VIVEKANANDA COLLEGE, THAKURPUKUR

NAAC Accredited Grade—A

STUDY MATERIAL

Subject : Physical Chemistry

Course Title : Applications of Thermodynamics II

Topic : **Phase Equilibrium- Discussion on** Binary solutions: Liquid vapour equilibrium for two component systems, Ideal solutions at fixed temperature and pressure, Duhem - Margules equation, Henry's law, Konowaloff's rule, Positive and Negative deviations from ideal system, Boiling pt.-composition diagrams, Azeotropic solution, Three component systems: Water-chloform-acetic acid system, triangular plot.

Paper : Physical Chemistry **– 3 (CODE: CEMA-CC-4-9-TH)**

Semester : 4th Semester

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Binary Solution:

Liquid vapour equilibrium for two component systems of Ideal solution:

When a binary liquid mixture remains in equilibrium with its vapour at a given temperature and pressure, then the chemical potential of each constituent must be the same in both the phases.

Therefore, $\mu_i\,(l) = \mu_i\,(vap)$

From the study of the vapour pressure of solutions of non-volatile solutes, Francoise Marie Raoult first established that the vapour pressure of the solution (p_i) is equal to the vapour pressure of the pure solvent ((p_i^o) multiplied by the mole fraction (xi) of the solvent in the solution at a given temperature. This is known as **Raoult's Law**. This law gives satisfactory result when dilute solutions are used. If the solutes be volatile in nature, the the above law holds good provided the components behave ideally. So, if a binary solution behaves ideally, then for the binary solution we can write, $p_1 = x_1 .\, p_1^o$; where the suffix 1 is used for the solvent and 2 for the solute in the case binary solution.

$$\mathbf{p_1 = x_1 .\, p_1^o}\ (\mathbf{p_1^o} \text{ is the vapour pressure of the pure solvent})$$

Let a binary solution or a mixture consists of component 1 and component 2 and also the mixture is regarded as ideal when the escaping tendency from the liquid state to the vapour state for any one of them is not influenced by the presence of the other. This implies that in the liquid state, the interaction between the molecules of 1 and 1, is the same as that for 1 and 2 or between 2 and 2. Under this condition, the partial pressures of any of the components would follow Raoult's law.

Therefore, $\mu_1\,(l) = \mu_1\,(vap)$.

But, $\mu_1\,(vap) = \mu_1^o\,(vap) + RT \ln (p_1 / p^o)$; where $p^o = 1$ atm

So, $\mu_1\,(l) = \mu_1^o\,(vap) + RT \ln (p_1 / p^o)$

$= \mu_1^o\,(vap) + RT \ln (x_1 .\, p_1^o / p^o)$

$= \mu_1^o\,(vap) + RT \ln (.\, p_1^o / p^o)$

$= \mu_1^o\,(vap) + RT \ln (p_1^o / p^o) + RT \ln x_1$

$= \mu_1^*(l) + RT \ln x_1$

$d\mu_1 (l) = RT.\ dlnx_1$.

From Gibbs – Duhem relations for the binary solutions, we can write,

$n_1\ d\mu_1 + n_2\ d\mu_2 = 0$;

or $x_1.\ d\mu_1 + x_2.\ d\ \mu_2 = 0$

or, $d\mu_{2\ n} = -\ (x_1/\ x_2).\ d\ \mu_1$

$= -(x_1/\ x_2).\ RT.\ dlnx_1$

$= -(\ x_1/\ x_2).\ RT\ dx_1\ /\ x_1$

$= RT.\ dlnx_2$

Therefore, $\mu_2 = RT.\ lnx_2$ + constant z

When $x_2 = 1$; then $\mu_2 = \mu_2^o + RT.\ lnx_2$

Thus, the expression of chemical potential for the volatile solute is similar to that for the solvent or the component1. Thus, $p_2 = x_2.\ p_2^o$. Therefore, for an ideal mixture of several components, $p_i = x_i.\ p_i^o$

Variation of Vapour pressure of binary liquid mixture with liquid phase (ideal solutions) and vapour phase composition:

Consider a liquid pair A and B which are **volatile**, **completely miscible** and **form an ideal mixture** having mole fractions x_A and x_B. Consider also the vapour pressures of them are P^o_A and P^o_B in their respective pure state. If p_A and p_B are are the partial vapour pressures of the liquid mixture or solution, then as per Raoult's law:

$p_A = x_A.\ P^o_A$ and $p_B = x_B.\ P^o_B$

Thus, total vapour pressure of the liquid mixture or solution, $P = p_A + p_B = x_A.\ P^o_A + x_B.\ P^o_B$;

$P = (1 - x_B).\ P^o_A + x_B.\ P^o_B = P^o_A + x_B.\ (P^o_B - P^o_A)$

$\therefore P = P^o_A + (P^o_B - P^o_A).\ x_B$ ....(3)

Thus, the plot of vapour pressure curve for the liquid mixture or solution against either of mole fraction of the liquid is linear and is given by

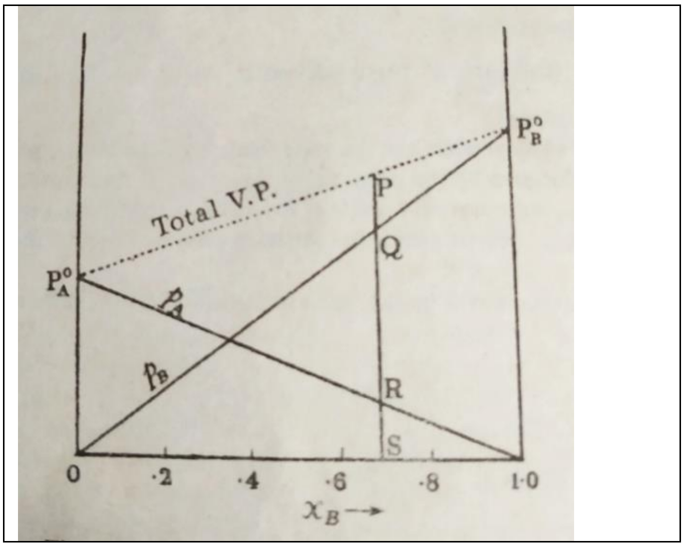


Figure 1

In the Figure 1, solid lines represent partial pressure of A (p_A) and partial pressure of B (p_B) and dashed line indicates the total vapour pressure of the liquid mixture or the solution. When $x_B = 1$, P becomes P^o_B and $x_B = 0$, then total vapour pressure = P^o_A.At certain composition S, the total vapour pressure SP = SR + SQ.

Equation (3) gives the relation vapour pressure of the solution or the liquid mixture. But at equilibrium, the liquid phase and the vapour phase compositions are not the same. Suppose q_B be the compositin of B in terms of mole fraction the vapour phase.

Then, $q_B = p_B / P = p_B / (p_A + p_B) = x_B . P^o_B / [P^o_A + (P^o_B - P^o_A). x_B]$ ……….(4)

Thus, x_B can be expressed in terms of q_B as given below:

$x_B = q_B . P^o_A / [P^o_B + (P^o_A - P^o_B). q_B$ …………….(5)

From equation (4) we can write, $q_B = x_B . P^o_B /(x_A . P^o_A + x_B . P^o_B)$

Or, $1 / q_B = 1 + x_A . P^o_A / x_B . P^o_B$

Or, $[(q_A + q_B) / q_B] - 1 = (x_A / x_B). (P^o_A / P^o_B)$

Or, $q_A / q_B = = (x_A / x_B). (P^o_A / P^o_B)$

When $P^o_B > P^oA$, then $q_A / q_B < x_A / x_B$

Or, $1 / q_B < 1 / x_B$

Or, $q_B > x_B$

Thus, when $P^o_B > P^o_A$, then $q_B > x_B$ which implies that the more volatile constituent is always present in greater percentage in vapour state than that in the liquid state.

With the values of x_B, the vapour composition diagram can be plotted as

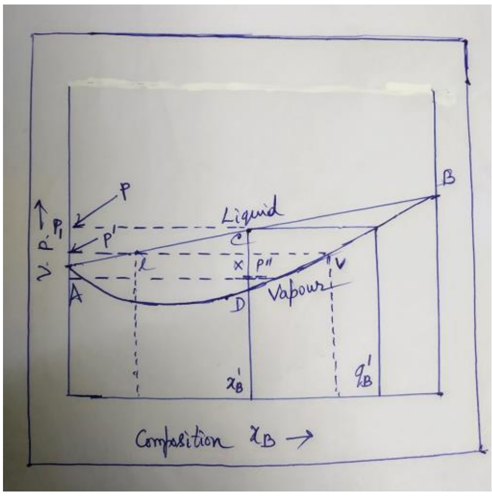


Figure 2

The vapour- composition curve is always found to be below the liquid – composition curve when plotted against pressure. If x'_B be the mole fraction of B in the liquid phase, then correspondingly q'_B will be the mole fraction of B in the vapour phase.at the pressure P1. It is obvious that the vapour will be richer in the more volatile component. Completely miscible liquid pairs in equilibrium with vapour are systems of two phases. Hence applying phase rule, we get F = 2-2 +2 = 2. Systems will be bivariant. Therefore, if temperature is fixed, then the pressure and composition would vary together, i.e. each composition will have definite vapour pressure**.** In **Figure 2** the upper line shows the liquid phase composition and the lower line is for the vapour phase composition. For the liquid phase, X axis shows the mole fraction of the constituent B i.e. (x'_B) in the liquid phase and q'_B gives the composition of the vapour phase in terms of mole fraction of B.

In the case of pure liquid at any given temperature if the superincumbent pressure is greater than the vapour pressure of the liquid, only liquid phase exists. Liquid remains in equilibrium with the vapour when the superincumbent pressure becomes equal to the vapour pressure of the liquid. If superincumbent pressure of the liquid is made infinitesimally less than the vapour pressure of the liquid, then the liquid phase disappears completely. When the pressure over the liquid mixture having mole fraction x''_B of the constituent B is made greater than the pressure at C, i.e. vapour pressure of the liquid mixture, then only the liquid phase exists. On lowering the pressure as it comes to Pvap, only, tit forms bubble and liquid remains in equilibrium with the vapour phase. So, the line ACB is also called **the bubble point line**.

When the pressure is further lowered to P′, the entire liquid phase does not disappear, rather both the liquid undergo vaporization at unequal rate – the more volatile liquid having higher vapour pressure vapourises to give higher percentage in the vapour phase. Thus, vapour phase becomes richer with the more volatile constituent B and the liquid phase becomes richer with less volatile component A. The intersection of the tie line cuts the liquid composition curve at l and the same tie line cuts the vapour phase composition curve at v respectively. Applying lever Rule, we get,

The amount of the liquid phase / The amount of the vapour phase = v-x/x-l

The area under ACBDA region shows liquid – vapour equilibrium.

Thermodynamic criteria of ideal solutions:

A solution is regarded as an ideal solution when each constituent obeys Raoult’s Law at any composition and temperature. Thermodynamic criteria of ideal solution:

i) The activity coefficient of each constituent is unity.

ii) $\Delta G_{mix} = \sum n_i(\mu_i - \mu^*) = RT\sum n_i \ln x_i = n. RT\sum x_i \ln x_i$, $\Delta G_{mix\ /mole} = RT\sum x_i \ln x_i$

iii) $\Delta S_{mix} = \partial / \partial T\ (\Delta G_{mix})_P = -nR. \sum x_i \ln x_i$

iv) $\Delta H_{mix\ /mole} = 0$;

v) $\Delta V_{mix\ /mole} = 0$;

This happens only when the constituents are of same molecular size, electronegativity difference is very small, valency is almost same and also have same crystal structure.

Vapour pressure composition relation of binary liquid mixture from thermodynamic consideration:

Let us consider a liquid mixture containing n_A and n_B moles A and B in equilibrium with its vapour having partial vapour pressures p_A and p_B respectively at T K. According to Gibbs – Duhem equation

$$n_A. d\mu_A + n_B. d\mu_B = 0$$

Dividing both sides by $(n_A + n_B)$, we get,

$x_A. d\mu_A + x_B. d\mu_B = 0$. ……………….(6)

where x_A and x_B are the mole fractions of the constituents A and B. Since the solution is always in equilibrium with its vapour, $\mu_A = \mu_B$ or, $d\mu_A = d\mu_B$

$\mu_A = \mu^o_A + RT \ln p_A$. (assuming the vapour behaves ideally and $(f_A = p_A)$
$d\mu_A = RT\ d\ln p_A$ and similarly $d\mu_B = RT\ d\ln p_B$

Thus, from equation (1), $x_A. RT\ d\ln p_A + x_B. RT\ d\ln p_B = 0$

$$\text{Or, } x_A / dx_A. RT\ d\ln p_A + x_B / dx_A. RT\ d\ln p_B = 0$$

Since, $dx_A = - dx_B$, therefore $x_A / dx_A. RT\ d\ln p_A - x_B / dx_B. RT\ d\ln p_B$

Or, $d\ln p_A / d\ln x_A = d\ln p_B / d\ln x_B$ ……………(7)

The equation (7) is called Duhem – Margules equation.

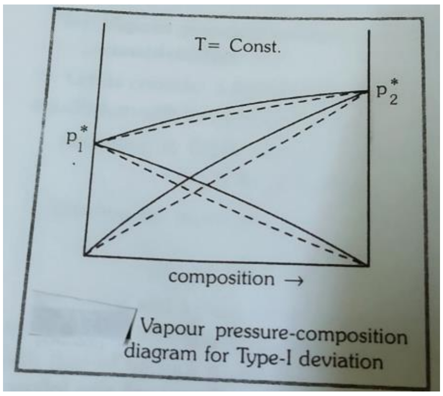
Let us consider component A obeys Raoult's law, $p_A = x_A. P^o_A$ or $\ln p_A = \ln x_A + \ln P^o_A$
Or, $d\ln p_A = d\ln x_A$

Or, $d\ln p_A / d\ln x_A = 1$

Therefore, $d\ln p_B / d\ln x_B = 1$

In real or non – ideal solutions, there is departure from Raoult's law.

Case I: These are the systems in which theo total vapour pressure is continuous and at any composition it is intermediate between the vapour pressure of the two pure components. Systems exhibiting such behavior are Found in water – methyl alcohol, benzene – toluene and carbon tetrachloride – benzene.



Type1-Figure 3

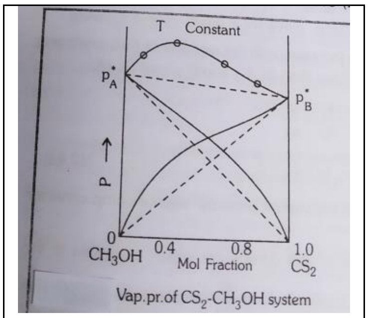
Case II: When one constituent A exhibits positive deviation from Raoult's law, then

$p_A > x_A . P^o_A$

or, $d\ln p_A / d\ln x_A > 1$

According to Duhem – Margules equation, $d\ln p_B / d\ln x_B > 1$

Thus, second constituent also exhibits positive deviation. Examples of solution exhibiting positive deviations are: Ethyl alcolhol- acetone, Toluene-carbon tetrachloride, Acetone-carbon disulfide etc.



Type II: Figure 4

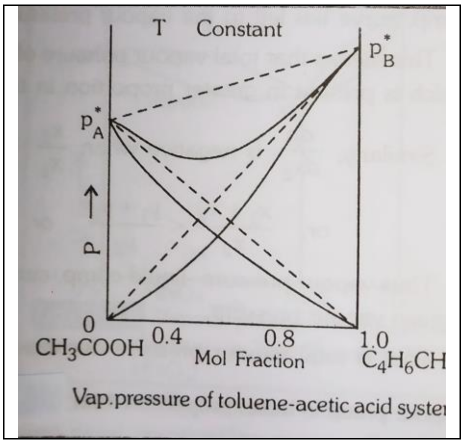
Case III: When one constituent A exhibits negative deviation from Raoult's law, then

$p_A < x_A . P^o_A$ and $p_B < x_B . P^o_B$

or, $d\ln p_A / d\ln x_A < 1$.

According to **Duhem – Margules equation**, $d\ln p_B / d\ln x_B < 1$

Thus, second constituent also exhibits negative deviation. Examples are: Acetone-chloroform, chloroform-ether, and chloroform-benzene etc.



Type III: Figure 5

<u>Explanation of positive deviations of TYPE -II:</u>

The positive deviations from the ideal behaviour or Raoult's law (**Figure 4**) indicate that the molecules have more tendency to escape from solution as compared to that for liquids. This is because that the intermolecular forces of attractions of A-B are weaker than that of A-A or B-B attractions e.g. consideration of a solution obtained by mixing ethyl alcohol and acetone. In pure ethyl alcohol, alcohol molecules are held together by intermolecular H bonding. When acetone is added into ethyl alcohol, the molecules of acetone tend to adjust themselves between alcohol molecules. Thus, in turn, some hydrogen bonds (relatively stronger) in ethyl alcohol break. The escaping tendency of alcohol and acetone molecules from solution increases. As a result, vapour pressure of the solution is more than that expected for an ideal solution.
Thus, ΔH_{mixing} becomes positive as energy is i) required to break the stronger intermolecular H bonds in ethyl alcohol; ii) ΔH_{mixing} is positive because molecules are held together less tightly.

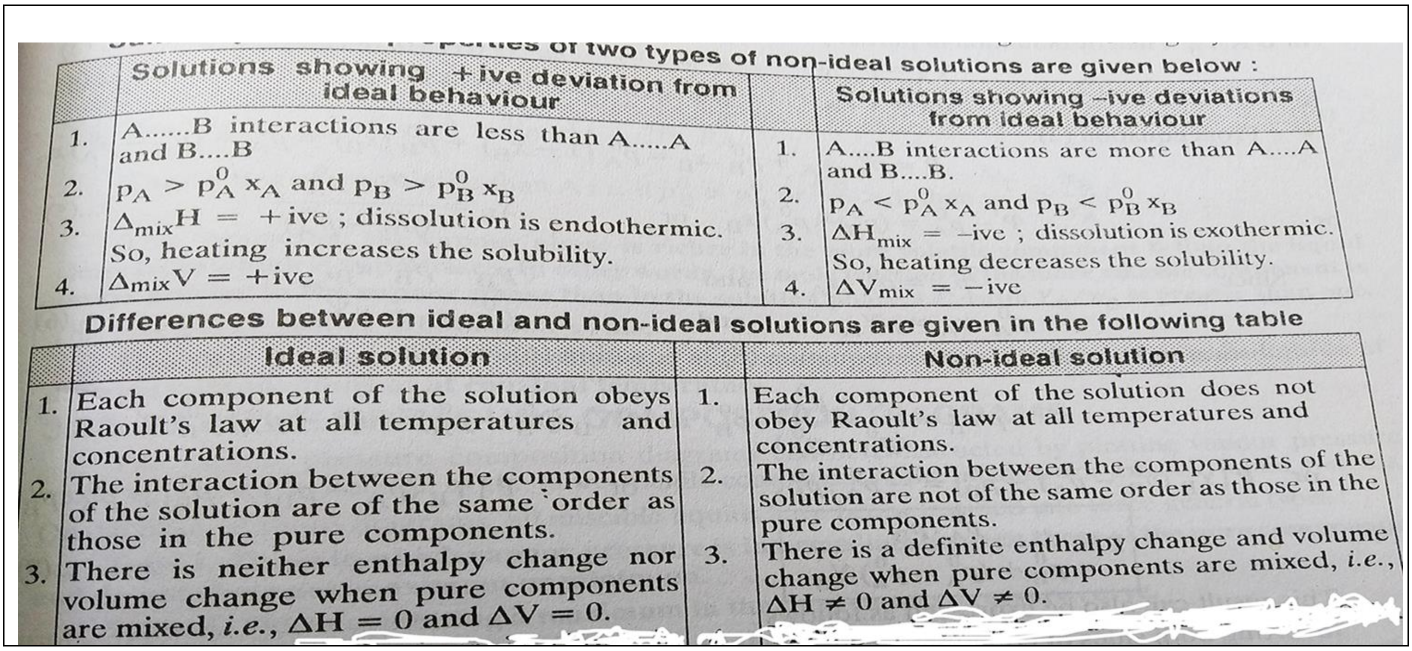
<u>Explanation of negative deviations of TYPE -III:</u>

From the **Figure 5**, it is clear that for any mole fraction, the total vapour pressure is less than the value expected on the basis of ideal behavior and the vapour pressure of the mixture curve dips to a minimum. Examples are: Examples are: Acetone-chloroform, chloroform-ether, and chloroform-benzene etc. The negative deviations from ideal behavior or Raoult's law indicate that the molecules have lesser tendency to escape from a solution than that from pure liquids. This is beca. use the intermolecular attractive forces between the molecules of A-B are stronger than those for either of the two pure liquids i.e. A-A and B-B. For example, consider a solution obtained by mixing water with sulphuric acid. In this solution, new attractive forces arise due to the inter-molecular hydrogen bonding shown below:

H_2O ……H– O– SO_2– O–H ….. ..OH_2

Due to this strong intermolecular H bonding, escaping tendency of molecules from the solution decreases and consequently vapour pressure of the solution is less than expected for an ideal solution. For this type of solution, **ΔH_{mixing} becomes negative due to increase of attractive forces and ΔV_{mixing} is negative as molecules are held together more tightly.**

Some main properties of two types of non-ideal solutions are given below:



perties of two types of non-ideal solutions are given below :

	Solutions showing +ive deviation from ideal behaviour		Solutions showing –ive deviations from ideal behaviour
1.	A......B interactions are less than A.....A and B....B	1.	A....B interactions are more than A....A and B....B.
2.	$p_A > p_A^0 x_A$ and $p_B > p_B^0 x_B$	2.	$p_A < p_A^0 x_A$ and $p_B < p_B^0 x_B$
3.	$\Delta_{mix}H = +$ive ; dissolution is endothermic. So, heating increases the solubility.	3.	$\Delta H_{mix} = -$ive ; dissolution is exothermic. So, heating decreases the solubility.
4.	$\Delta_{mix}V = +$ive	4.	$\Delta V_{mix} = -$ive

Differences between ideal and non-ideal solutions are given in the following table

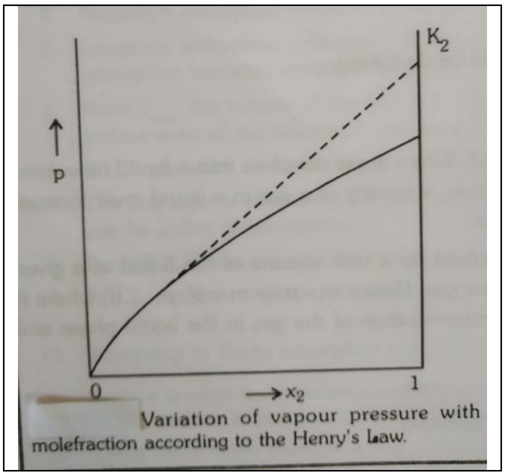
	Ideal solution		Non-ideal solution
1.	Each component of the solution obeys Raoult's law at all temperatures and concentrations.	1.	Each component of the solution does not obey Raoult's law at all temperatures and concentrations.
2.	The interaction between the components of the solution are of the same order as those in the pure components.	2.	The interaction between the components of the solution are not of the same order as those in the pure components.
3.	There is neither enthalpy change nor volume change when pure components are mixed, *i.e.*, $\Delta H = 0$ and $\Delta V = 0$.	3.	There is a definite enthalpy change and volume change when pure components are mixed, *i.e.*, $\Delta H \neq 0$ and $\Delta V \neq 0$.

[redacted]

HENRYS LAW:

Henry's law considers the solubility of a gas into liquid. When a gas dissolves into a liquid, its volume decreases. Hence, according to Le Chatelier's principle, solubility of a gas in a liquid must increase with the increase in pressure at a given temperature.
Henry's law states that mass (m) of a gas dissolved by a unit volume of the liquid at a given temperature is propotional to the pressure (P) of the gas. Hence $m_2 = k'. P_2$
Since m_2 is also proportional to mole fraction x2 in solution, we have, $x_2 = k. P_2$
Therefore, $P_2 = (1/k). x_2 = k_2 x_2$

Henry's law is valid when the gas does not react chemically with the solvent. Solubility of a gas in a liquid is in general an endothermic process as ΔS is negative. Exceptions are observed with liquid ammonia., molten silver. Solubility of a gas in water decreases in water in presence of electrolyte. Thus, concept of dilute real solution can be developed from Henry's law. If the vapour pressure of a solute obeys Henry's law, then then the chemical potential of the solute in solution be represented as



Variation of vapour pressure with molefraction according to the Henry's Law.

Figure 6

$\mu_{i\,(sol)} = \mu_{i(vap)} =$

$$= \mu^o_{i(vap)} + RT \ln (p_i/p^0)$$

$$= \mu^o_{i(vap)} + RT \ln (k_i x_i /p^0)$$

$$= \mu^o_{i(vap)} + RT \ln (k_i /p^0) + RT \ln x_i$$

$$= \mu^o_{i(sol)} + RT \ln x_i$$

Henry's law is valid when the solution is infinitely dilute. So, Henry's constant k_2 is obtained by extrapolating p vs x_2 plot for the ideal solution of $x_2 = 0$ and $x_2 = 1$ where $p = k_2$.

For the solute, $\mu_{2(l)} = \mu_{2(v)} = \mu^o_{2(v)} + RT \ln (p_2/p^0) = \mu^o_{2(v)} + RT \ln (k_2.x_2/p^0)$

$d\mu_{2(l)} = RT\, d\ln x_2 = RT\, dx_2/ x_2$

From, Gibbs- Duhem equation: $n_1 d\mu_1 + n_2 d\mu_2$

Or, $x_1\, d\mu_1 + x_2\, d\mu_2 = 0$

Or, $x_1\, d\mu_1 + RT\, dx_2 = 0$

Or, $d\mu_1 = RT\, dx_1/ x_1$

or, $\mu_1 = \mu^o_1 + RT \ln x_1$

Thus, Raoult's law can be derived from Henry's law.

Konowaloff's Rule:

The effect of change of liquid phase composition on the variation of vapour pressure of the solution can be understood from thermodynamic considerations:

Let x_A and x_B be the mole fractions of the constituents A and B in the liquid phase and y_A and y_B their mole fractions of the constituents A and B in the vapour phase.

Total vapour pressure $P = p_A + p_B$

$\because \quad dP/dx_B = dp_A/dx_B + dp_B/dx_B = - dp_A/dx_A + dp_B/dx_B$ …………(8)

From Gibbs – Margules equation,

$(dp_A / p_A) / (dx_A / x_A) = (dp_B / p_B) / (dx_B / x_B)$

Or, $dp_A / dx_A = (x_B . p_A / x_A . p_B) . (dp_B / dx_B)$

Putting the value of dp_A / dx_A in equation (8), we get

$dP / dx_B = (dp_B / dx_B) [1 - x_B .]$

$= (dp_B / dx_B) [1 - x_B . y_A / x_A . y_B]$

Now, (dp_B / dx_B) is always positive, in order to become dP / dx_B positive if $(x_B . y_A / x_A . y_B) < 1$

Or, $x_B / x_A < y_B / y_A$

Or, $(x_A / x_B) > y_A / y_B$

Or, $(x_A + x_B) / x_B > (y_A + y_B) / y_B$

Or, $1/x_B > 1/y_B$

Or, $x_B < y_B$

So long dp/dx_B = + ve, mole fraction of the second constituent (B) in the liquid phase is than that for the constituent (B) in the vapour phase and similarly $xA > yB$ i.e. vapour pressure-liquid comp. curve lies left to the vapour pressure -vapour comp. curve for a given vapour phase.

This means that the total vapour pressure of the solution increases with the addition of that constituent which is present in greater proportion in the vapour phase than in the liquid phase. **……………….(A)**

If, dP / dx_B is negative $(x_B . y_A / x_A . y_B) > 1$

Or, $(x_B / x_A) > y_B / y_A$

Or, $(x_A / x_B) < y_A / y_B$

Or, $1/x_B < 1/y_B$

Or, $x_B > y_B$

Thus, vapour pressure-liquid comp. curve lies right to the vapour pressure- vapour comp. curve for a given vapour pressure.

Therefore, total vapour pressure decreases on addition of that constituent which is present in the vapour phase in lesser proportion than in the liquid phase. **………………………………..(B).**

So, long dP/dx_B remains (-ve) mole fraction of the second constituent in the liquid phase is less than that in the vapour phase.

At the maxima or minima in the vapour pressure- composition diagram,
$dP/dx_B = 0$ or $dP/dx_A = 0$

So, $x_A / x_B = y_A / y_B$

Hence, maxima or minima in the vapour pressure-composition curve is observed when both the liquid and the vapour phase have same composition. Under this condition, liquid mixture have the same composition as that of the vapour phase, is called ***azeotrope mixture***.

Generalisation of **(A)** and **(B)** are called **Konowaloff's Rule.**

In type I the vapour -composition and liquid-composition curves are both continuous and at all concentrations, the composition in the two phases are different. A liquid mixture of composition x will be in equilibrium with vapour mixture of composition x'. Obviously, the vapour will be richer in the component which is more volatile.

In type II and III, the vapour- composition curve touches the liquid – composition curve at the maximum or minimum points. This means that the liquid mixture – composition will be in equilibrium with the vapoure phase-composition corresponding to maximum or minimum point. Thus, the diagrams of **II & III** are made up of two portions namely: i) one between the pure component A and a solution of maximum or minimum vapour pressure and (ii) the other pure component B and the solution vapour of maximum or minimum pressure.

In type II liquid mixtures having composition between A and O will have vapour rich in B than that in solution i.e. a liquid composition x will be in equilibrium with vapour- composition x'. But for the liquid mixtures having composition between O and B will have vapour rich in A as compared to that in solution. So, liquid composition y will be in equilibrium with vapour composition y'.
In type III, liquid mixtures having composition between A and O will have solution rich as compared to the vapour phase and it is indicated by x and x'. But between B and O, vapour compostion will be richer than the solution composition as indicated by y' and y.

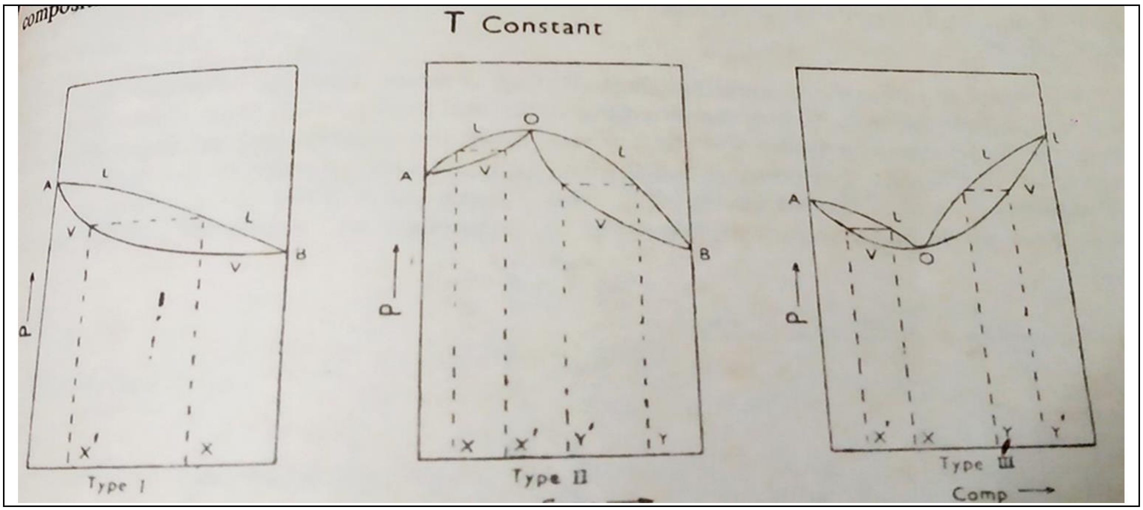
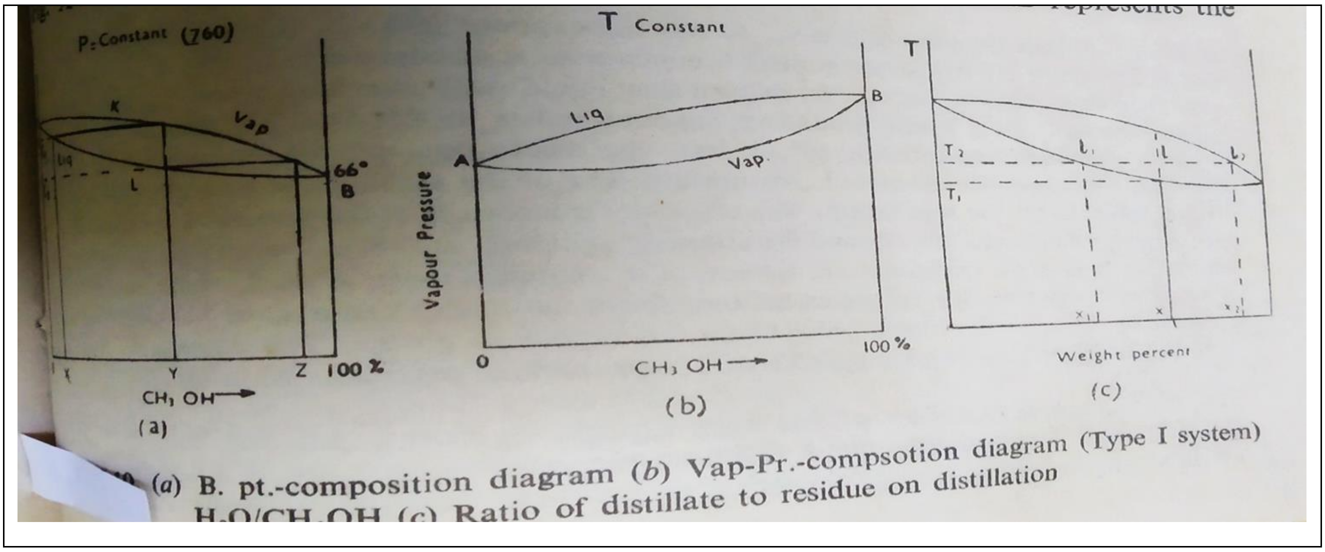


Figure 7: Vapour pressure-composition curve for Type – I, II, III (Boiling Point-Composition Diagrams)

The vapour pressure of a mixture of two liquids changes with the variation in composition. The higher the vapour pressure of a mixture, the lower will be its boiling point. Thus, a liquid mixture of **Type II**, which shows maximum vapour pressure at a particular composition will have a minimum boiling point compared to mixtures with any composition. In other words, the temperature-composition diagram will be the inverted in shape of vapour pressure-composition diagram. The boiling point-composition diagrams for all three types of liquid mixtures are shown below:



(*a*) B. pt.-composition diagram (*b*) Vap-Pr.-compsotion diagram (Type I system) H_2O/CH_3OH (*c*) Ratio of distillate to residue on distillation

Figure 8

In **Figure8**, ALB is the b.pt.-liquid -composition curve and AKB represents b.pt.-vapour-composition curve. A liquid mixture, having a composition x will boil at t_1 °C and the vapour in equilibrium with the liquid will have the composition y; the b.pt. decreases with increase in concentration of B. If this vapour be removed and condensed, the liquid will have the composition y. If this condensed liquid be boiled again, it will boil at t_2°C and the vapour which is in equilibrium, will have the composition z. On removing the vapour and condensing, a liquid of composition z will be obtained. On repeating this process of boiling and condensing, ultimately the pure component B will be obtained. In the residual liquids, the percentage of A component will increase gradually. Thus, the two liquids can be gradually separated from a mixture of Type I. The tedious process of successive evaporation and condensation is in practice is usually avoided by fractional distillation technique.

Boiling Point-Composition Diagram with no Maxima or Minima:

In practice distillation is conveniently carried out at constant pressure and at constant temperature. Therefore, if we examine the boiling point-composition diagram, then we see that the more component has a higher vapour pressure and hence lower boiling point. So, **Figure 8A** shows that at a constant temperature (below the boiling point), liquid phase is the most stable one. During fractional distillation, the solution at point **a** is allowed to evaporate (**a** →**b**). The vapour which is richer in benzene, is condensed (**b**→**c**) and then

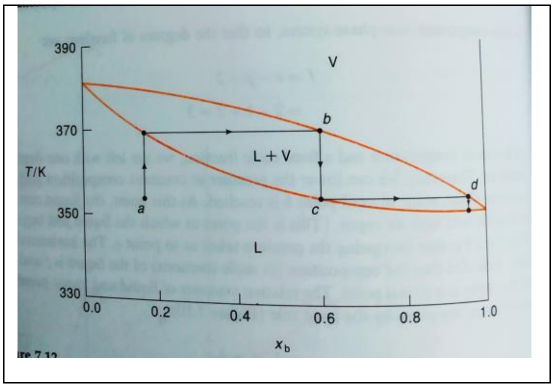
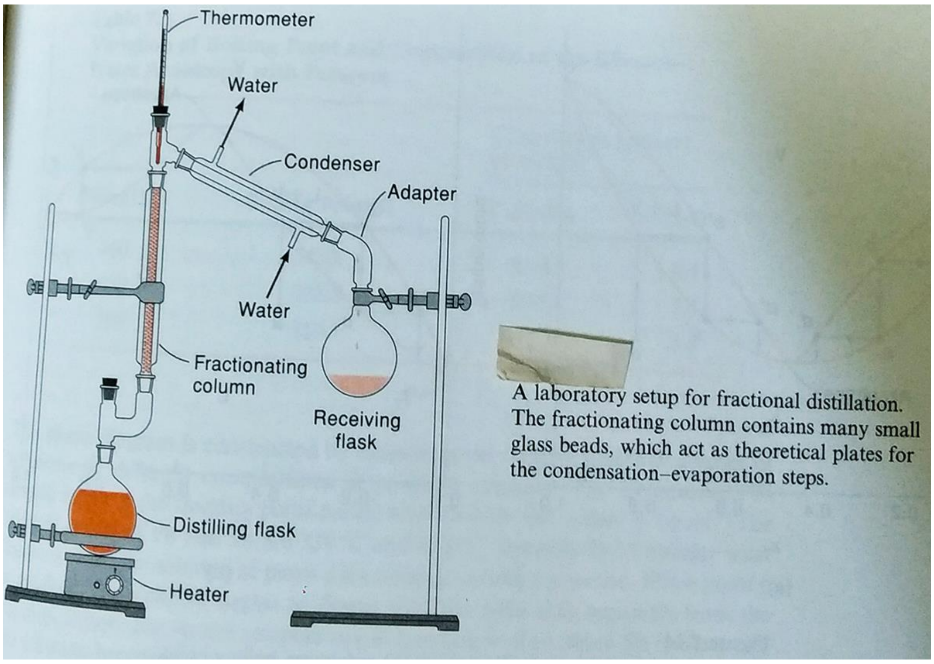


Figure 8A: **Boiling pt.-composition diagram of benzene-toluene.**

evaporated (**c→d**). Repeating the process, will eventually separate the two components completely. This procedure is called fractional distillation. Each evaporation - condensation step is called a theoretical plate.



A laboratory setup for fractional distillation. The fractionating column contains many small glass beads, which act as theoretical plates for the condensation–evaporation steps.

Figure 9

In the laboratory, chemists use an apparatus like that shown in **Figure 9** to separate volatile liquids. The round-bottom flask containing the benzene-toluene solution is allowed to fit with a long column packed with glass beads. When the solution boils, the vapour condenses on the beads of the lower part of the column and the liquid correspondingly falls back into the distilling flask. As time goes on, the beads gradually heat up, allowing the vapour to move upward slowly. Actually, the packing material gives the column many theoretical plates and causes the benzene-toluene mixture to flow continuously in the column throgh numerous vaporization-condensation steps. At each step, the composition of the vapour in the column will be richer in the more volatile or lower boiling point component. The vapour that rises to the top of the column is essentially pure benzene, which is then condensed and collected into the recei ving flask. Petroleum refineries are used to similar process for the crude oil. Actually, crude oil is a mixture of several compounds and by heating- condensing principle, the crude oil is used to pass through 80-meter-high column packed with hundreds of theoretical plates to obtain the desired petroleum fraction.

Boiling Point-Composition Diagram with Minima:

In this type of system, the vapour pressure reaches a maximum for a certain composition. Hence the corresponding boiling point-composition diagram must have minimum at the same composition. Since liquid phase is more stable below the boiling point, liquid composition curve lies below the vapour composition curve. Boiling point of liquid having higher vapour pressure at room temperature, is less than that of the other liquid. The boiling point-composition curve in the **Figure 10** can be described as two simple parts. One is between the liquid (A) and the azeotropic mixture and the other is between the liquid (B) and the azeotropic mixture. Fractional distillation of the liquid mixture having composition in the range AO results in the separation liquid (A) and the azeotropic mixture. Azeotropic mixture is obtained as the distillate while liquid (A) remains in the distilling flask.in the above **Figure 10. Further distillation of the azeotropic mixture is not possible as the composition of the azeotropic mixture remains same in the liquid as well as in the vapour phase. Therefore, an azeotropic mixture can be regarded as *<u>constant boiling mixture</u>*.** While the region OB yields pure liquid (B) as the residue and the azeotropic mixture as the distillate. In case of water-ethyl alcohol system azeotropic mixture contains 95.6 % ethyl alcohol having boiling point 78.1 ºC.

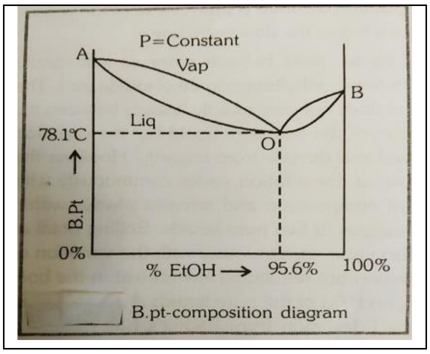


Figure 10

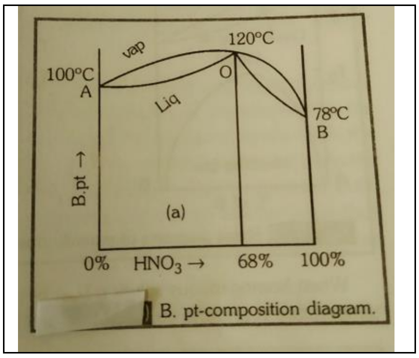


Figure 11

Boiling Point-Composition Diagram with Minima:

The b.pt.-composition curve **Figure 11** has the maxima and here also the curve has two parts- one between A and O and the other between O and B. In the case of H_2O-HNO_3 system, the azeotropic mixture contains 68 % HNO_3 with b.pt. at 120 ºC. When a dilute solution containing less than 68 % HNO_3 is distilled, the solution is separated into pure water and the azeotropic water being collected as distillate while azeotrope itself being collected as residue. Similarly, the OB part shows distillation of concentrated solution of HNO_3. Pure HNO_3 being collected as distillate and azeotrope as residue.

In case of azeotropic mixture, liquid phase and vapour phase both have the same composition. Applying this restriction in the case of Phase rule, we get, $F = C-P+2-1 = C - P + 1 = 2-2+1 = 1$ and at constant it becomes $F = 1-1 = 0$; i.e. at constant pressure azeotropic mixture will have definite boiling point. From this it seems that azeotrope behaves like a compound, but the following evidences suggest that it is a mixture and not a compound:

(i) The composition depends upon the pressure
(ii) The composition does not correspond to stoichiometric proportion of the components.
(iii) No spectroscopic evidence of formation of compound between the components is available.
(iv) Azeotropic mixture cannot be separated into pure components by distillation.

THHREE COMPONENT SYSTEMS

A three component (or ternary) system has F = C-P+2 = 3-P+2 = 5 - P. If P =1, there are four degrees of freedom. To make the two-dimensional plot, we must fix two variables say T and P. for a one phase system, the two variables will be taken as x_A and x_B, mole fractions of A and B. For multiphase systems, x_A and x_B. will be taken as mole fractions of A and B in the system. Once x_A and x_B are fixed, x_C is also fixed. Gibbs suggested the use of an equilateral-trangle plot, and this has become standard for ternary systems.

The triangular coordinate system is based on the following theorem. Let D be the arbitrary point inside a equilateral triangle in **Figure 12 (a)**.

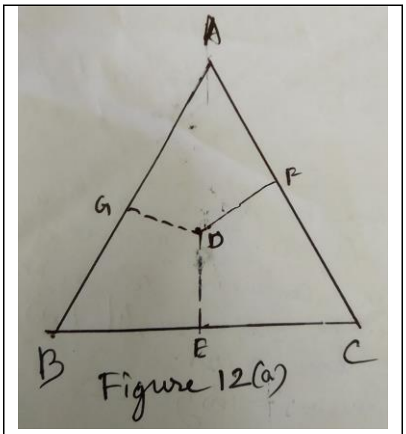


Figure 12(a)

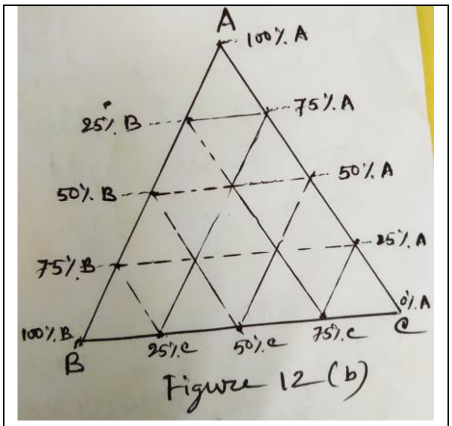


Figure 12 (b)

If perpendiculars are drawn from D to the sides of the triangle, the sum of these three lines is a constant which is equal to the triangle's height 'h'. If particulars are drawn from the point D to the sides of the triangle, then sum of these perpendiculars i.e. DE +DF+DG = h. We take the height 'h' =1, then, the lengths DE, DF, DG correspond to the mole fractions of components of A, B and C respectively. Thus, the perpendicular distance from point D to the side of the triangle opposite the vertex A i.e. DE represents the mole fraction x_A. Similar things are happening for the other components B and C. In the **Figure 12 (b)**

(i) Equally spaced lines have been drawn parallel to each side. The sides of the triangle represent the composition of different binary systems. So, AB represents the binary system (A+B). On the line AB, the overall mole fraction of the component C is constant and it is zero. The line AC represents the binary system (A+C) and the composition of the B component is zero. Similarly, side BC corresponds to the binary system (B+C) and the composition of the component A is zero. On lines parallel to the AC, the composition of B is constant and on lines parallel to BC, the concentration A is constant.

(ii) The vertices of A, B and C of the equilateral triangle represents three pure components.

(iii) Any point within the equilateral triangle will represent the composition of a mixture of three components.

Calculation of the concentration of each component

Location of the point within the triangle when the composition of each component is known separately. Let x_A = a, x_B = b and x_C = c, be the mole fractions of the three components A, B and C respectively. The sides of the triangle are equally divided into 100 or 20 or 5 parts. A portion BX_2 = a is measured off on line AB which will give the concentration of A; a portion AX_1 = b measured off on the line AB will be the concentration of component B. The remainder X_1X_2 = c will be equal to the concentration of C. Now the lines are drawn parallel to the sides of the triangle and intersection of the two parallel lines to give the gross composition of the ternary mixture.

Example:

Locate the point inside the equilateral triangle for a ternary mixture with 50 % A, 20 % B and 30 % C.

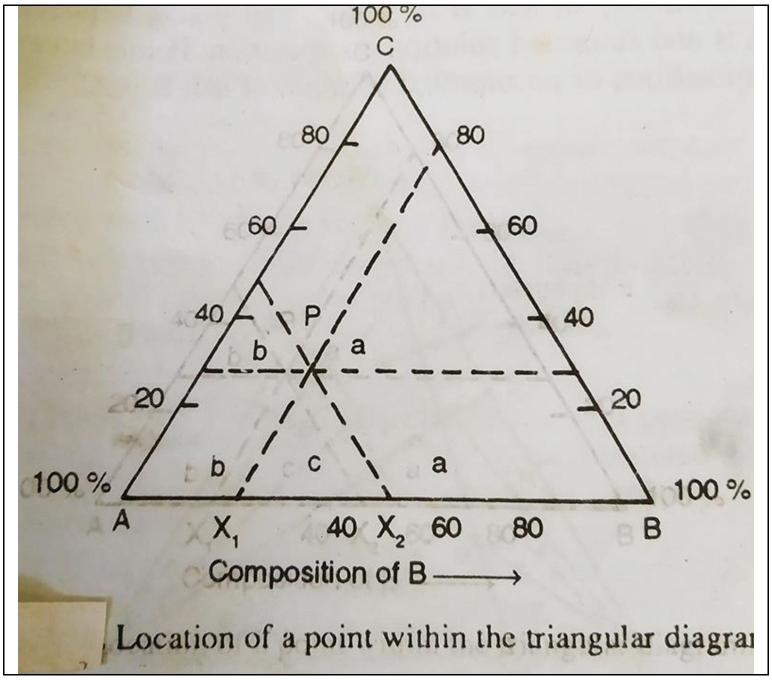
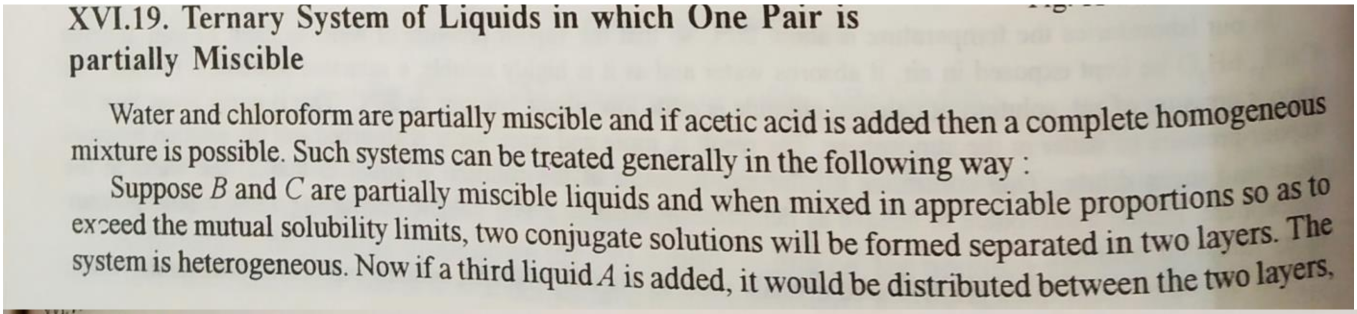


Figure 13

As a first step divide the sides of a equilateral triangle into 5 equal parts and measure **50 % A** on the line BA, given by BX_2. Then **20 % B** is measured on the line AB, given by AX_1. At point A, percentage of A is 100 % and that of B is 0 %. From point X_1 draw a line parallel to the side AC, and from point X_2, draw a line parallel to side BC. These two parallel lines intersect at point P within the triangle. This point P represents the composition of the mixture **50 % A, 20 % B and 30 % C.**

Three component systems: Water-chloroform-acetic acid system:

From: PHYSICAL CHEMISTRY – *Dr. P. C. Rakshit*



XVI.19. Ternary System of Liquids in which One Pair is partially Miscible

Water and chloroform are partially miscible and if acetic acid is added then a complete homogeneous mixture is possible. Such systems can be treated generally in the following way :

Suppose B and C are partially miscible liquids and when mixed in appreciable proportions so as to exceed the mutual solubility limits, two conjugate solutions will be formed separated in two layers. The system is heterogeneous. Now if a third liquid A is added, it would be distributed between the two layers, A being completely miscible with B and also with C. The miscibility of B and C is, it is found, enhanced by the presence of A. And when sufficient amounts of A are added to the system, the two layers are converted into a single homogeneous mixture. The temperature throughout is kept constant.

The variation in the miscibility of B and C when increasing amounts of A are added is shown in Fig. XVI.37. Suppose we have a mixture of B and C in the proportion as at point Z. This mixture will separate into two layers of conjugate solutions having comosition x and y. As A is gradually added, the composition (overall) of the mixtures of three-components will change along AZ. For a mixture of composition Z_1, the system is still heterogeneous and the two ternary conjugate layers will have concentrations denoted by x_1 and y_1. The line x_1y_1 passing through z_1 is called a *tie-line*. The tie-line is a measure of the miscibility gap. As more and more A is added, the tie-lines become shorter and shorter till these merge to a point a K. the curve xKy, obtained by joning the terminuses of the tie-lines, (*i.e.*, the limiting values of the miscibilities of B in C and C in B in presence of A) demarcates the zone of heterogeneous existence of the system. Outside this curve xKy for any composion, the ternary system will be homogeneous and inside the system is heterogeneous. The curve xKy is called the binodal curve. Complete miscibility by merging of two layers would occur only at K, *i.e*, the compositon of the two layers at this point become identical and the point K is called the *plait-point* of the system.

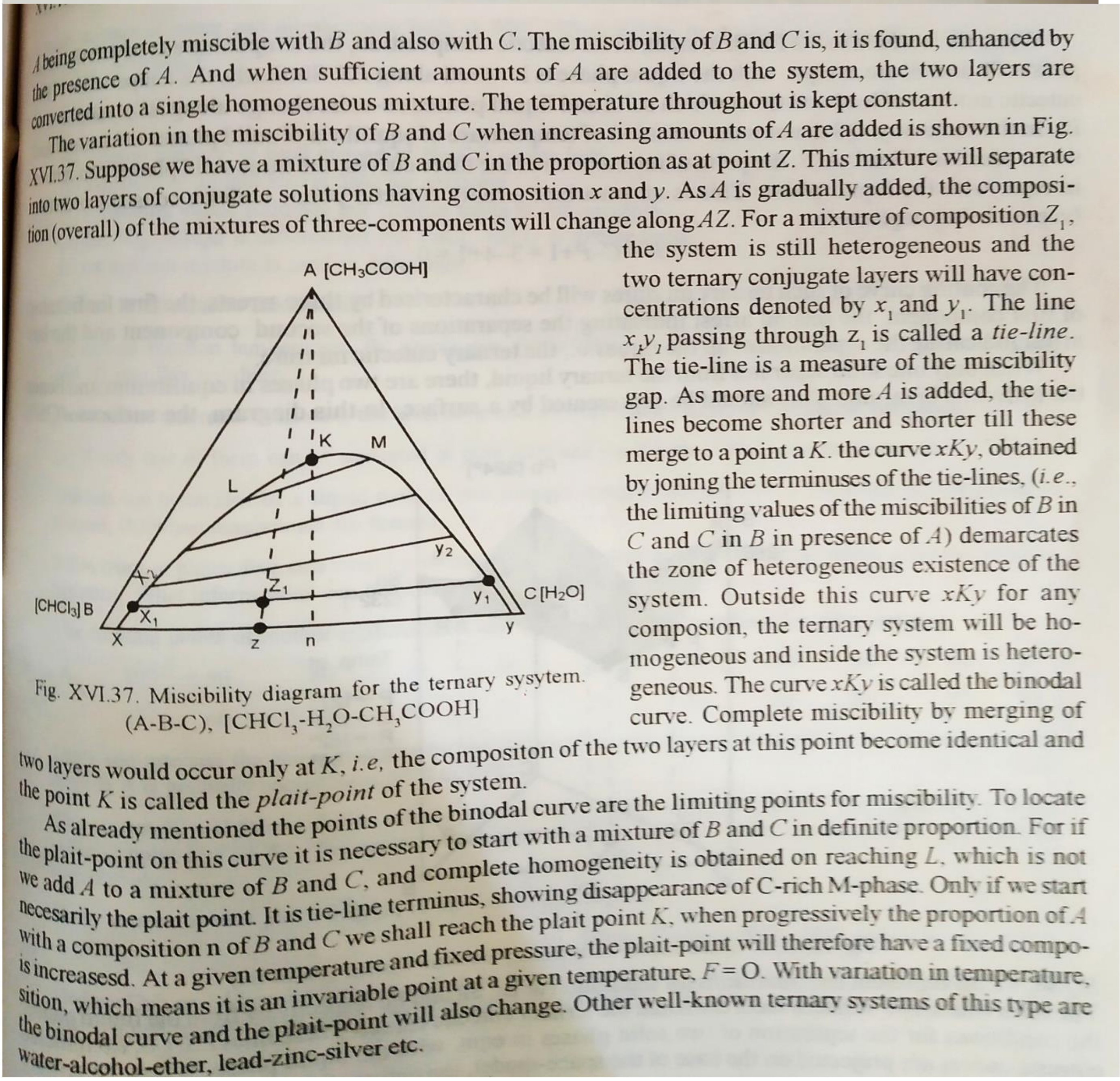


Fig. XVI.37. Miscibility diagram for the ternary sysytem. (A-B-C), [$CHCl_3$-H_2O-CH_3COOH]

As already mentioned the points of the binodal curve are the limiting points for miscibility. To locate the plait-point on this curve it is necessary to start with a mixture of B and C in definite proportion. For if we add A to a mixture of B and C, and complete homogeneity is obtained on reaching L, which is not necesarily the plait point. It is tie-line terminus, showing disappearance of C-rich M-phase. Only if we start with a composition n of B and C we shall reach the plait point K, when progressively the proportion of A is increasesd. At a given temperature and fixed pressure, the plait-point will therefore have a fixed composition, which means it is an invariable point at a given temperature, F = O. With variation in temperature, the binodal curve and the plait-point will also change. Other well-known ternary systems of this type are water-alcohol-ether, lead-zinc-silver etc.

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