

PHYSICAL EQUILIBRIA

Some common terms;

Solution

- Is the mixture of two or more non chemically reactive substance whose composition/ relative amounts vary within certain limits.
- A solution is homogeneous (i.e. the same all through) mixture of two substances.
- can be gaseous, liquid or solid of variable composition.

Binary solution

- Is a solution which consists of only two components e.g.
 - (i) Solution of volatile component such as **carbon dioxide in water**
 - (ii) Solution of non-volatile component such as **bromine in water**

For each of the above cases, the major component is the solvent and the minor component is the solute.

SOLUTION OF A VOLATILE COMPONENT

- when a binary solution contains a volatile solute, the vapour from the solution would contain both molecules of the solution and the solvent.
- Vapour pressure of each component above the liquid mixture will be lowered at particular temperature.
- When one liquid dissolves in another, the saturated vapour pressure of the solution depends on the saturated vapour pressures of the components and on the composition of the mixture.
 - One way of expressing the composition of the mixture of the liquids is to state the **mole fraction** of each component or constituent.
 - By definition, mole fraction refers to the number of moles of a given component divided by the total number of moles of all the components in the mixture.
 - i.e. mole fraction of A in a mixture of A and B = $\frac{\text{Number of moles of A}}{\text{Total number of moles}}$
 - mole fraction is abbreviated as X, thus $X_A = \frac{n_A}{n_A+n_B}$ and $X_B = \frac{n_B}{n_A+n_B}$

NB. Presence of non-volatile solute at the surface of the solution; reduces the escaping tendencies of the solvent molecules; lowering its vapour pressure resulting in the boiling point of the solution to be raised.

TWO COMPONENT LIQUID MIXTURES (Binary solution)

These include completely miscible liquid and immiscible liquids.

1. MISCIBLE LIQUIDS

Miscible liquids are liquids which completely dissolve in one another in all proportions to form a homogeneous mixture of solution.

Examples include ethanol and water, petrol and kerosene.

Completely miscible liquids may form an ideal solution or a non-ideal solution on mixing.

THE IDEAL SOLUTION AND RAOULT'S LAW

An ideal solution is one in which the inter molecular force A-A, A-B and B-B are all equal; and obeys Raoult's law exactly.

Alternatively, an ideal solution can be defined using its properties: thus, it's a solution which obeys Raoult's law exactly; has equal intermolecular forces of attraction i.e. A-A, A-B and B-B: there is no change in volume when then two components are mixed (total volume of the solution is equal to the sum of the individual volumes) and no heat change on mixing (no heat is evolved nor gained when the two components of the ideal solution are mixed)

PROPERTIES OF IDEAL SOLUTION

- No heat change on mixing.
- No volume change in mixing; total volume of the solution is equal to the sum of the individual volumes.
- Equal intermolecular forces of attraction i.e. A-A, A-B and B-B if A and B are the two components of an ideal solution.

In reality an ideal solution does not exist but there are some solutions which approximate to ideal behavior

Example of the mixtures that form ideal solution include:

- 1) Water and methanol
- 2) Chlorobenzene and bromobenzene
- 3) Heptane and octane
- 4) Benzene and methylbenzene.
- 5) Aminopentane and amino hexane
- 6) Liquid mixture of Nitrogen and oxygen

Question

- a) Explain what is meant by the term ideal solution.
- b) Explain why most solutions deviate considerably from ideal behavior.

Solution

- a) An ideal solution is one that obeys Raoult's law throughout its composition. The solution is formed with no volume change and temperature change. In such a solution, the cohesive forces (A-A and B-B) between the molecules of components are equal in magnitude and kind to the adhesive forces(A-B) between the molecules of the components in the mixture.
- b) For solutions that do not obey Raoult's law or non-ideal solutions, the forces of attraction in mixture between the molecules (cohesive forces) are not equal in magnitude and kind to the forces of attraction between unlike molecules (adhesive forces). Such solutions are formed with volume and temperature changes.

RAOULT'S LAW

Raoult's law states that *"For an ideal solution, partial pressure of a given component, above the liquid mixture; is directly proportional to its mole fraction in the liquid mixture"*

OR

The partial vapour pressure of a component in an ideal liquid mixture (ideal solution) is equal to the vapour pressure of the pure component at that temperature multiplied by its mole fraction in that ideal liquid mixture.

It should be noted that Raoult's law only works for ideal mixtures.

i.e

$$P_i \propto x_i$$

$$P_i = P_i^0 X_i$$

Where P_i = Partial pressure of component, i

X_i = Mole fraction of the component, i

P_i^0 = saturated water vapour of the component, i

OR:

For a dilute ideal solution, partial pressure of a given component above the liquid mixture; is equal to its saturated vapour pressure multiplied by its mole fraction.

Consider a liquid mixture of two components A and B which obeys Raoult's law

$$P_A = P_A^0 \cdot X_A \quad \text{and} \quad P_B = P_B^0 \cdot X_B$$

$$\begin{aligned} X_A &= n_A / (n_A + n_B) & \text{where } n_A \text{ and } n_B \text{ are the moles of the components A and B respectively} \\ X_B &= n_B / (n_A + n_B) & X_A \text{ and } X_B \text{ are the mole fractions of the components A and B respectively} \end{aligned}$$

$$\text{But } P_A + P_B = P_{\text{total}} \quad \text{thus} \quad P_{\text{total}} = P_A^0 X_A + P_B^0 X_B$$

Note that the total mole fraction or the composition of two components in an ideal solution is considered to be 1 or 100%.

Thus $X_A + X_B = 1$ or 100%.

$$\text{And } X_A = 1 - X_B$$

Limitations of Raoult's law/conditions under which Raoult's law hold;

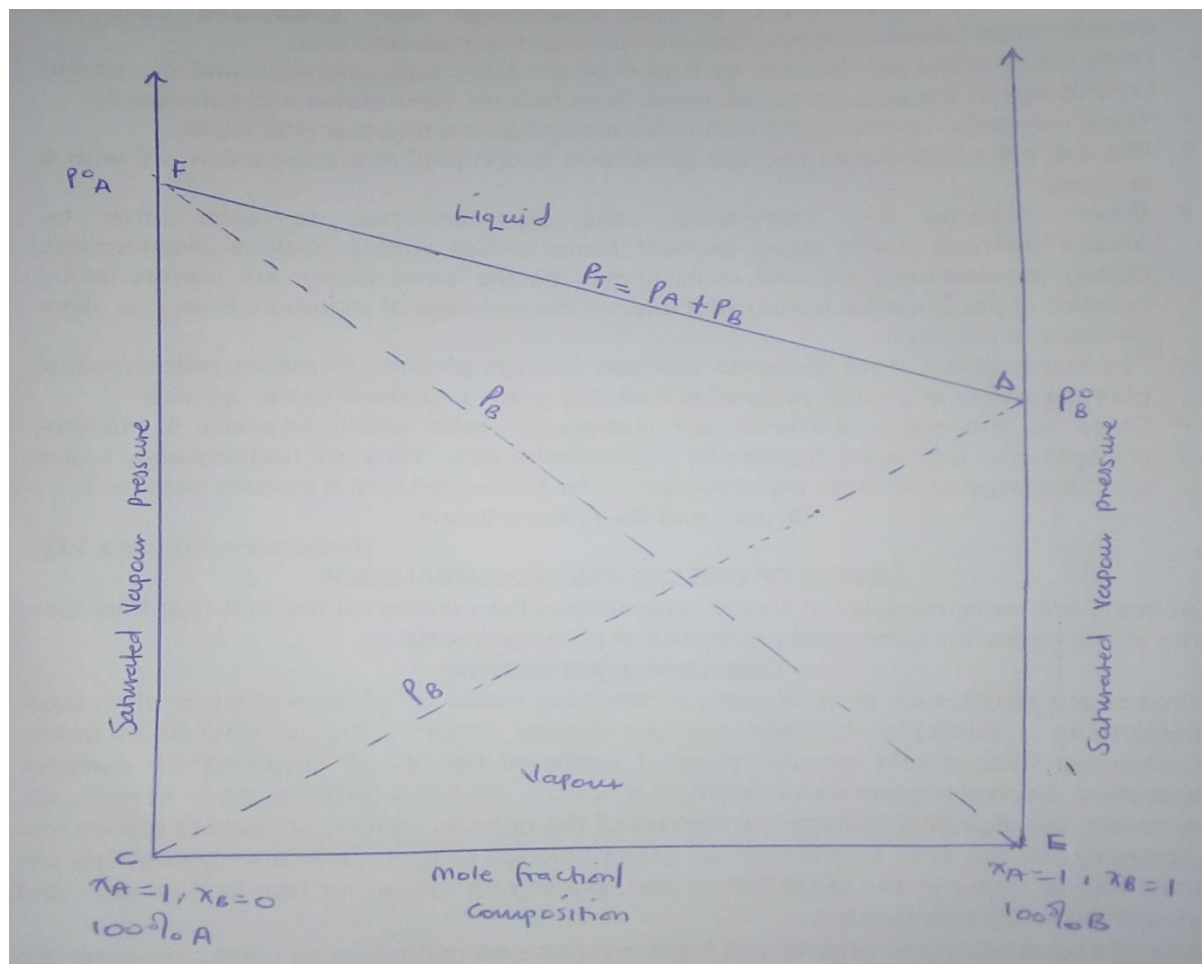
- Ideal solution should be sufficiently dilute
- Temperature must be constant
- Solute should be non-volatile

VAPOUR PRESSURE COMPOSITION DIAGRAM FOR A BINARY SOLUTION THAT OBEYS RAOULT'S LAW

Raoult's Law can be used to obtain the vapour pressure composition diagram for an ideal solution. Consider a binary solution containing components A and B

- From $P_A = P_A^0 X_A$ When $X_A = 1$, $X_B = 0$ for $X_A + X_B = 1$, $P_A = P_A^0$
- Similarly, $P_B = P_B^0 X_B$

Where $X_B = 1$ and $X_A = 0$; $P_B = P_B^0$



Note from the diagram

- P_A and P_B are partial vapour pressures of A and B respectively in the binary solution.
- P_A^0 and P_B^0 are vapour pressures of pure A and B respectively.

CURVES:

CD; - Shows the variation of vapour pressure of component B with its composition

EF; - Shows the variation of vapour pressure of component A with its composition

FD; -Variation in total vapour pressure of the solution with composition

- The more volatile component has a higher saturated vapour pressure at a given temperature if the composition is the same.
- It can also be seen from the diagram that A is more volatile than B since A exerts a higher vapour pressure than B at a given temperature.
- The importance of vapour pressure composition diagram is to tell the shape of the boiling point composition diagram that is used to describe how a mixture of two liquids can be separated using fractional distillation.
- If the solution is ideal, the composition of the liquid boiling at a particular temperature is given $P_{\text{total}} = P_A + P_B$, thus $P_{\text{total}} = P_A^0 X_A + P_B^0 X_B$
- The vapour composition in terms of the mole fraction of components A and B is given by;
 $y_A = P_A / P_{\text{total}} = (P_A^0 \cdot X_A) / P_{\text{total}}$
 $y_B = P_B / P_{\text{Total}} = (P_B^0 \cdot X_B) / P_{\text{total}}$

Examples

1(a). Calculate the composition benzene- toluene mixture which at 760mmHg boil at 88oc if the saturated vapour pressure of benzene and Toluene at this temperature are 957 and 378mmHg respectively.

(b). Calculate the composition of the vapour obtained when the liquid mixture in A boil.

(c) Which of the two liquids is more volatile? Give a reason for your answer.

a)

$$P_{\text{total}} = 760 \text{ mmHg}$$

$$P_{\text{Benzene}}^0 = 957 \text{ mmHg}$$

$$P_{\text{Toluene}}^0 = 378 \text{ mmHg}$$

$$P_{\text{total}} = P_{\text{toluene}} + P_{\text{Benzene}}$$

$$= (P_{\text{toluene}} X_{\text{toluene}}) + (P_{\text{Benzene}} X_{\text{Benzene}}) \quad \text{But } X_T + X_B = 1$$

$$\rightarrow X_B = (1 - X_T)$$

$$P_{\text{total}} = P_T^0 X_T + P_B^0 (1 - X_T)$$

$$P_{\text{total}} = P_T^0 X_T + P_B^0 - P_B^0 X_T$$

$$760 = 378 X_T + 957 - (957 X_T)$$

$$760 - 957 = 378 X_T - 957 X_T$$

$$-197 = -579 X_T$$

$$X_T = 0.34$$

$$X_B = 1 - 0.34$$

$$= 0.66$$

$$\text{b) } Y_T = P_{oT} X_T / P_{\text{total}} \\ = 378 \times 0.34 / 760$$

$$= 0.169 \approx 0.17$$

$$Y_B = P_{oB} X_B / P_{\text{total}}$$

$$= 957 \times 0.66 / 760$$

$$= 0.83$$

c) Benzene is more volatile

➤ Because it has the highest vapour composition

2. Calculate the composition of a liquid mixture of A and B which at 760mmHg boils at 98°C if the vapour composition of A and B are equal given that the saturated vapour pressure of A and B are 950mmHg and 320mmHg respectively.

SOLUTION

Vapour composition of A ; $y_A = P_A / P_{\text{total}}$

Vapour composition of B; $y_B = P_B / P_{\text{total}}$

$$y_A = y_B$$

$$P_B / P_{\text{total}} = P_A / P_{\text{total}}$$

$$P_A = P_B$$

$$P_A^0 X_A = P_B^0 X_B, \quad X_A + X_B = 1, \quad X_B = 1 - X_A$$

$$\rightarrow P_A^0 X_A = P_B^0 (1 - X_A), \quad 950 X_A = 320 (1 - X_A), \quad 950 X_A = 320 - 320 X_A$$

$$1270 X_A = 320$$

$$X_A = 0.25$$

$$X_B = 1 - 0.25$$

$$X_B = 0.75$$

3. At 50°C the vapour pressure of hexane is 54KPa and that of heptane is 22KPa

(a) Calculate the vapour pressure above the liquid mixture of 4.3g of hexane and 5g of heptane at this temperature.

(b) Determine the composition of the vapour above the liquid mixture in (a) above.

Solution

Let hexane be A and heptane be B

$$\begin{aligned} \text{(a) } R_{\text{mm}}(\text{C}_6\text{H}_{14}) &= (6 \times 12) + (14 \times 1) = 86 \\ \text{Moles of hexane}(n_A) &= 4.3 / 86 = 0.05 \end{aligned}$$

$$\begin{aligned} R_{\text{mm}}(\text{C}_7\text{H}_{16}) &= (7 \times 12) + (16 \times 1) = 100 \\ \text{Moles of heptane}(n_B) &= 5 / 100 \\ &= 0.05 \end{aligned}$$

$$\text{Total moles} = 0.05 + 0.05$$

$$\begin{aligned} P_{\text{hexane}} &= X_A P_A^0 \\ &= 0.05 / 0.1 \times 54 \\ &= 27 \text{ KPa} \end{aligned}$$

$$\begin{aligned} P_{\text{heptane}} &= X_B P_B^0 \\ &= 0.05 / 0.1 \times 22 \\ &= 11 \text{ KPa} \end{aligned}$$

$$\begin{aligned} \text{Vapour pressure } (P_{\text{total}}) &= P_{\text{hex}} + P_{\text{hept}} \\ &= 27 + 11 \\ &= 38 \text{ KPa} \end{aligned}$$

$$\begin{aligned} \text{(b) For heptanes} &= 11 / 38 \times 100 \\ &= 28.9\% \end{aligned}$$

$$\begin{aligned} \text{For hexane} &= 27 / 38 \times 100 \\ &= 71.1\% \end{aligned}$$

4. The vapour pressure of ethanol at 20°C is 43.6 mmHg while that of benzene at the same temperature is 75.2 mmHg. The mole fraction of benzene is 0.09 for the mixture of benzene and ethanol at 20°C

Calculate

(i) The vapour pressure of the mixture

$$V.P_{\text{ethanol}} = 43.6 \text{ mmHg}; \quad V.P_{\text{benzene}} = 75.2 \text{ mmHg}; \quad X_{\text{benzene}} = 0.09$$

$$\begin{aligned} \text{From: vapour pressure of the mixture} &= P_{\text{ethanol}}^0 \cdot X_{\text{ethanol}} + P_{\text{benzene}}^0 \cdot X_{\text{benzene}} \\ &= (1 - 0.09) \times 43.6 + 0.09 \times 75.2 \\ &= 39.7 + 6.8 \\ &= 46.5 \text{ mmHg} \end{aligned}$$

(ii) The mole fraction of benzene in the vapour phase

Vapour pressure of benzene = $X_{\text{benzene}} \cdot \text{total V.P of mixture}$

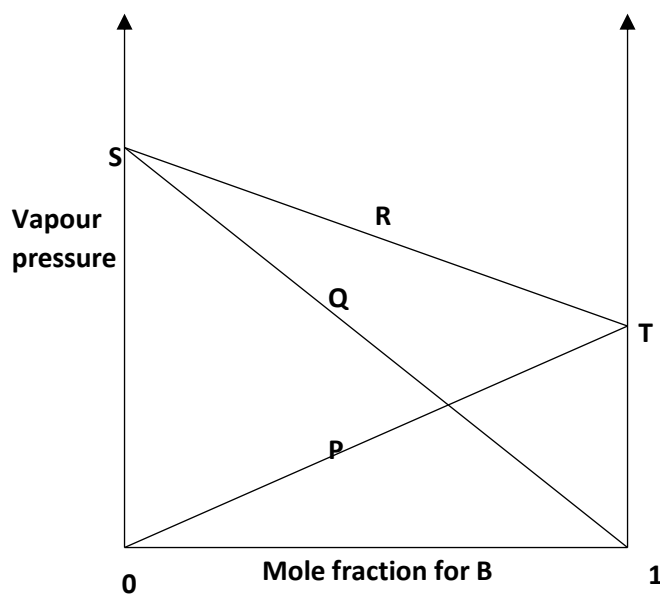
Therefore; $X_{\text{benzene}} = \text{V.P}_{\text{benzene}} / \text{total V.P of mixture}$

$$= 6.8/46.5$$

$$= 0.15$$

ASSIGNMENT

- The vapour pressure of ethanol at 20°C is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. the mole fraction of Benzene is 0.09 for a mixture of benzene and ethanol at 20°C. Calculate the total vapour pressure of the mixture .
- Calculate the mole fraction of benzene at the vapour phase
- State three properties of an ideal solution
- The vapour pressure – composition diagram of an ideal solution of liquids A and B is shown below. The mole fraction shown on the diagram is for liquid B.



- Identify lines, **P**, **Q** and **R** and the points **S** and **T**.
- Draw a fully labelled boiling point – composition diagram for a mixture of liquids **A** and **B**.
- State what would be obtained as the distillate and the residue if a liquid mixture containing 40% of A is fractionally distilled.
- Briefly what takes place during fractional distillation.

BOILING POINT CURVES

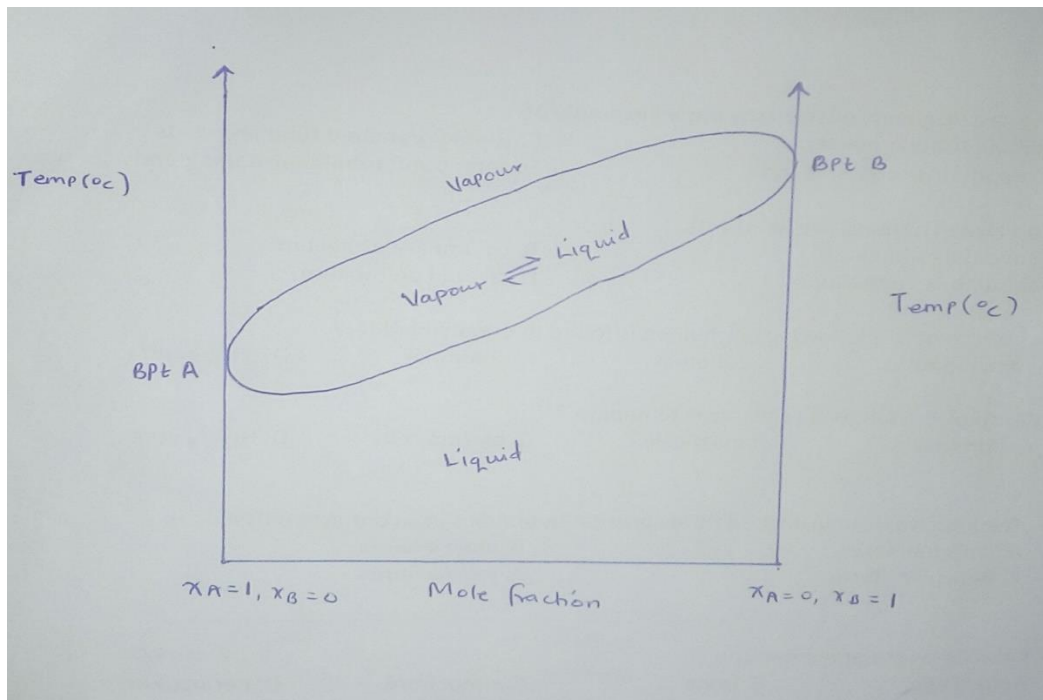
Boiling point curve;

- a graph of temperature at which the mixture boils when plotted against composition.
- Increasing temperature increases the vapour pressure of both liquids in the mixture, but the vapour pressure of a more volatile component increases more rapidly, such that the vapour above the liquid mixture boiling is richer in the more volatile component,
- So the composition of the vapour lies on the other side of straight line joining boiling point
- The component with a high vapour pressure has a low boiling point whereas the compound with a low vapour pressure has a high boiling point. If a liquid has a high vapour pressure at a particular temperature, it means that its molecules are escaping easily from the surface. Similarly, if at the same temperature, a second liquid has a low vapour pressure, it means its molecules are not easily escaping.

Explanation

Liquids boil when their vapour pressure becomes equal to the external atmospheric pressure. If the liquid has a high vapour pressure at some temperature, it means that you will not have to increase the temperature very much until the vapour pressure reaches the external atmospheric pressure. On the other hand, if the vapour pressure is low, you will have to heat the liquid to higher temperatures for its vapour pressure to rise and equal to the atmospheric (external) pressure for boiling to occur.

BOILING POINT COMPOSITION DIAGRAM OF AN IDEAL SOLUTION



It should be noted that a binary solution containing two components i.e A and B can be separated into individual components by **fractional distillation**.

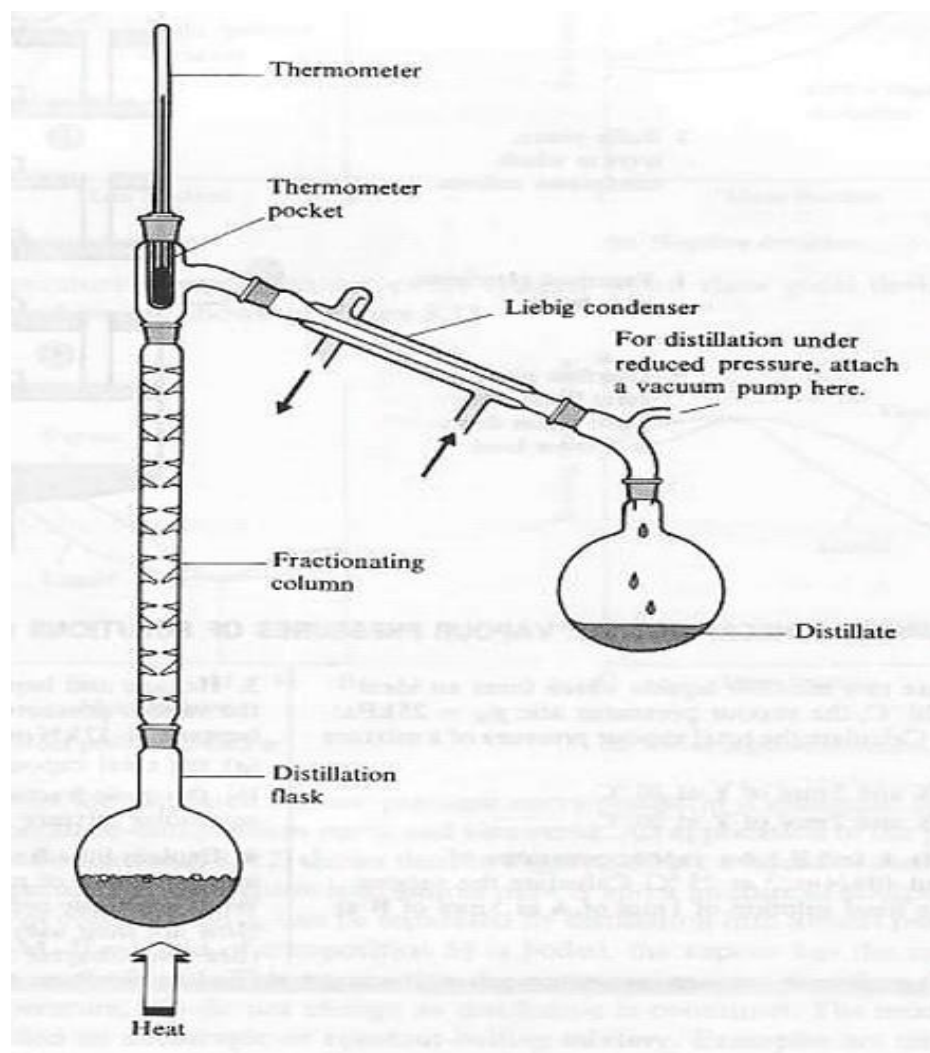
FRACTIONAL DISTILLATION

Defn; This a method of separating the components of a mixture of liquids that have different boiling points (boiling temperatures).

During fractional distillation, equilibrium is established between the vapour and the liquid in the fractional distilling column, the vapour becomes progressively richer in the more volatile component and it's the more volatile component that is collected as a distillate.

Repeated heating and condensation is tedious therefore fractional distillation is achieved using a fractionating column ; the fractionating column has a large surface area on which ascending vapour and descending liquid come into contact. A mixture rich in the most volatile component distils over the top of the column where the thermometer registers its boiling temperature. As distillation continues, the temperature rises towards the boiling temperature of the next volatile component. The receiver is changed to collect the second component. In this way, the components are distilled over at their *boiling temperatures*.

Arrangement of the apparatus for fractional distillation

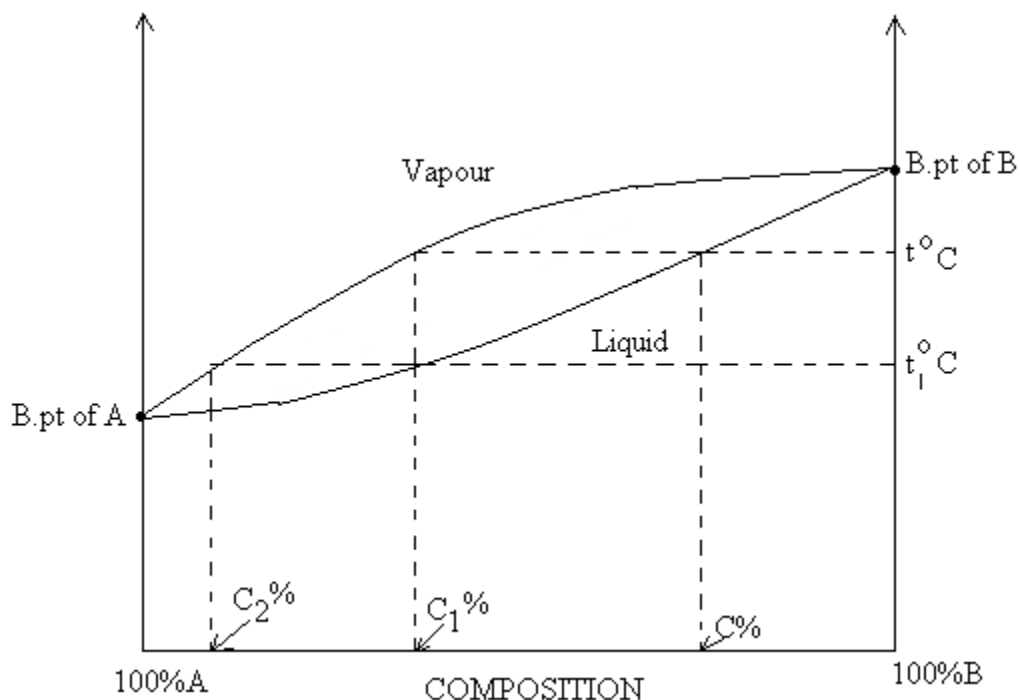


When the liquid mixture is heated, it produces the vapour which ascends up in the column, it is cooled down by the glass beads packed in the column to produce a liquid that descends the column. The descending liquid meets with ascending vapour and an equilibrium between the liquid and vapour is established within the column. This results into formation of a vapour that is richer in the more volatile component. Therefore when a liquid mixture of two components is fractionally distilled the vapour within the fractionating column becomes progressively richer in the more volatile component until the more volatile component is collected as distillate.

Hence, fractional distillation works on the principle that when a liquid mixture is fractionally distilled, the vapour becomes progressively richer in the more volatile component.

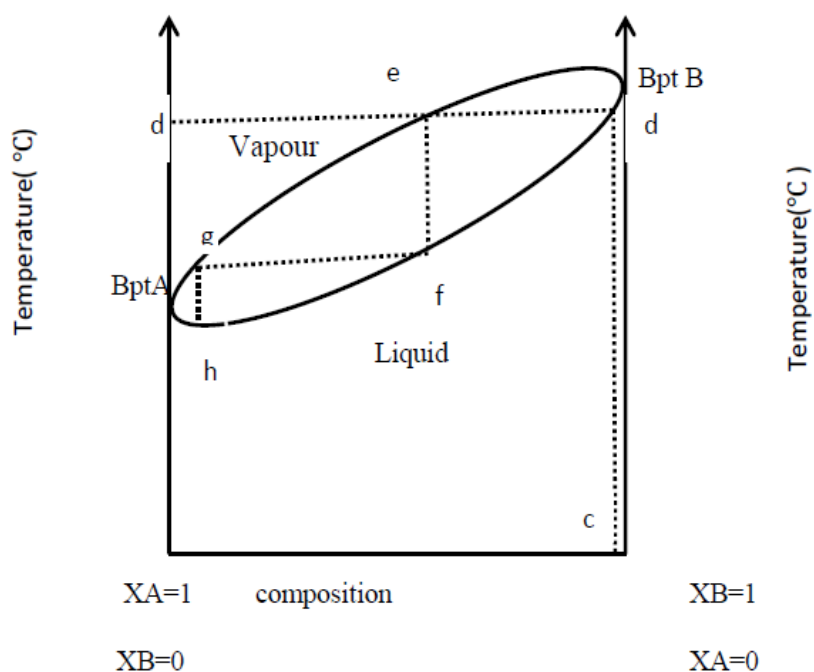
The diagram can be used to describe how a solution of A and B can be fractionally distilled as follows;

BOILING POINT COMPOSITION DIAGRAM FOR COMPOUND A AND B



Consider a liquid mixture of A and B containing $C\%$ of A. when the liquid mixture is heated it boils at $t^\circ\text{C}$. At this temperature the liquid mixture is in equilibrium with a vapour whose composition is $C_1\%$ of A. when the vapour is condensed, the liquid mixture containing $C_1\%$ A is obtained when the liquid mixture is heat, it boils at temperature $t_1^\circ\text{C}$. At this temperature, the liquid is in equilibrium with a vapour whose composition is $C_2\%$ of A. when the vapour is condensed the liquid mixture that is richer in A is obtained. Therefore, according to the diagram when a liquid mixture containing $C\%$ A is fractionally distilled the mixture will separate into pure A as the distillate and B as the residue.

describe how fractional distillation can be used to separate a binary solution containing components A and B of a given composition say “c” as shown in the figure below.



- Heating a liquid of composition C richer in B, It boils at a temperature d; giving off a vapour of composition e, at the same temperature.
- Condensing the vapour, the liquid of the same composition, f is formed
- The liquid when boiled gives a vapour of composition g, at boiling point P which when condensed gives a liquid, h of the same composition as the vapour at g.
- A series of successive boiling and condensation finally produces the pure vapour of the more volatile component A while the residue in the flask becomes richer in the less volatile component B.
- Pure vapour when condensed gives pure liquid A.

This is the principle of fractional distillation; a process of separation of two miscible liquids with different boiling points.

Question.

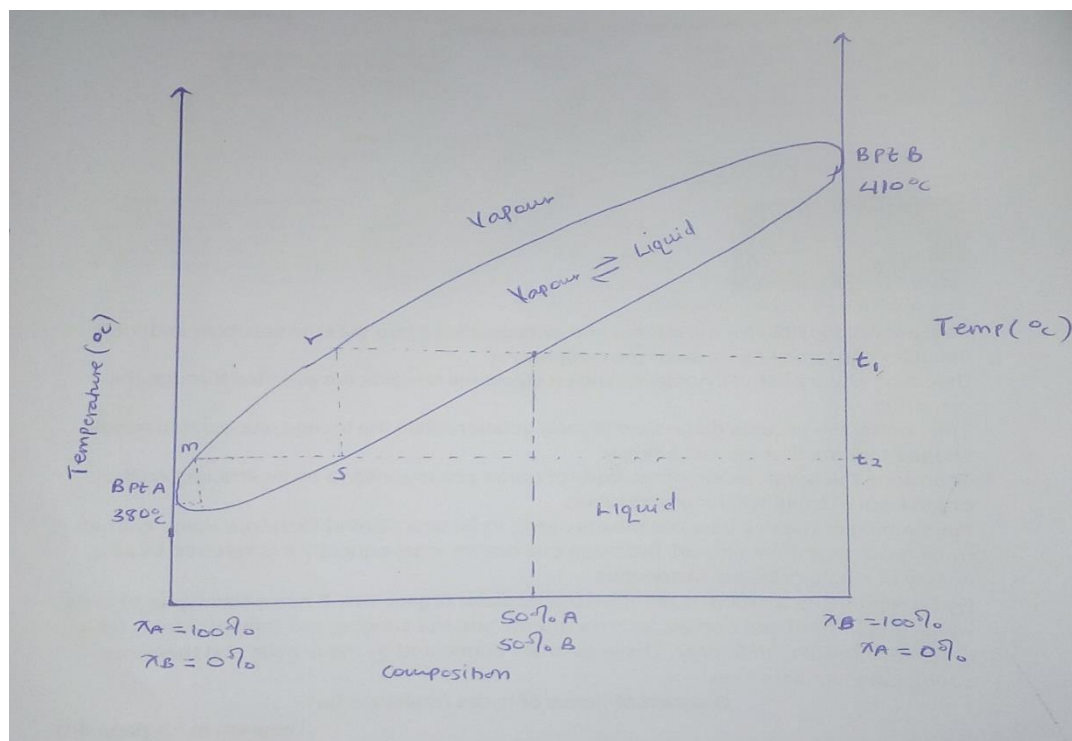
Compound A, Boiling point 380°C and compound B boiling point 410°C forms an ideal solution

(a). Sketch a labeled boiling point composition diagram for the mixture.

(b). Using the diagram, describe and explain how pure B can be obtained from a mixture containing 50%A and 50%B.

Solution

a) **Boiling point composition diagram for compound A and B**



b)

- A liquid mixture containing 50% B is heated ; boiling at temperature t_1 ; to give vapour of composition r, richer in more volatile component A than the less volatile component B
- Condensing the vapour, liquid mixture of composition s, and so on until pure A is obtained as distillate and the residue will be pure B.

Assignment 1

- The normal boiling point of liquids A and B are 80°C and 110°C respectively. The mixture of A and B can be assumed to obey Raoult's law. Show how the two substances can be separated by fractional distillation and explain the principle involved in the process.
- Compound A (bp 372°C) and compound B (bp 399°C) form an ideal solution.
 - Explain what is meant by the term ideal solution.
 - Sketch a labeled boiling/composition diagram for the mixture
 - Using the diagram, describe and explain how pure B can be obtained from a mixture containing 50% B.

ASSAIGNMENT 2

- Propanone was mixed with trichloromethane
 - State what was observed. Explain your answer

- II. Sketch a labeled diagram for the vapour pressure – composition for the mixture of propanone and trichloromethane. (The boiling point of propanone is lower than that of trichloromethane)
- III. Describe what would happen if a mixture of trichloromethane and propanone was fractionally distilled.
- IV. Explain the process of fractional distillation

NON IDEAL/REAL/IMPERFECT SOLUTION.

- A real solution is the one which shows deviation from ideal behavior i.e. Raoult's law,
- Thus, ***a real solution is one which deviates from Raoult's law.***
- These deviations arise from the differences in the intermolecular forces of attraction between the molecules of pure components and the molecules of different components.
- Vapour pressure of such solution is either higher or less than those predicted from Raoult's law and therefore, the deviation are either positive or negative.

NOTE

Some liquids are miscible but when mixed they form solutions that do not obey Raoult's Law; such solutions which do not obey Raoult's Law are called non-ideal solutions. That is a non-ideal solution is a solution in which the intermolecular forces of attraction are different from those in pure and separate components. A solution that does not obey Raoult's Law is said to deviate from ideal behavior.

a) NEGATIVE DEVIATION

- ✓ Occurs when the vapour pressure of the system is lower than that expected by Raoult's law.
- ✓ This is because of the greater bond of attraction between molecules of different kind, A.....B than those of molecules of the same kind, A.... A or B... B.
- ✓ this attraction leads to a reduction in the rate of escape of the molecules to the vapour phase, decreasing volume and evolving heat.

Examples of solution which show negative deviations from Raoult's

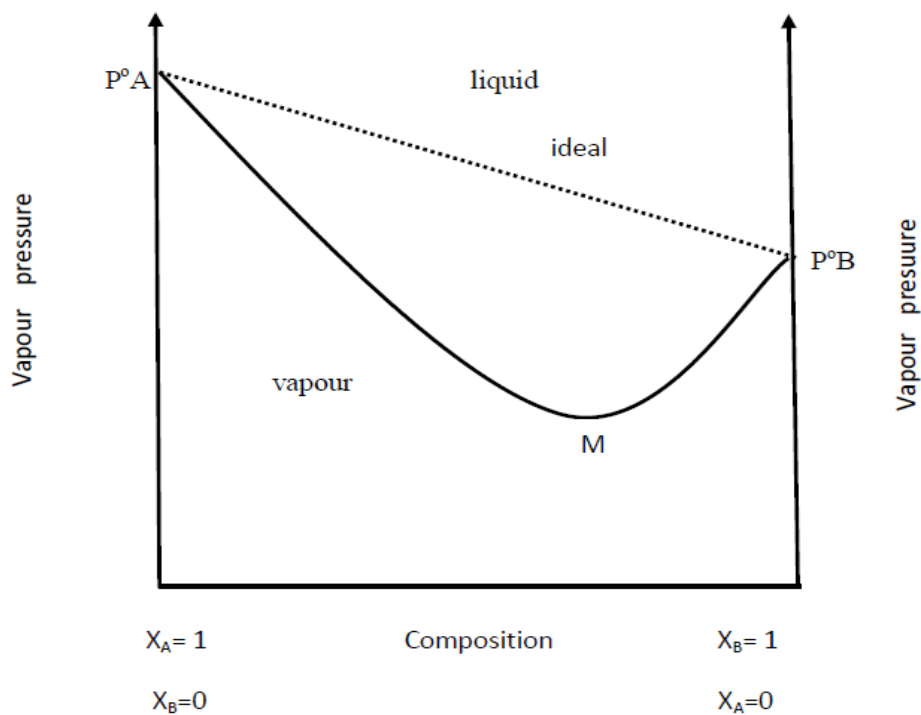
<i>Liquid mixture / solution</i>	<i>Reasons for deviation</i>
I. HCl/HNO ₃ and water	<ul style="list-style-type: none"> • Acid ionizes in water producing ions, and as ions are hydrated, strong ion –dipole attraction are formed compared to Van der-Waals forces in acid and hydrogen bonds in water. • This reduces the escaping tendency of molecules into vapour state

II. Trichloromethane/Chloroform and propanone	<ul style="list-style-type: none"> Intermolecular hydrogen bonding between the chloroform and acetone formed, evolves a lot of heat and reduces the volume of the mixture which reduces the escaping tendency of the molecules into vapour state.
III. Phenol-Phenyl amine mixture	<ul style="list-style-type: none"> Intermolecular hydrogen bond formed by the phenol and phenyl amine due to the differences in their polarities outweighs cohesive force in phenol and phenyl amine . Heat is evolved and the volume decreases on mixing, reducing the escaping tendency of the molecules into vapour state.

PROPERTIES OF MIXTURE WHICH DEVIATE NEGATIVELY FROM RAOULT'S LAW.

- Total volume decrease when the liquids are mixed
- Heat energy is evolved
- Adhesive forces between components are stronger than the cohesive forces in the individual component

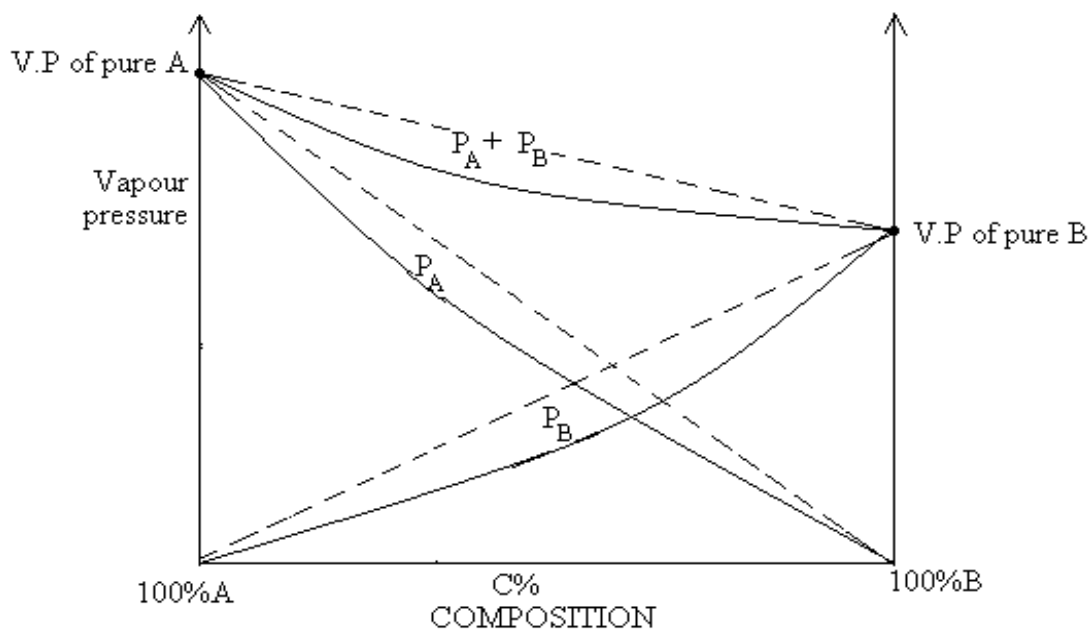
Vapour pressure composition diagram of a liquid mixture showing negative deviation from Raoult's law



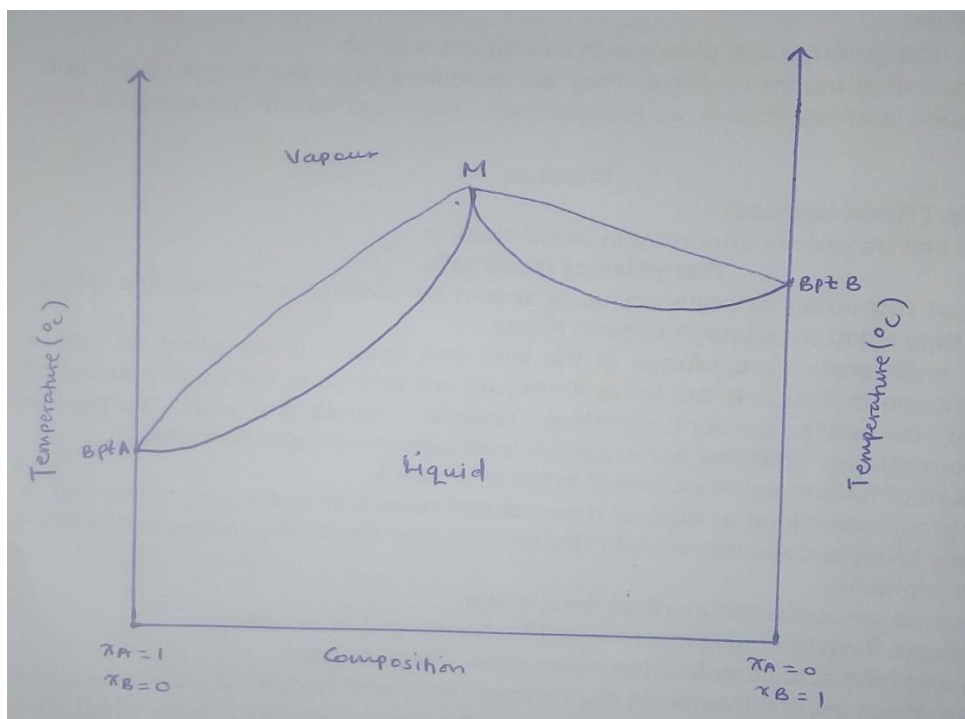
Note

Minimum, M in the diagram above implies that the solution will have to be heated more in order for its vapour pressure to reach atmospheric pressure hence a **maximum boiling point**.

ALTERNATIVELY(for graph above)



Boiling point composition diagram for a liquid mixture showing negative deviation



At **M**, vapour and liquids are indistinguishable i.e. the liquid mixture giving off vapour of the same composition behaving as a pure liquid mixture is called **maximum boiling azeotrope or constant boiling mixture**.

Definition.

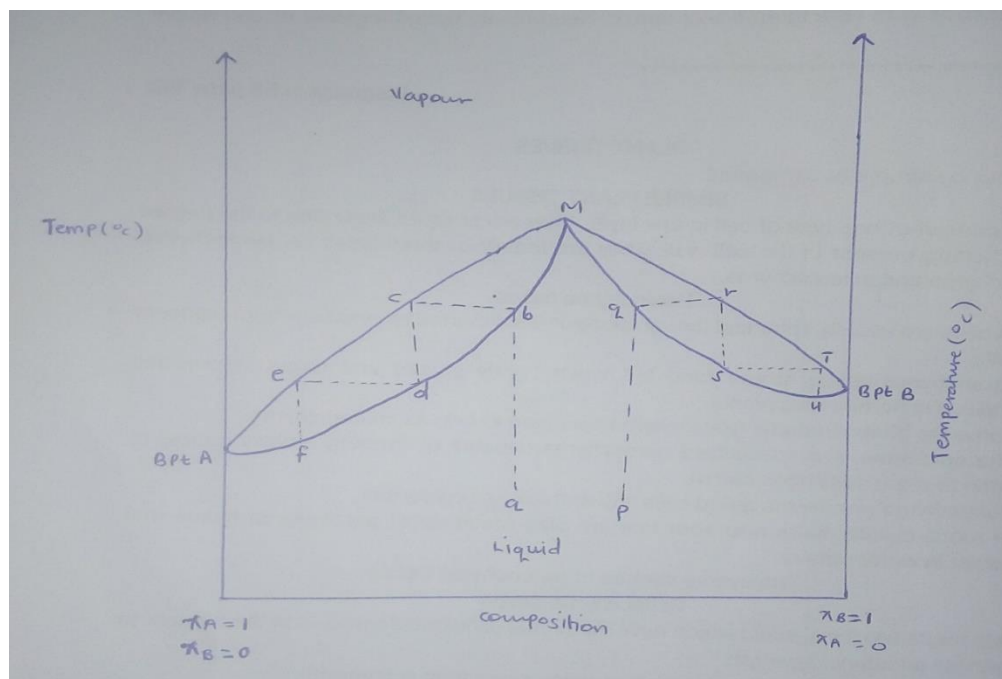
An **azeotrope** is the liquid mixture that boils at a constant temperature ; yielding vapour of the same composition as that of liquid at a constant pressure.

Or

An azeotropic mixture is a liquid mixture which at constant pressure boils at a constant temperature to give a vapour of the same composition. Therefore, an azeotropic mixture is a constant boiling point mixture which distills unchanged. It behaves as a compound yet it is a mixture because.

- Its composition changes with changes in pressure yet for compounds their compositions are constant regardless of the pressure
- It can be separated by any physical means such as the technique of azeotropic distillation yet compounds can not be separated by such physical means.

Fractional distillation of liquid mixture of composition a and p



- Successive boiling and condensation of a liquid mixture of composition **a**, along **a,b,c, d e**, and **f** gives off pure A in the vapour phase while the residue in the flask tends towards a mixture of composition M (mixture of A and B).
- At M, any further boiling and condensation produces no change in composition
- Similarly for original mixture of composition **P**, boiling and condensation proceeds along **p,q,r,s,t,u**.

- Component B will be distilled off in the vapour phase while the residue in the flask tends towards M.
- Frictional distillation therefore cannot completely separate the two components.

Reasons

- Separation by friction distillation is possible for mixture with components that differ in their boiling point.
- However azeotropic mixture boils at a fixed constant temperature; with no change in composition; hence volatile vapour of any component can be obtained from azeotropic mixture thus cannot be separated by friction distillation.

Assignment

1) At a constant temperature, a mixture of 11.95g of Trichloromethane and 14.5g propanone deviates from Raoult's law and has a total vapour pressure of 300mmHg. If the saturated vapour pressure of propanone and Trichloromethane are 380mmHg and 300mmHg respectively

(a). State the types of deviation from Raoult's law and briefly explain them.

(b). How does the mixture of Trichloromethane and propanone deviate from Raoult's law? Show your working (C=12, O=16, H=1, Cl=35.5)

(c). (i) State what is observed when propanone is mixed with trichloromethane .

ii) Explain your answer in c (i)

2. a) Nitric acid (boiling point 86°C) and water (boiling point 100°C) are completely miscible and yet their mixture cannot be completely separated by a single frictional distillation .

(i). Explain why a mixture of nitric acid and water which is miscible even with a marked difference in boiling point of 14°C cannot be completely separated by fractional distillation.

(b). The table below shows the composition of nitric acid in the liquid mixture and vapour above in various temperatures.

Temperature(°C)	86	100	120	111	103	100
% of nitric acid in liquid	100	81	68	50	20	0
% of nitric acid in vapour	100	87	68	30	06	0

- Plot a graph of temperature against vapour and liquid composition. Label the axes.
- Write the coordinates of the azeotropic point and mark it on the graph as S
- How many distillations are needed to obtain a distillate from a mixture of 50% nitric acid by mass? Identify the distillate
- Calculate the volume of the residue of frictional distillation of any mixture that would completely react with marble chips to produce 448cm³ of carbon dioxide at s.t.p (density of solution = 1.866gcm⁻³)

(b). POSITIVE DEVIATION

- Total vapour pressure of the system is higher than that expected from Raoult's law.
- This is because of the less attraction (greater repulsion) between the molecules of different components(adhesive forces) than that of the pure component(cohesive forces).
- Bonding of A-A and B-B are broken on mixing two components.
- This causes the molecules of A and B to have greater tendency to escape from a liquid phase to vapour phase giving higher vapour pressure.

Properties of mixtures which deviate positively from Raoult's law

- Increase in volume of the resultant solution
- Heat energy is absorbed
- Adhesive force between different components are weaker than cohesive force of the pure component.

Examples of mixtures which deviate positively from Raoult's law

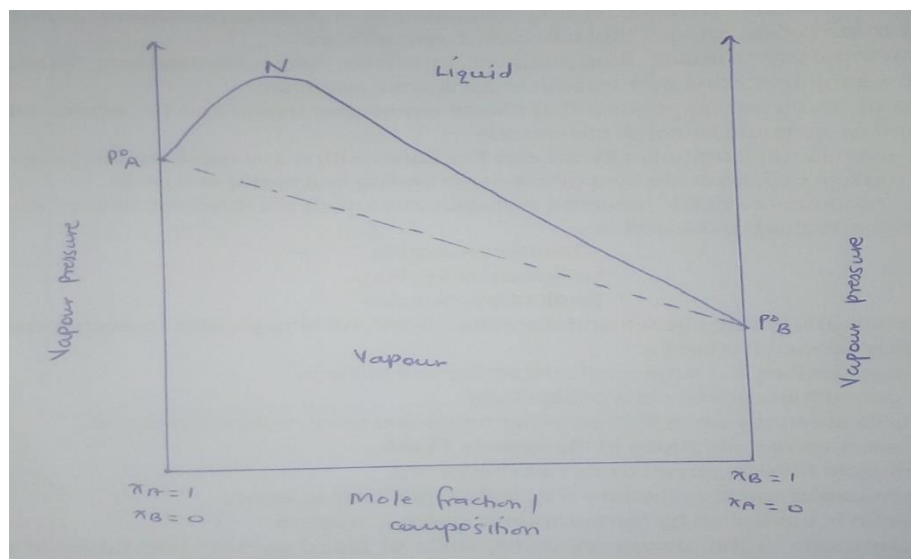
Liquid mixture/solution	Reason for deviation
Benzene-ethanol mixture	<ul style="list-style-type: none">• Benzene has no polar molecules with only van der waal forces of attraction present.• Ethanol has polar molecules which can associate through hydrogen bonding . Those two forces are different in nature and when the components are put together, there will be great repulsion between the molecules of benzene and ethanol.• This increase escaping tendencies of the molecules in the mixture to vapour state.
Water-ethanol mixture	<ul style="list-style-type: none">• Water and ethanol associate through a strong intermolecular hydrogen bonding.• Mixing the two, hydrogen bonds are broken down; causing less attraction between the molecules of ethanol and water mixture than the average attraction between the molecules of the pure component of ethanol –ethanol and water- water molecules hence increasing the escaping tendency in vapour phase.

Other examples include;

- Cyclohexane and methanol mixture
- Carbon disulphide and ethanol mixture
- carbontetrachloride and methanol mixture
- Acetone and Carbon disulphide
- Benzene and cyclohexane

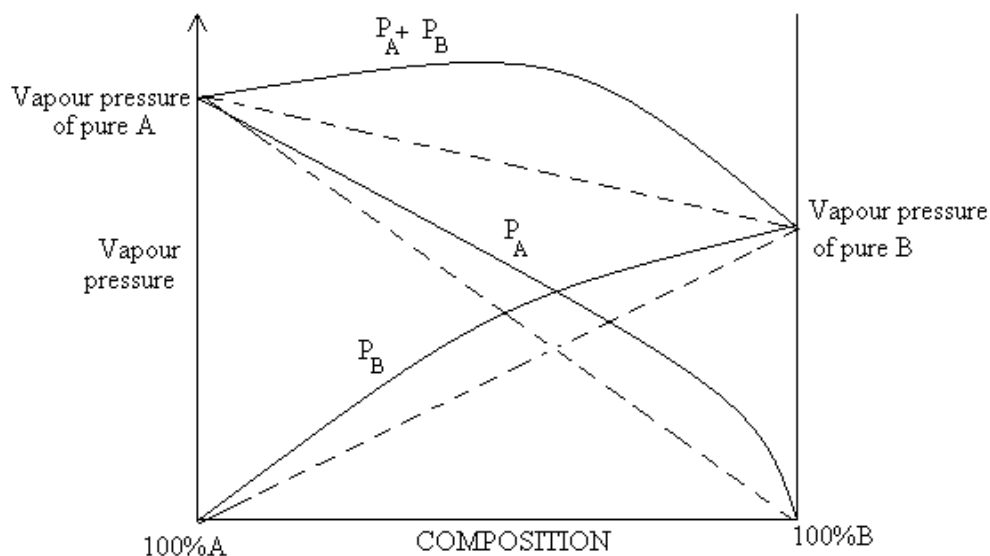
- Chloroform and ethyl alcohol.

Vapour pressure composition diagram of a liquid mixture showing positive deviation from Raoult's law

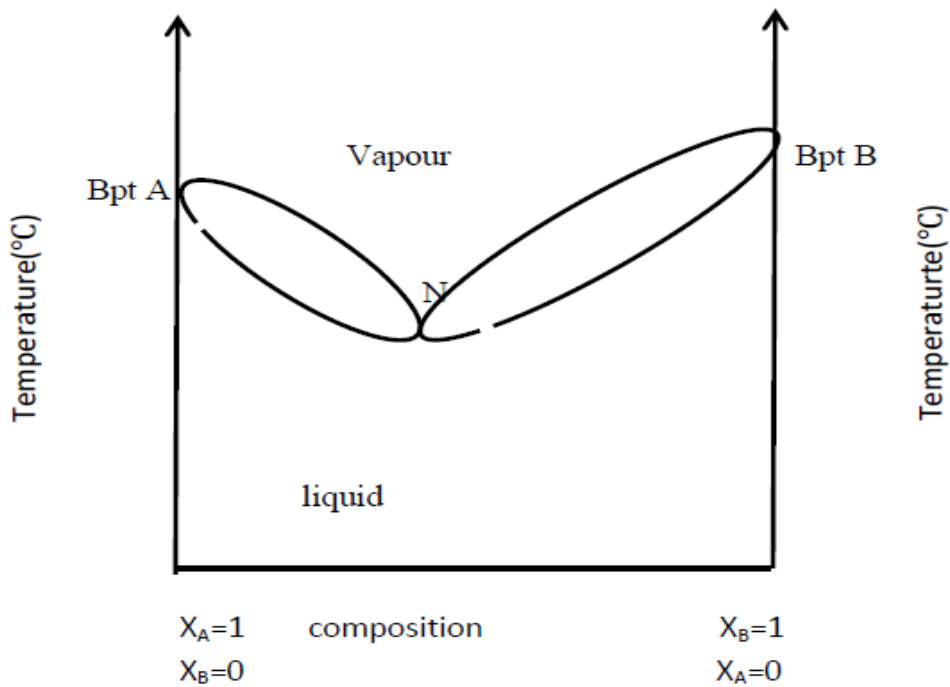


Maximum N, in the vapour phase means that the mixture(solution) requires less heat for its vapour pressure to reach to the atmospheric pressure hence **minimum boiling point**.

ALTERNATIVELY

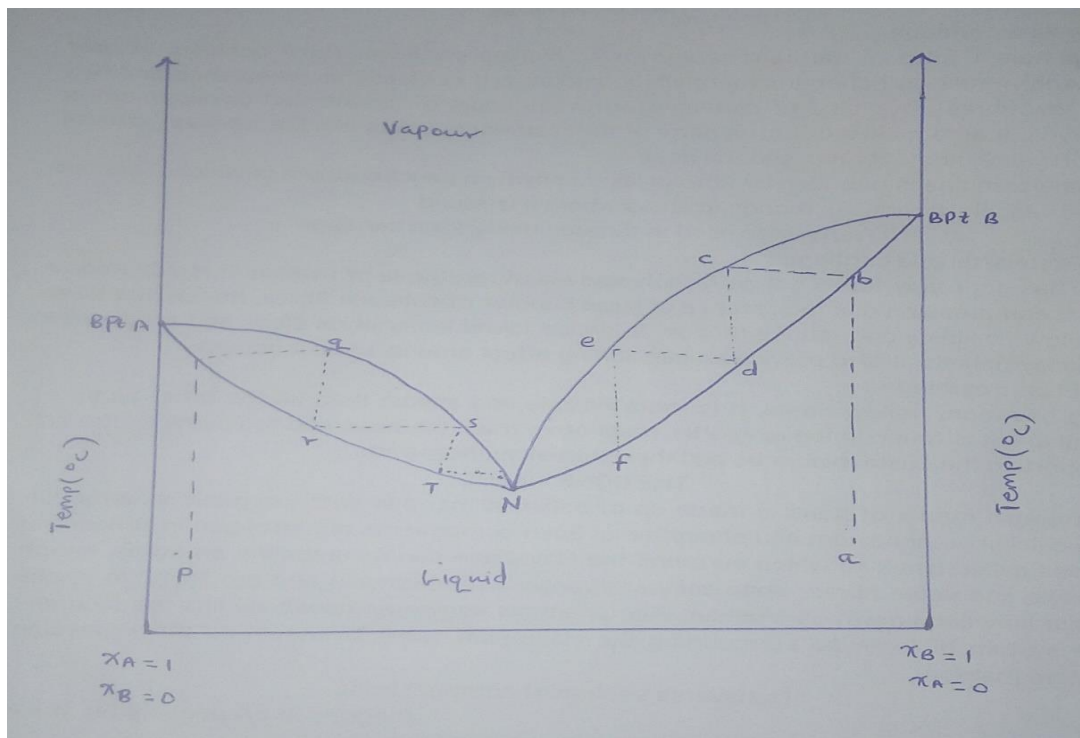


Boiling point composition diagram for a liquid mixture showing a positive deviation



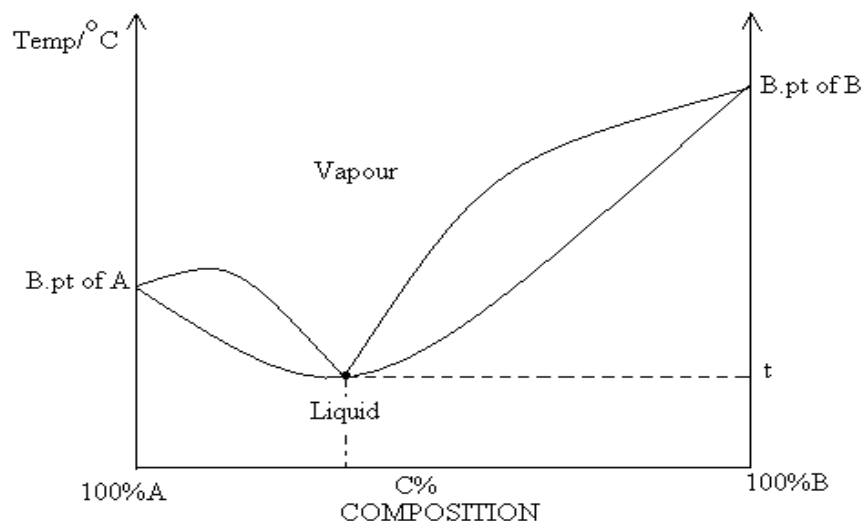
At minimum N, the composition of vapour and liquid is indistinguishable. The liquid mixture giving off vapour of the same composition behaving as a pure liquid mixture is called **minimum boiling azeotrope** or **constant boiling mixture**.

Fractional distillation of a liquid mixture of composition a and p



- When a liquid of composition **a**, is heated, successive boiling and condensation along **a, b, c, d, e, f** gives off a vapour richer in azeotropic mixture while the residual liquid mixture in the flask becomes richer in B.
- Also, if a liquid mixture of composition **p** is heated, successive boiling and condensation proceeds along **p, q, r, s, t** giving off vapour richer in the azeotropic mixture whereas the residue liquid in the flask becomes richer in A
- It's also not possible to completely separate components by fractional distillation.

Note (extra explanation)



When a liquid mixture whose composition is C% of B is heated, it will boil at a constant temperature, $t^{\circ}\text{C}$ to give a vapour whose composition is C% of B. A liquid mixture that produces a vapour whose composition is the same as that of the liquid mixture when the liquid is boiled is called an azeotropic mixture or an azeotrope such a mixture cannot be separated by fractional distillation since it boils at constant temperature and the vapour composition remains constant.

When a liquid mixture containing less than C% of B is fractionally distilled, the vapour becomes progressively richer in the azeotropic mixture which is then collected as a distillate, the residue is pure A.

Similarly, when a liquid mixture containing more than C% of B is fractionally distilled, the vapour becomes progressively richer in the azeotropic mixture and is collected as the distillate, the residue in the flask is pure B.

Differences between mixtures that deviate negatively and positively from Raoult's law.

Positive deviation	Negative deviation
Cohesive forces are stronger than adhesive forces	Cohesive forces are weaker than adhesive forces

There is an increase in volume on forming the liquid mixture	There is a decrease in volume on forming the liquid mixture
The mixture has a higher vapour than expected from Raoult's law	The mixture has a lower V.P than expected from Raoult's law.
Heat is absorbed on forming the liquid mixture therefore the liquid mixture therefore the container becomes cold	Heat is given off on forming the liquid mixture and the container becomes warm.

Question

- (i) A constant boiling point mixture(azeotrope) of hydrochloric acid and water is 20% by mass of HCl and has a density of 1.18 cm^{-3} . calculate the volume of the acid needed to prepare 1 litre 2M HCl solution.

Density of a zoetrope = 1.18 gcm^{-3}

Composition of a zoetrope = 20% HCl

Density of HCl alone = $\frac{20}{100} \times 1.18 = 0.236 \text{ gcm}^{-3}$

Mass of acid in gl^{-1}

1 cm^3 of acid contain 0.236g

1000 cm^3 of acid contain $0.236 \times 1000 = 236 \text{ gl}^{-1}$

RFM od HCl

$(1 \times 1) + (35.5 \times 1) = 36.5$

Majority of original acid = $\frac{\text{conc } (\text{gl}^{-1})}{\text{RFM}} = \frac{236}{36.5} = 0.647 \text{ M}$

0.647 moles are contained in 1000 cm^3 of acid

2 moles are contained in $\frac{1000 \times 2}{0.647} \text{ cm}^3$ of the acid

= 309.1 cm^3

Alternatively

Calculating the number of moles in 1 liter 2 M HCl solution

1000 cm^3 of HCl contains 2 moles

1 cm^3 of HCl contains $(2/1000)$

1000 cm^3 of HCl contains $(2/1000) \times 1000$ moles

=2 moles

Converting the moles of HCl into mass

$$\text{RFM of HCl} = (1 \times 1) + (35.5 \times 1) = 36.5$$

Therefore; 1 mole of HCl weighs 36.5

$$2 \text{ moles of HCl weigh } (36.5 \times 2) = 73\text{g}$$

But a constant boiling mixture of HCl and water has a composition of 20% HCl

Therefore; let the total mass of the boiling point mixture be x

$$\text{Where: } 73/x \times 100 = 20$$

$$= 365$$

But density = mass/volume

$$1.18 = 365/\text{volume}$$

$$= 365/1.18$$

$$= 309.3 \text{ cm}^3$$

Or

1.18g is contained in 1 cm³ of solution

1 g is contained in (1/1.18) cm³

365 g is contained in (1/1.18) x 365 cm³

$$= 309.3 \text{ cm}^3$$

Thus, to prepare 2M solution of hydrochloric acid measure 309.1cm³ of the original acid and transfer into 1 litre volumetric flask and then top up the solution mark with distilled water.

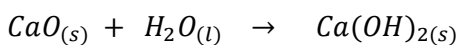
Properties of an azeotropic mixture

- Constant boiling point of the liquid mixture.
- Liquid and vapour have fixed compositions.

Separation of azeotropic mixtures

(i) Chemical methods

- Involves addition of quick lime (CaO) which removes the water e.g. azeotropic mixture of water and ethanol.



(ii) Distillation by use of third component

- E.g. an azeotropic mixture of ethanol and water can be separated by the addition of benzene and then distilling mixture of the 3 components.
- First distillation yields an azeotropic mixture of the three components.
- The second distillation produces the mixture of ethanol and benzene and on distilling the mixture, pure ethanol is obtained.

(iii) **solvent extraction**

- One component can be extracted using a solvent in which it dissolves.

(iv) **Adsorption**

- Always effective by addition of charcoal or silica gel which absorbs one of the components.

Assignment

Two liquids are usually classified according to whether they obey Raoult's law.

- a) State Raoult's law and draw a diagram to show how the vapour pressure of an ideal binary mixture vary with composition
 - (i) Give an example of a binary mixture which shows positive deviation from Raoult's law and draw a labeled diagram of temperature against composition.
 - (ii) Explain in terms of molecular interaction the reasons for the deviation
- b) Explain why the mixture in (i) above cannot be separated by fractional distillation.

Homework 1

- (a) State four methods that can be used to separate azeotropic mixtures.
- (b) What is meant by the term partially miscible liquids.
- (c) Define the term upper critical solution temperature and lower critical solution temperature as applied to partially miscible liquids.
- (d) Give an example of a pair of liquids that have
 - (i) Upper critical temperature.
 - (ii) Lower critical temperature.
 - (iii) Both upper and lower critical temperature

Homework 2

- (a). When a mixture of water and methanol is distilled, a constant boiling mixture containing 85% methanol is obtained at 70°C (*the boiling point of pure water and methanol are 100°C and 75°C respectively*)
 - (i). Draw a boiling point – composition diagram for the mixture of methanol and water
 - (ii). Explain the shape of diagram
 - (iii). Describe what would happen if a mixture containing less than 80% methanol was fractionally distilled
- (b). (i). Calculate the vapour pressure of a solution containing 18.5g of a non-volatile solute X in 30g of solvent Y at 298K. (*The molecular masses of X and Y are 280 and 74 respectively. The vapour pressure of Y is 1.2×10^4 at 298K*)
 - (ii). Explain the effect of increasing concentration of X on the boiling point of Y.

Homework 3

(a). State **Raoult's** law.

(b). A mixture of liquid **Y** and **Z** obeys Raoult's law. If the vapour pressure of Y and Z are 9.50 kNm⁻² and 3.20 kNm⁻² respectively at 20°C.

- Calculate the composition of the vapour containing 0.5 mol of each liquid at 20°C
- State which of the two liquids is more volatile. Explain your answer.

(c). The boiling points of liquid **Y** and **Z** are 368°C and 395°C respectively.

(i). Sketch a labelled boiling point – composition diagram of the mixture of the liquids

(ii). Using the diagram, describe how pure liquid **Z** can be obtained from a mixture containing 50%

(d). Explain why some liquids show negative deviation from Raoult's law

(e). If the mixture of liquids **Y** and **Z** in (b) was to deviate negatively from Raoult's law, sketch a labelled boiling point – composition diagram for the mixture.

Homework 4

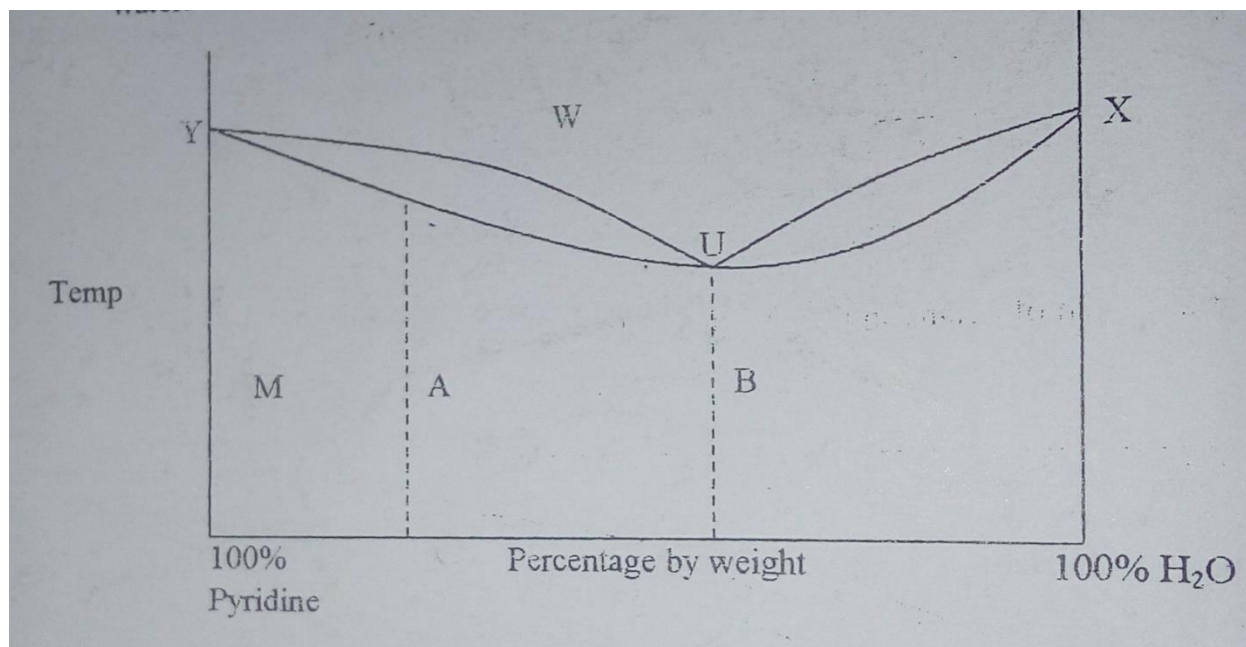
The following data were obtained for a mixture cyclohexane (Bpt = 81°C) in methanol (Bpt = 65°C)

Bpt (°C) of the mixture	Mole fraction of methanol in	
	Liquid mixture	Vapour above the mixture
70	0.12	0.27
60	0.31	0.47
55	0.50	0.56
57	0.82	0.69
61	0.94	0.83

- Plot a graph of boiling point against composition for the solution of cyclohexane in methanol.
- State the type of deviation from Raoult's law.
- Use your graph to obtain the composition of the azeotrope and explain why it cannot be separated into pure components by fractional distillation.
- Explain what would happen if a liquid mixture containing 40% methanol is fractionally distilled.

Question

The figure below shows the boiling composition diagram for the mixture of pyridine and water.



(i) What do the points W, M, U, and X represent?

W= vapour phase, M = liquid phase, Y= boiling point of pyridine, X= boiling point of water, U= azeotropic point.

(ii) What do the lower and upper curves represent?

Lower curve shows how the boiling points of the mixture varies as composition changes

Upper curve shows the composition of the vapour with change in the composition of the mixture.

(iii) State the deviation from Raoult's law that is shown by the diagram

Positive deviation

(iv) State two characteristics of the mixture shown at U

- Volume of solution increases
- Heat is absorbed when U is formed

(v) State two characteristics of the mixture at U

(vi) Explain why the mixture at U has a minimum boiling point

(vii) Explain carefully what happens when the mixtures at A and B are separately distilled from a simple flask

2. IMMISCIBLE LIQUIDS

Are liquids which do not mix at all conditions.

These are liquids which are insoluble in one another such that when mixed in any proportion they form two separate layers. E.g. Benzene and water, Trichloromethane and water, Tetrachloromethane and water, Chlorobenzene and water, Water and petrol, water and oil, aniline (phenylamine) and water, Nitrobenzene and water etc.

In a mixture of two immiscible liquids:

- Each liquid exerts its own vapour pressure corresponding to its pure state at a particular temperature independent of the other.
- vapour pressure above the liquid mixture will be the sum of vapour pressure of the two pure components at that temperature.
- A mixture of two immiscible liquids will boil at a temperature lower than the normal boiling point of the two liquids. This is because the total vapour pressure of the liquid reaches the given external pressure at a lower temperature than either liquid alone.
- This is the principle of steam distillation

NOTE

- The above principle of immiscible liquids is the basis of steam distillation (distillation under reduced pressure).
- When a liquid mixture of immiscible liquid is heated, each component of the mixture exerts vapour pressure independently. The vapour pressure increases with temperature and when the total vapour pressure equal to the external atmospheric pressure, the liquids boil. Therefore, a liquid mixture of immiscible liquids boils at a temperature that is lower than the boiling point of either of the components. This is because the total vapour pressure equal to the external atmospheric pressure at a temperature lower than the boiling point of either of the components.

EXAMPLE 1:

(a). mixture of Chlorobenzene (bpt 131) and water (bpt 100) boils at 91°C

(b). mixture of amino benzene (bpt 180) and water (bpt 100) boils at 96.5°C

EXAMPLE 2

The vapour pressure of aniline at 98°C is $7.065 \times 10^3 \text{ Nm}^{-2}$ and that of water at the same temperature is $94.260 \times 10^3 \text{ Nm}^{-2}$, therefore the total vapour pressure of the mixture at 98°C = $(7.065 + 94.260) \times 10^3$ = $101.325 \times 10^3 \text{ Nm}^{-2}$

Which is equal to the external atmospheric pressure. Therefore, a mixture of aniline and water will boil at 98°C, although the boiling point of water is 100°C and that of aniline is 184°C.

This principle is applied in steam distillation that is steam distillation works on the principle that when immiscible liquids are heated and agitated, they exert, vapour pressure independently such

that the total vapour pressure equal the external atmospheric pressure(760mmHg) at a temperature lower than the boiling point of either of the components.

Example 3

Pure water boils at 100°C while phenyl Amine boils at 184°C at 760mmHg. A mixture of phenyl Amine and water boils at 98°C at 760mmHg. Explain

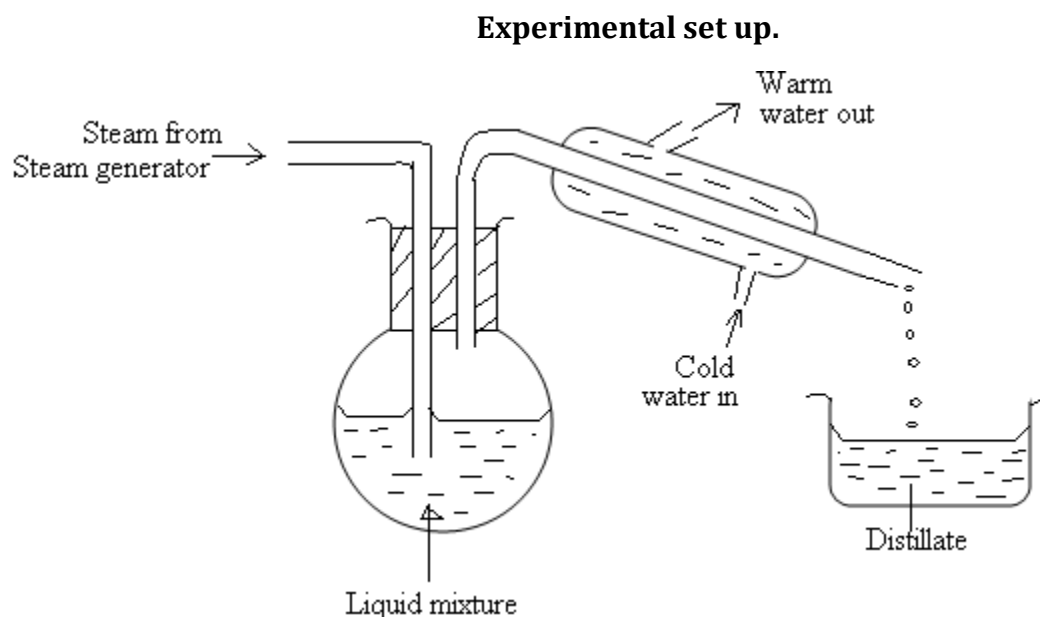
Answer:

Phenyl Amine and water are immiscible liquids and each of the liquids exerts its own vapour pressure independent of the vapour pressure of the other liquid at a given temperature. Therefore, the vapour pressure of the mixture is higher than the vapour pressure of the individual liquids at a given temperature hence on heating the vapour pressure of the mixture balances with the atmospheric pressure at a lower temperature for the mixture to boil.

STEAM DISTILLATION

This is a technique of separating an immiscible substance with water at a temperature below its boiling point by bubbling steam through the mixture.

steam distillation can also be defined as *a technique that is used to separate volatile substances from their non-volatile impurities by passing steam through the heated mixture*. It is mainly used in purifying of organic compounds from their non-volatile inorganic impurities. In this case the organic compound along with steam condense as they pass through the Liebig condenser and collect as a distillate. The non-volatile impurity remains in the distillation flask, and since water and the organic compound are immiscible, they are separated using a separating funnel.



Procedure

- Flask containing immiscible mixture is gently heated and steam is passed through the container having an impure mixture to be purified.
- Distillate is collected in the receiver and it contains two purified immiscible liquid e.g. water and organic compound.
- Organic compound is then isolated using a separating funnel, dried using a drying agent.

Alternative procedure(same)

When steam is passed through the liquid mixture, it heats up the mixture and agitates it such that one of the components of the mixture evaporates together with steam. The component together with water are collected as a distillate after condensation by the help of the condenser. Since the components collected, with water is immiscible with water the distillate in form of layers is separated using a separating funnel.

Example: e.g. A mixture of 2-nitrophenol and 4-Nitrophenol is separated by steam distillation. 2-Nitrophenol is isolated first with water because it has a lower boiling point (more volatile) than 4-Nitrophenol (less volatile). 2-Nitrophenol and water are then separated using a separating funnel.

NB: steam is preferred to liquid water because: -

- ❖ It keeps the mixture agitating
- ❖ Equilibrium between the vapors and the two liquids is rapidly attained.

CONDITIONS FOR STEAM DISTILLATION

- Components should have high RMM. This enables a reasonable mass of the substance to be obtained in the distillate.
- One of the components should be immiscible with water.
Reason: It enables the components of the mixture to exert their own vapour pressure independent of vapour pressure of the mixture.
The substance can easily be separated from water when it selects as a distillate using a separating funnel.
- Impurities in the mixture should be nonvolatile, so that they do not appear in the distillate.
- Components being separated should have a considerable saturated vapour pressure at temperature near the boiling point of water. This enables the substance to exert a reasonable vapour pressure at a given temperature.

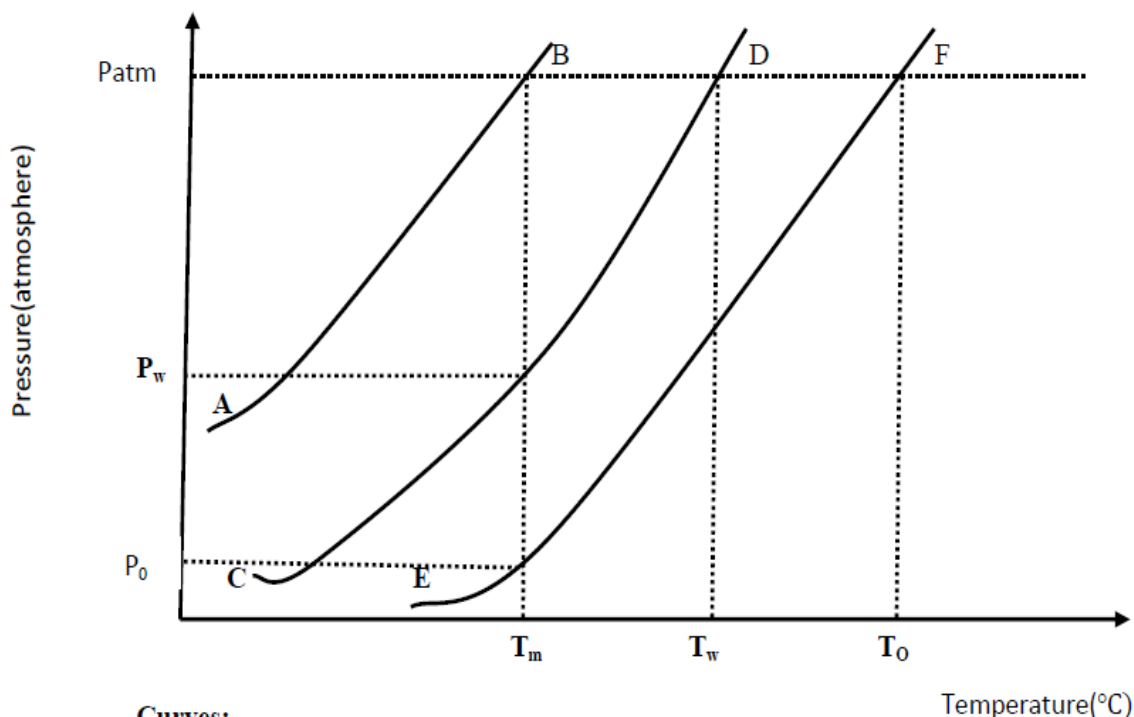
Advantages of steam distillation.

- Used for purification of organic compounds which decompose near their boiling points.
- Thermal decomposition of compounds which occurs at high temperature doesn't take place.
- It enables separation of miscible liquids whose components have high boiling points which are not close to each other. In this case the component with the lowest boiling is isolated first with water as the distillate.

NOTE

The amount of the component collected with water as the distillate is proportional to the vapour pressure exerted by that component.

Graphical determination of composition of distillate.



Curves:

AB-variation of total vapour pressure of water and organic compound with temperature

CD-variation of vapour pressure of water with temperature

EF- variation of vapour pressure of pure organic compound with temperature.

From Dalton's law; **Partial vapour pressure of a gas is directly proportional to its mole fraction**

$$\text{Partial pressure} = \text{mole fraction} \times P_{total} ; \quad P_w = X_w \times P_{total}$$

$$X_w = \frac{n_w}{n_w + n_o}$$

$$P_w = \frac{n_w}{n_w + n_o} P_{total} \dots\dots\dots (i)$$

$$\text{Similarly } P_o = \frac{n_o}{n_w + n_o} P_{total} \dots\dots\dots (ii)$$

Divide (i) by (ii)

$$\frac{P_w}{P_o} = \frac{n_w}{n_o}$$

But $n_w = \frac{m_w}{M_w}$ where $m_w = \text{mass of water}$; $M_w = \text{relative molecular mass of water}$

$n_o = \frac{m_o}{M_o}$ $m_o = \text{mass of organic compound}$; $M_o = \text{RMM of organic compound}$

$$\frac{P_w}{P_o} = \frac{m_w/M_w}{m_o/M_o} , \quad \frac{P_w}{P_o} = \frac{m_w \cdot M_o}{m_o \cdot M_w}$$

$$\frac{m_w}{m_o} = \frac{P_w/M_w}{P_o/M_o}$$

$$\text{Thus } \frac{\text{Mass of wter}}{\text{Mass of organic compound}} = \frac{\text{Partial pressure of water} \times \text{RMM of water}}{\text{Partial pressure of organic compoud} \times \text{RMM of organic compoud}}$$

Examples

- 1) When an organic compound P is steam distilled at normal atmospheric pressure of 760mmHg. The distillate was found to contain 80% by composition of P. At this temperature, Vapour pressure of water is 640mmHg. Calculate the RMM of P.

Solution

$$\frac{\text{Mass of wter}}{\text{Mass of organic compound}} = \frac{\text{Partial pressure of water} \times \text{RMM of water}}{\text{Partial pressure of organic compoud} \times \text{RMM of organic compoud}}$$

Total pressure = 760mmHg, % mass of P = 80% , % mass of water is (100-80) = 20%, Partial pressure of water = 640mmHg, Partial pressure of organic compound = total pressure – partial pressure of water = (760 – 640) mmHg = 120mmHg

RMM of water = 18 , RMM of organic compound = ?

$$\frac{20}{80} = \frac{1}{4} = \frac{640 \times 18}{120 \times \text{RMM of P}}$$

$$\text{RMM of P} = \frac{640 \times 18 \times 4}{120}$$

$$= 384$$

The RMM of the organic compound P is 384

Example 2

When Bromo benzene is steam distilled at normal atmospheric pressure of 760. The temperature of distillation was found to be 95.7°C. At this temperature, the vapour pressure of water is 640mmHg. Calculate the percentage composition of Bromo benzene in the distillate.

Solution

Partial pressure of bromo benzene = Total pressure – partial pressure of water

$$= (760 - 640) \text{ mmHg}$$

$$= 120 \text{ mmHg}$$

Partial pressure of water = 640 mmHg

RMM of water = 18g, RMM of $\text{C}_6\text{H}_5\text{Br}$ = 72 + 5 + 80 = 157

Let the mass of water be Xg; mass of Bromo benzene be Yg

$$\frac{\text{Mass of water}}{\text{Mass of organic compound}} = \frac{\text{Partial pressure of water} \times \text{RMM of water}}{\text{Partial pressure of organic compound} \times \text{RMM of organic compound}}$$

$$\frac{X}{Y} = \frac{640 \times 18}{120 \times 157}$$

$$\frac{X}{Y} = \frac{11520}{18840}$$

Mass of water = 1152, mass of $\text{C}_6\text{H}_5\text{Br}$ = 1884

Total mass of distillate = X + Y

$$\% \text{ mass of } \text{C}_6\text{H}_5\text{Br} = \left(\frac{\text{mass of } \text{C}_6\text{H}_5\text{Br}}{\text{total mass}} \times 100\% \right)$$

$$= \frac{1884 \times 100}{3036}$$

$$= 62.06\%$$

Exercise 1

1. A mixture of naphthalene ($C_{10}H_{18}$) and water distilled at 98.3°C and 753mmHg . Calculate the composition of distillate as percentage by mass given that the vapour pressure of water at 98°C is 715mmHg .
2. At 744mmHg , the steam distillation of a certain liquid takes place at 90°C . The vapour pressure of water at this temperature is 634mmHg , and the distillate contains 50% by mass of liquid T. calculate the RMM of T.
3. (a) what is steam distillation
(b) Explain the principle behind isolation of substance by steam distillation.
(c) Describe briefly how you would perform steam distillation in a laboratory.

Exercise 2

1. When 490g of an organic compound X containing carbon and hydrogen only was burnt in oxygen, 15.78g of carbon dioxide and 5.38g of water were formed.
 - (i) Calculate the empirical formula of X.
 - (ii) X was steam distilled at 80°C and 760mmHg and the distillate was found to contain 90.8% by mass of X (The vapour pressure of water at 80°C is 240mmHg). Calculate the formula mass of x
2. The vapour pressure (V.P.) of water and of an immiscible liquid X at different temperatures are given in the table below;

Temperature/ $^\circ\text{C}$	92	94	96	98	100
V.P. of X /KPa	6	8	12	15	17
V.P of H_2O /KPa	74	80	88	94	101
V.P of mixture/KPa	80	88	100	109	118

- (a) On the same axes, plot graphs of vapour pressure against temperature. (02 marks)
- (b) (i) Determine the vapour pressure of the mixtures of X and water at the temperatures given in the table above. (02 marks)
(ii) On the same axes of the graph in (a), plot a graph of the vapour pressure of the mixture versus temperature. (02 marks)
- (c) The distillate obtained from the mixture at 101KPa contained 1.6g of water and 1.1g of X.
Calculate the relative molecular mass of X using the information from the graphs you have drawn.
 $RFM = 91.78$, $P_{\text{H}_2\text{O}} = 89\text{KPa}$, $P_x = 12\text{KPa}$. (05 marks)
- (d) (i) Explain the principles in separation of mixtures by steam distillation. (05 marks)
(ii) State any two advantages of steam distillation. (02 marks)

Solution for some selected parts

(c) From the graph; the vapour of x = 12 KPa, vapour pressure of water = 89 KPa

$$\text{RFM of H}_2\text{O} = (1 \times 2) + (1 \times 16)$$

$$= 18$$

$$\text{From; } \frac{P^0_{\text{H}_2\text{O}}}{P^0_x} = \frac{\text{mass of H}_2\text{O} / \text{molar mass of H}_2\text{O}}{\text{mass of x} / \text{molar mass of x}}$$

$$\frac{89}{12} = \frac{1.6 / 18}{1.1 / \text{molar mass}}$$

$$89 \times 18 \times 1.1 = 12 \times 1.6 \times \text{molar mass of x}$$

$$\begin{aligned} \text{Hence; molar mass of x} &= \frac{1762.2}{19.2} \\ &= 91.78 \end{aligned}$$

D(i)

- *The substance to be steam distilled must be miscible with water*
- *The two substances in the mixture contribute vapour pressures independent of the other*
- *The vapour pressure above the liquid is sum of the vapour pressures of the pure components in the mixture*
- *The substance should have a high molecular mass so that a lot of it is distilled off*
- *Impurities in the mixture should be non-volatile so that they don't appear in the distillate*
- *On heating; the vapour pressure increases so that the sum of the vapour pressure equals that of the atmospheric pressure so that the mixture boils at a lower boiling temperature than the boiling points of either liquids.*

Miscellaneous question

(1)

(a) Explain what is meant by the term ideal solution.

(b) At standard atmospheric pressure, hydrochloric acid and water form a constant boiling point mixture having a boiling point of 110°C and a composition of 20% by mass of hydrochloric acid.

(i) Define a constant boiling mixture

(ii) Sketch a labelled diagram of the boiling point – composition for hydrochloric acid and water system. [boiling point of water and hydrochloric acid are 100 and 85°C respectively]

(c) A constant boiling mixture of hydrochloric acid and water has a density of 1.18gcm⁻³. Calculate the volume of the acid needed to prepare one litre of 2M hydrochloric acid solution.

(d) The vapour pressure of ethanol at 20°C is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. The mole fraction of benzene is 0.09 for a mixture of benzene and ethanol at 20°C. Calculate

(i) The vapour pressure of the mixture

(ii) The mole fraction of benzene in the vapour phase

(2)

(a) Define the term partial pressure

(b) The vapour pressure of pure chloroform and carbon tetrachloride are 199.1 and 114.5 mmHg respectively at 25°C. Assuming that the mixture behaves ideally. Calculate

(i) The partial pressure of each component in the mixture

(ii) The total pressure.

(c) Calculate the percentage of carbon tetrachloride in the vapour in equilibrium with the liquid mixture containing 0.4 mole fraction of chloroform

(3)

Ethanol (boiling point 78.5°C) and tetrachloromethane (boiling point 76.8°C) form an azeotropic mixture of boiling point 65.0°C and 38% ethanol by composition

(i) What is an azeotropic mixture?

(ii) Draw a well labelled boiling point – composition diagram for the ethanol – tetrachloromethane mixture

(iii) Explain why ethanol and tetrachloromethane form an azeotropic mixture?

(b) Describe the changes that take place when a mixture containing 45% ethanol is fractionally distilled.

END