PHYSICAL / PHASE EQUILIBRIA

This involves the study of behaviour of substances as they change phase.

Solid, liquid, and gaseous states of a particular substance are known as physical states because they are chemically indistinguishable.

Physical equilibrium is the equilibrium established between molecules of a substance in one physical state and molecules of the same substance in another physical state. i.e

Solid $\rightleftharpoons$ liquid equilibrium e.g. Ice $\rightleftharpoons$ liquid water

Liquid $\rightleftharpoons$ vapour equilibrium e.g. liquid water $\rightleftharpoons$ steam.

Solid $\rightleftharpoons$ vapour equilibrium e.g. Ice $\rightleftharpoons$ steam.

The characteristics of a physical equilibrium include;
- the equilibrium is attained in a closed system.
- at equilibrium, the measurable properties of a system become constant.
- at equilibrium, there is a dynamic balance between the two opposite processes.

Each of the three homogeneous physical states (solid, liquid and gas) in which a substance can exist is also known as a phase.

A phase is a homogeneous and physically distinct part of a system which is separated from the other parts by a definite boundary.

Phase equilibria involves the study of the conditions (temperature, pressure and concentration) under which different phases are in equilibrium.

Equilibrium can only be achieved in a closed system when the rate of movement of molecules from one phase to the other is exactly balanced by the opposing process.

Note:
(i)   One liquid layer makes one phase whether it is of a pure substance or a mixture.
(ii)   Two liquid layers in contact show two phases e.g in a liquid mixture of water and kerosene, there are two phases because there is a line of separation between the two liquids.
(iii)   A mixture of gases always makes one phase because the system is homogeneous.
(iv)   An immiscible mixture of water and tetrachloromethane in which iodine has been added contains three components, two phases and has one boundary.

Phase diagrams

A phase diagram is a plot showing conditions of temperature and pressure under which the different physical states of a substance are stable / in equilibrium.

In a phase diagram, a phase is represented by a <u>region</u>. The lines or curves represent the conditions under which two phases can exist in equilibrium.

Phase diagrams for One – component system.
(i)   Water system
The various equilibria which can exist when water is held at various pressure and temperatures are summarised in the pressure – temperature diagram below.
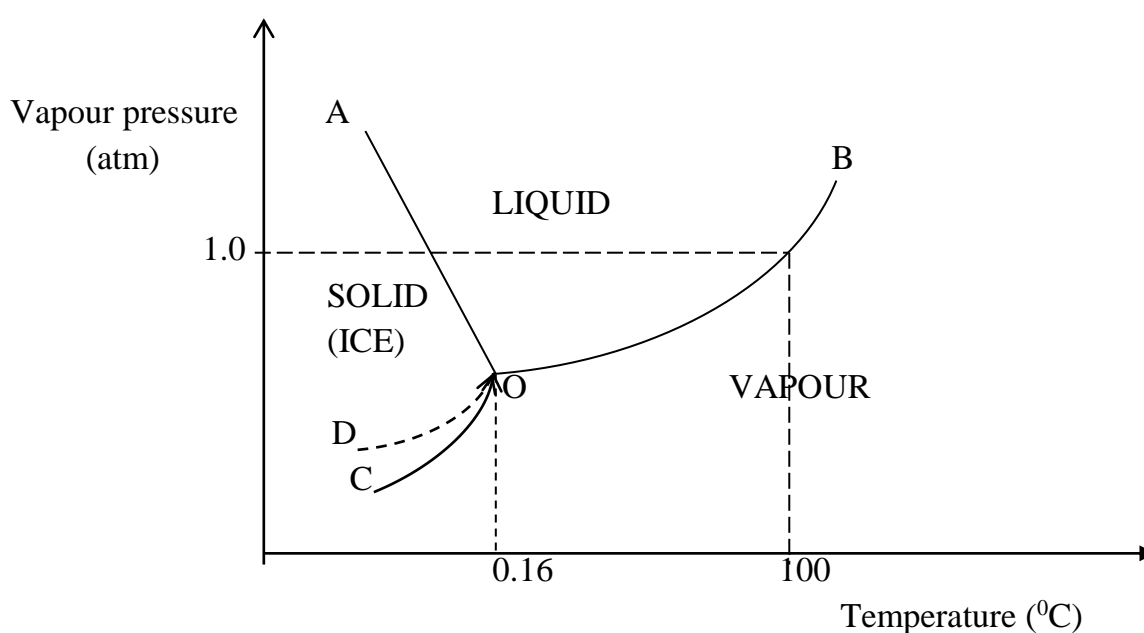
- At conditions of low temperature and low pressure, water exists as Ice (solid state).
- At conditions of high temperature and low pressure, water exists as vapour.
- At high temperature and high pressure, water largely exists as liquid.

Line OB is the vapour pressure curve or vaporisation curve of liquid water. It shows the effect of pressure on the boiling point of water. i.e. an increase in pressure results into increase in boiling point.
Any particular temperature along this curve gives the boiling point of liquid water at that pressure.

Note:
Boiling point is the constant temperature and pressure at which the liquid turns into a vapour.

Line CO is the sublimation curve for ice. It shows the combination of temperature and pressure at which ice and its vapour are in equilibrium.

The imaginary line OD shows a condition known as <u>super cooling</u>. This is the process of lowering the temperature of a liquid below its freezing point without it becoming a solid.

Super cooling occurs when temperature is decreased with an increase in pressure.

Line OA is the melting point curve of ice or freezing point curve of liquid water.

The line shows the effect of pressure on the melting point if ice or freezing point of liquid water.

The line shows that the melting point of ice is lowered by an increase in pressure . i.e. increase in pressure favours melting.

Explanation.

When water freezes, its volume increases due to the stronger intermolecular hydrogen bonds formed. This results into a tetrahedral open structure of ice.
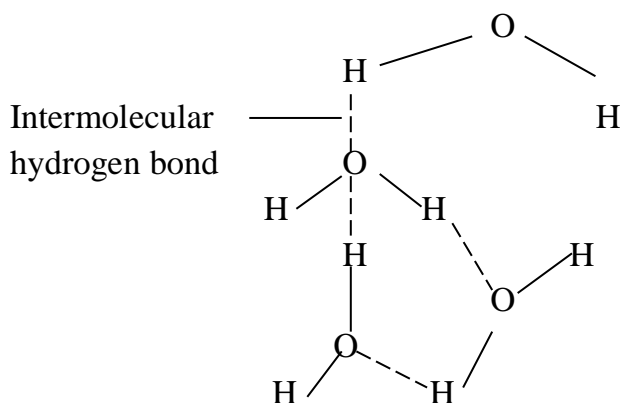
When pressure is applied to this structure, the hydrogen bonds breakdown and the open structure is destroyed making ice to melt.

Note.

The melting points of Bismuth and Antimony also decrease with increase in pressure.

Point O is the _triple point_.

A triple point is a point that shows conditions of temperature and pressure under which all the three phases co-exist in equilibrium with each other.

Point B is called the _Critical point_

A critical point is a point above which liquification of vapour is impossible however much the pressure is increased.

(ii)   Carbondioxide system

Carbondioxide is an example of substances whose melting point increases with increase in pressure.
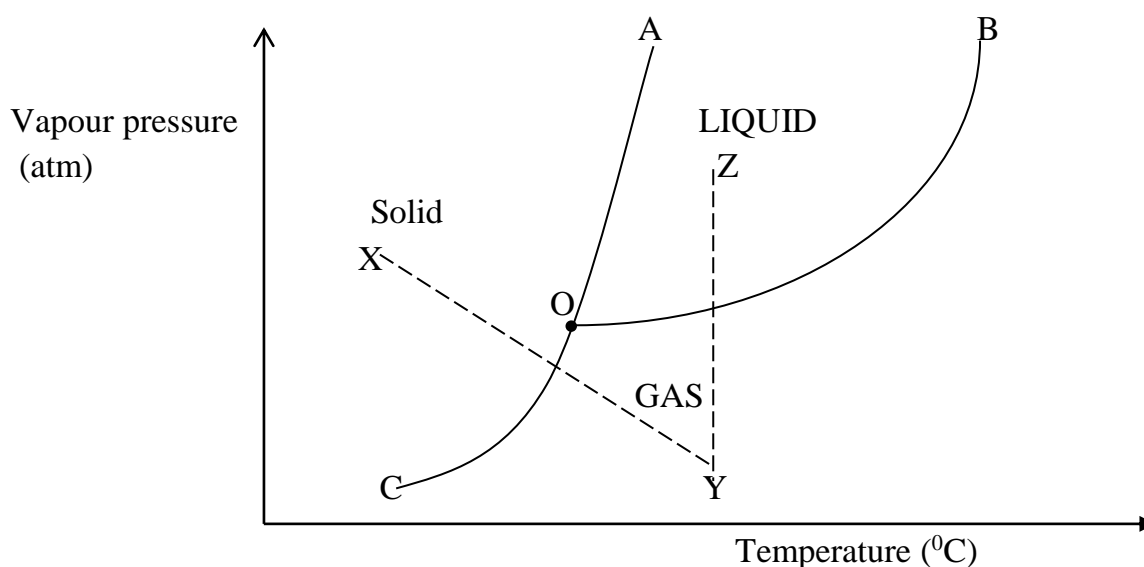
The above phase diagram differs from that of water in the following ways;
-   the line OA slopes away from the vapour pressure axis indicating that the melting point of solid carbondioxide increases with increase in pressure. This is because molecules of carbondioxide in the solid phase are packed more closely than in the liquid phase unlike in water.
-   the triple point of carbondioxide occurs at a higher vapour pressure than that of water.

A system at point X is in solid phase and changes to vapour phase along XY when heated at reduced pressure. i.e. sublimation takes place along XY.

At point Y, the system is in vapour phase. When compressed at a constant temperature, it changes to a liquid along YZ.

Point O is the triple point for carbondioxide.

This point is greater than 1 atm. This implies that solid carbondioxide boils without passing through the liquid state. i.e. it sublimes.


(iii)   The Sulphur system.

Sulphur exists in two allotropic forms. i.e;
-   Rhombic sulphur (α - sulphur)
-   Monoclinic sulphur (β - sulphur)

At ordinary temperatures, the stable allotrope is the rhombic form.

The temperature at which the two allotropes are in equilibrium is called the <u>transition temperature</u>, which is 96^{0}C.

When rhombic sulphur is gently heated, it is converted to monoclinic sulphur at 96^{0}C. Further heating results into monoclinic sulphur changing to liquid sulphur at 119^{0}C.
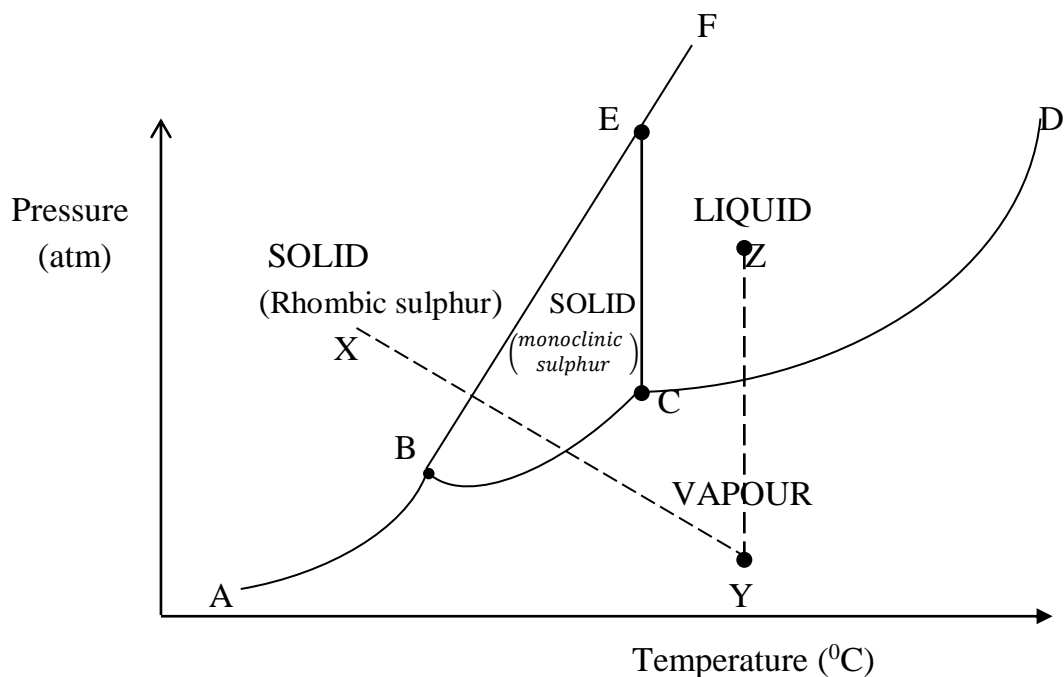
Curve **AB** is the sublimation curve of rhombic sulphur. It shows the variation of the vapour pressure of rhombic sulphur with temperature.

Curve **BC** is the sublimation curve of monoclinic sulphur.

Curve **CD** is the vaporisation curve / vapour pressure curve of liquid sulphur. It shows the variation of vapour pressure of liquid sulphur with temperature.

Curve **BE** is called the transition curve. It shows the effect of pressure on the transition temperature between rhombic sulphur and monoclinic sulphur. Along this line, monoclinic sulphur is in equilibrium with rhombic sulphur.

Curve **CE** is the fusion curve of monoclinic sulphur. It shows the effect of pressure on the melting point of monoclinic sulphur.

Curve **EF** is the fusion curve of rhombic sulphur.

Point **B** is the triple point for rhombic sulphur, monoclinic sulphur and vapour sulphur.

Point **C** is the triple point for monoclinic sulphur, liquid sulphur and the sulphur vapour.

Point **E** is the triple point for rhombic sulphur, monoclinic sulphur and liquid sulphur.

Point **D** is the critical point.

When any of the phases is subjected to a change in temperature or pressure, it will disappear and another dominates. e.g. Rhombic sulphur at X when heated at reduced pressure along XY changes to monoclinic sulphur before turning into vapour.

Sulphur at point Y is in vapour state. When compressed at a constant temperature changes to liquid sulphur along YZ.

PHASE DIAGRAMS FOR TWO – COMPONENT SYSTEMS

A two – component system is one in which two chemical individual components are involved in the equilibrium.

Examples include;

- Solid – liquid equilibrium mixtures (eutectic mixtures)
- Liquid – liquid equilibrium mixtures (miscible liquid mixtures.)

SOLID – LIQUID EQUILIBRIUM MIXTURES (EUTECTIC MIXTURES)

When a liquid form of a pure substance is cooled, a certain temperature is reached where the liquid is converted to its solid state at a constant temperature and pressure.

The constant temperature at which the solid and liquid forms of a pure substance are in equilibrium with each other is called the freezing point.

Below the freezing points, the liquid will change completely into a solid.

Consider the following cooling curve for molten lead.
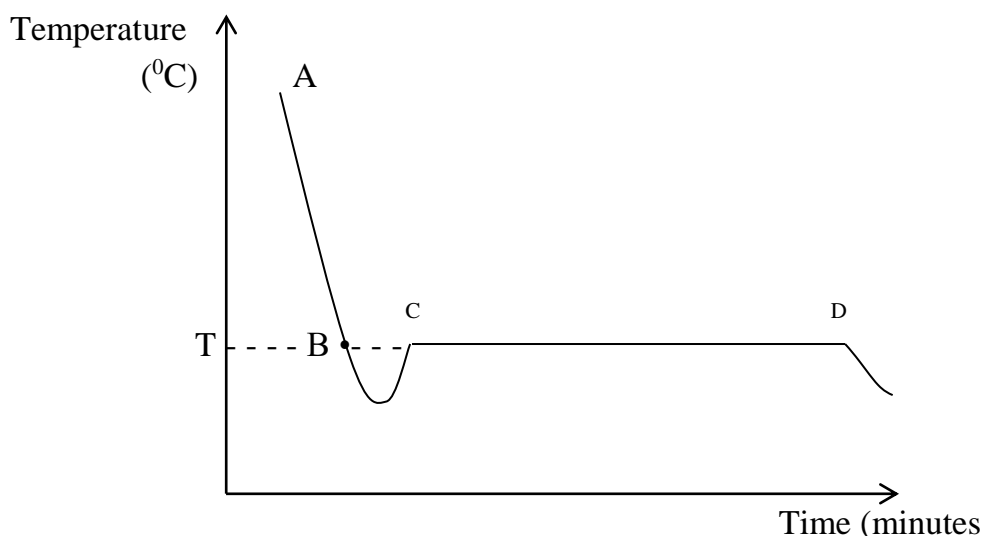
Along AB, molten lead is cooling as temperature decreases steadily.

Along CD, an equilibrium is established between molten lead and solid lead and this occurs at a constant temperature.

Line BC shows a condition known as super cooling. However, after the first crystal has formed, heat is absorbed from the surrounding and further solidification occurs at a constant temperature.

T is the freezing point / melting point of lead.

Note:

The freezing point of a liquid is depressed when another substance is added to it.

The decrease in freezing point is approximately proportional to the relative amount of substance (solute) added.

Cooling curves for mixtures are obtained by varying the amount of each component in the mixture, and then determining the temperature at which the mixture begins to freeze at each composition. The component with a higher composition solidifies out first.

Consider the cooling curve of the liquid Tin – lead mixture, when a liquid mixture containing 25% tin and 75% lead by mass is cooled at a fixed pressure, a temperature, T_1, is reached when solid lead (because it has a higher composition) separates out of the mixture. This temperature will be lower than the actual freezing point of molten lead.

As cooling is continued, the crystallisation of lead makes the liquid mixture less richer in lead until a certain composition where both components of the mixture solidify together at a fixed temperature, T_2.
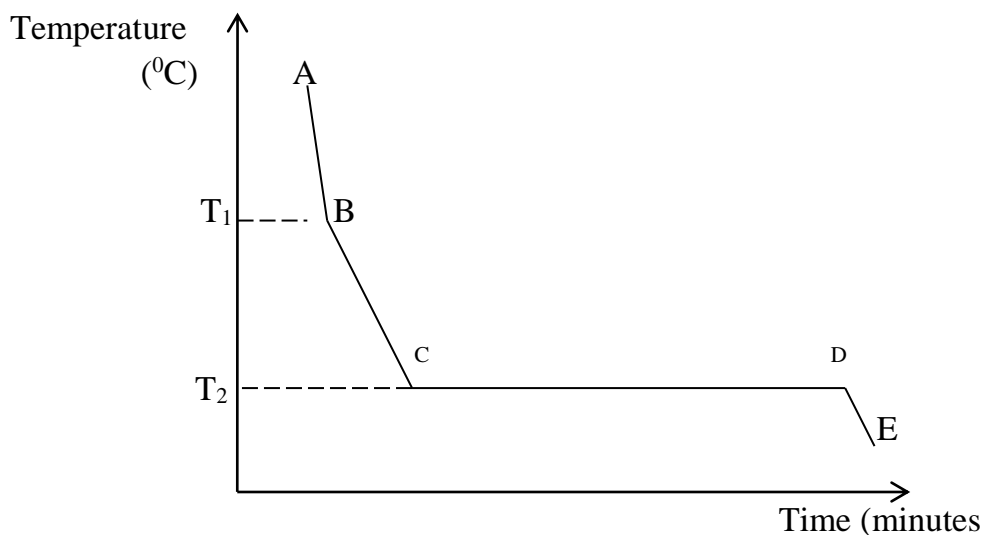
Along AB, the liquid mixture is cooling.

Along BC, lead is crystallising out of the mixture.

Along CD, both lead and tin solidify / crystallise out together.

Along DE, the solid mixture is cooling.

Points T_1 and T_2 are known as <u>arrest points</u> or freezing points of lead and the mixture respectively.

Question:

Explain how phase diagrams for solid – liquid mixture (eutectic mixtures) are obtained.

Soln

- *Cooling curves for molten mixtures of various compositions, but equal total mass are first plotted. These give the arrest points (freezing points) for these mixtures.*
- *The temperatures corresponding to the arrest points for a number of mixtures are plotted against composition of the mixtures to obtain the phase diagram.*

Constructing a phase diagram of the Tin and Lead mixture.

- Pure tin and pure lead are heated separately until they melt.
- Each molten mixture is allowed to cool while stirring and the constant temperature at which they freeze is recorded.
- Mixtures of various compositions of solid tin and lead are prepared.
- Each mixture is heated separately until it melts.
- The temperatures corresponding to freezing points are plotted against composition to obtain a phase diagram of the following shape.
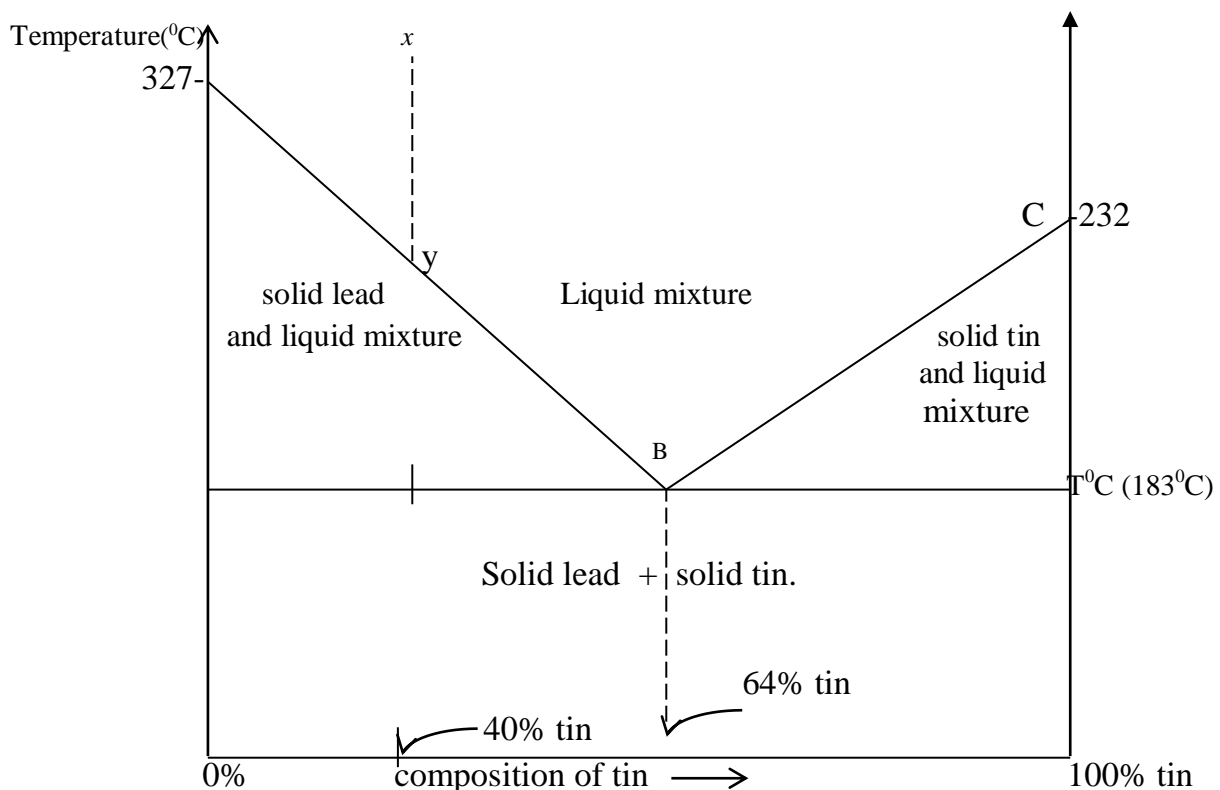
Point B is the eutectic point, and the eutectic mixture contains 64% tin and 36% lead. The above diagram generally shows that addition of tin to molten lead results into lowering of the freezing point of lead.

As the mixture cools, pure lead crystallises out. The liquid mixture thus becomes richer in tin as more lead crystallises out hence the freezing point of lead continues to be lowered.

At a certain temperature, T^0C both lead and tin crystallise out of the liquid mixture, and this temperature remains constant until the whole mixture has solidified.

Note:
- AB shows the variation of freezing point of lead as tin is added or; lowering of freezing point of lead as the percentage of tin increases.
- BA shows the variation of freezing point of lead as the percentage of tin is reduced.
- BC shows variation in the freezing point of tin as the percentage of lead in the mixture is reduced.

  Or, increase in melting point of tin as concentration of lead decreases.
- CB shows variation of freezing point of tin as lead is added

  Or; lowering of freezing point of tin as percentage of lead increases.
- The phases at point B are; solid lead, solid tin, and liquid.

Question:
Describe the changes that would take place when a liquid mixture of the above system containing 40% tin is cooled from 400^0C to 100^0C.

Soln:
The liquid mixture containing 40% tin cools without change in phase along xy, with a fixed composition up to point y where solid lead begins to crystallise out.

As lead solidifies out with further cooling, the liquid mixture becomes more saturated with tin and the freezing point of lead is further decreased along yB up to the composition of the eutectic at B, 64% tin.

At B, the temperature (183^0C) remains constant and both lead and tin solidify out together until all the liquid has solidified.

Further cooling below 183^0C results into no change in phase of the solid mixture.

Simple eutectic systems involving salt and water sodium nitrate – water system.
The phase diagram for such a system is obtained through the following steps.
- Pure water is allowed to cool while stirring and the constant temperature at which it freezes is recorded.
- Solutions of various compositions of sodium nitrate and water are prepared.
- Each solution is allowed to cool while stirring and the constant temperature at which they freeze is recorded.

- A graph of freezing point / temperature against composition is plotted to give a phase diagram.
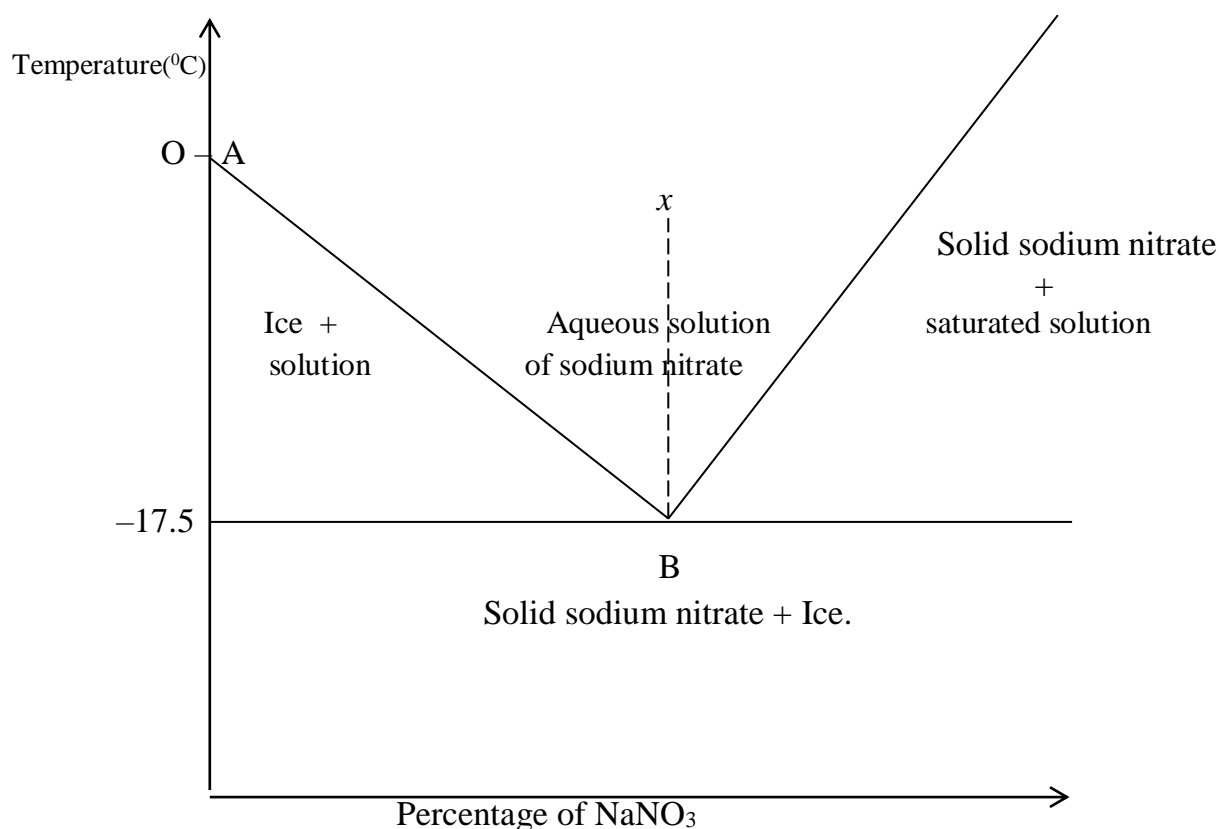
The phase diagram of a system involving a salt and water is almost similar to that of a simple eutectic system involving two metals or two salts.

The only fundamental difference is that with the water – salt system, the melting point of the salt in the phase diagram cannot be realised. This is because the melting point of the salt is generally much higher than the critical temperature of water in the solution.

Note:
- Point A (0^0C) is the freezing point of water.
- Line AB shows the lowering of the freezing point of water as more sodium nitrate is added to it.
- Point B is the eutectic point. It is the lowest temperature which can be reached before the whole system solidifies. It is also the only point at which ice, solid sodium nitrate and the saturated solution of sodium nitrate are in equilibrium.
- Line BC shows the solubility of sodium nitrate in water with increasing temperature i.e solubility increases with increase in temperature.

Explanation of the above phase diagram.

Along AB, a dilute solution of sodium nitrate is being cooled below 0^0C. Pure ice begins to crystallise out at a temperature less than 0^0C because the added solute lowers the freezing point of water, and ice comes out first because the solution is dilute.

As ice is formed, the solution becomes more concentrated with sodium nitrate hence freezing point is decreased further and more ice is deposited.

As the remaining solution gets more concentrated, eventually both ice and sodium nitrate begin to crystallise out together at a fixed temperature, -17.5^0C until the whole solution solidifies.

Similarly, when a concentrated solution of sodium nitrate is cooled, along CB, crystals of pure sodium nitrate will be deposited until at -17.5^0C, when both ice and sodium nitrate crystallise out together.

Note:

When a solution of composition x is slowly cooled, it does so without change in phase along xB with a fixed composition. At point B, the solution solidifies at a constant temperature, -17.5^0C, until when all the solution has solidified into ice and sodium nitrate crystals.

Examples of other mixtures that form eutectics.
- Cadmium and zinc
- Naphthalene and camphor
- Tin and Bismuth
- Antimony and lead
- Benzene and naphthalene

- An eutectic mixture is a heterogeneous solid mixture which when heated at constant pressure will melt at a constant temperature giving a liquid of the same composition as the solid

  or;

  it is a liquid mixture which at a constant pressure solidifies at constant temperature to form a heterogeneous solid of the same composition as the liquid.

- An eutectic point is a point at which two components of a liquid mixture solidify simultaneously without change in composition at a fixed temperature and pressure.

- An eutectic temperature is the constant temperature at which a liquid mixture solidifies at constant pressure to give a heterogeneous solid of the same composition as that of the liquid.

Conditions for the formation of eutectic mixture
- Pure crystals of the components should separate from mixture on cooling.
- The two substances involved must be completely miscible when melted.

Eutectic mixtures behave like compounds or pure metals in the following ways;
- Both have sharp melting points at a fixed pressure.
- Both produce similar cooling curves.
- They have a fixed composition at a constant pressure.

Reasons why eutectic mixtures are not compounds.
- Their compositions vary with pressure.
- They can be separated by physical means.
- Microscopic examination shows that eutectic mixtures are heterogeneous, made of crystals of different substances.
- Composition of an eutectic mixture does not correspond to any known compound.

Application of eutectic mixtures.
- formation of alloys e.g. solder, brass.
- formation of solders for joining metals at relatively low temperatures.
- used in safety appliances as plugs.
- Determination of identity of unknown organic compounds.
- In industries for lowering melting point of some substances.

Questions
1. The table below shows the melting points of various mixtures of naphthalene – biphenyl system.

Percentage of naphthalene	12.5	27.5	62.5	80.0
Melting point (^{0}C)	63.0	53.0	54.0	69.0

a) Draw a fully labelled phase diagram of the naphthalene – biphenyl system. (the melting points of naphthalene and biphenyl are 86^0C and 71^0C respectively)
b) Using the phase diagram, determine the;
i)   eutectic temperature.
ii)   Composition of the eutectic mixture.

---

c) Describe the changes that would take place if a liquid mixture of the above system containing;

(i)   15% naphthalene was cooled from 90^0C to room temperature.

(ii)   48% naphthalene was cooled from 90^0C to room temperature.

d) Determine the mass of biphenyl that crystallises out if 200g of the liquid mixture containing 10% naphthalene is cooled from 95^0C to 50^0C.

Soln:

b)(i) 40^0C

(ii)   48% naphthalene and 52% biphenyl

d)   A perpendicular is drawn from 95^0C to 50^0C at 10% naphthalene.
A horizontal line is then drawn through 50^0C to find the composition of liquid mixture at 50^0C.

From the graph, percentage composition of naphthalene in the liquid mixture is 34%.

- *Mass of naphthalene in liquid mixture before cooling $\frac{10}{100}$ x 200 = 20g.*
- *Thus mass of biphenyl in liquid mixture before cooling = 200 – 20*
  = 180g.

Since only biphenyl crystallises out on cooling, the mass of naphthalene remains unchanged = 20g.
Let the mass of biphenyl remaining in liquid mixture be mg..

Percentage of naphthalene in liquid mixture at 50^0C;

$\frac{20}{m+20}$ x 100 = 34

2000 = 34m + 680

m = 38.8g

Mass of Biphenyl that crystallises out = 180 – 38.8
= 141.2g

2.   The table below shows the melting points and composition of various mixtures of bismuth and cadmium.

Percentage of cadmium	20	35	50	65	80	95
Melting point (^{0}C)	226	190	156	184	242	300

a) Draw a well labelled phase diagram for the cadmium – bismuth system.
b) Use your diagram to determine the;
   i)   melting points of pure cadmium and pure bismuth.
   ii)   composition and melting point of the eutectic mixture.

c) Describe what happens when a liquid mixture containing 10% of cadmium at 350^{0}C is gradually cooled.

d) Determine the mass of bismuth that crystallised when 200g of the mixture containing 25% cadmium was cooled from 300^{0}C to 168^{0}C

e) State <u>two</u> similarities and <u>two</u> differences between an eutectic mixture and a pure compound.

3.   The table below shows composition and melting points of various mixtures of ethanoic acid and water.

Percentage of ethanoic acid	0	20	40	60	80	100
Melting point (^{0}C)	0	–10	–20	–19	–1	18

a) Draw a well labelled temperature – composition phase diagram for the ethanoic acid – water system.

b) Using your diagram, determine the composition of the eutectic mixture.

c) Explain the phase changes that would take place if a liquid mixture containing 20% ethanoic acid at 15^{0}C is cooled to – 30^{0}C.

d) 135g of the liquid mixture of composition 16% ethanoic acid at 5^{0}C was cooled to 22^{0}C. Calculate the mass of ice that crystallised out.

LIQUID – LIQUID EQUILIBRIUM MIXTURES.

When two liquids which do not chemically react are mixed, there is formation of either a miscible liquid mixture or an immiscible liquid mixture.

MISCIBLE LIQUID MIXTURES

These are formed of liquids that completely dissolve in each other in any proportion to give a homogeneous solution.

Miscible liquid mixtures are of two types;

 (i) Ideal solutions

 (ii) Non – ideal solutions.

IDEAL SOLUTIONS

This is a solution in which forces of attraction between the unlike molecules of the components are equal in magnitude to those between the like molecules of the pure and separate components. The solution is formed with no change in volume or heat, and obeys Raoult's law.

Examples of solutions that approximate to the ideal behaviour are;

- Benzene and methyl benzene mixture.
- Hexane and heptane mixture.
- Methanol and water
- Propan-1-ol and propan-2-ol.

Characteristic properties of Ideal solutions.

 (i) Forces of attraction between molecules of the unlike components are equal in magnitude to those between like molecules of the components in their pure and separate state.

 (ii) There is no heat change when such a solution is formed.

 (iii) The total volume of the solution is equal to the sum of the volumes of the individual components.

 (iv) The solution obeys Raoult's under all conditions.

Raoult's law of vapour pressures.

The partial vapour pressure of a component of an Ideal solution at a particular temperature is the product of its mole fraction and the vapour pressure it exerts in its pure state at that temperature.

The total vapour pressure above the mixture / solution depends on the composition of the mixture, and the partial vapour pressure of each component in the mixture is calculated using Raoult's law.

Consider an ideal solution composed of liquids A and B where the vapour pressure of pure A is P_A^o and that of pure B is P_B^o while the mole fractions of A and B are X_A and X_B respectively.

Partial vapour pressure of A, $P_A = X_A\, P_A^o$.
Partial vapour pressure of B, $P_B = X_B\, P_B^o$.

The total vapour pressure exerted by the solution / mixture is obtained using the expression;

$$P_{Total} = P_A + P_B.$$
$$= X_A P_A^o + X_B P_B^o$$

Note:
$X_A + X_B = 1$ or 100%

Relationship between Dalton's and Raoult's laws.
The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures.
For a component A,

$$P_A = X_{A(Vapour)}\, P_T$$

Thus, relating two expressions;
$$P_A = X_{A\,(vapour)}\, P_T \quad \_\,\_\,\_\,\_ \ (i)$$
$$P_A = X_A\, P_A^o \quad \_\,\_\,\_\,\_\,\_\,\_\,\_\,\_\,\_\ (ii)$$

$$X_{A\,(vapour)}\, P_T = X_A P_A^o$$

Hence;
$$X_{A(vapour)} = \frac{X_A P_A^o}{P_T}$$

Examples:

1. A mixture of benzene and methylbenzene forms an ideal solution.
    a) Calculate the vapour pressure of a solution containing 1.95g of benzene and 4.6g of methylbenzene at 20⁰C. (The vapour pressures of pure benzene and pure methyl benzene at 20⁰C are 10.0Kpa and 8.2Kpa respectively)

    b) Determine the composition of the vapour above the solution in (a)

Solution:

(a) *Formula mass of;*
$C_6H_6 = (12 \times 6) + (1 \times 6) = 78g$
Methyl benzene, $C_7H_8 = (12 \times 7) + (1 \times 8) = 92g$

Moles of;
benzene $= \dfrac{1.95}{78} = 0.025moles$

methyl benzene $= \dfrac{4.6}{92} = 0.05$ moles

Total moles of the mixture $= 0.025 + 0.05 = 0.075$ moles.
Let benzene be B, and methyl benzene be M

$$P_{Total} = P_B + P_M$$
$$= (X_B P_B^o) + (X_M P_M^o)$$
$$= \left(\frac{0.025}{0.075} \times 10.0\right) + \left(\frac{0.05}{0.075} \times 8.2\right)$$
$$= 8.80Kpa$$

(b) $X_{B(vapour)} = \dfrac{X_B P_B^O}{\rho_T} = \dfrac{3.33}{8.80}$

$X_{B(vapour)} = 0.378$

$X_{M(vapour)} = 1 - 0.378$
$$= 0.622$$

2. Methanol and ethanol form an ideal solution.

(a) Calculate the vapour pressure of a solution containing 2 moles of methanol and 1 mole of ethanol at 335K. (The vapour pressures of methanol and ethanol at 335K are 8.1 x 10⁴ Pa and 4.5 x 10⁴Pa respectively).

(b) Calculate the composition of the vapour formed from the mixture in (a) above.

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

Solution;

(a) Let methanol be M, and ethanol be E.

$$P_{Total} = P_m + P_E$$
$$= (X_M P_M^o) + (X_E P_E^o)$$
$$= \left(\frac{2}{3} \times 8.1 \times 10^4\right) + \left(\frac{1}{3} \times 4.5 \times 10^4\right)$$
$$= 5.4 \times 10^4 + 1.5 \times 10^4$$
$$= 6.9 \times 10^4 Pa$$

(b) $X_{M(vapour)} = \dfrac{X_M P_M^o}{P_{Total}} = \dfrac{5.4 \times 10^4}{6.9 \times 10^4}$
$$= 0.783$$

$$X_E = 1 - 0.783$$
$$= 0.217$$

(c) Methanol is more volatile. This is because it has a higher composition in vapour phase.

3. The vapour pressure of ethanol at 20^0C 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 20^0C. Calculate the;
   (i) Vapour pressure of the mixture.
   (ii) Mole fraction of benzene in vapour phase.

Solution;

   (i) *Mole fraction of ethanol* $= 1 - 0.09$
   $$= 0.91$$

$$P_{Total} = P_{ethanol} + P_{Benzene}$$
$$= (X_E P_E^o) + (X_B P_B^o)$$
$$= \left(\frac{0.91}{1} \times 43.6\right) + (0.09 \times 75.2)$$
$$= 39.676 + 6.768$$
$$= 46.444mmHg.$$

   (ii) $X_{B(vapour)}$ $= \dfrac{X_B P_B^o}{P_{Total}}$

   $$= \frac{6.768}{46.444}$$
   $$= 0.146$$

4. The saturated vapour pressure of benzene and Toluene are 957mmHg and 378mmHg respectively.
   a) Calculate the composition of benzene – toluene mixture at 760mmHg.
   b) Calculate the composition of benzene in vapour phase.
   c) State which one of the two liquids is more volatile and give a reason for your answer.

Solution;

   (a) Let benzene be B, and Toluene be T.

   $$P_{Total} = P_B + P_T$$
   $$= (X_B P_B^o) + (X_T P_T^o)$$

   Since $X_B + X_T = 1$
   $$X_B = 1 - X_T$$

   $760 = 957 (X_T - 1) + 378 X_T$
   $760 = 957 - 957X_T + 378X_T$
   $-197 = -579X_T$
   $X_T = 0.34$, *Hence* $X_B = 1 - 0.34$
   $$= 0.66$$

(b) $X_{B(vapour)} = \dfrac{X_B P_B^0}{P_T} = \dfrac{0.66 \times 957}{760}$

$$= 0.83$$

(c) Benzene is more volatile. This is because it has a higher vapour composition.

5. Two pure liquids A and B have vapour pressure of 1.5×10^4 Pa and 3.5×10^4Pa respectively at 20^0C. If the mixture of A and B obeys Raoult's law, calculate the;

(i) Composition of the liquid mixture of A and B which has a total vapour pressure of 2.9×10^4 Pa at 20^0C.

(ii) Composition of the vapour.

6. The vapour pressures of methanol and water are 125.9mmHg and 23.8mmHg respectively at 20^0C. Calculate the;

(i) Vapour pressure of a mixture containing 21.0g of methanol and 89.0g of water at 20^0C. (Assume the two liquids form an ideal solution.)

(ii) Composition of the vapour above the mixture.

Vapour pressure – composition diagram for an ideal solution

In a liquid mixture that behaves ideally, the partial vapour pressure of each component is proportional to its mole fraction.

Consider an ideal solution composed of liquids A and B;
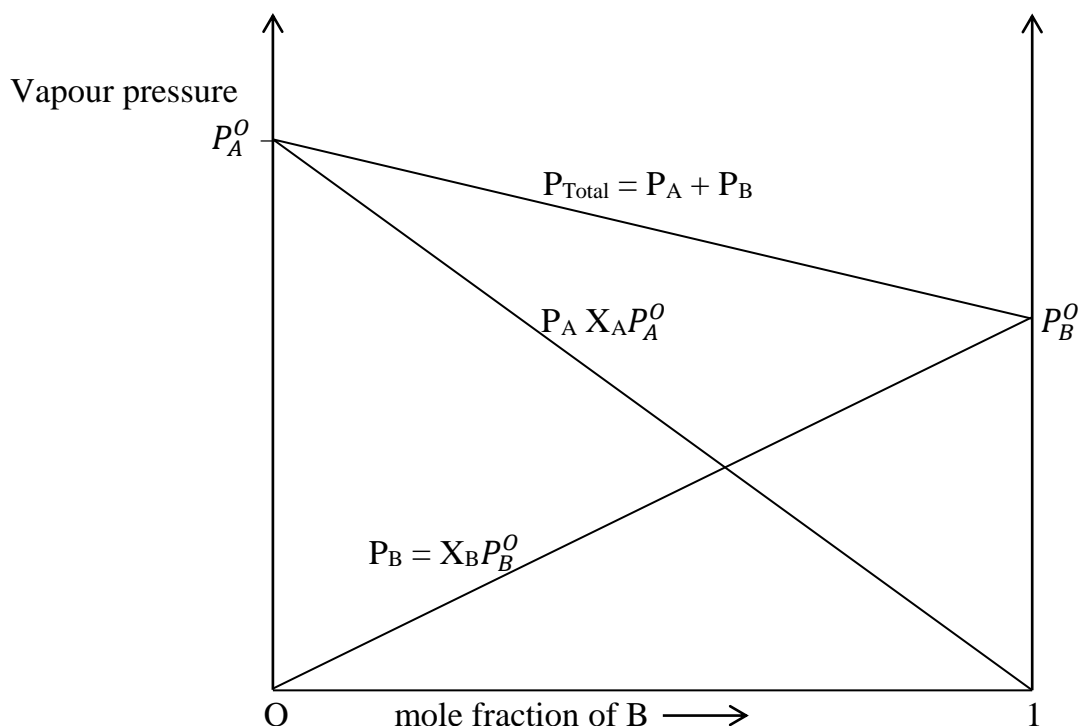
P_A^o is the vapour pressure of pure A.

P_B^o is the vapour pressure of pure B.

Line P_B shows the variation of the partial vapour pressure of B with composition.

Line P_A shows the variation of the partial vapour pressure of A with composition.

Line P_{Total} shows the variation of the total vapour pressure of the solution with composition.

P_A^o is higher than P_B^o showing that component A is more volatile than component B.

The partial vapour pressure of each component increases with increase in its composition in the liquid mixture, and at any given composition the total vapour pressure is equal to the sum of the partial vapour pressures of the two components at that particular composition.

The vapour pressure – composition diagram can be used to predict the shape of the boiling point – composition diagram as shown below;
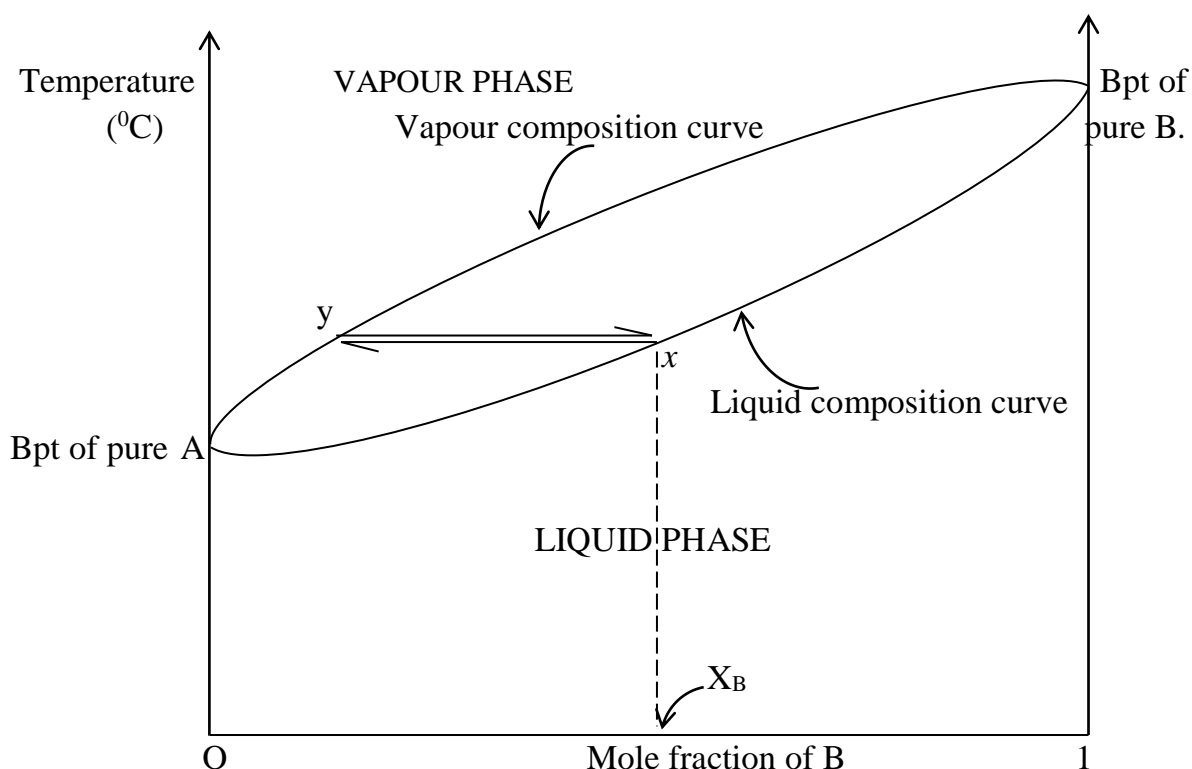
The diagram shows that an increase in the composition of the less volatile component B results into increase in boiling point of the mixture.

Similarly, an increase in the composition of the more volatile component A from right to left results into decrease in boiling point of the mixture.

When a liquid mixture of any given composition is heated, the vapour obtained is richer in the more volatile component e.g the <u>tie – line</u> xy shows the liquid – vapour equilibrium established when a liquid mixture of composition X_B is heated. It gives a vapour of composition y, which is richer in the more volatile component A.

Note;

Since liquids A and B have different boiling points, they can be separated by <u>fractional distillation</u>.

This separation is only possible when the vapour phase has a composition different from that of the boiling liquid mixture.

In this method;

- The liquid mixture is heated to its boiling point. This gives a vapour richer in the more volatile component.

- The vapour is then condensed by cooling to give a liquid of the same composition as the vapour.
- Progressive / repeated heating and condensation gives the more volatile component as the distillate while the less volatile component is obtained as the residue.

Consider the processes taking place in the phase diagram
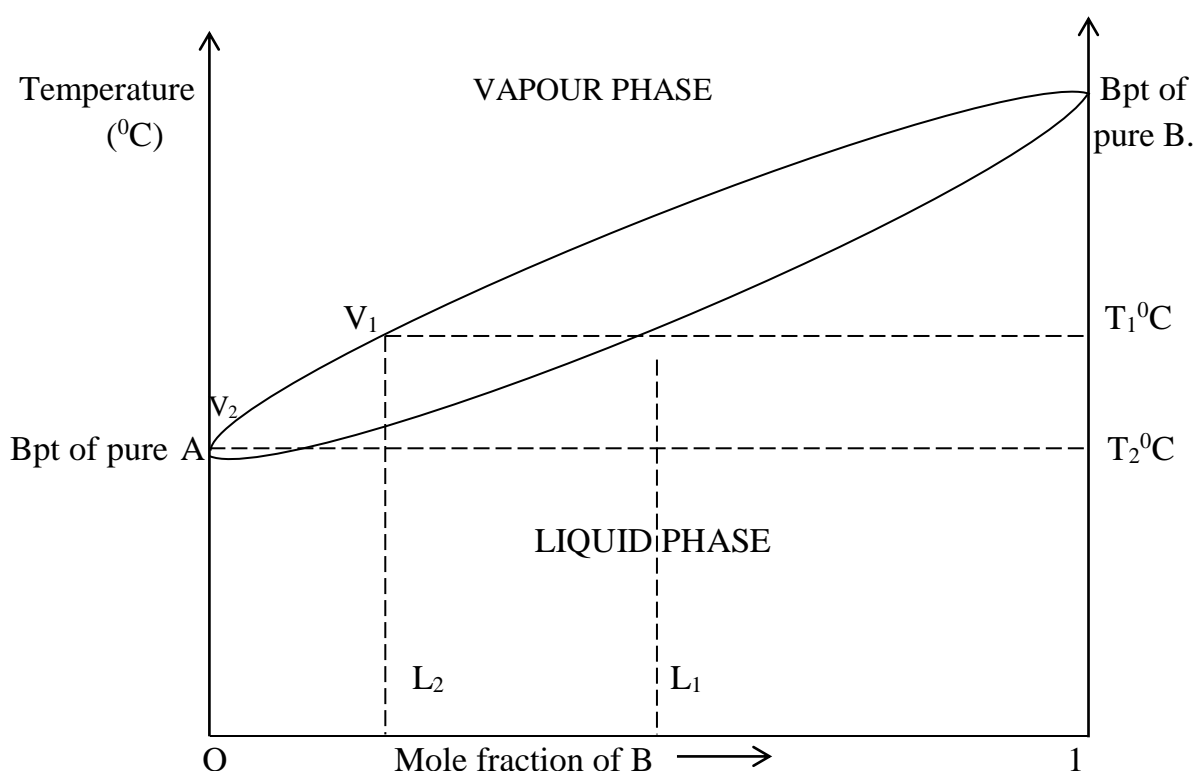
When a liquid mixture of composition L_1 is heated, it boils at a temperature $T_1 {}^0C$ to give a vapour V_1 which is richer in component A compared to the composition of the liquid mixture L_1.

On condensing the vapour V_1, a liquid mixture L_2 with the same composition as that of the vapour V_1 is obtained.

Heating a liquid mixture L_2 results into it boiling at temperature $T_2 {}^0C$ to give a vapour V_2 much richer in the more volatile component.

Hence progressive heating and condensation results into obtaining pure A as the distillate and pure B as the residue.

The process of fractional distillation using a fractionating column.

When a liquid mixture of a given composition is heated, a vapour richer in the more volatile component ascends the fractionating column as it is being cooled down by the large surface area provided by the glass beads in the column. This results into formation of a liquid that descends the column.

The descending liquid comes into contact with more of the ascending vapour and at each point in the column an equilibrium is established between the liquid and vapour, hence boiling takes place.

This results into formation of the vapour that is richer in the more volatile component at the top of the column, which condenses within the leibig condenser and is collected as the distillate.

Application of fractional distillation.
- Purification / refining of crude oil.
- Obtaining nitrogen and oxygen from liquid air.
- Concentration of alcohols in breweries.

Question:
The table below shows how the vapour pressure of the mixture of A and B varies with the mole fraction of A at a certain temperature.
(The mixture of A and B is assumed to be ideal)

Mole fraction of A, (X_A)	0.0	0.2	0.4	0.6	0.8	1.0
Total vapour pressure of the mixture (atm)	308	318	328	338	348	358

a) Plot a graph of vapour pressure against mole fraction of A.

b) From the graph, determine the;
   (i) Saturated vapour pressures of pure A and B.
   (ii) Partial vapour pressures of A and B when the mole fraction of B is 0.3
   (iii) Mole fraction of A at which the partial vapour pressures of A and B are the same.

c) Sketch the boiling point – composition diagram for this mixture and briefly explain how the mixture containing 40% of B can be fractionally distilled.

NON – IDEAL SOLUTIONS.
Question:
Explain why some liquid mixtures do not obey Raoult's law.
Due to the difference in the molecular structures of the components of the liquid mixture, the forces of attraction formed between molecules in the liquid mixture happen to be different in strength from those between molecules of the pure and separated components.

To overcome these forces as the molecules in the liquid mixture tend to escape into vapour phase, there is a change in volume and heat, and finally either a higher or lower vapour pressure than that expected from Raoult's law is exerted.

Note:
A non – ideal solution is a solution that does not obey Raoult's law of vapour pressures. i.e. it deviates from Raoult's law.
The two types of deviation from Raoult's law are;
- Positive deviation
- Negative deviation

POSITIVE DEVIATION
This occurs when the vapour pressure exerted by the solution is greater than that expected of an ideal solution / predicted by Raoult's law.

Positive deviation arises when the forces of attraction formed between the unlike molecules of the components of the solution are <u>weaker than</u> those between molecules of the pure and separate components.
This implies that heat is absorbed as weak intermolecular forces are formed in the liquid mixture and the escaping tendency of the molecules into vapour phase <u>increases</u> resulting into a higher vapour pressure exerted at the surface of the liquid mixture.

Properties of liquid mixtures that deviate positively from Raoult's law
- The volume of the solution is greater than the sum of the individual volumes of the components.
- Heat is absorbed during formation of the solution.
- The forces of attraction between the unlike molecules of the components are weaker than those between molecules of the pure and separate components.

Vapour pressure – composition diagram for a liquid mixture deviating positively from Raoult's law.
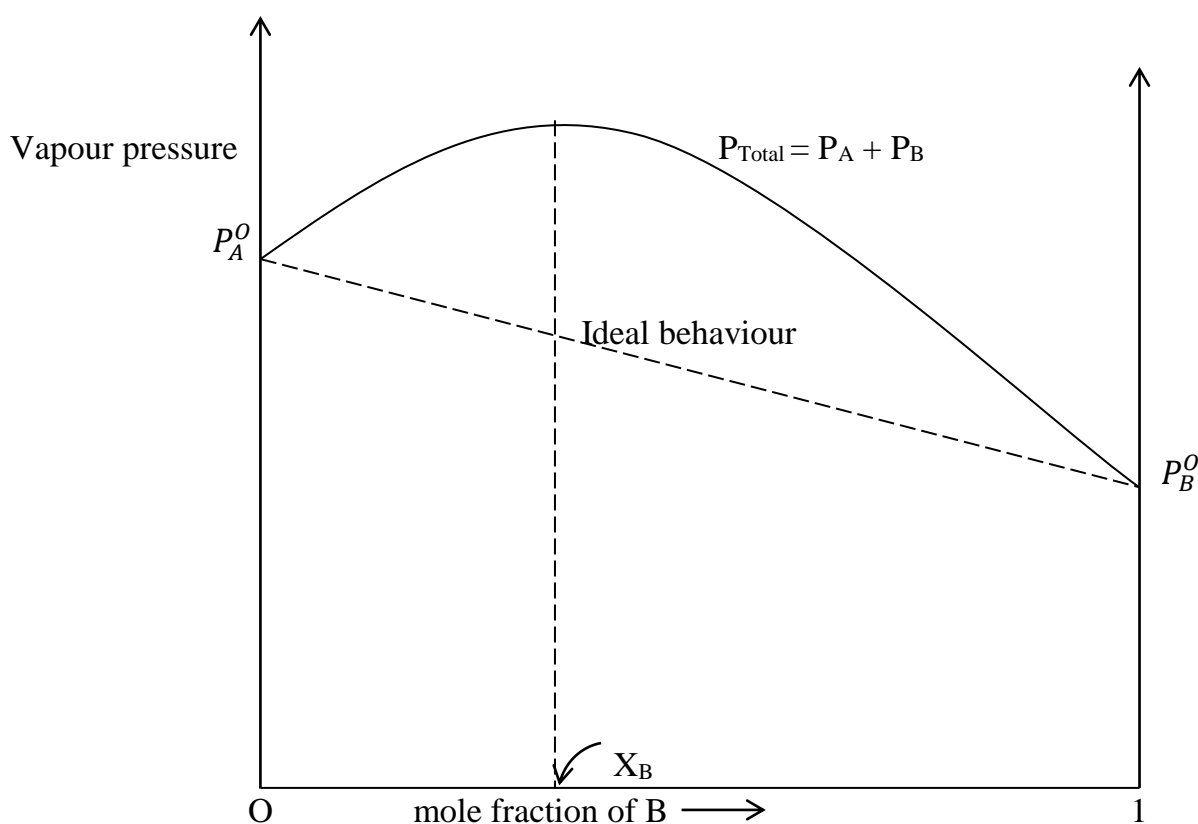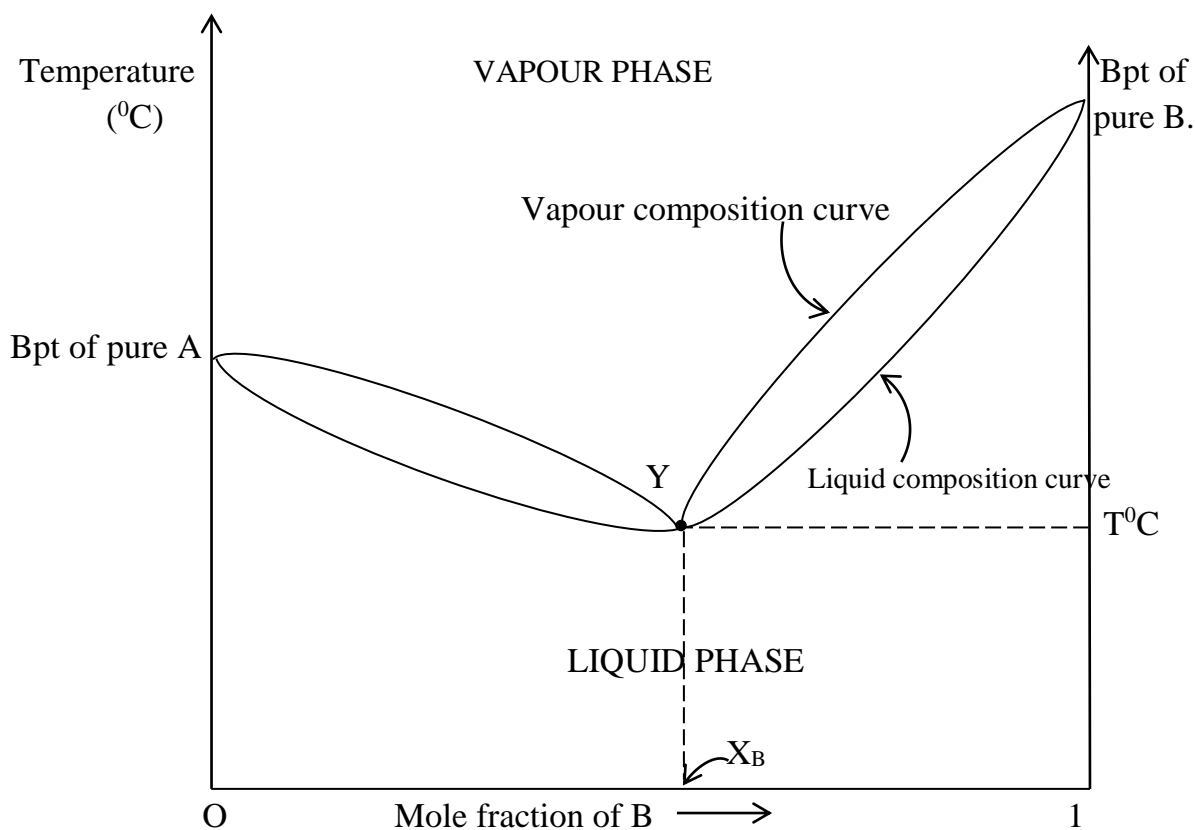

The phase diagram shows that addition of liquid B to liquid A results into an increase in the vapour pressure exerted by the solution due to the weak intermolecular forces formed. At composition X_B of B, the intermolecular forces formed are the weakest, hence a maximum vapour pressure is exerted.

Similarly, addition of A to B results into an increase in vapour pressure up to composition X_B where the intermolecular forces between molecules of the components are the weakest.

Boiling point – composition diagram for a liquid mixture deviating positively from Raoult's law.

The maximum vapour pressure at composition X_B of B in the vapour pressure – composition diagram corresponds to the minimum boiling point at the same composition in the boiling point – composition diagram.

The phase diagram shows that addition of liquid B to liquid A results into a decrease in boiling point up to point Y where the composition of the liquid mixture is X_B of B, and the mixture boils at a constant minimum temperature, T^0C.

Similarly, addition of liquid A and B results into a decrease in boiling point of the mixture up to composition X_B of B where the mixture boils at a constant minimum temperature, T^0C.

This shows that addition of one component to the other results into formation of weaker intermolecular forces between the components and hence the escaping tendency of the molecules from the liquid mixture into vapour phase increases such that at any given composition, the exerted vapour pressure becomes equal to the external atmospheric pressure at a lower temperature corresponding to lower boiling points.

At composition X_B of B, the mixture boils at a constant temperature giving a vapour of the same composition as that of the liquid.

Note:

A liquid mixture of composition X_B of B is called an <u>azeotropic mixture</u> or <u>constant boiling point mixture</u> or <u>azeotrope.</u>

An azeotropic mixture is a liquid mixture which at a fixed pressure boils at a constant temperature to give a vapour of the same composition as that of the liquid.

Fractional distillation of a liquid mixture that deviates positively from Raoult's law.

Consider the following boiling point – composition diagram for a liquid mixture of A and B.
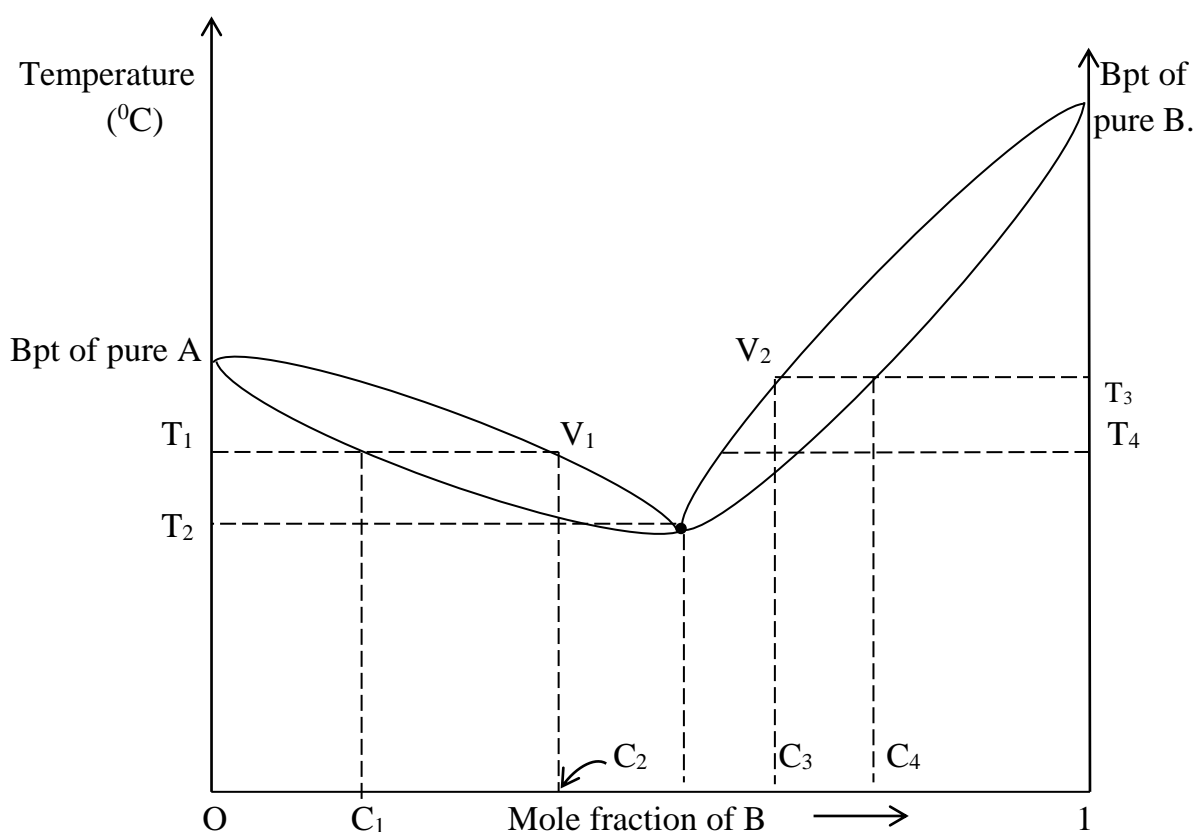
When a liquid mixture of composition C_1 of B is heated, it boils at a temperature $T_1 {}^0C$ producing a vapour V_1 which is richer in B.

Condensation of this vapour produces a liquid of the composition C_2 which is similar to that of the vapour V_1.

Progressive heating and condensation results into obtaining the azeotropic mixture as the distillate while liquid A remains as the residue.

When a liquid mixture of composition C_4 of B is heated, it boils at a temperature T_3 ^{0}C producing a vapour V_2 which is richer in A.

Condensation of this vapour produces a liquid of composition C_3 which is similar to that of the vapour V_2

Progressive heating and condensation results into obtaining the azeotropic mixture as the distillate while liquid B is collected as the residue.

Note:

Examples of liquid mixtures that deviate positively from ideal behaviour include,
- Water and ethanol
- Benzene and ethanol
- Cyclohexane and methanol
- Carbondisulphide and ethanol
- Tetrachloromethane and methanol

Questions:

1. The table below shows the boiling points and mole fractions of methanol in mixtures of methanol and cyclohexane in liquid and vapour phase.
    (The boiling point of pure methanol is 65^{0}C while that of pure cyclohexane is 81^{0}C)

Boiling point of mixture(^{0}C)	Mole fraction of methanol in the liquid mixture	Mole fraction of methanol in vapour phase
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

   a) Plot a boiling point – composition diagram and label it fully.
   b) Explain the shape of the diagram
   c) From your diagram explain what happens when a mixture containing 0.2 mole fraction of cyclohexane is fractionally distilled.

2. (a)(i) State Raoult's law and mention its limitations.
   (ii) Explain what is meant by an ideal solution.
   (iii) Explain why some liquid mixtures do not obey Raoult's law

   b) The vapour pressure of solution containing 1 mole of A and 4 moles of B is 0.75atm at 25^{0}C.
   (i) Calculate the vapour pressure of the liquid mixture assuming it was ideal.
   (ii) State how the mixture deviates from Raoult's law. Explain your answer.
   (iii) Calculate the composition of the vapour above the liquid mixture assuming it is ideal
   c) Sketch a labelled boiling point – composition diagram for a liquid mixture of A and B

NEGATIVE DIVIATION.

This occurs when the vapour pressure exerted by the solution is less than that expected of an ideal solution / predicted by Raoult's law.

Negative deviation arises when the forces of attraction formed between the unlike molecules of the components of the solution are <u>stronger</u> than those between molecules of the pure and separate components.

This implies that heat is evolved as stronger intermolecular forces are formed in the liquid mixture and the escaping tendency of the molecules into vapour phase <u>decreases</u> resulting into a lower vapour pressure exerted at the surface of the liquid mixture.

Properties of liquid mixtures that deviate negatively from Raoult;s law.
- The volume of the solution is lower than the sum of the individual volumes of the components.
- Heat is evolved during formation of the solution.
- The forces of attraction between the unlike molecules of the components are stronger than those between molecules of the pure and separate components.

Vapour pressure – composition diagram for a liquid mixture deviating negatively from Raoult's law.
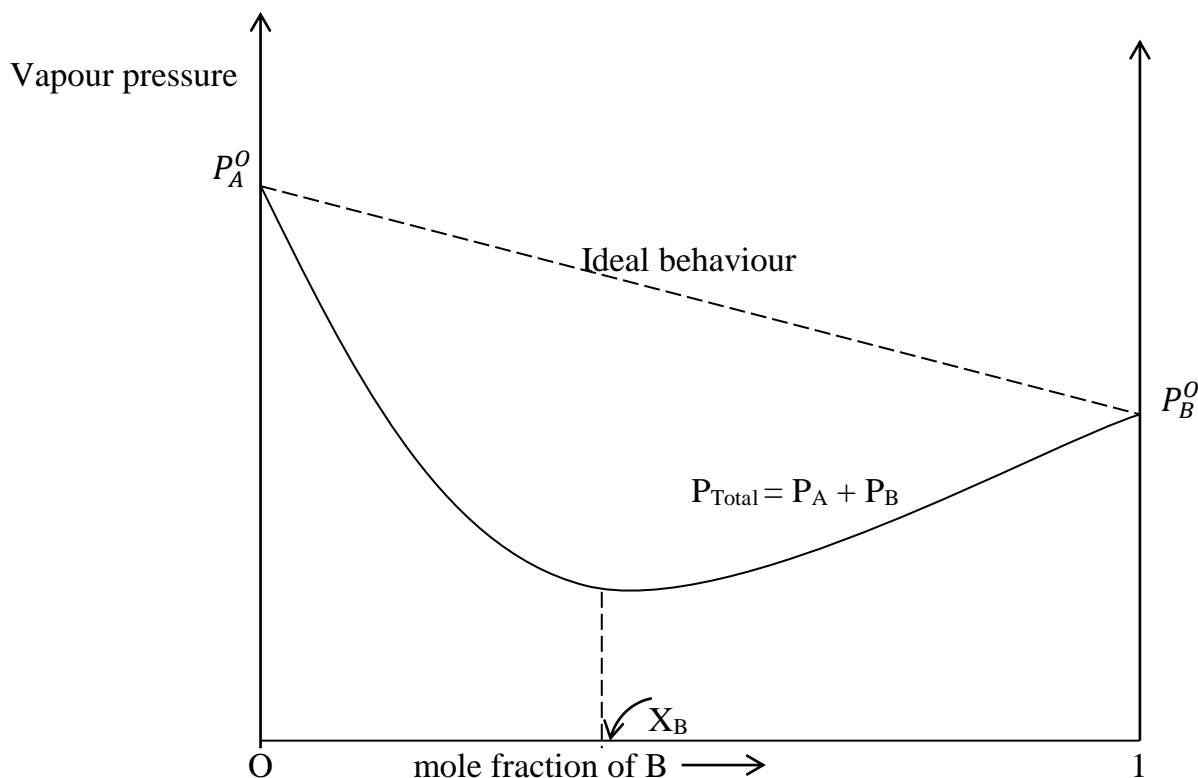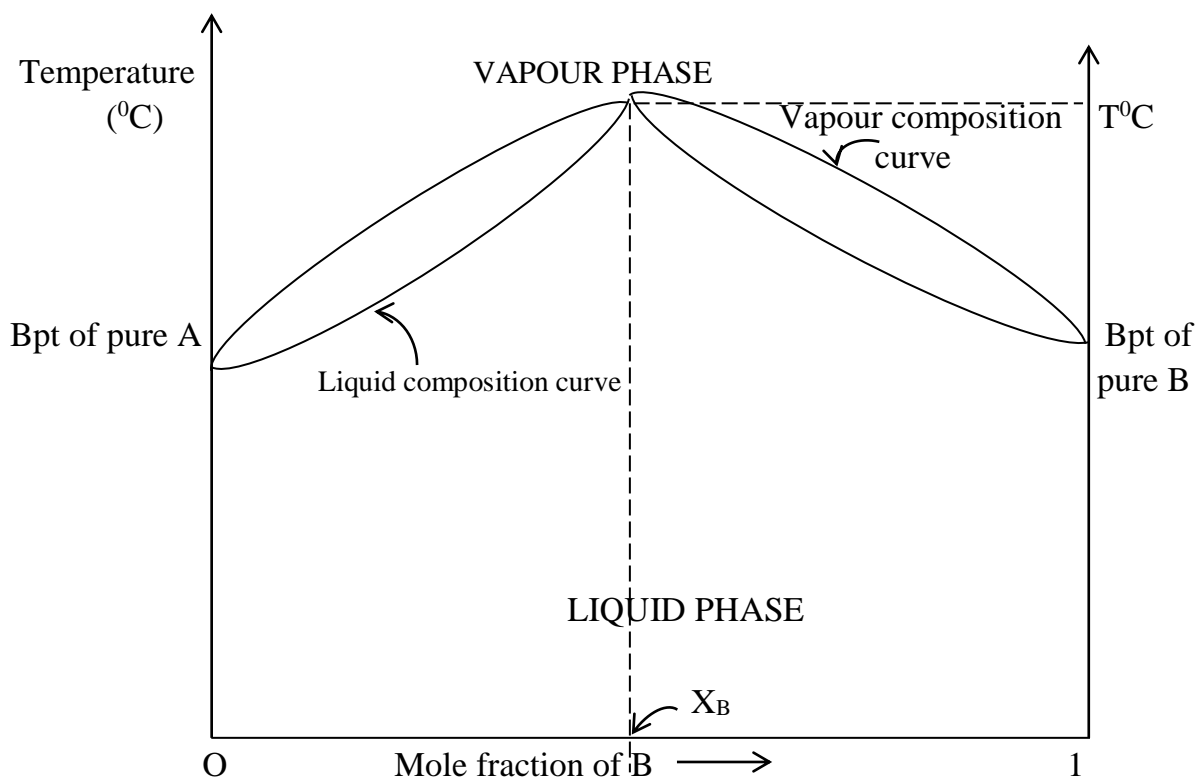

The phase diagram shows that addition of liquid B to A results into a decrease in the vapour pressure exerted by the solution due to the stronger intermolecular forces formed between the unlike molecules.

At composition X_B of B, the intermolecular forces formed are the strongest hence a minimum vapour pressure is exerted.

Similarly, addition of A to B results into a decrease in vapour pressure up to composition X_B where the forces of attraction between unlike molecules of A and B are the strongest.

Boiling point – composition diagram for a liquid mixture deviating negatively from Raoult's law.

The minimum vapour pressure at composition X_B of B in the vapour pressure – composition diagram corresponds to the maximum boiling point at the same composition in the boiling point – composition diagram.

The phase diagram shows that addition of liquid B to liquid A results into an increase in boiling point up to point Y where the composition of the liquid mixture is X_B of B, and the mixture boils at a constant maximum temperature, T^0C.

Similarly, addition of liquid A to liquid B results into an increase in boiling point of the mixture up to composition X_B of B where the mixture boils at a constant maximum temperature, T^0C.

This shows that addition of one component to another results into formation of stronger intermolecular forces between the components in the liquid mixture and hence the escaping tendency of the molecules from the solution into vapour phase decreases such that at any given composition, the exerted vapour pressure becomes equal to the external atmospheric pressure at a higher temperature corresponding to higher boiling points.

At composition X_B of B, the mixture is an azeotrope and it boils at a constant temperature giving a vapour of the same composition as that of the liquid.

Fractional distillation of a liquid mixture that deviates negatively from Raoult's law.

Consider the following boiling point – composition diagram for a liquid mixture of A and B.
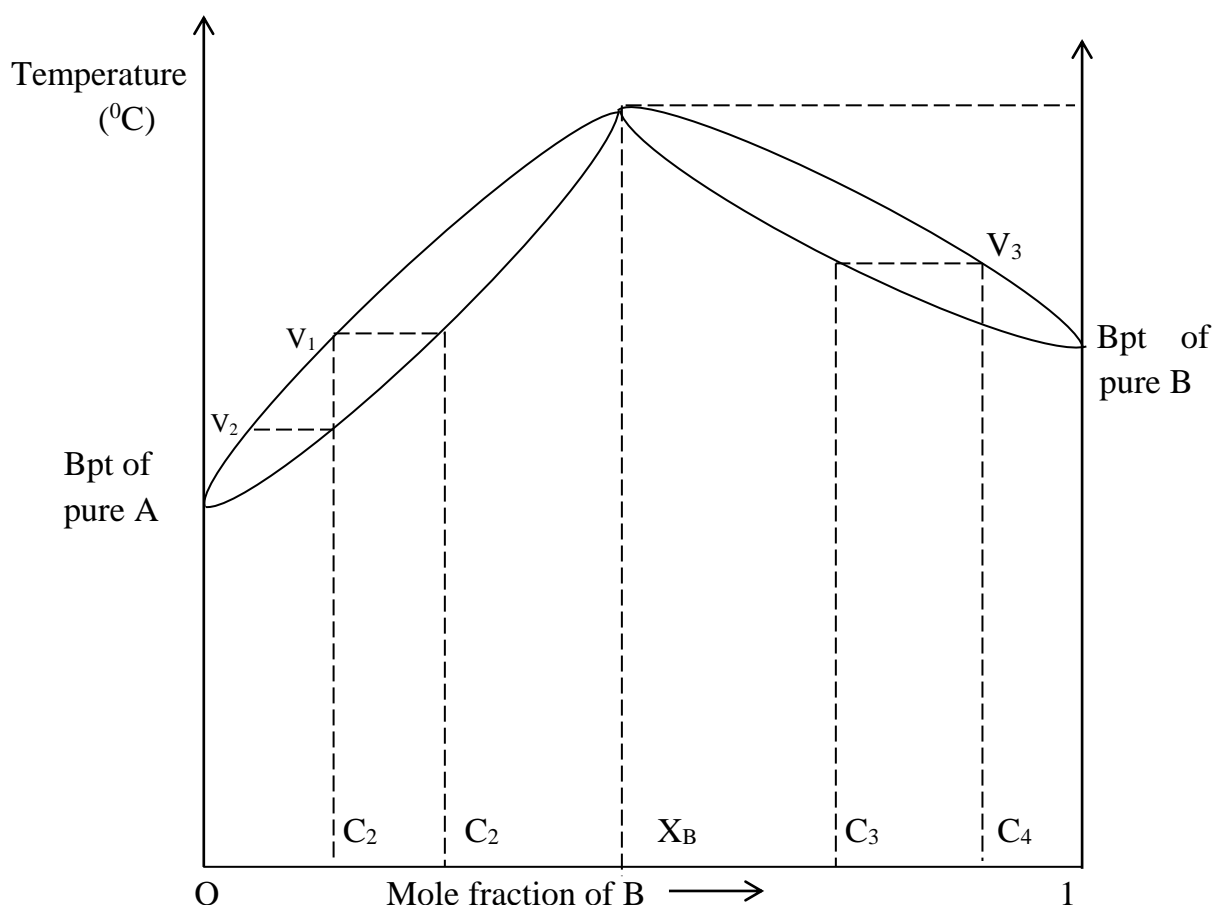
When a liquid mixture of composition C_1 of B is heated, it boils at a temperature $T_1\,^0C$ producing a vapour V_1 which is richer in A compared to the composition of liquid mixture C_1.

Condensation of this vapour produces a liquid of composition C_2 which is similar to that of the vapour, V_1.

Progressive heating and condensation results into obtaining pure A as the distillate while azeotropic mixture is obtained as the residue.

When a liquid mixture of composition C_3 of B is heated, it boils at a temperature, $T_2\,^0C$, producing a vapour, V_3, which is richer in B.


Condensation of this vapour produces a liquid of composition C_4 which is similar to that of the vapour, V_3.

Progressive heating and condensation results into obtaining liquid B as the distillate while the azeotropic mixture is obtained as the residue.

Note:

(i)   Examples of liquid mixtures which deviate negatively from Roault's law include;

- Chloroform (trichloromethane) and propanone.
- Phenol and phenylamine.
- Nitric acid and water
- Hydrochloric acid and water.

For the liquid mixture of chloroform and propanone, both components are polar compounds. The carbon to oxygen double bond in propanone and carbon to chlorine bonds in chloroform are polarised. When the two compounds are mixed, the negative charge on the oxygen atom of propanone and the positive charge on the hydrogen atom of chloroform strongly attract one another forming hydrogen bonds.

```
CH₃              Cl
|                |
C  = O - - H—C— Cl
|                |
CH₃              Cl
```
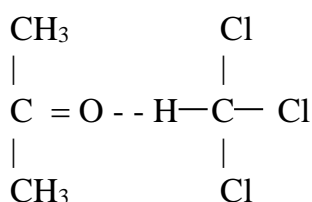
This results into evolution of heat because the hydrogen bond formed is stronger than the van der waals forces between molecules of pure propanone and pure chloroform.

For the liquid mixture of nitric acid and water, there is ionisation of the covalent molecules of the acid in water.

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$
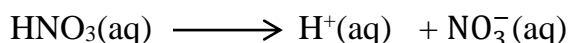
As the formed ions are hydrated, stronger ion – dipole attractions are formed compared to the Van –der waals forces in nitric acid and hydrogen bonds in water molecules. This results into evolution of heat and consequently a reduction in volume.

(ii)   Azeotropic mixtures are of two types; i.e.

- Minimum boiling point azeotropic mixtures.
- Maximum boiling point azeotropic mixtures.

Differences between the types of azeotropic mixtures.

Maximum boiling point azeotrope	Minimum boiling point azeotrope
- Obtained from liquids whose mixture deviates negatively from Raoult's law	- Obtained from liquids whose mixture deviates positively from Raoult's law.
- Its boiling point is higher than the boiling points of either of the components.	- Its boiling point is lower than the boiling point of either of the components
- Obtained as a residue during fractional distillation	- Obtained as a distillate during fractional distillation

Azeotropic mixtures behave like pure substances or compounds in the following ways;
- Both have fixed compositions at a constant pressure.
- Both have fixed boiling points at a constant pressure.

Differences between azeotropic mixtures and pure compounds.
- Azeotropic mixtures can be separated by physical means.
- Azeotropes cannot be represented by simple general molecular formulae.
- Boiling point and composition of azeotropes changes with change in pressure
- Freezing of an azeotropic mixture takes a wide range of temperatures while freezing of a compound takes a narrow range.

Methods of separating azeotropic mixtures
a) **Distilling with a third component**
   The third component should mix with one of the components of the azeotrope to form an ideal solution, and immiscible with the other component. The mixture is then separated using a separating funnel.
   The components of the ideal solution are separated by fractional distillation.
   An azeotropic mixture of ethanol and water can be separated by addition of benzene.

b) **Chemical method**
   (i) By adding another component that has a stronger affinity for one of the components of the azeotrope e.g
       In an azeotropic mixture of water and ethanol, calcium oxide can be added to combine with water, and the mixture is filled.
       The filtrate is re-distilled to obtain 100% pure ethanol.

   (ii) By adsorption. Charcoal or silica gel can be added to absorb and retain one of the components of the azeotrope.

c) **Solvent extraction**

One of the components can be obtained by adding a solvent in which it is more soluble.

Questions:

1. (a) State three reasons why azeotropes are considered to be mixtures and not compounds.

   b) The total vapour pressure of a mixture of propanone and trichloromethane, and the mole fraction of trichloromethane at a constant temperature are given in the table below;

Mole fraction of trichloromethane	0.0	0.2	0.4	0.6	0.8	1.0
Vapour pressure of the mixture (mmHg)	347	305	267	244	256	293

   (i) Plot a graph of total vapour pressure of the mixture against the mole fraction of trichloromethane.

   (ii) Using the graph, deduce how the mixture deviates from Raoult's law. Give a reason for your answer.

   (iii) Explain the cause for the deviation you have stated in b(ii) above.

   (iv) Determine the composition of the azeotrope.

2. (a) A mixture of liquids Y and Z obeys Raoult's law. If the vapour pressure of Y and Z are $9.50KNm^{-2}$ and $3.20KNm^{-2}$ respectively at 20^0C,

   (i) Calculate the composition of the vapour containing 0.5 moles of each liquid at 20^0C.

   (ii) State which of the two liquids is more volatile. Give a reason for your answer.

   b) The boiling points of liquids y and Z are 368^0C and 395^0C 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% Z.

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

   d) 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.

3. (a) Methanoic acid (HCOOH) with boiling point 80^0C, and water with boiling point 100^0C, are miscible in all proportions. They form a maximum boiling point mixture containing 77% methanoic acid which boils at 108^0C.

   (i) Sketch a labelled boiling point – composition diagram for the mixture of methanoic acid and water.

   (ii) Explain the factors that lead to methanoic acid and water forming a maximum boiling point mixture.

   (iii) Describe briefly what happens when a mixture containing 40% methanoic acid is distilled.

   b) At standard atmospheric pressure, hydrochloric acid and water form a constant boiling point mixture having a boiling point of 110^0C and composition 20% by mass of hydrochloric acid. The constant boiling point mixture has a density of $1.18gcm^{-3}$. Calculate the volume of the acid needed to prepare 1 litre of 2M hydrochloric acid solution.

4. Propanone was mixed with trichloromethane

   (a) State what was observed and explain your answer.
   - *The two liquids are completely miscible forming a <u>warm</u> homogeneous <u>colourless solution.</u> The volume of the formed solution is lower than the sum of the individual volumes of the components.*
   Explanation: (Refer to notes.)

   (b) The table below shows the mole fractions of trichloromethane and partial vapour pressures of trichloromethane and propanone in the mixture.

Mole fraction of trichloromethane		0.0	0.2	0.4	0.6	0.8	1.0
Partial vapour pressure of; (mmHg)	Propanone	0	35	82	142	219	293
	trichloromethane	347	270	185	102	37	0

   (i) Plot a graph of vapour pressure of mixture against mole fraction of trichloromethane.
   (ii) State the type of deviation.
   (iii) Explain your answer in b(ii) above

IMMISCIBLE LIQUID MIXTURES

These are mixtures made of liquids that are insoluble in one another such that when mixed in any proportion, the liquids form different layers.

Examples of immiscible liquid mixtures include;

- Phenylamine and water
- Carbondisulphide and water
- Chlorobenzene and water
- Nitrobenzene and water

Question:

What boils at 100^0C at 101.3Kpa. At the same pressure methylbenzene boils at 111^0C whereas a mixture of water and methyl benzene boils at 96^0C. Explain this observation.

Solution

Methylbenzene is immiscible with water. When this mixture is heated each component exerts its own vapour pressure independently. The vapour pressure of the mixture therefore is the sum of the independent vapour pressures, and increases with increase in temperature.

When the sum of the vapour pressures equals the external atmospheric pressure, the mixture boils and this happens at a temperature lower than the boiling point of either of the components.

STEAM DISTILLATION

This is the method used to separate a volatile component, which is immiscible with water, from other non – volatile impurities by passing steam through the impure sample, and boiling occurs below 100^0C.

The purified sample is then obtained from the distillate using a separating funnel.

Note:

This method is generally used in the laboratory and in industry for the purification of those liquids which decompose when heated to their normal boiling points. These are mainly organic substances that are immiscible with water.

The process of steam distillation.

The apparatus used in steam distillation is arranged as shown below;
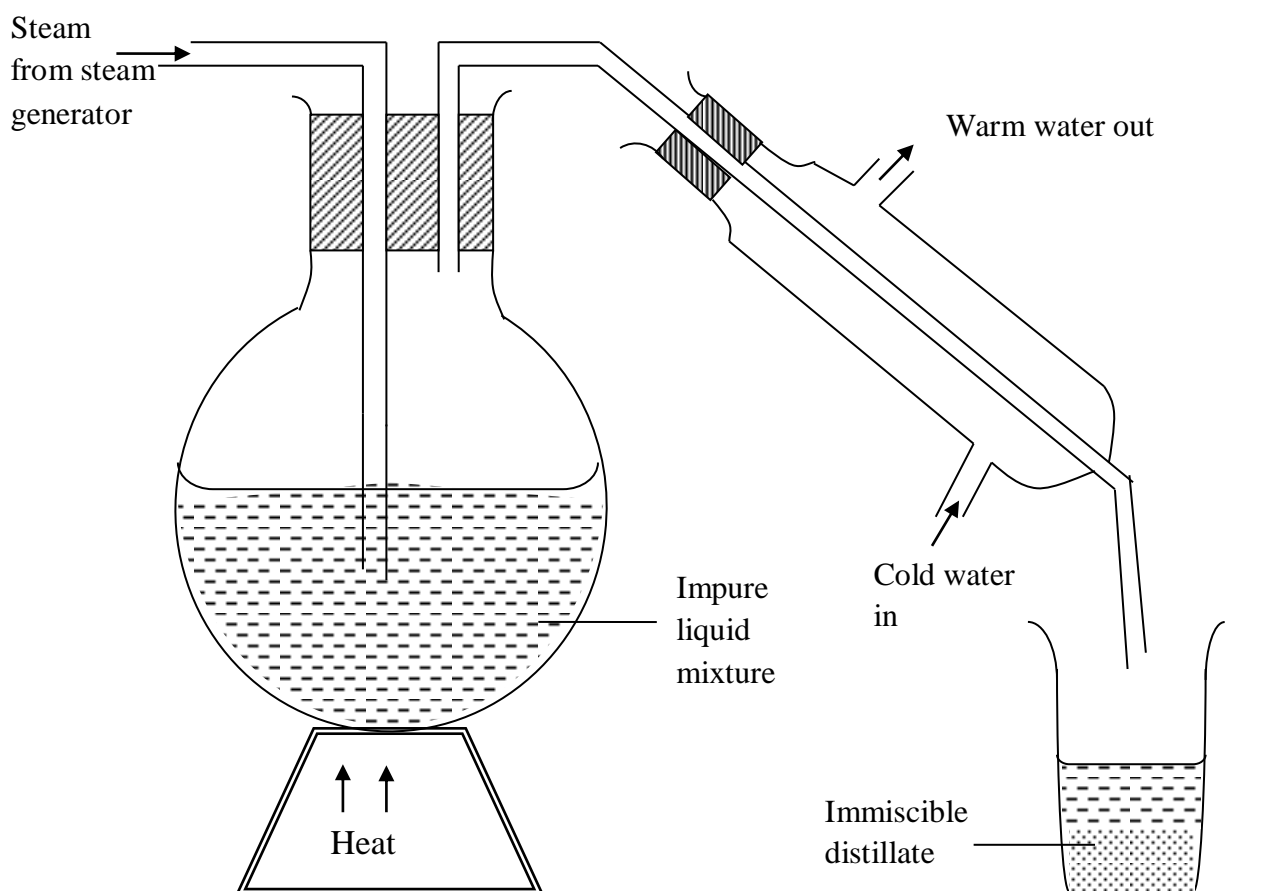
When steam from the steam generator (or generated from a boiler) is passed through the mixture, it heats up the mixture and the more volatile of the components evaporates together with steam.

The vapour is condensed to give an immiscible distillate of the volatile substance and water.

The immiscible distillate is then separated using a separating funnel and the pure distillate can be dried using a suitable drying agent.

Note:

Steam is preferred to liquid water because it keeps the mixture agitated and thus the equilibrium between the liquid and vapour is rapidly attained.

Condition / properties of a substance that enable it to be purified by steam distillation.
- The substance should be immiscible with water.
- The substance should exert a high vapour pressure at the boiling point of water
- The substance should have a fairly high relative molecular mass.

Principles of steam distillation

When a mixture of two immiscible liquids is heated, each component exerts own vapour pressure independently. The vapour pressure of the mixture is the sum of the vapour pressures of the components.

Vapour pressure of the mixture increases with increase in temperature.

When the sum of the vapour pressures of the mixture equals the external atmospheric pressure, the mixture boils and this happens at a temperature lower than the boiling point of any of the two components of the mixture.

Question:

Explain how the above properties enable a substance to be purified by steam distillation.
- *The substance should be immiscible with water so that at a given temperature each of the components produces vapour independent of their proportions in the mixture and hence boil at a much lower temperature than the boiling point of the volatile component.*
- *The substance should be more volatile than its impurities so that it exerts a higher vapour pressure near the boiling point of water and the mixture boils below 100^0C. This also has an advantage of most of it being obtained in the distillate.*
- *The substance should have a high relative molecular mass such that a good quantity of it is obtained in the distillate.*

Advantages of isolating substances by steam distillation.
- Distillation occurs at a lower temperature than the boiling point of any of the components of the distillate.
- Enables purification of substances that decompose at a temperature closer to their boiling points.

Application of steam distillation

    (i)   Used in purification of organic compounds which decompose near their boiling points.

    (ii)   Used in extraction of some natural products such as oils from plants.

    (iii)   It is used in determining relative molecular mass of some compounds.

Determining the composition of the distillate obtained by steam distillation.

Consider a distillate containing liquid A and water.

Let the vapour pressure exerted by A be P_A, and the mole fraction of A in the distillate be X_A.

Since composition is determined from the exerted vapour pressure, Dalton's law is used. i.e.

$$P_A = X_A P_{Total} _____ (i)$$

and for water,

$$PH_2O = XH_2O \, P_{Total} _____ (ii)$$

From the above expressions;

$$\frac{P_A}{PH_2O} = \frac{X_A}{XH_2O}$$

But $X_A = \dfrac{\cap_A}{\cap_A + \cap_{H_2O}}$, and $X_{H_2O} = \dfrac{\cap_{H_2O}}{\cap_A + \cap_{H_2O}}$

Thus; $\dfrac{P_A}{PH_2O} = \dfrac{\cap_A}{\cap_{H_2O}}$

$$\cap_A = \frac{mass\ of\ A}{rfm\ of\ A}, \text{ and } \cap_{H_2O} = \frac{mass\ of\ H_2O}{RFM\ of\ H_2O}$$

Hence,

$$\frac{P_A}{PH_2O} = \frac{mass\ of\ A \times RFM\ of\ H_2O}{mass\ of\ H_2O \times RFM\ of\ A}$$

And,

$$\boxed{\frac{mass\ of\ A}{mass\ of\ H_2O} = \frac{P_A \times RFM\ of\ A}{PH_2O \times RFM\ of\ H_2O}}$$

Examples;

1. A mixture containing a substance R was steam distilled at 760mmHg and 98^0C. The distillate contained 85% by mass of water. If the vapour pressure of water is 734mmHg at 98^0C, calculate the molar mass of R.

   Solution

   Percentage by mass of R = 100 – 85 = 15%
   Vapour pressure of R = 760 = 734 = 26mmHg.

   $$\frac{mass\ of\ R}{mass\ of\ H_2O} = \frac{P_R \times RFM\ of\ R}{PH_2O \times RFM\ of\ H_2O}$$

   $$\frac{15}{85} = \frac{26 \times RFM\ of\ R}{743 \times 18}$$

   $$RFM\ of\ R = \frac{15 \times 734 \times 18}{85 \times 26}$$

   $$= 89.67$$

2. A mixture of naphthalene, $C_{10}H_8$, and water distils at 98.3^0C and 753mmHg. Calculate the percentage of mass of naphthalene in the distillate.
   (The vapour pressure of water at 98.3^0C is 715mmHg, C = 12, H = 1)

   Solution
   Let the percentage by mass of naphthalene be x%
   Thus, percentage by mass of water = (1000 – x)%
   Molar mass of $C_{10}H_8$ = (12 x 10) + (1 x 8) = 128.
   Vapour pressure of naphthalene = (753 – 715)
   = 38mmHg.

   $$\frac{mass\ of\ naphthalene}{mass\ of\ water} = \frac{P_{naphthalene} \times RFM\ of\ naphthalene}{P_{water} \times FRM\ of\ water}$$

   $$\frac{x}{100-x} = \frac{38 \times 128}{715 \times 18}$$
   4864 (100 – x) = 1280x
   x = 27.3
   percentage by mass of naphthalene = 27.43%

3. (a) When an organic compound, Y, containing carbon and hydrogen was burnt in excess oxygen, 31.5g of carbondioxide and 10.7g of water were formed. Calculate the empirical formula of Y.

   b) Y was steam distilled at 70⁰C and 760mmHg, and the distillate was found to contain 91.1% by mass of Y.
   (The vapour pressure of water at 70⁰C is 234mmHg)

   (i) Calculate the formula mass of Y.
   (ii) Deduce the molecular formula of Y.

   c) When 1 mole of Y was completely hydrogenated in the presence of a catalyst, one mole of hydrogen gas was absorbed. Write the structural isomers of Y.

   Solution

   (a) *Mass of carbon* $= \dfrac{31.55 \times 12}{44} = 8.60g$

   Mass of hydrogen $= \dfrac{10.76 \times 2}{18} = 1.20g$

	C	H
Moles:	$\dfrac{8.60}{12}$	$\dfrac{1.20}{1}$
	$=0.717$	1.20
Mole ratio	$\dfrac{0.717}{0.717}$	$\dfrac{1.20}{0.717}$

   $= (1 \quad : \quad 1.67) \times 3$

   $= \quad 3 \quad : \quad 5$

   Empirical formula $= C_3H_5$

   b)(i) *Percentage by mass of* $H_2O = 100 - 91.1 = 8.9\%$

   Vapour pressure of Y $= 760 - 234 = 526mmHg$

   $\dfrac{mass\ of\ Y}{mass\ of\ H_2O} = \dfrac{V.\rho\ of\ Y \times RFM\ of\ Y}{V.\rho\ of\ H_2O \times RFM\ of\ H_2O}$

   $\dfrac{91.1}{8.9} = \dfrac{526 \times RFM\ of\ Y}{234 \times 18}$

   RFM of Y $= \dfrac{91.1 \times 234 \times 18}{8.9 \times 526}$

   $= 81.96$

   Formula mass of Y $= 82g$.

(ii) $(C_3H_5)n = 82$

         $(12 \times 3)n + (1 \times 5)n = 82$ *Molecular formula* $= C_6H_{10}$

         $41n = 82$

         $n = 2$

c)   *The compound should have a double bond*
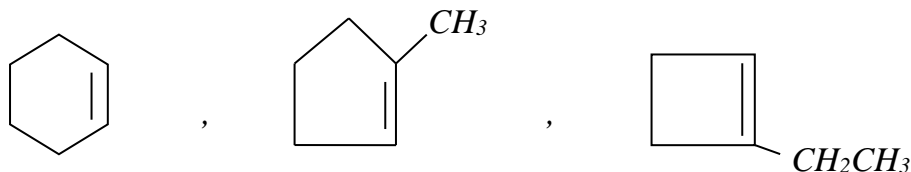
4.   (a)   State the effect on the vapour pressure of water, and one the total vapour pressure of the system when small amounts of the following substances are separately added to water at 25^0C.

Substance added to water	Effect on;	
	Vapour pressure of water	Total vapour pressure of the system
(i) Sodium chloride	Decreases	Decreases
(ii) Propanone	Increases	Increases
(iii) Tetrachlomethane	Remains constant	Increases.

    (b) Explain your answers in a(i), (ii) and (iii)

Solution

In a (i) sodium chloride is a non – volatile solute. When added to water, its particles occupy the water surface and hinder the escaping tendency of water molecules into vapour phase hence the vapour pressure exerted by water is reduced, and consequently the vapour pressure of the solution is reduced.

In a (ii), both propanone and water molecules are polar but the hydrogen bonds in water are stronger than the van der waal's forces between propanone molecules.
When the two liquids are mixed, weaker intermolecular forces are formed between the unlike molecules due to repulsion between similar polarities.
This results into an increase in the escaping tendency of the molecules from solution into vapour phase hence increase in vapour pressure exerted both by water and the water – propanone.

In a (iii), tetrachloromethane is immiscible with water. Each component in the mixture exerts an independent vapour pressure.
Thus the vapour pressure of water remains constant.
Each component contributes its vapour pressure to sum up to the total vapour pressure of the system. Thus the vapour pressure of the system increases.

5. The following data was obtained for the steam distillation of Bromobenzene at a pressure of 760mmHg.

Temperature (^{0}C)		90	92	94	96	98	100
Vapour pressure (mmHg)	Water	526	567	610	658	707	760
	Bromobenzene	98	106	115	123	132	141

a) On the same axes, plot graphs of vapour pressure against temperature for water, bromobenzene and the mixture of water and bromobenzene.

b) From the graphs, determine;
   (i)   the temperature at which distillation occurred.
   (ii)   the vapour pressures exerted by water and bromobenzene at the distillation temperature.

c) Calculate the percentage by mass of bromobenzene that would be obtained.

d) Explain how bromobenzene can be isolated from the distillate.
   - *The distillate is put in a separating funnel and when the layers of the liquid (bromobenzene) and water have settled, the bromobenzene layer is run off. Bromobenzene is then dried using anhydrous calcium chloride and filtered.*

THREE – COMPONENT SYSTEMS
Distribution of a solute between two immiscible solvents in contact
If a solute (solid or liquid) is shaken with two immiscible solvents in contact at a given temperature and it is soluble in both, the solute distributes or partitions itself between the two solvents until equilibrium is established.

At equilibrium, the ratio of concentration of the solute in one solvent to the concentration in the second solvent is always constant at a fixed temperature.

The partition or distribution law.
"A solute soluble in two immiscible solvents in contact will distribute itself between the two liquids such that the ratio of its concentration in one solvent to its concentration in the other at equilibrium is constant at a fixed temperature provided the solute remains in the same molecular state in both solvents".

The constant ratio is known as the Partition or Distribution coefficient, K_D.

The partition or distribution coefficient, K_D .

This is the constant ratio of molar concentrations of a solute dissolved in two immiscible solvents in contact and when equilibrium has been established at a fixed temperature and the molecular state of the solute is the same in both solvents.

If a solute X is shaken between two immiscible liquids A and B in contact at a fixed temperature, then at equilibrium,

$$\frac{[\,X\,]\,in\,A}{[\,X\,]\,in\,B} = a\ constant,\ K_D.$$

The value of K_D is independent of volume of the solvents used and the mass of the solute.

Question:

10g of butanoic acid was added to $100cm^3$ of water and shaken with $150cm^3$ of ether at 25^0C.

At equilibrium, 3.6g of butanoic acid had remained in the aqueous layer.

   (a)   Calculate the distribution coefficient of butanoic acid between;

         (i)   water and ether.

         (ii)   ether and water

   (b)   Comment on the solubility of butanoic acid in water.

Solution

(a)(i)   mass of butanoic acid in ether = 10 – 3.6

$$= 6.4g$$

$$K_D = \frac{[Butanoic\ acid]ether}{[butanoic\ acid]water}$$

$$= \frac{3.6/_{100}}{6.4/_{150}}$$

$$K_D = \ 0.844$$

(ii) $K_D = \dfrac{[Butanoic\ acid]ether}{[butanoic\ acid]water}$

$$= \frac{6.4/_{150}}{3.6/_{100}}$$

$$K_D = 1.185$$

---

b)   Butanoic acid is less soluble in water than it is in ether i.e. it is 1.185times more soluble in ether than in water.

$$\frac{[Butanoic\ acid]ether}{[butanoic\ acid]water} = 1.185$$

[Butanoic acid] ether = 1.185 [Butanoic acid] water.

Limitations of the partition or distribution law.
-   The temperature of the mixture should be kept constant
-   The solute should be soluble in both solvents
-   The solute must not dissociate or associate in either solvent i.e. it should remain in the same molecular state in both solvents.
-   The solute must not react with either solvent.
-   The solute should not saturate either solvent

DETERMINATION OF DISTRIBUTION COEFFICIENT OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS IN CONTACT.

A known mass of the solute is dissolved in known volumes of two immiscible solvents in contact in a separating funnel.

The mixture is shaken so that the solute can completely dissolve in both solvents, and it is then allowed to stand for equilibrium to be established.

The layers are then separated and the concentration of the solute in each layer is determined by titration.

The standard solution selected depends on the nature of the solute. e.g;
-   If the solute is acidic, an alkaline solution such as sodium hydroxide solution is used as the standard solution.
-   If the solute is alkaline, an acidic solution such as hydrochloric acid is used as the standard solution.
-   If the solute is iodine, standard sodium thiosulphate solution is used.

The end-point is detected by indicators that are selected depending on the titrant.

a) **Determination of partition coefficient of butanedioic acid (Succinic acid) between water and ether.**

A known mass of butanedioic acid is added to a known volume of water in a separating funnel, and a known volume of ether is also added.

The mixture is shaken, left sealed and allowed to settle such that equilibrium is established at a constant temperature.

The layers are separated and a fixed volume of the aqueous layer is pipette and titrated against a standard solution of sodium hydroxide using phenolphthalein indicator.

$$C_2H_4(COOH)_2 \text{ (aq)} + 2\,NaOH(aq) \longrightarrow C_2H_4(COONa)_2(aq) + 2H_2O(l)$$

From the volume of standard sodium hydroxide solution used, the concentration of butanedioic acid in the aqueous layer is determined.

The concentration of the acid in the organic layer is then obtained by subtraction.

The partition coefficient, K_D is obtained from the expression;

$$K_D = \frac{[C_2H_4(COOH)_2] water}{[C_2H_4(COOH)_2] ether}$$

b) **Determination of partition coefficient of iodine between water and tetrachloromethane**

A known mass of iodine is added to a known volume of tetrachloromethane in a separating funnel to make a solution.

A known volume of water is added to the mixture and the funnel is stoppered.

The mixture is shaken and then allowed to settle so that equilibrium is established at a constant temperature.

The layers are separated and a fixed volume of the aqueous layer is pipette and titrated with a standard solution of sodium thiosulphate using starch indicator.

$$2S_2O_3^{2-} \text{ (aq)} + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$
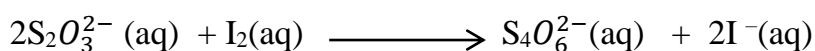
From the volume of standard sodium thiosulphate solution used, the concentration of iodine in aqueous layer is determined.

The concentration of iodine in the organic layer can then be determined by subtraction.

Partition coefficient, K_D is obtained from the expression;

$$K_D = \frac{[I_2] \text{ water}}{[I_2] \text{ CCl}_4}$$

c) **Determination of the partition coefficient of ammonia between water and chloroform**

An aqueous solution of ammonia of a known concentration is prepared and a known volume of this solution is transferred into a separating funnel.

A known volume of trichloromethane (chloroform) is added to the solution in the separating funnel.

The mixture is shaken and then left sealed to stand at a constant temperature such that equilibrium is established.

The layers are separated and a fixed volume of the organic layer is pipetted and titrated against a standard solution of hydrochloric acid using phenolphthalein indicator.

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$
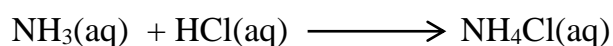
From the volume of standard hydrochloric acid used, the concentration of ammonia in the organic layer is determined while concentration remaining in the aqueous layer can be obtained by subtraction.

The partition coefficient is then obtained from the expression.

$$K_D = \frac{[NH_3] \text{ water}}{[NH_3] \text{ CCl}_3}$$

Examples

1. In an experiment to determine the partition coefficient of ammonia between water and trichloromethene, $10cm^3$ of the aqueous layer required $13.2cm^3$ of 0.25M hydrochloric acid for complete neutralisation.
   $25cm^3$ of the trichloromethane layer required $6.60cm^3$ of 0.05M hydrochloric acid for complete reaction.
   Calculate the value of the partition coefficient.

Solution

[NH₃] in the aqueous layer;

$$Moles\ of\ HCl = \left(\frac{13.2\ x\ 0.25}{1000}\right)$$

$$= 3.3\ x\ 10^{-3}\ moles$$

NH₃(aq) + HCL(aq) ⟶ NH₄Cl(aq)
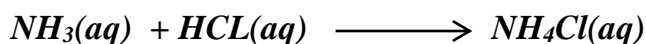
Moles of NH₃ = moles of HCl
$$= 3.3\ x\ 10^{-3} moles$$

$10cm^3$ of the aqueous layer contain $3.3\ x\ 10^{-3}$ moles of NH₃.

$1000cm^3$ of the aqueous layer contain $\left(\frac{1000\ x\ 3.3\ x\ 10^{-4}}{10}\right)$

$$= 0.33M$$

[NH₃] in the organic layer;

$$Moles\ of\ HCl = \left(\frac{6.60\ x\ 0.05}{1000}\right) = 3.3\ x\ 10^{-4} moles.$$

Moles of NH₃ = mole of HCl
$$= 3.3\ \ x\ 10^{-4} moles$$

$25cm^3$ of the organic layer contain $3.3\ x\ 10^{-4}$ moles of NH₃

$1000cm^3$ of the organic layer contain $\left(\frac{1000\ x\ 3.3\ x\ 10^{-4}}{25}\right)$
$$= 0.0132M$$

$$K_D = \frac{[NH_3]water}{[NH_3]organic}$$

$$= \frac{0.33}{0.0132}$$
$$= 25$$

2.   50cm^3 of 1.5M ammonia solution was shaken with 50cm^3 trichloromethane in a separating funnel.

After the layers had settled, 20cm^3 of the trichoromethane layer was pipetted and titrated with 0.05M hydrochloric acid.

22.90cm^3 of the acid was required for complete neutralisation.

(i)   Write the expression for the partition coefficient, K$_D$, for ammonia between water and trichloromethane.

ii)   Calculate the value of the partition coefficient.

Solution:

(i) $\mathbf{K_D} = \frac{[NH_3]water}{[NH_3]CHCl_3}$

(ii)   [NH$_3$] in the organic layer;

Moles of HCl = $\left(\frac{22.9 \text{ x } 0.05}{1000}\right)$ = 1.145 x 10^{-3} moles
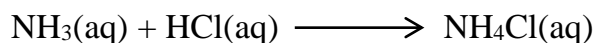
NH$_3$(aq) + HCl(aq) $\longrightarrow$ NH$_4$Cl(aq)
Moles of NH$_3$ = moles of Hcl
            = 1.145 x 10^{-3} moles.

20cm^3 of the organic layer contain 1.145 x 10^{-3} moles of NH$_3$

1000cm^3 of the organic layer contain $\left(\frac{1.145\text{x }10^{-3}\text{ x }1000}{20}\right)$
                                            = 0.05725M

Initial [NH$_3$ in aqueous layer = 1.5M
[NH$_3$ remaining in aqueous = 1.5 – 0.05725
                    = 1.44275M

K$_D$ = $\frac{1.44275}{0.05725}$
      = 25.2

3. (a) Iodine in aqueous potassium iodide was shaken vigorously with an equal volume of tetrachloromethane
   (i) State the role of potassium iodide solution
   (ii) State and explain the observation made in (a)

   b) A certain amount of iodine was shaken with 50.0cm^3 of tetrachloromethane and 50.0cm^3 of water in a separating funnel
   25.0cm^3 of the aqueous layer required 6.70cm^3 of 0.05M sodium thiosulphate solution, while 25.0cm^3 of the organic layer required 27.20cm^3 of 1.15M sodium thiosulphate solution.
   Calculate the distribution coefficient for iodine between CCl$_4$ and water.

Solution

(a)(i) Potassium iodide provides iodide ions which combine with iodine molecules to form a soluble complex of triodide ions.

$$I_2(aq) \; + I^-(aq) \; \rightleftharpoons \; I_3^-(aq)$$
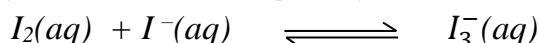
Otherwise, iodine is sparingly soluble in water.

(ii) The colourless tetrachloromethane layer becomes purple.
This is because the iodine that was making the aqueous layer brown dissolves more in the organic layer. The aqueous layer finally becomes faint brown / pale –brown.

b) *[I$_2$] in the aqueous layer*
moles of $S_2O_3^{2-} = \left(\dfrac{6.7 \; x \, 0.005}{1000}\right)$

$$= \; 3.685 \; x \; 10^{-4} \; moles$$
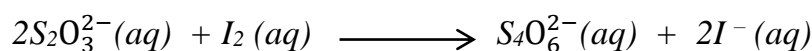
$2S_2O_3^{2-}(aq) \; + I_2\,(aq) \; \longrightarrow \; S_4O_6^{2-}(aq) \; + \; 2I^-\,(aq)$
2 moles of $S_2O_3^{2-}$ *react with 1 mole of I$_2$*
3.685 x 10^{-4} moles of $S_2O_3^{2-}$ *react with* $\left(\dfrac{3.685 \; x \; 10^{-4}}{2}\right)$
$$= 1.8425 \; x \; 10^{-4} \; moles$$

25cm^3 of the aqueous layer contain 1.8425 x 10^{-4} moles of I$_2$
1000cm^3 of the aqueous layer contain $\left(\dfrac{100 \; x \, 1.8425 \; x \; 10^{-4}}{25}\right)$
$$= 0.00737M$$

[I_2] in the organic layer;

Moles of $S_2O_3^{2-}$ $= \left(\frac{27.20 \times 1.15}{1000}\right)$

$= 3.128 \times 10^{-2}$ moles

2 moles of $S_2O_3^{2-}$ react with 1 mole of I_2

3.128 $\times$ 10^{-2} moles of $S_2O_3^{2-}$ react with $\left(\frac{3.128 \times 10^{-2} \times 1}{2}\right)$

$= 1.564 \times 10^{-2}$ *moles*

$25cm^3$ of the organic layer contain 1.564×10^{-2} moles of I_2

$1000cm^3$ of the organic layer contain $\left(\frac{100 \times 1.564 \times 10^{-2}}{25}\right)$

$= 0.6256M$

$\frac{[I_2]CCl_4}{[I_2]water} = \frac{0.6256}{0.00737}$

$K_D = 84.88$

4. 0.9656g of iodine was added to a mixture of $50cm^3$ of water and $50cm^3$ of tetrachloromethane.

   $25cm^3$ of the aqueous layer required $4.40cm^3$ of 0.01M sodium thiosulphate solution for complete reaction.

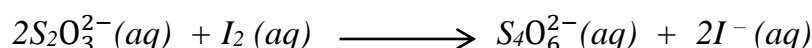   Determine the distribution coefficient of iodine between CCl_4 and water (I = 127)

Solution

Initial [I_2] in the aqueous layer;

$50cm^3$ of the aqueous layer contain 0.09656g of I_2

$1000cm^3$ of the aqueous layer contain $\left(\frac{1000 \times 0.9656}{50}\right)$

$= 19.312gl^{-1}$

[I_2] remaining in the aqueous layer;

Moles of $S_2O_3^{2-}$ $= \left(\frac{4.40 \times 0.01}{1000}\right)$

$= 4.4 \times 10^{-5}$ *moles*

$2S_2O_3^{2-} (aq) + I_2 (aq) \longrightarrow S_4O_6^{2-} (aq) + 2I^- (aq)$

2 moles of $S_2O_3^{2-}$ react with 1 mole of I_2

4.4 $\times$ 10^{-5} moles of $S_2O_3^{2-}$ react with $\left(\frac{4.4 \times 10^{-5} \times 1}{2}\right)$

$= 2.2 \times 10^{-5}$ *moles of I_2.*

$25cm^3$ of the aqueous layer contain 2.2×10^{-5} moles of I_2

$1000cm^3$ of the aqueous layer contain $\left(\dfrac{100 \times 2.2 \times 10^{-5}}{25}\right)$

$$= 8.8 \times 10^{-4} \text{ M}$$

Formula mass of $I_2 = 127 \times 2$
$$= 254g$$
$[I_2] = 254 \times 8.8 \times 10^{-4} = 0.22352gl^{-1}$

$[I_2]$ in organic layer $= 19.312 – 0.22352$
$$= 19.08848 \ gl^{-1}$$

$$K_D = \frac{[I_2]CCl_4}{[I_2]water}$$

$$= \frac{19.08848}{0.22352}$$

$K_D = 85.4$

Application of the distribution / portion law
- Solvent extraction
- Investigation of complex ions
- Distinguishing bromides from iodides
- Ion exchange
- Partition chromatography

(a) SOLVENT EXTRACTION

This involves separating one component from a mixture by shaking it with the extraction solvent in which the component is more soluble.

Each layer is then collected and the solute can be obtained by distilling off the extracting solvent.

Solvent extraction is the partial removal of a solute from a solvent or its aqueous solution by introducing another solvent immiscible with the first solvent but in which the solute is more soluble.

The process is commonly applied in the purification of organic compounds present in aqueous solution together with ionic impurities.

Organic compounds and non – polar substances are extracted using organic solvents such as carbon tetrachloride, ether or benzene.

Ether is usually preferred as an extracting solvent because;
- It is very volatile and therefore easily distilled off.
- It is a good organic solvent.
- It is generally inert, thus can not react with organic compounds.
- It is immiscible with water.

Note:
The extracting solvent should be used in several small portions than all being used at once. This is because more solute is extracted by using several small portions of the solvent.

Examples:
1. Calculate the mass of an organic compound, Q that can be extracted from $100cm^3$ of an aqueous solution containing 5.0g of Q by using;
   a) $100cm^3$ of ether
   b) 2 successive portions of $50cm^3$ of ether.
   (K_D of Q between ether and water is 3)

Solution
   a) Let the mass of Q extracted by $100cm^3$ of ether be xg.
   Mass of Q remaining in the aqueous layer = (5 – x)g.

$$\frac{[Q]ether}{[Q]water} = K_D$$

$$\frac{\frac{x}{100}}{\frac{5-x}{100}} = 3$$

$$\frac{x}{5-x} = 3$$
$$x = 15 = 3x$$
$$x = 3.75g.$$

   b) Let mass of Q extracted by the 1ˢᵗ $50cm^3$ portion of ether be x_1g
   Mass of Q remaining in aqueous layer = (5 – x_1)g

$$\left(\frac{\frac{x_1}{50}}{\frac{5-x_1}{100}}\right) = .03$$

$$2x_1 = 15 = 3x_1$$
$$5x_1 = 15$$
$$x_1 = 3g$$

$$\frac{2x_1}{5-x_1} = 3$$

   After extraction with the first portion;
   Mass of Q remaining in aqueous layer = (3 – 5) = 2g
   Let the mass of Q extracted using the 2ⁿᵈ $50cm^3$ portion be x_2g

Thus, mass of Q remaining in aqueous solution = (2 − x₂)g

$$\frac{\frac{x_2}{50}}{\frac{2-x_2}{100}} = 3$$

$$\frac{2x_2}{2-x_2} = 3$$

$2x_2 = 6 = 3x_2$

$5x_2 = 6$

$x_2 = 1.2g$

Total mass extracted by the 2 successive portions = x₁ + x₂

$= 3 + 1.2$

$= 4.2g$

2. Calculate the percentage by mass of iodine extracted from 100cm³ of water using;
   a) 100cm³ of benzene
   b) 2 successive portions of 50cm³ of benzene
      (K_D of iodine between benzene and water is 5)

Solution;

(a) Let the percentage by mass of iodine extracted by 100cm³ of benzene be y%
Thus percentage by mass of I₂ remaining in aqueous = (100 − y)%

$$\frac{[I_2]benzene}{[I_2]water} = 5$$

$$\frac{\frac{y}{100}}{\frac{100-y}{100}} = 5$$

$$\frac{y}{100-y} = 5$$

$y = 500 - 5y$

$y = 83.33\%$

(b) Let the percentage by mass of iodine extracted by the 1ˢᵗ 50cm³ portion of benzene be x₁%

$$\frac{\frac{x_1}{50}}{\frac{100-x_1}{100}} = 5$$

$$\frac{2x_1}{100-x_1} = 5$$

$2x_1 = 500 - 5x_1$

$7x_1 = 500$

$x_1 = 71.43\%$

Thus, percentage by mass of iodine remaining in aqueous layer = (100 – 71.43) = 28.57%

Let the percentage by mass of iodine extracted by the 2nd 50cm³ portion of benzene be x_2%

$$\frac{\frac{x_2}{50}}{\frac{28.57 - x_2}{100}} = 5$$

$$\frac{2x_2}{28.57 - x_2} = 5$$

$2x_2 = 5 (28.57 – x_2)$

$x_2 = 20.42\%$

Total mass of iodine extracted by the two portions
$$= 71.43 + 20.41$$
$$= 91.84\%$$

3. 50cm³ of a solution containing 0.966g of iodine in tetrachloromethane was shaken with 50cm³ of water.

   (i) Calculate the amount of iodine that remained in the tetrachloromethane layer.

   (K_D for iodine between CCl_4 and water = 85.25)

   (ii) Explain how your answer in (i) would be affected if the iodine solution in tetrachloromethane was shaken with aqueous potassium iodide instead of water.

Solution;

(i) *Let the mass of I_2 extracted by 50cm³ of water be ag*

Thus, mass of I_2 remaining in CCl_4 will be (0.966 – a)g

$$\frac{[I_2]CCl_4}{[I_2]water} = 85.25$$

$$\frac{\frac{0.966-a}{50}}{\frac{a}{50}} = 85.25$$

$$\frac{0.966-a}{a} = 85.25$$

$0.966 = 86.25a$

$a = 0.0112g$

Amount of iodine remaining in organic layer = 0.966 – 0.0112
$$= 0.9548g$$

(ii)   *The mass of iodine remaining in the tetrachloromethane layer would reduce.*

The iodide ions in potassium iodide solution combine with iodine to form a soluble complex.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

This reduces the concentration of iodine in the aqueous layer.

For equilibrium to be established, more iodine moves from the organic layer to the aqueous layer.

4. A solid Q is three times as soluble in solvent X as in solvent Y.

Q has the same relative molecular mass in both solvents. Calculate the mass of Q that would be extracted from a solution of 4g of Q in $12cm^3$ of Y with;

(i) $12cm^3$ of X

(ii) $6cm^3$ successive portions of X

Solution

This implies;

$$[\,Q\,]_X = 3[\,Q\,]_Y$$

Hence,

$$\frac{[Q]_X}{[Q]_Y} = 3$$

(b)   Investigation of complex ions

Many ions undergo complexation when a ligand substance is added to their aqueous solution.

The formular of the formed complex and hence the number of ligand molecules coordinated to the central metal ion can be determined by the application of the partition law.

Consider the reaction between copper (II) ions and ammonia,

$$Cu^{2+}(aq) + n\ NH_3(aq) \rightleftharpoons [Cu(NH_3)_n]^{2+}(aq)$$
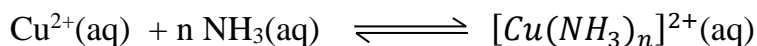
Determining the number of moles, n, of ammonia combining with one mole of copper (II) ions can not be done by direct titration because the acid will react with ammonia in the complex as well as free ammonia.

However, when an organic solvent is added to the aqueous solution, the complex ion formed can not dissolve in the organic solvent.

Only the free ammonia molecules will be partitioned between the aqueous layer and the organic layer.

Therefore, the total concentration of ammonia in the aqueous layer consists of complexed ammonia and the free ammonia.

Determination of the formula of a complex formed between copper (II) ions and ammonia $[Cu(NH_3)_n]^{2+}$.

Excess aqueous ammonia is added to a solution of copper (II) sulphate of a known concentration in a separating funnel.

An equal volume of trichloromethane is added to the solution in the funnel. The mixture is shaken and allowed to settle at a constant temperature for equilibrium to be established as the layers separate.

The layers are removed from the funnel and a known volume of the organic layer is pipette and titrated with standard hydrochloric acid using methyl orange indicator to determine the concentration of ammonia in the organic layer.

From the known value of the partition coefficient of ammonia between water and trichloromethane, the concentration of free ammonia in the aqueous layer is got from the expression

$$K_D = \frac{[NH_3]free}{[NH_3]organic}$$

A fixed volume of the aqueous layer is also pipetted and titrated with standard hydrochloric acid using methyl orange indicator. This gives the total concentration of both the complexed and uncomplexed ammonia in the aqueous layer.

The concentration of the complexed ammonia in the aqueous layer is then obtained using the expression;

$$[NH_3 \text{ complexed} = [NH_3]_{Total} - [NH_3] \text{ free}$$

The number of molecules of ammonia combining with copper (II) ions to form a complex is then obtained from the ratio of the concentration of complexed ammonia to that of copper (II) ions.

$$n = \frac{[NH_3] \, complexed}{[Cu^{2+}]}$$

Examples

1. Excess ammonia was shaken with equal volume of trichloromethane and a 0.05M aqueous solution of copper (II) sulphate and allowed to stand. Some ammonia reacted with copper (II) ions to form a complex, $[Cu(NH_3)_n]^{2+}$.

   At equilibrium, the concentrations of ammonia in the trichloromethane and aqueous layers were 0.021M and 0.725M respectively.

   (K_D for ammonia between water and trichloromethane = 25)

   (a) Calculate the concentration of;
   (i)   free ammonia in the aqueous layer.
   (ii)   ammonia that formed a complex with copper(II) ions.

   (b) Determine the value of n in the complex.

Solution

a)(i)

$$K_D = \frac{[NH_3]free}{[NH_3]organic}$$

   [NH₃] free = K_D x *[NH₃] organic*
   = 25 x *0.021*
   = *0.525M*

   (ii) [NH₃] complexed = *[NH₃]ₜₒₜₐₗ* − *[NH₃]free*
   = *0.725 − 0.525*
   = *0.2M*

b)   *0.05 moles of Cu²⁺ complex with 0.2 moles of NH₃.*
   1 mole of Cu²⁺ complexes with $\left(\frac{1\ x\ 0.2}{0.05}\right)$
   = *4 moles of NH₃*

   Formula of complex = $[Cu(NH_3)_4]^{2+}$

2. Ions of a metal M react with excess ammonia to form a complex according to the equation

   M⁺(aq) + n NH₃(aq) $\rightleftharpoons$ $[M(NH_3)_n]^+$(aq)
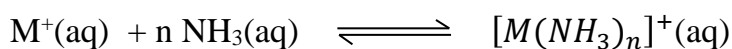
   25cm³ of ammonia solution was added to 25cm³ of a 0.1M aqueous solution of metal m ions, followed by 50cm³ of trichloromethane.

   The mixture was shaken and allowed to reach equilibrium at 20⁰C.

The aqueous layer required 27.5cm^3 of 1.0M nitric acid and the trichloromethane layer required 18.0cm^3 of 0.05M nitric acid for complete neutralisation. Calculate the;

(i)   concentration of ammonia in trichloromethane layer.

(ii)   concentration of ammonia that formed a complex with M^+
        (K_D for ammonia between water and $CHCl_3$ is 25 at 20^0C)

(iii)   value of n in the complex

Solution

(i)   *1000cm^3 of HNO$_3$ solution contain 0.05moles*

        18cm^3 of HNO$_2$ solution contain $\left(\frac{18 \times 0.05}{1000}\right)$

$$= 9 \times 10^{-4} \text{ moles of HNO}_3$$
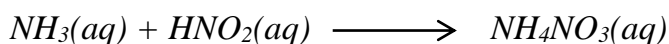
$NH_3(aq) + HNO_2(aq) \longrightarrow NH_4NO_3(aq)$
1 mole of HNO$_3$ reacts with 1mole of NH$_3$
Thus, moles of NH$_3$ reacting $= 9 \times 10^{-4}$

50cm^3 of CHCl$_3$ layer contain 9×10^{-4} moles of NH$_3$
1000cm^3 of CHCl$_3$ layer contain $\left(\frac{1000 \times 9 \times 10^{-4}}{50}\right)$

$$= 0.018M$$

(ii)   *1000cm^3 of HNO$_3$ solution contain 1.0 moles*

        27.5cm^3 of HNO$_3$ solution contain $\left(\frac{27.5 \times 1.0}{1000}\right)$

        1 mole of HNO$_3$ reacts with 1 mole of NH$_3$
        Thus, moles of NH$_3$ reacting $= 0.0275$ moles

        50cm^3 of aqueous layer contain 0.0275 moles of NH$_3$
        1000cm^3 of aqueous layer contain $\left(\frac{1000 \times 0.0275}{50}\right)$
$$= 0.55M$$

$[NH_3]$ complexed $= [NH_3]$Total in aqueous $- [NH_3]$ free
But; $[NH_3]$ free $= K_D \times [NH_3]$ organic
$$= 25 \times 0.018$$
$$= 0.45M$$
$[NH_3]$ complexed $= 0.55 - 0.45$
$$= 0.1M$$

(iii) $1000cm^3$ of M^+ solution contain 0.1 moles

$25cm^3$ of M^+ solution contain $\left(\frac{25 \times 01}{1000}\right)$

$$= 2.5 \times 10^{-3} \text{ moles}$$

$50cm^3$ of the aqueous layer contain 2.5×10^{-3} moles

$1000cm^3$ of the aqueous layer contain $\left(\frac{1000 \times 2.5 \times 10^{-3}}{50}\right)$

$$= 0.05M \text{ of } M^+ \text{ ions}$$

0.05 moles of M^+ ions complex with 0.1 moles of NH_3

1 mole of M^+ ions complexes with $\left(\frac{1 \times 0.1}{0.05}\right)$

$$= 2 \text{ moles of } NH_2$$
$$Hence \; n = 2$$

3. $25cm^3$ of excess ammonia solution were added to $25cm^3$ of 0.1M copper (II) sulphate solution and the resultant solution shaken with trichloromethane.

   After the layers had settled, $50cm^3$ of the trichloromethane layer needed $25.5cm^3$ of 0.05M hydrochloric acid for neutralisation, while $20cm^3$ of the aqueous layer required $33.3cm^3$ of 0.5M hydrochloric acid for neutralisation.
   (The partition coefficient of ammonia between water and trichloromethane is 25).
   Determine the formula of the complex ion formed.

Solution

$1000cm^3$ of HCl solution contain 0.5 moles

$25.5cm^3$ of HCl solution contain $\left(\frac{25.5 \times 0.05}{1000}\right)$

$$= 1.275 \times 10^{-3} \text{ moles}$$
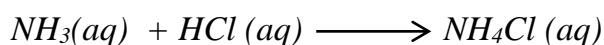
$NH_3(aq) + HCl\,(aq) \longrightarrow NH_4Cl\,(aq)$
Thus, moles of NH_3 reacting $= 1.275 \times 10^{-3}$ moles.

$50cm^3$ of $CHCl_3$ layer contain 1.275×10^{-3} moles of NH_3

$1000cm^3$ of $CHCl_3$ layer contain $\left(\frac{1000 \times 1.275 \times 10^{-3}}{50}\right)$

$$= 0.0255M$$

$1000cm^3$ of HCl solution contain 0.5 moles

$33.3cm^3$ of HCl solution contain $\left(\frac{33.3 \times 0.5}{1000}\right)$

$$= 1.665 \times 10^{-2} \text{ moles.}$$

From the reaction ratio;

Moles of NH_3 reacting aqueous layer = 1.665 x 10^{-2}moles

20cm³ of the aqueous layer contain 1.665 x 10^{-2} moles of NH_3

1000cm³ of the aqueous layer contain $\left(\dfrac{1000 \times 1.665 \times 10^{-3}}{20}\right)$

$$= 0.8325M$$

$[NH_3]$ free in aqueous = K_D x $[NH_3]$organic

$$= 25 \times 0.0255$$
$$= 0.6375M$$

$[NH_3]$ complexed = = $[NH_3]$Total in aqueous − $[NH_3]$ free

$$= 0.8325 − 0.6375$$
$$= 0.195M$$

Moles of Cu^{2+} in aqueous layer = $\left(\dfrac{25 \times 0.1}{1000}\right)$

$$= 2.5 \times 10^{-3} \text{ moles}$$

50cm³ of the aqueous layer contain 2.5 x 10^{-3} moles of Cu^{2+}

1000cm³ of the aqueous layer contain $\left(\dfrac{2.5 \times 10^{-3} \times 1000}{50}\right)$

$$= 0.05M$$

0.05 moles of Cu^{2+} complex with 0.195 moles of NH_3

1 mole of Cu^{2+} complexes with $\left(\dfrac{0.195 \times 1}{0.05}\right)$

$$= 3.9$$
$$\cong 4 \text{ moles of } NH_3$$

Formula complex = $[Cu(NH_3)_4]^{2+}$

4. 8g of an ore of zinc was dissolved in excess ammonia and the resultant solution was diluted to one litre with water, shaken with trichloromethane and left to settle.

   50cm³ of the trichlormethane layer required 25cm³ of 0.05M hydrochloric acid for complete neutralisation, while 25cm³ of the aqueous layer required 40cm³ of 0.5M hydrochloric acid.

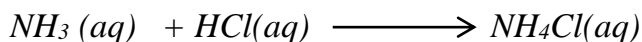   (The partition coefficient for ammonia between water and $CHCl_3$ is 25)

Calculate the;

(i)   Concentration of zinc ions in the complex formed.

(ii)   Percentage of zinc in the ore.

Solution

(i)   *Moles of HCl used in the CHCl₃ layer* $= \left(\frac{25 \times 0.05}{1000}\right)$

$$= 1.25 \times 10^{-3} \text{ moles}$$

$NH_3 (aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$
1 mole of HCl reacts with 1mole of NH₃
Therefore; moles of NH₃ in CHCl₃ = 1.25 x 10⁻³ moles

50cm³ of CHCl₃ layer contain 1.25 x 10⁻³ moles of NH₃

1000cm³ of CHCl₃ layer contain $\left(\frac{1000 \times 1.25 \times 10^{-3}}{50}\right)$

$$= 0.025M$$

Moles of HCl used in the aqueous $= \left(\frac{40 \times 0.5}{1000}\right)$

$$= 0.02 \text{ moles}$$

1 mole of HCl reacts with 1 mole of NH₃.
Therefore, moles of NH₃ = 0.02 moles

25cm³ of the aqueous layer contain 0.02 moles of NH₃

1000cm³ of the aqueous layer conation $\left(\frac{1000 \times 0.02}{25}\right)$

$$= 0.8M$$

[NH₃] free in aqueous = K_D x [NH₃]organic

$$= 25 \times 0.025$$
$$= 0.625M$$

[NH₃] complexed = = [NH₃]Total − [NH₃] free

$$= 0.8 - 0.625$$
$$= 0.175M$$

$$Z_n^{2+}(aq) + 4 NH_3(aq) \longrightarrow [Zn(NH_3)_4]^{2+}(aq)$$
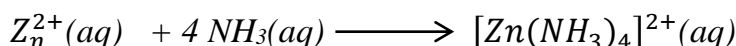
4 moles of NH₃ complex with 1 mole of Zn²⁺

0.175 moles of NH₃ complexes with $\left(\frac{0.175 \times 1}{4}\right)$

$$= 0.04375 \text{ moles.}$$

Concentration of $Zn^{2+} = 0.04375M$.

(ii)   *Mass of pure Zn in the ore = 0.04375 x 65*

$$= 2.844g$$

Percentage of Zn $= \frac{2.844}{8}$ x 100%

$$= 35.55$$

5.   Cobalt (II) ions form a complex $[Co(NH_3)_n]^{2+}$, with ammonia.

The table below shows the results of partition of ammonia between 0.1M cobalt (II) sulphate and trichloromethane.

[NH$_3$] in 0.1M CoSO$_4$	0.72	0.94	1.19	1.43	1.70	1.92
[NH$_3$] in CHCl$_3$	0.01	0.03	0.05	0.07	0.09	0.11

(i)   Plot a graph of [NH$_3$] in 0.1M CoSO$_4$ against [NH$_3$] in CHCl$_3$
(ii)   Determine the value of n in the complex.

Note:

The number of moles of NH$_3$ that complexed with 0.1M solution of Co^{2+} is determined by extrapolating the graph to cut the y – axis i.e. the intercept gives the moles.

At the intercept, the concentration of NH$_3$ in CHCl$_3$ is zero and therefore all the NH$_3$ present has complexed with Co^{2+}.

c)   Determination of the equilibrium constant, Kc.

The partition law can be used to determine the equilibrium constant between a covalent species and an ionic species in equilibrium.

Consider iodine (a covalent species) dissolving in excess potassium iodide solution to form a complex, triodide ions according to the equation;

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
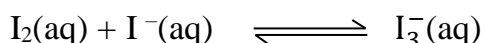
The equilibrium constant, Kc, for the reaction is obtained from the expression;

$$Kc = \frac{[I_3^-]}{[I_2][I^-]}$$

The following steps are taken;

- A known volume of aqueous solution of iodine in potassium iodide is shaken with carbon tetrachloride in a separating funnel and allowed to stand at constant temperature for equilibrium to be established as the layers separate.
- A fixed volume of each layer is pipetted into separate conical flasks and each is titrated against standard solution of sodium thiosulphate using starch indicator.
- From the volume of sodium thiosulphate that reacts with each layer the concentration of iodine in each layer is determined using the equation;

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}$$
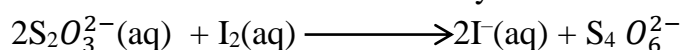
Part of the iodine in the aqueous layer react with iodide ions to form a complex, while the remaining iodine distributes itself between the aqueous layer and the organic layer.

Only the covalent iodine molecules, I_2, will dissolve in the organic solvent.
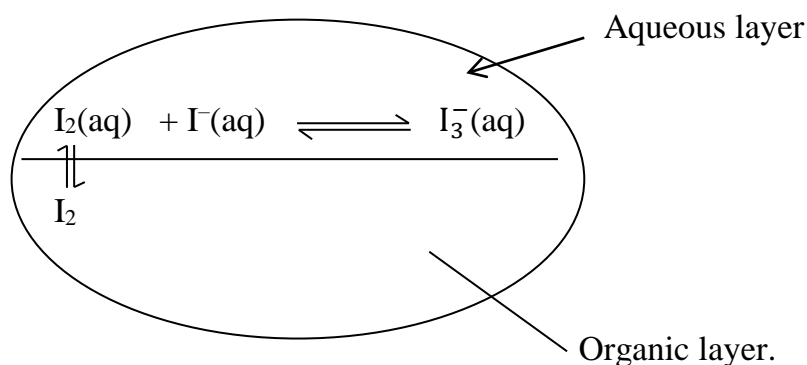
From a known value of partition coefficient of Iodine between the organic and aqueous layer, the concentration of free iodine in the aqueous layer is determined using the expression;

$$K_D = \frac{[I_2]\ organic}{[I_2]\ free\ in\ aqueous}$$

$[I_2]$ complexed $= [I_3^-] = [I_2]_{Total} - [I_2]$ free.
Then;
$[I^-]$ at equilibrium $= [I^-]$ initial $- [I_2]$ complexed.
And;

$$K_c = \frac{[I_3^-]\ organic}{[I_2]\ free\ [I^-]}$$

Example

Iodine in 0.3M aqueous potassium iodide solution was shaken with carbon disulphide and the mixture allowed to settle for some time at a fixed temperature.

When the mixture was titrated with sodium thiosulphate solution, the carbon disulphide layer was found to contain 32.3gdm^{-3} of iodine, while the aqueous layer contained 1.14gdm^{-3} of iodine .

(K_D) for iodine between CS_2 and water is 585)

a) Calculate the molar concentration at equilibrium of;

i) **free iodine in aqueous.**

RFM of I_2 = 127 x 2

$\qquad$ = 254

$[I_2]$ in CS_2 = $\frac{32.3}{254}$ 0.127M

$\frac{[I_2]CS_2}{[I_2]free\ in\ aq}$ = 585

$[I_2]$ free = $\frac{0.127}{585}$ = 2.17 x 10^{-4}M.

ii) **triiodide ions**

$[I_2]_{Total}$ in aq = $\frac{1.14}{254}$ 0.00449M

$[I_3^-]$ = $[I_2]$ complexed = $[I_2]$ $_{total}$ – $[I_2]$ free

$\qquad$ = 0.00449 – 2.17 x 10^{-4}

$\qquad$ 0.00427M

iii) **Iodide ions.**

$[I^-]$ = Initial concentration – $[I_2]$ complexed

$\qquad$ = 0.3 – 0.00427

$\qquad$ = 0.296M

b) Calculate the equilibrium constant, Kc, for the reaction.

Kc = $\frac{[I_3^-]}{[I_2]_{free}[I^-]}$

= $\frac{0.00427}{2.17\ x\ 10^{-4}\ x\ 0.296}$

= 66.48 mol^{-1} dm^3

d) Distinguishing between bromides and iodides.

To the test solution is added dilute nitric acid followed by bleaching powder. Then tetrachloromethane is added, the mixture is shaken and allowed to stand.

- Formation of a brown colouration in the tetrachloromethane layar shows the presence of bromide ions.
- Formation of a purple colouration in the tetrachloromethane layer shows the presence of iodide ions.