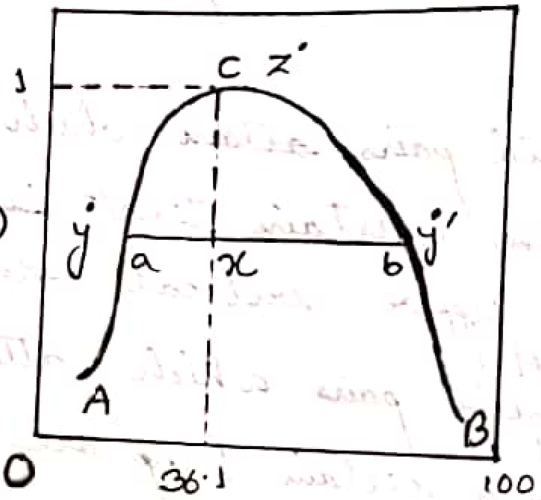


Fig: Phenol - water system

{ab line is called tie line}.

y = phenol in H_2O.

y' = H_2O in phenol.

x = conjugate soln.

Phenol- water system is a typical example which shows an upper critical solution temp^r. Phenol and water are partially miscible at ordinary temp^r. When equal volume of phenol and water are mixed. two ~~bilay~~ layers are formed. The upper layer is saturated solution of phenol in water while the lower one is saturated solution of water in phenol. These two solutions are in eq^m with each other and ~~are~~ are called conjugate solution.

On increasing the temp^r, the mutual solubility of phenol and water increases. At a certain temp^r, the composition of two conjugated soln becomes the same. Thus, phenol and water become completely miscible forming a single solution. This temp^r at which the two layers become completely miscible is called upper critical soln temp^r (UCST).

The critical soln temp for phenol-water system is 68.1°C, The composition ~~of~~ corresponding to CST is called critical solution composition. Here, composn is 36.10% phenol and 63.90% water.

Another example are aniline-hexane system, aniline-water system and cyclohexane - methanol system.

② Triethylamine – Water system (LCST):

In Triethylamine-water system, the mutual solubility increases with decrease in Temp^{r}. i.e. LCST. The Temp^{r} is 18·5°C. Above this Temp^{r}, the liquids give rise to two distinct layers but below this

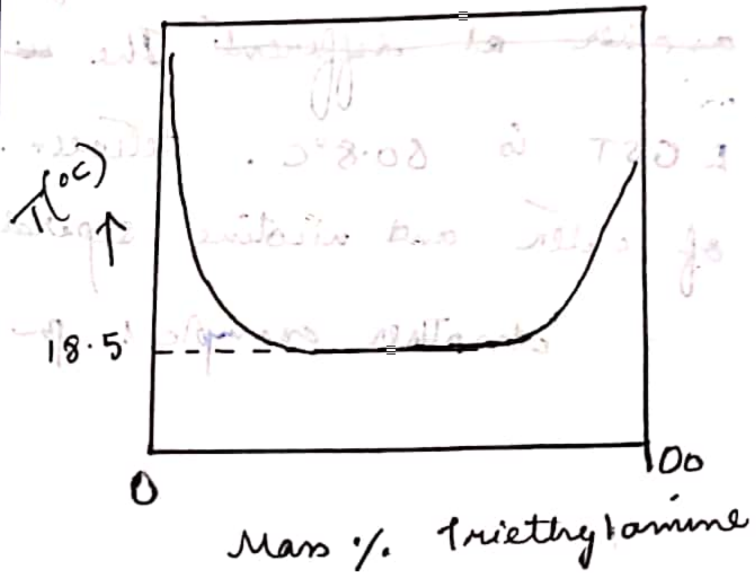


fig: Triethylamine system

temp^r they are completely miscible in all proportions. Another example: $(C_2H_5)_2NH + H_2O$ system.

③ Nicotine-water system (UCST and LCST):

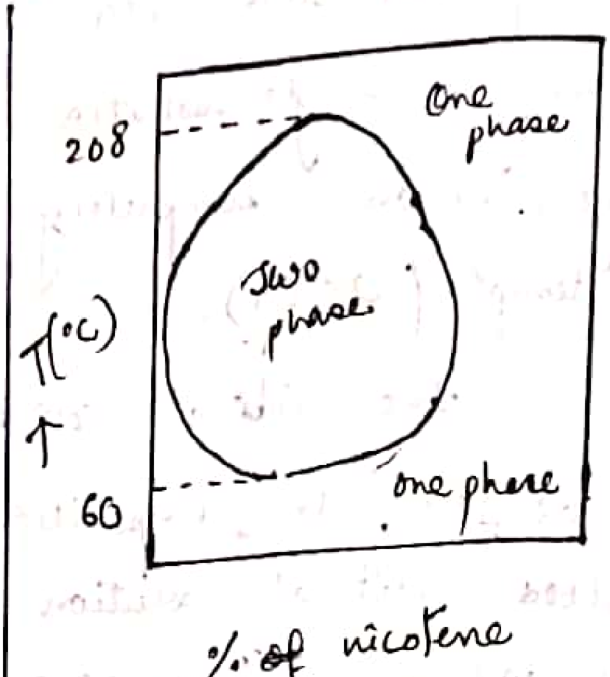


Fig: Nicotene-water system

Nicotine-water system shows UCST as well as LCST. i.e. these liquids are completely miscible above a certain critical temp^r (upper consolute temp^r) and again below a certain critical temp^r (lower console temp^r). Between these two limiting temp^r's, they are partially miscible. ~~The solubilities of these liquids in one another at different~~ The ~~w~~ UCST is 208·0°C and LCST is 60·8°C. Between these two temp^r's, mixtures of water and nicotine separate into two liquid layers.

Another example:- β-picoline ~~an~~ $-H_2O$ system.

Steam distillation :

Steam distillation is used in the purification of organic compounds which have high boiling points and are almost ~~completely~~ immiscible in water. e.g. Aniline Its normal boiling point is 180°C. But it can be made to boil and distil over of a much lower tempr by passing steam through it.

Apparatus: The steam is generated in a metal can. The solution to be distilled is placed in the round-bottomed flask, clamped at an angle so as to prevent the solution from being splashed into the condenser. The tube carrying the steam from the can dips below the liquid in the flask. The distillation flask is kept heated gently ~~at~~ on a sand bath in order to avoid too much condensation of water into it. The vapours of ~~a~~ the organic compound mixed with steam pass over and are condensed in the receiver. The boiling point here is 98.5°C which is much lower than the original boiling point of aniline (180°C).

The vapour pressures of water and aniline at 98.5°C are 717 torr and 43 torr, respectively. As the molar masses of the liquids are 18 and 93 g mol-1 respectively, the relative masses of the two liquids in the distillate willbe given by:

$$\frac{\text{Mass of water}}{\text{Mass of aniline}} = \frac{18\ \text{g/mol} \times 717\ \text{torr}}{93\ \text{g/mol} \times 43\ \text{torr}} = 3.23.$$

Nernst Distribution Law:

A solute distributes itself between two non-miscible solvents in contact with each other in such a way that at eqm the ratio of concentration of the solute in the two layers is ~~contact~~ constant at a given temperature, provided the molecular state of solute is same in both the solvents.

$$\frac{\text{conc}^n \text{ of } x \text{ in solvent } A}{\text{conc}^n \text{ of } x \text{ in solvent } B} = \frac{C_A}{C_B} = K_D.$$

K_D is called Partition coefficient or distribution coefficient.

Conditions reqd :

① Tempr should be kept constant.

② Two solvents should be immiscible.

③ The mutual solubility of the two solvents should not be affected by addition of solute.

④ The solutions should be different.

⑤ The molecular state ~~by~~ of solute should be same in both the solvents.

Thermodynamic derivation of Nernst distribution law:

At eqm, $\mu_A = \mu_B$. where μ_A and μ_B are the chemical potentials of solvent A and B respectively.

we know, $\underset{(T,P)}{\mu} = \underset{(T)}{\mu^\circ} + RT\ln a$ activity (a).

$$\therefore \mu_A = \mu_A^\circ + RT\ln a_A \longrightarrow ①.$$

$$\mu_B = \mu_B^\circ + RT\ln a_B \longrightarrow (\text{II}).$$

$$\mu_A^\circ + RT\ln a_A = \mu_B^\circ + RT\ln a_B.$$

$$\Rightarrow RT\ln a_A - RT\ln a_B = \mu_B^\circ - \mu_A^\circ.$$

$$\Rightarrow RT\left[\ln a_A - \ln a_B\right] = \mu_B^\circ - \mu_A^\circ.$$

$$\Rightarrow \ln\frac{a_A}{a_B} = \frac{\mu_B^\circ - \mu_A^\circ}{RT} \longrightarrow (\text{III}).$$

At const. Temp^r,

$$\ln\frac{a_A}{a_B} = \text{constant}.$$

$$\Rightarrow \frac{a_A}{a_B} = \text{constant}.$$

~~At~~ for dilute solutions,

$$\boxed{\frac{C_A}{C_B} = \text{constant.} = K_D.}$$

This is the Nernst distribution law.