CHEMISTRY

(Major)

(1st Semester)

Course No.: **CHM-DSC-102**

(Physical Chemistry -I)

States of Matter and Solution

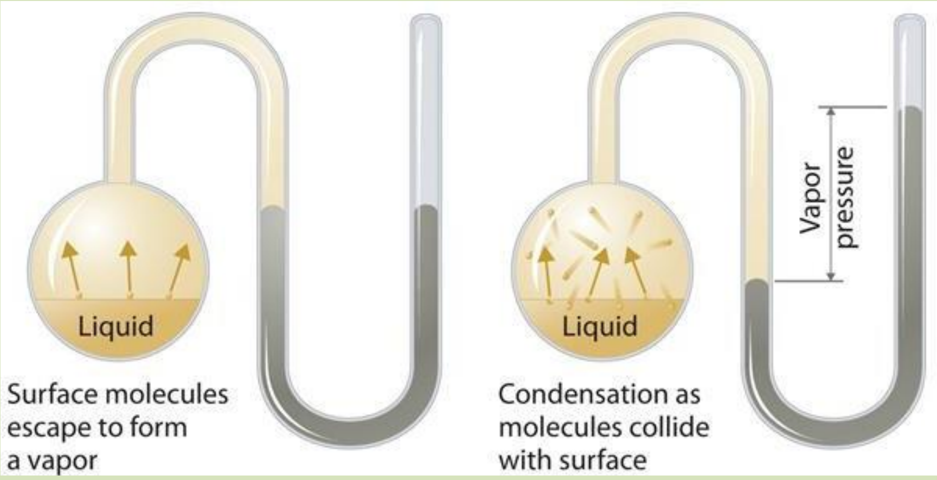
Unit 5: Solutions

[Ideal solutions: Ideal solutions and Raoult's law, deviations from Raoult's law; non-ideal solutions. Vapour pressure-composition and temperature-composition curves of ideal and non-ideal solutions. Distillation of solutions. Azeotropes. Partial miscibility of liquids: Critical solution temperature; effect of impurity on partial miscibility of liquids. Immiscibility of liquids- Principle of steam distillation. Nernst distribution law and its applications, solvent extraction]

VAPOURPRESSURE

Consider a pure liquid in a beaker is covered with a jar. Some molecules on the liquid surface evaporate and fill the vacant space available to them. The molecules in the vapour phase move randomly in the vacant space, during this motion, they strike the surface of the liquid and condensed. This process of evaporation and condensation go on and an equilibrium is established between evaporation and condensation. The pressure exerted by vapours over the liquid surface at equilibrium is called vapour pressure of the liquid.

If solute is non-volatile solid or liquid the vapour pressure of solution is equal to partial vapour pressure of solvent in the solution and if the solute is volatile solid or liquid, then vapour pressure will be equal to the sum of partial vapour pressure of solute and that of solvent.



RAOULT’SLAW:

In 1986, a French Chemist named Francois Marte Raoult proposed a quantitative relation between partial pressure and mole fraction of volatile liquids. The law states that mole fraction of the solute component is directly proportional to its partial pressure.

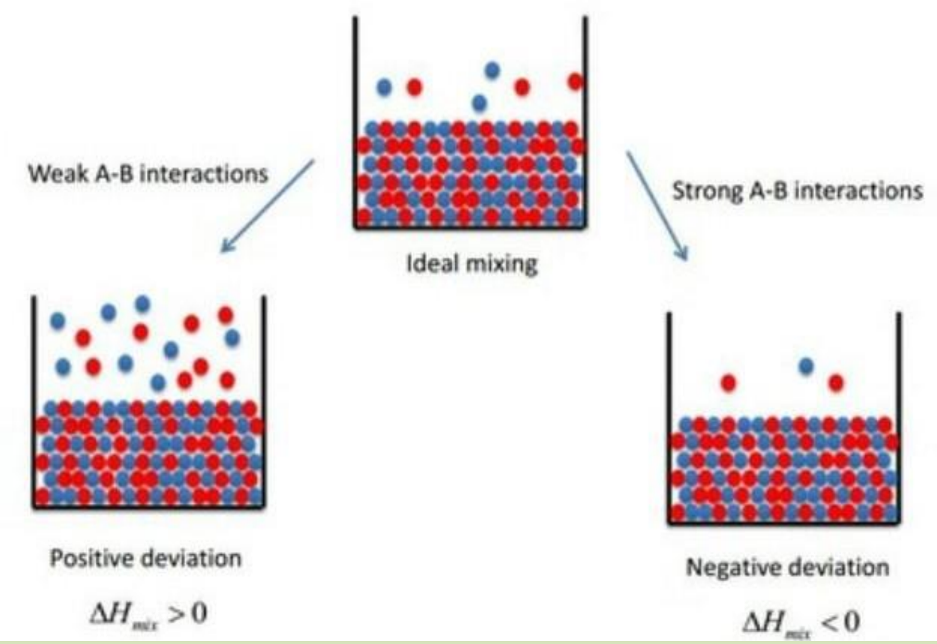


Image1: Types of Solutions

On the basis of Raoult's Law, liquid-liquid solutions are classified into two types of solutions, they are:

- Ideal Solutions
- Non-ideal Solutions

Ideal and Non– Ideal Solutions

Ideal and Non – Ideal Solutions The solutions which obey Raoult's law at all compositions of solute in solvent at all temperature are called ideal solutions. Ideal solutions can be obtained by mixing two components with identical molecular size, structure and they should have almost same inter molecular attraction e.g., two liquids A and B form an ideal solution when A –A and B–B molecular attractions will be same and hence A–B molecular atrraction will be almost same as A–A and B–B molecular attraction.

An ideal solution should have following characteristic

- It should obey Raoult's law i.e., $P_A = X_A$ and $P_B = X_B$
- $\Delta H_{mix} = 0$, i.e. no heat should be absorbed or evolved during mixing
- $\Delta V_{mix} = 0$, i.e. i.e. no expansion or contraction on mixing

Examples of Ideal solutions

- Ethylchloride and ethyl bromide
- n–hexane and n–heptane
- CCl_4 and $SiCl_4$

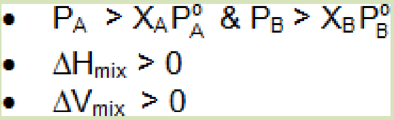
The solution which deviate from ideal behaviour are called **non *ideal solution*** or **real solutions** and they do not obey Raoult's law over entire range of composition.

It has been found that on increasing dilution, a non ideal solution tend to be ideal.
For non ideal solutions,

- $P_A \neq X_A \mathbf{P^0_A}, P_B{}^1 \neq X_B \mathbf{P^0_B}$ i.e, they do not obey Raoult's law
- $\Delta\ H_{mixing} \neq 0$,
- $\Delta\ V_{mixing} \neq 0$

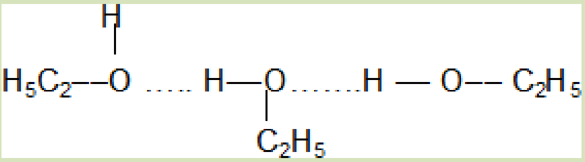
Here we may have two cases

Case 1:



- $P_A > X_A P^0_A$ & $P_B > X_B P^0_B$
- $\Delta H_{mix} > 0$
- $\Delta V_{mix} > 0$

Such a solution shows ***positive deviation*** from Raoult's Law and the observed boiling point of such solutions is found to be less than the calculated value. e.g. cyclohexane and ethanol. In ethanol the molecules are held together due to hydrogen bonding, when cyclohexane is added to ethanol the molecules of cyclohexane tend to occupy the space between ethanol molecules due to which some hydrogen bonds break due to which intermolecular attraction between cyclohexane and ethanol is reduced and hence show higher vapour pressure.



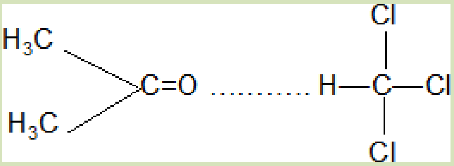
$$H_5C_2-\overset{\overset{H}{|}}{O}\cdots\cdots H-\underset{\underset{C_2H_5}{|}}{O}\cdots\cdots H-O-C_2H_5$$

Examples of solutions showing positive deviation:

- Acetone + Ethanol
- Acetone- Benzene
- Water+ Methanol
- Water+ Ethyanol

Case 2:

$$P_A < X_A P_A^0, \quad P_B < X_B P_B^0$$
$$\Delta H_{mix} < 0$$
$$\Delta V_{mix} < 0$$



Solutions of above type show negative deviation from Raoult’s law and their observed boiling point is found to be higher than the calculated value eg. When acetone and chloroform are mixed together a hydrogen bond is formed between them which increases inter molecular attraction between them and hence decreases the vapour pressure

Examples of solutions showing negative deviation:

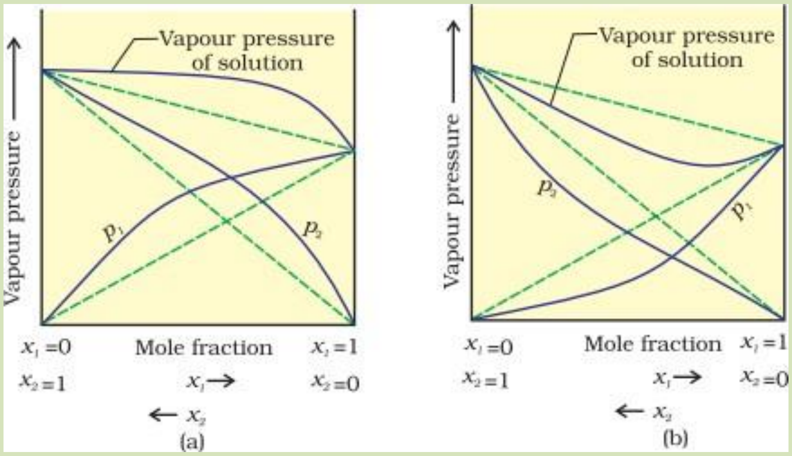
- Acetone + Aniline
- Chloroform+ Diethylether
- Chloroform+ Benzene
- Water+ HCl

(a) Condition for forming non-ideal solution showing positive deviation
Two liquids A & B on mixing form this type of solutions (Fig a)

- When A-B attractive force should be weaker than A-A and B-B attractive force.
- “A” and “B” have different shape, size and character.
- “A” and “B” escape easily showing higher vapour pressure than the expected value.

(b) Condition for forming non-ideal solution showing negative deviation
Two liquids A & B on mixing form this type of solutions (Fig b)

- When A-B attractive force should be greater than A-A and B-B attractive force.
- “A” and “B” have different shape, size and character.
- Escaping tendency of both “A” and “B” is lower showing lower vapour pressure than expected ideally.



Thermodynamics of mixing (see class notes)

Gibbs Duhem equation (see class notes)

Partial miscibility of liquids: Critical solution temperature

Some liquid pairs do not give homogeneous Solutions at all compositions. Such liquid pairs are said to be partially miscible liquids. phenol-water, ether-water, aniline-water Etc. Two solutions of partially miscible liquids, which are in equilibrium are called **conjugated Solutions** at a particular temperature. The two layers of a conjugated solutions become completely miscible at a certain temperature whose value depends upon the nature of the two liquids.

“**The temperature at which two partially miscible liquids become completely miscible at all proportions is called the Critical Solution Temperature (CST) or Mutual Solubility Temperature (MST) or consulate temperature of the system**”

When the critical solution temperature is lower than the room temperature, it is known as Lower Critical Solution Temperature which may be achieved by lowering the temperature of the system. On the other hand, when the critical solution temperature is higher than the room temperature, it is known as Upper Critical Solution Temperature which may be achieved by raising the temperature of the system.

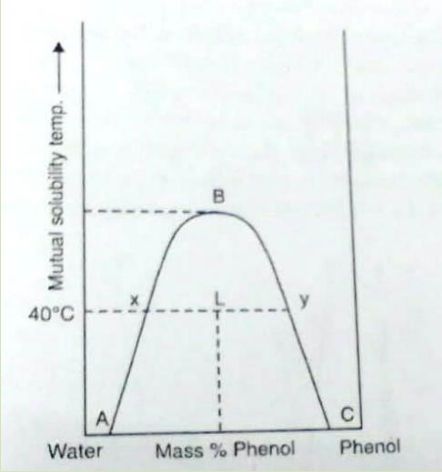
Depending upon the Critical Solution Temperature, partially miscible systems are categorized into three classes.

1. **Type I**: Partially miscible systems with Upper critical solution temperature (UCST), e.g.: phenol- water system
2. **Type II**: Partially miscible systems with Lower critical solution temperature (LCST), e.g.: triethylamine-water system
3. **Type III**: Partially miscible systems with Upper CST and Lower CST, e.g.: nicotinewater system

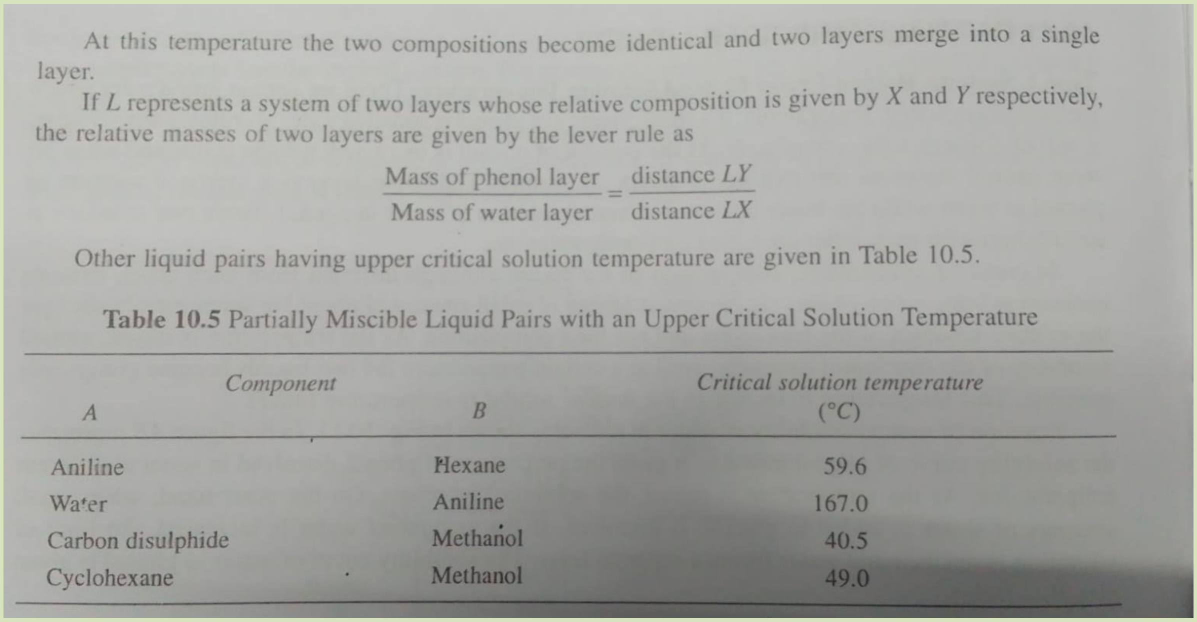
Type I: Partially miscible systems with Upper critical solution temperature

Variation of mutual solubility of water in phenol is shown in fig. below. In the figure AB represents the solubility curve of phenol in water. It gives the % of phenol in water at different temperatures. As the temperature is raised, the solubility increases. On the other hand, when a small amount of water is added to phenol, it dissolves. If the amount of water is increased, the limit of saturation is reached and water forms a separate layer. The solubility curve of water in phenol is given by CB.

At a temperature (say 40°C), point x represents the composition of phenol dissolved in water and point y represents the composition of water in phenol. Thus at a point between x and y completely miscible and homogeneous solutions will result. Between x and y all mixtures yield two layers of compositions x and y, while a point on the left of x or the right of y will correspond to a homogeneous solution. ABC is thus a boundary between homogeneous and heterogeneous phases.



Any point lying on the curve corresponds to the coexistence of two liquid phases, and the area outside the curve represents a single-layer homogeneous solution. The temperature (66 °C) corresponding to the maximum in the curve (point B, having composition 33 % phenol by mass) at and above which two liquids become completely miscible in all proportions is called Upper CST.



At this temperature the two compositions become identical and two layers merge into a single layer.

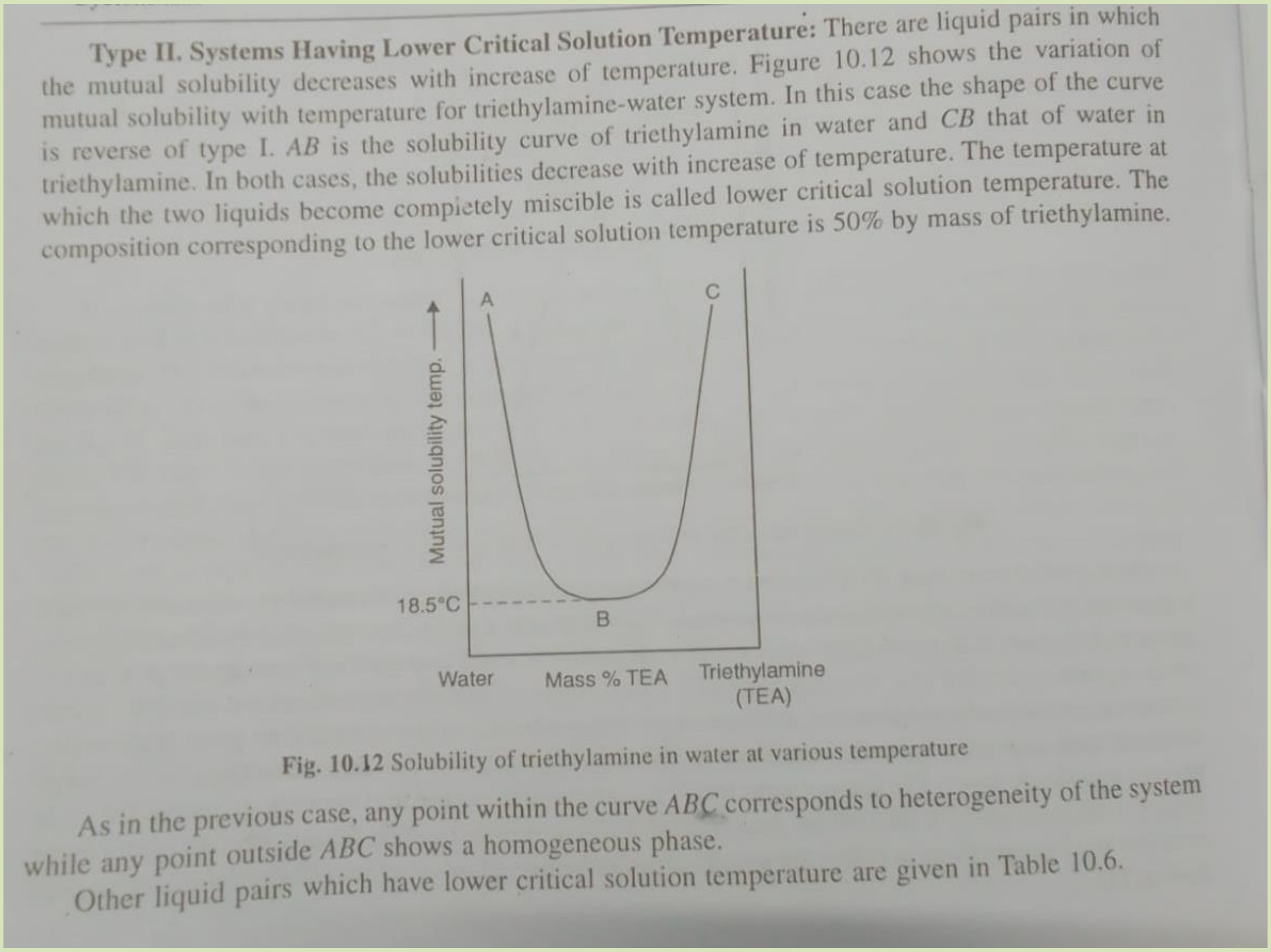
If L represents a system of two layers whose relative composition is given by X and Y respectively, the relative masses of two layers are given by the lever rule as

$$\frac{\text{Mass of phenol layer}}{\text{Mass of water layer}} = \frac{\text{distance } LY}{\text{distance } LX}$$

Other liquid pairs having upper critical solution temperature are given in Table 10.5.

Table 10.5 Partially Miscible Liquid Pairs with an Upper Critical Solution Temperature

Component *A*	*B*	*Critical solution temperature* (°C)
Aniline	Hexane	59.6
Water	Aniline	167.0
Carbon disulphide	Methanol	40.5
Cyclohexane	Methanol	49.0



Type II. Systems Having Lower Critical Solution Temperature: There are liquid pairs in which the mutual solubility decreases with increase of temperature. Figure 10.12 shows the variation of mutual solubility with temperature for triethylamine-water system. In this case the shape of the curve is reverse of type I. AB is the solubility curve of triethylamine in water and CB that of water in triethylamine. In both cases, the solubilities decrease with increase of temperature. The temperature at which the two liquids become completely miscible is called lower critical solution temperature. The composition corresponding to the lower critical solution temperature is 50% by mass of triethylamine.

Fig. 10.12 Solubility of triethylamine in water at various temperature

As in the previous case, any point within the curve ABC corresponds to heterogeneity of the system while any point outside ABC shows a homogeneous phase.

Other liquid pairs which have lower critical solution temperature are given in Table 10.6.

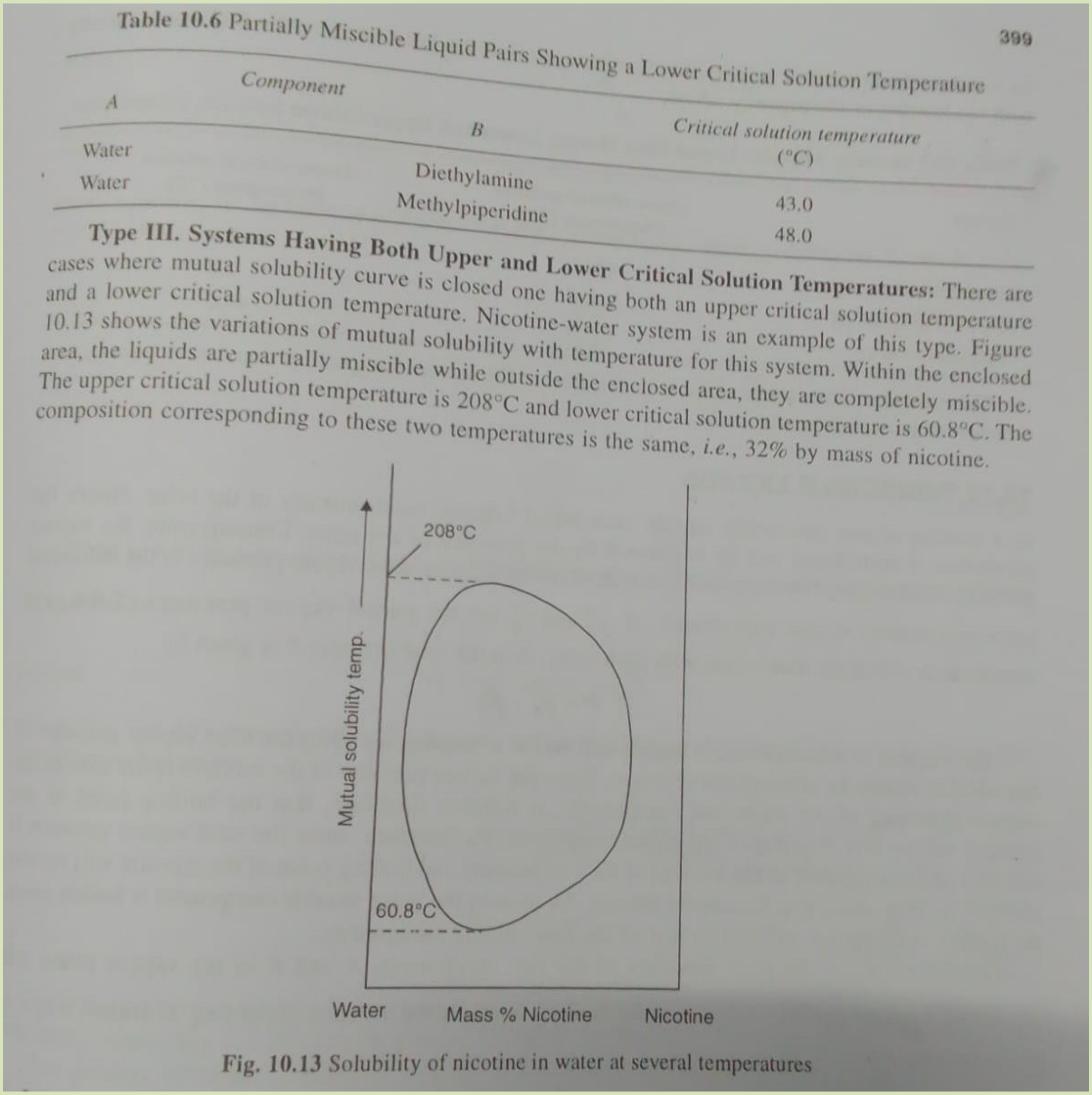


Table 10.6 Partially Miscible Liquid Pairs Showing a Lower Critical Solution Temperature

Component *A*	*B*	*Critical solution temperature (°C)*
Water	Diethylamine	43.0
Water	Methylpiperidine	48.0

Type III. Systems Having Both Upper and Lower Critical Solution Temperatures: There are cases where mutual solubility curve is closed one having both an upper critical solution temperature and a lower critical solution temperature. Nicotine-water system is an example of this type. Figure 10.13 shows the variations of mutual solubility with temperature for this system. Within the enclosed area, the liquids are partially miscible while outside the enclosed area, they are completely miscible. The upper critical solution temperature is 208°C and lower critical solution temperature is 60.8°C. The composition corresponding to these two temperatures is the same, *i.e.*, 32% by mass of nicotine.

Fig. 10.13 Solubility of nicotine in water at several temperatures

Effect of impurity on partial miscibility of liquids

- If an impurity is soluble in one of the two liquids, the CST of the system increases. Eg., a conc. of 0.1 M naphthalene per dm^3 of water raises the CST of phenol-water system by 20 ^{o}C. This increase is due the salting out of the water.
- When the added substance dissolves in both the liquids, the CST is lowere due to negative salting out effect. Eg. Addition of succinic acid in phenol-water system.

AZEOTROPES:

Azeotropes are defined as a mixture of two liquids which has a constant composition in liquid and vapour phase at all temperatures. Azeotropes can't be separated by fractional distillation, as the composition of vapour phase remains same after boiling. Because of uniform composition azeotropes are also known as Constant Boiling Mixtures.

There are two types of Azeotropes:

- Maximum Boiling Azeotrope
- Minimum Boiling Azeotrope

1. Maximum Boiling Azeotrope: Maximum Boiling Azeotrope is formed when we mix two non-ideal solutions at some specific composition, showing large negative deviation from Raoult's law.
   Examples:
   - Nitric Acid (HNO_3) (68%) and water (32%) form maximum boiling azeotrope at boiling temperature of 393.5 K
   - Hydrochloric Acid (HCl) (20.24%) and water form maximum boiling azeotrope at boiling temperature of 373 K
2. Minimum Boiling Azeotrope: Minimum Boiling Azeotrope is formed when we mix two non-ideal solutions at some specific composition, which shows large positive deviation from Raoult's Law.
   Example: Ethanol (95.5 %) and water (4.5 %) form minimum boiling azeotrope at boiling temperature of 351.5 K.

Immiscible liquids

For two immiscible liquids, $\frac{w_1}{w_2} = \frac{p_1^0 M_1}{p_2^0 M_2}$ (For derivation, check class notes)

DISTILLATION

Purification of Liquid Organic Compounds

Distillation is the process of separating the component or substances from a liquid mixture by selective evaporation and condensation. Distillation is the most basic method used for the purification of liquids and for the separation of liquid mixtures. Distillation involves the heating of a liquid to boiling and then collecting their vapours to condense them in liquid state.

By this method,

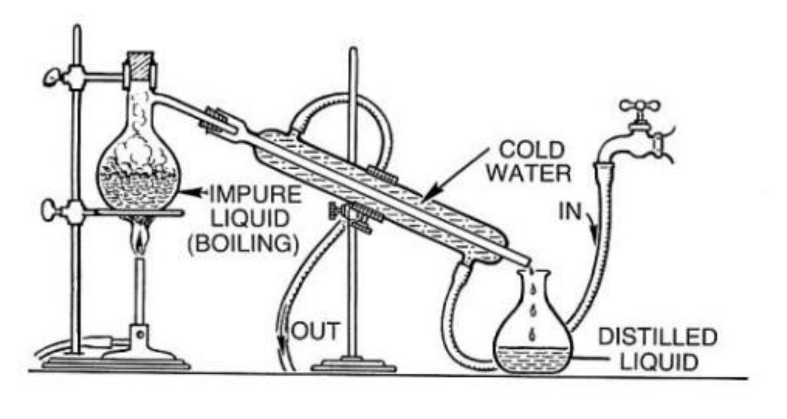
- Separation of the liquids of the mixture, having a few degrees different boiling points,
- Separation of a liquid from non-volatile components,
- Purification of the liquid is carried out

Distillation is mainly applied in 6 different form according to the nature of the substance to be purified or removed.

1. Simple Distillation
2. Fractional Distillation
3. Steam Distillation
4. Vacuum Distillation
5. Molecular Distillation
6. Fractional Distillation Under Reduced Pressure

1.Simple Distillation

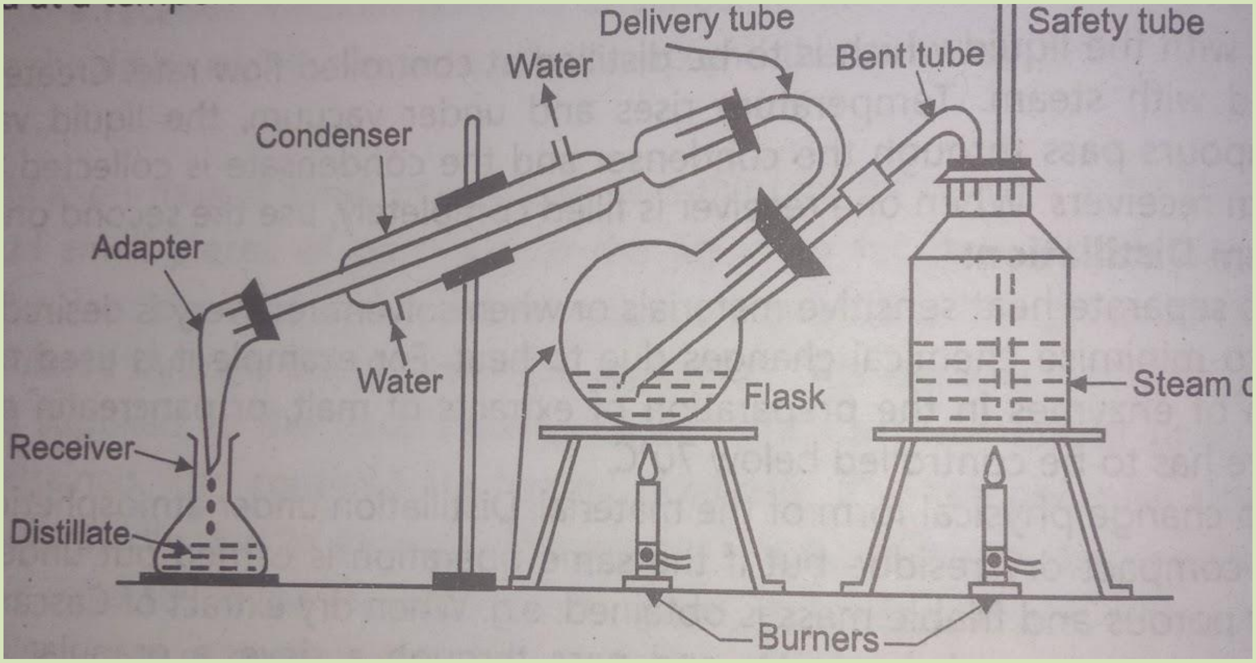
Distillation of the substances in simple structure, that are readily volatile and resistant to their own boiling heat, can be carried out under ordinary pressure . For example; hydrocarbons, alcohols, esters, small molecule fatty acids, amines are purified by this method. Simple distillation is a procedure by which two liquids with different boiling points can be separated. Simple distillation (the procedure outlined below) can be used effectively to separate liquids that have at least 80℃ difference in their boiling points. As the liquid being distilled is heated, the vapors that form will be richest in the component of the mixture that boils at the lowest temperature. Purified compounds will boil, and thus turn into vapors, over a relatively small temperature range (2 or 3°C); by carefully watching the temperature in the distillation flask, it is possible to affect a reasonably good separation. As distillation progresses, the concentration of the lowest boiling component will steadily decrease. Eventually the temperature within the apparatus will begin to change; a pure compound is no longer being distilled. The temperature will continue to increase until the boiling point of the nextlowest-boiling compound is approached. When the temperature again stabilizes, another pure fraction of the distillate can be collected. This fraction of distillate will be primarily the compound that boils at the second lowest temperature. This process can be repeated until all the fractions of the original mixture have been separated.



2. Steam Distillation

Steam distillation is a separation process used to purify or isolate temperature sensitive materials, like natural aromatic compounds. Steam or water is added to the distillationapparatus, lowering the boiling pointsof the compounds. These compounds should be immiscible with water. The goal is to heat and separate the components at temperatures below their decomposition point. The advantage of steam distillation over simple distillation is that the lower boiling point reduces decomposition of temperature-sensitive compounds. Steam distillation is useful for the purification of organic compounds, although vacuum distillation is more common. When organics are distilled, the vapor is condensed. Because water and organics tend to be immiscible, the resulting liquid generally consists of two phases: water and the organic distillate.

Steam distillation is the preferred method used to isolate essential oils. It is also used for "steam stripping" in petroleum refineries and to separate commercially important organic compounds, such as fatty acids.



Nernst distribution law

When two immiscible solvents A and B taken in a beaker, they form separate layers. Now a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from B to A. finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.

$$\frac{Concentration\ of\ X\ in\ A}{Concentration\ of\ X\ in\ B} = a\ constant\ \ldots\ldots\ldots\ldots(1)$$

Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's Distribution law or Nernst's Partition law or simply Distribution law or Partition law. It states that, " if a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents."

$$\frac{Concentration\ of\ X\ in\ A}{Concentration\ of\ X\ in\ B} = K_D\ \ldots\ldots\ldots\ldots(2)$$

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B, Nernst's Distribution law can be expressed as

$$\frac{C_1}{C_2} = K_D \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

The constant K_D(or simply K) is called the distribution coefficient or Partition coefficient or Distribution ratio.

Applications of the Nernst Distribution law:

1. Study of Association of a solute
2. Study of Dissociation of a solute
3. Distribution indicators
4. Study of complex ions
5. Solvent extraction: The most important application of the distribution law is in the process of extraction, in the laboratory as well as in industry

Solvent extraction

Solvent extraction, sometimes called liquid-liquid extraction, involves the selective transfer of a substance from one liquid phase to another. Usually, an aqueous solution of the sample is extracted with an immiscible organic solvent. For example, if an aqueous solution of iodine and sodium chloride is shaken with carbon tetrachloride, and the liquids allowed to separate, most of the iodine will be transferred to the carbon tetrachloride layer, whilst the sodium chloride will remain in the aqueous layer. The extraction of a solute in this manner is governed by the Nernst partition or distribution law which states that "at equilibrium, a given solute will always be distributed between two essentially immiscible liquids in the same proportions”. Thus, for solute A distributing between an aqueous and an organic solvent

$$[\mathrm{A}]_{\mathrm{o}}/[\mathrm{A}]_{\mathrm{aq}} = K_{\mathrm{D}} \quad \text{-----------} \quad (1)$$

K_D is known as the equilibrium distribution or partition coefficient which is independent of total solute concentration. It should be noted that constant temperature and pressure are assumed, and that A must exist in exactly the same form in both phases. Equilibrium is established when the chemical potentials (free energies) of the solute in the two phases are equal and is usually achieved within a few minutes by vigorous shaking. The value of K_D is a reflection of the relative solubilities of the solute in the two phases.

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