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- Now, HOD–Chemistry, St. Mary's College Kisubi.

1.2 About the book (U.A.C.E Physical Chemistry Compendium).

- Complete, well researched and simplified notes [illegible] Chemistry.
- Logically presented, in the form of bulleted facts which are s[illegible] for learners.
- Well illustrated experiments and detailed treatment of results.
- Many worked examples, typical explanations and challenging tasks.

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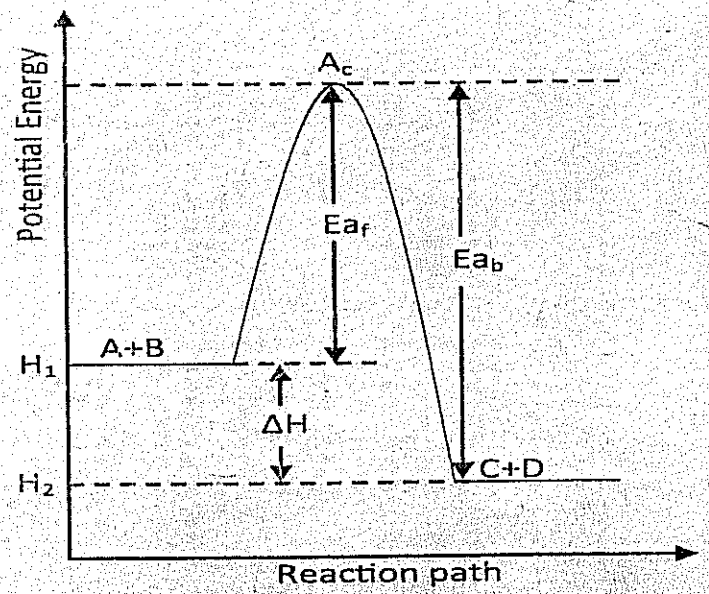
UACE PHYSICAL CHEMISTRY

COMPENDIUM

Researched, Simplified & Shared



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CHAPTER ONE: THE PARTICULATE NATURE OF MATTER:

1.0 Introduction:

- Matter is an infinite assembly of tiny invisible particles. These particles are; atoms, molecules or ions.
- Depending on prevailing temperature and pressure, any pure substance can exist in three different states/phases i.e; solid, liquid and gas. The fourth state of matter, plasma is still a subject of research.
- Plasma is an ionized gas formed when a gas is heated to a very high temperature. At this temperature electrons acquire sufficient energy to escape nuclear attraction and leave behind positive ions.
- Over 99% of the matter in the universe appears to exist as plasma! The sun and stars are examples.

1.1 The kinetic theory of matter:

- The kinetic theory of matter is an explanation put forward to explain why matter/substances exist in three physically distinct states yet chemically are indistinguishable.
- It is called kinetic theory because according to the theory, matter is viewed as made of particles which are in state of constant motion. Therefore, matter has kinetic energy.
- The differences between the three states are due to the different ways in which the individual particles move.

Solid state:

- According to the theory, in solid state:
- The particles are closely packed and firmly held together by binding forces of cohesion (forces of attraction between particles of the same substance).
- Particles are held together in a fixed position and hence can only vibrate (can only move to and fro, about a mean position).

- Solids have definite shapes and volumes because of the fixed position of their particles.
- Solids cannot flow because the particles that form them are fixed relative to their neighbours.
- When a sample of solid is heated, the particles gain the heat energy and vibrate with greater amplitudes. The more energy applied the greater the vibration.
- Finally a temperature is reached and the solid is converted into liquid, at a constant temperature known as melting point. This involves breaking down of regular structure of solids.
- However, for some solids, on being heated, they bypass the liquid phase and change direct to gaseous phase. These solids are said to sublime and the process is sublimation.

Liquid state:

- According to kinetic theory of matter:
- Liquids have more kinetic energy than solids and the particles are not held in a fixed position.
- Particles are in constant translational motion colliding and bouncing off with each other.
- Particles are as well closely packed but less close to one another than in a solid state. The forces of attraction between them are weaker.
- Liquids therefore flow, have fixed volume but takes the shape of the container.
- The surface of a liquid is always flat except near the wall of the container. This is due to particles at the surface being continuously attracted inwards and sideways by the remaining particles.
- At the same time, fastest particles at the surface of a liquid escape into vapour by a process of evaporation which increases with temperature.

- If a liquid is kept in a closed container, the escaped particles collide in the space above the surface of the liquid.
- Collisions between the particles of this vapour and the wall of the container generate vapour pressure.
- When the vapour pressure becomes equal to external atmospheric pressure, the liquid boils and gets fully converted into vapour.

Gaseous state:

- According to kinetic theory of matter, in gases:
- There is almost no cohesive force of attraction between the particles hence particles in gases are completely free to move.
- The movement of particles is only restricted by the wall of the container.
- A gas therefore has no definite shape and volume because of freedom of motion of gaseous particles. It occupies the whole volume of the container.
- A gas can be compressed since the particles are far apart.

1.2 Evidences for the kinetic theory of matter:

- As mentioned, kinetic theory of matter is an argument that asserts that:

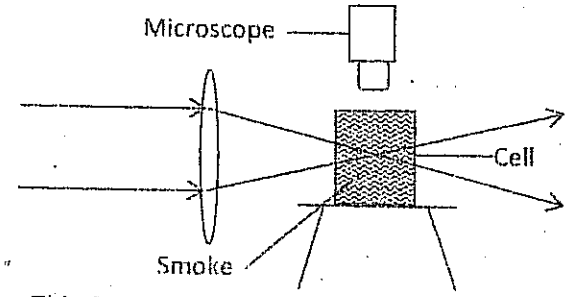
i. Matter is not continuous, but rather granular (made of particles) and
ii. Particles in matter are in a state of random motion.

- There are two main evidences that logically support the notion of the kinetic theory of matter, and these are:

a. Brownian motion and
b. Diffusion.

Brownian motion:

- It is called Brownian motion because it was a botanist, Robert Brown, who first observed this kind of motion when; he sprinkled pollen grains on water, spread on a slide and observed under a high power magnification of microscope.
- He observed the grains to move randomly (in a zig – zag fashion), and later, this motion was named Brownian motion.
- The random motion of the otherwise stationary pollen grains was due to it being continuously knocked by invisible water molecules which are in a state of random motion.
- Hence liquids are made of particles (molecules) which are in a state of random motion.
- Brownian motion can also be demonstrated in gases. Here:
- The smoke of methylammonium chloride is suspended in a glass cell, placed horizontally upright and horizontally illuminated by rays from a strong source.
- The smoke cell is then viewed through a low magnification microscope, which is then seen to portray Brownian motion



- This Brownian motion is again due to the bombardment of visible and otherwise stationary smoke particles by invisible air particles.
- Hence, air and all gases are made of particles (molecules), which are in a state continuous motion.

Diffusion:

- Diffusion literally means spreading out or intermingling. Diffusion takes place in all the three states of matter.
- Technically, diffusion is the movement of particles from a region of high concentration to that of low concentration.
- This movement from high concentration to low concentration is also described as movement down the concentration gradient.
- Hence diffusion is the movement of particles down its concentration gradient.
- The diffusion is not an explosive process, but rather spread in some time duration, and takes place at different rates in the three states of matter. It is fastest in the gaseous state and slower in the liquid state and slowest in the solid state.
- The taking of some time by diffusion is due to collision between the randomly moving (diffusing) particles. The slow rates of diffusion in liquids and solids are due to the closer pack of their particles, making their spreading particles to frequently collide with one another, hence retarding the rate of diffusion.
- Hence diffusion, does not only account for the particulate nature of matter and the random motion of the particles, but also the degree of compactness of the particles in the different states of matter.

Applications of diffusion:

a. Small scale applications:

- Food flavour/dye tends to be uniform in food due to diffusion of food colour.
- Animals, both the wild and domestic use diffusion of particles from other animals. This helps them locate their own members and enemies.

- Diffusion helps in identification of gases. For example because of diffusion of ammonia and hydrogen sulphide, we are able to detect the smell and hence identify the gases.
- Deodorants for human body use its ability to diffuse slowly for a long period of time to sustain the scent.
- Determination of formula masses.

b. Large scale applications:

i. Extraction of helium from natural gas.

- The mixture of helium and natural gas is made to diffuse through a thin sheet of Pyrex glass.
- Helium being the lightest amongst the components diffuses fastest and is thus extracted first.

ii. Separation of isotopes:

- Isotopes of an element have different masses and so diffuse at different rates under similar conditions – lightest isotope diffusing fastest.
- This has been employed in partial separation of isotopes of chlorine and neon.
- However, a major use of diffusion in separation of isotopes has been achieved using uranium in nuclear energy plants.
- Here, a sample of uranium containing uranium – 235 and uranium – 238 are converted to uranium hexafluoride, vapourised and made to diffuse through porous nickel barrier.
- The lighter vapour of uranium – 235 hexaflouride diffuses faster than vapour of uranium – 238 hexaflouride and thus separated.

1.3 The gas laws:

- The behaviours of gases are quite different from those of solids and liquids. Due to these observations, more detailed assumptions are made basing on the kinetic theory of matter to explain the gaseous state.

Detailed assumptions of the kinetic theory of gases:

- The pressure exerted by a gas is due to its molecules which are in a continuous and random motion colliding with the walls of the vessel containing the gas.
- The collisions between the gas molecules and the wall of the container are perfectly elastic such that there is no loss in kinetic energy of the molecules.
- The average kinetic energy of the molecules is proportional to the absolute temperature.
- The forces of attraction between the molecules and the molecules and the wall of the container are negligible.
- The actual volume of the gas molecules is negligible compared to the volume of the container.
- The behaviours of gases which are summarized into laws can be described in terms of four important variables:

i. The temperature of the gas,
ii. The volume of the gas,
iii. The pressure of the gas, and
iv. The amount of the gas (mass or number of moles)

- A gas law states how two of these variables and others change with one another, when the others are constant.

Boyle's law:

It states that "at a fixed temperature, the volume of a given mass of a gas is inversely proportional to its pressure".

- If 'V' is the volume and 'P' is the pressure of a given mass of gas at a fixed temperature, then:

$$P \alpha \frac{1}{V} \quad \text{.....1.1}$$

$\Rightarrow V = \frac{k}{P}$, where k is the constant of proportionality.

$$PV = k \quad \text{.....1.2}$$

- The law of inverse proportion means: if one quantity is doubled the other one is halved. If one quantity is tripled (trebled) the other one is reduced by one third.
- If a fixed mass of a gas at a given temperature has a volume of 'V_1' and pressure of 'P_1'. Then, if at the same temperature the volume is changed to 'V_2'; then pressure will change inversely to 'P_2'.

From equation 1.2,

$$P_1V_1 = k \quad \text{.....1.3}$$

Also,

$$P_2V_2 = k \quad \text{.....1.4}$$

Equation 1.3 = equation 1.4

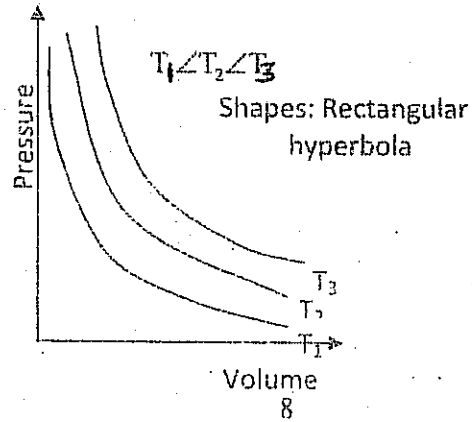
$$P_1V_1 = P_2V_2 \quad \text{.....1.5}$$

Generally,

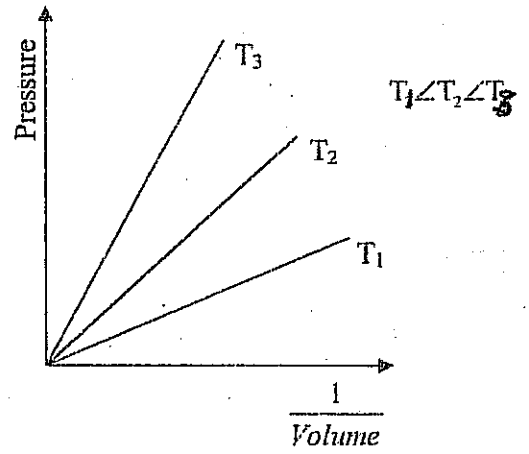
$$P_1V_1 = P_2V_2 = P_3V_3 = \ldots\ldots = P_{(n-1)}V_{(n-1)} = P_nV_n \quad \text{.....1.6}$$

- Boyle's law can as well be stated as "at a fixed temperature, the pressure of a fixed mass of a gas is inversely proportional to its volume".
- The variation of volume of a fixed mass of a gas with pressure at a constant temperature gives a graph known as an **isothermal.**

Pressure versus volume isothermal:



Pressure versus $\frac{1}{\text{Volume}}$ *isothermal:*



Charle's law:

The law states that "at a given pressure the volume of a fixed mass of a gas is directly proportional to the absolute or Kelvin temperature".

- Absolute temperate scale/thermodynamic/Kelvin scale has -273^0C as its 0.
- If V is the volume of a fixed mass of gas and T is the absolute temperature, from Charles law:

$V \alpha T$ 1.7

$\Rightarrow V = kT$ 1.8

Where k is the constant of proportionality.

Hence

$\frac{V}{T} = k$ 1.9

- If a gas has a volume V_1 and temperature T_1 at a given pressure; and the temperature is changed to T_2 at the same pressure, the new volume becomes V_2 in accordance to direct proportionality.

- From equation 1.9,

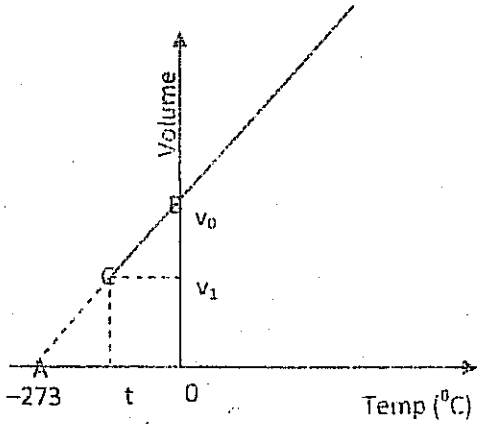
$\frac{V_1}{T_1} = \frac{V_2}{T_2}$ 1.10

Generally,

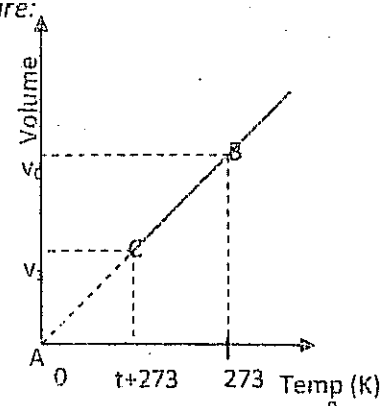
$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2} = ... = ... = \frac{V_{(n-1)}}{T_{(n-1)}} = \frac{V_n}{T_n}$ 1.11

- Charles's law comes from the observation that at 0^0C the volume of a gas is changed by $\frac{1}{273}$ units per degree rise/fall in temperature.

Vatiation of volume with temperature (^0C) at a constant pressure:



Variation of volume with temperature (K) at a constant pressure:



- V_0 is the volume of the gas at 0^0C (Celcius scale) or at 273K (Kelvin scale)
- At point C, the gas is liquefied. So, AC is an imaginary portion of the graph.
- Point A, corresponding to a temperature of -273^0C on Celsius scale and 0K on Kelvin scale is the theoretical lowest temperature that can be reached by a gas. At this temperature, the gas theoretically has zero volume. However, all gases liquefy above this temperature.
- The temperature of -273^0C on Celsius scale or 0K on Kelvin scale is called the absolute zero.

Definition:

The absolute zero is the lowest temperature at which a gas would theoretically have zero volume at a constant pressure.

- Charle's law was modified by pressure and stated as Pressure's law or Gay – Lusaac's law, which states:

"The pressure of a fixed mass of gas is directly proportional to Kelvin temperature if volume is constant.

The ideal gas equation/equation of state:

- Boyle's and Charle's laws can be combined to give an equation that connects temperature, pressure and volume of a fixed mass of a gas under different conditions.
- The equation is called ideal gas equation because it only holds if the gases behave as ideal or perfect. However, such gases do not exist.
- Consider a fixed mass of the ideal gas of volume V_1 and pressure P_1 at a temperature T_1. If the volume is changed to V_x, at constant temperature T_1, the new pressure P_2 is obtained from Boyle's law.

$P_1V_1 = P_2V_x$ 1.12

- If now T_1 is changed to T_2, V_x changes to V_2 according to Charles' law.

$$\Rightarrow \frac{V_x}{T_1} = \frac{V_2}{T_2} \quad \text{.....1.13}$$

- Combining equations 1.11 and 1.12,

$$\Rightarrow \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{.....1.14}$$

Generally;

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \ldots = \ldots = \frac{P_{(n-1)}V_{(n-1)}}{T_{(n-1)}} = \frac{P_nV_n}{T_n} \quad \text{..... 1.15}$$

- The equation 1.15 above is known as the ideal gas equation or the equation of state.

The molar gas constant:

a. ***When pressure is in*** Nm^{-2} ***and volume is in*** m^3

- From the equation 1.15,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \ldots = \ldots = \frac{P_{(n-1)}V_{(n-1)}}{T_{(n-1)}} = \frac{P_nV_n}{T_n}$$

$\Rightarrow \frac{PV}{T}$ is a constant.

$PV = KT$ 1.16

K is a constant.

For one mole of a gas,

$PV = RT$ 1.17

Where R is the universal molar gas constant.

For n moles of a gas;

$PV = nRT$ 1.18

- For one mole of a gas under standard temperature (273K) and pressure (760mmHg), $V = V_m = 22.4dm^3$

$p = \rho hg$

$p = 13600 \times \frac{760}{1000} \times 9.8$

$\Rightarrow 13600 \times \frac{760}{1000} \times 9.8 \times \frac{22.4}{1000} = 1 \times R \times 273$

$R = 8.31Jmol^{-1}K^{-1}$

b. When pressure is in atmospheres and volume is in dm^3/l.

- For one mole of a gas under standard temperature (273K) and pressure (760mmHg = 1atm), $V = V_m = 22.4dm^3$/litre

$PV = nRT$

$\Rightarrow 1 \times 22.4 = 1 \times R \times 273$

$R = 0.082 dm^3 atmmol^{-1} K^{-1}$

Worked example:1.1

0.8g of a gas X occupies $560cm^3$ at s.t.p. calculate the molar mass of the gas.

Solution:

m=0.8g, $V=560cm^3=\frac{560}{1000000}m^3$, R=8.31J/mole/K, T=298K

and $P = 13600 \times \frac{760}{1000} \times 10$ =103360Pa

From pV = nRT,

$\Rightarrow 103360 \times \frac{560}{1000000} = \frac{0.8}{M_r} \times 8.31 \times 298$

M_r=34

Worked example:1.2

The volume of a gas at s.t.p is $1.37dm^3$. Calculate the volume of the gas at 12^0C and 745mmHg.

Solution:

P_1=760mmHg, $V_1=1.37dm^3$, T_1=298K

P_2=745mmHg, V_2=?, T_2=(12+273)=285K

From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\Rightarrow \frac{760 \times 1.37}{298} = \frac{745 \times V_2}{285}$

$V_2=1.3366dm^3$

Task:1.1

A certain mass of a gas has a volume of $250m^3$ at 20^0C and a pressure of 100500Pa. Calculate its volume at s.t.p.

Task:1.2

a. Calculate the molar gas volume of carbon dioxide at:

i. S.t.p

ii. 30^0C and 760mmHg

iii. 40^0C and 760mmHg.

iv. 0^0C and 860mmHg.

v. 0^0C and 960mmHg.

b. Explain the variation in volumes of carbon dioxide between:

i. i), ii) and iii)

ii. i), iv) and v)

Task:1.3

2.2g of a certain gas at 288K and a pressure of $102700Nm^{-2}$ occupied 1177l. Calculate the universal constant R, in:

i. J/mole/K and

ii. latm/mole/K, at the above temperature and pressure.s

Dalton's law of partial pressures:

- For a mixture of gases that do not chemically combine in a container, the total pressure is contributed by each component in the container.
- The pressure out of the total pressure contributed by each component is called the partial pressure of that component.

Definition:

Partial pressure of a gas in a given gaseous mixture at a given temperature is the pressure that the gas would exert if it alone had occupied the volume of the mixture, at the same temperature.

The statement of the law:

"For a given mixture of gases that do not chemically react, the total pressure is given by the sum of the partial pressures of the gases, at a given temperature".

- In a ternary gaseous mixture of gases A, B and C:

$$P_t = P_a + P_b + P_c \quad \text{.....1.19}$$

Where:

P_t Is the total pressure of the mixture.

P_a Is the patial pressure of component A.

P_b Is the patial pressure of component B.

P_c Is the patial pressure of component C.

- The partial pressure of a given component in a mixture is equal to the product of its mole fraction and the total pressure of the mixture at a given temperature.

Mole fraction is the ratio of number of moles of a given component to the total number of moles in the system.

- The mole fraction of a component 'i' in a system is given by the symbol, X_i

Worked example:1.3

A mixture is made of 0.2 moles of nitrogen gas, 0.4 moles of carbon dioxide and 0.6 moles of oxygen. Calculate the mole fraction of each gas in the mixture.

Solution:

Total moles=0.2+0.4+0.6=1.2moles

$$X_N = \frac{0.2}{1.2} = \frac{1}{6}$$

$$X_{CO_2} = \frac{0.4}{1.2} = \frac{1}{3}$$

$$X_O = \frac{0.6}{1.2} = \frac{1}{2} = 0.5$$

- Total mole fraction is one (unity)

Task:1.4

A solution of sodium hydroxide contains 4g of sodium hydroxide and 76g of water. What is the mole fraction of sodium hydroxide in the solution?

Task:1.5

Calculate the mole fraction of glucose in an 18% solution of glucose in water.

$$P_N = \frac{1}{13} \times 2.6 \times 10^4 = 2000 Pa$$

$$P_O = \frac{10}{13} \times 2.6 \times 10^4 = 20{,}000 Pa$$

Worked example:1.6

A 10dm^3 vessel at 25^{0}C contains 3g of ethane, 4g of methane and 2.2g of propane.

a. Calculate the total pressure of the mixture, assuming the mixture behaves as the ideal gas.
b. Calculate the partial pressures of each component in the mixture.
c. What would the partial pressure of each component be if the volume of the vessel was reduced to 5dm^3 at the temperature of 25^{0}C?

Solution:

a. RMM of CH_4=(12x1)+(1x4)=16

Number of moles of methane=$\frac{4}{16} = 0.25$

RMM of C_2H_6= (12x2) + (1x6) =30

Number of moles of ethane=$\frac{3}{30} = 0.1$

RMM of C_3H_8= (12x3) + (1x8) =44

Number of moles of propane=$\frac{2.2}{44} = 0.05$

Total number of moles= (0.25+0.1+0.05) =0.4

P=?, V=10dm^3=$\frac{10}{1000} m^3$, R=8.31J/mole/K, T= (25+273) =298K

and n=0.4moles

From PV=nRT,

$$\Rightarrow P \times \frac{10}{1000} = 0.4 \times 8.31 \times 298$$

P=99,055.2Pa.

b. Let methane=M, ethane=E and propane=P

$$X_m = \frac{0.025}{0.4} = \frac{5}{8}$$

$$P_M = \frac{5}{8} \times 99{,}055.2 = 61{,}909.5 Pa$$

$$X_E = \frac{0.1}{0.4} = \frac{1}{4}$$

$$P_E = \frac{1}{4} \times 99{,}055.2 = 24{,}763.8 Pa$$

$$X_P = \frac{0.05}{0.4} = \frac{1}{8}$$

$$P_P = \frac{1}{8} \times 99{,}055.2 = 12{,}381.9 Pa$$

c. Total pressure would double according to Boyle's law.
New total pressure=198,110.4Pa.

$$P_M = \frac{5}{8} \times 198{,}110.4 = 123{,}819 Pa$$

$$P_E = \frac{1}{4} \times 198{,}110.4 = 49{,}527.6 Pa$$

$$P_P = \frac{1}{8} \times 198{,}110.4 = 24{,}763.8 Pa$$

If you compare the values of the partial pressures in b) and these ones, intuitively, when total pressure of the mixture is doubled, and the mole fractions of the components remained constant, the partial pressures double.

Task:1.7

A mixture of gases at s.t.p contains 40% carbon dioxide, 10% nitrogen, 20% carbon monoxide and 30% propane by volume. What are the partial pressures of these gases?

Task:1.8

An enclosed vessel contains 3.55g of chlorine, 14g of nitrogen and 1.6g of oxygen at 1atm and 0^0C. What will the partial pressures of each gas be if the temperature is raised to 57^0C?

Worked example:1.7

100cm^3 of hydrogen gas were collected over water at 27^0C and at an atmospheric pressure of 100,000Pa. Find the volume of dry hydrogen at s.t.p (saturated vapour pressure of water at 27^0C is 37,000Pa).

Solution:

Pressure of dry hydrogen, P_1= (100,000 – 37,000)
=63,000Pa.

T_1=(27+273)=300K, V_1=100cm^3, $P_2 = \frac{760}{1000} \times 9.8 \times 13{,}600$,V_2 = ? and T_2 = 273K

From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\Rightarrow \frac{63{,}000 \times 100}{300} = \frac{101{,}292.8 \times V_2}{273}$$

$$V_2 = 56.9830cm^3$$

Worked example:1.8

When 0.65g of zinc powder was reacted with excess dilute hydrochloric acid at 20^0C and pressure of 92,340Pa, 400cm^3 of moist hydrogen gas was collected. If the saturated vapour pressure of water at 20^0C is 2340Pa, calculate the volume of dry hydrogen at 20^0C.

Solution:

$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

65g of zinc produce 22,400cm^3 of hydrogen at s.t.p

0.65g will produce $\frac{0.65 \times 22{,}400}{65} = 224cm^3$ of hydrogen at s.t.p

Vapour pressure of dry hydrogen, P_1 = (92,340 – 2,340) = 90,000, T_1 = (20 + 273) = 293K, V_1 = ?, P_2 = 101,292.8, V_2 = 224, T_2 = 273K

From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\Rightarrow \frac{90{,}000 \times V_1}{393} = \frac{101{,}292.8 \times 224}{273}$$

V_1 = 362.9226cm^3

Task1.9

2.125g of hydrogen peroxide were exposed to sun light. The oxygen gas produced was collected over water at 300K and a pressure of 95000Nm^{-2}. Calculate the volume of dry ~~hydrogen~~ oxygen gas collected if the saturated vapour pressure of water at 300K is 36000Nm^{-2}.

Task:1.10

At a certain temperature, 20dm^3 of nitrogen at a pressure of 9.5x10^{4}Nm^{-2} and 50dm^3 of hydrogen at a pressure of 2.0x10^{4}Nm^{-2} were mixed into a 25dm^3 vessel. Calculate;

a. The partial pressures of the gases.
b. The total pressures of the gases.

Task:1.11

A gaseous mixture at a pressure of 1.05x10^{5}Nm^{-2} is made of 40% carbon dioxide, 20% nitrogen, 10% oxygen and 30% propane by volume.

a. Calculate the partial pressures of each of the gases.
b. What will the partial pressures of the other gases be if the carbon dioxide was removed by addition of of caustic potash?

Applications of partial pressures:

a. ***In the design of anaesthesia.***

- Anaesthesia is designed taking in consideration the partial pressures of the different gases. This partial pressure of a gas required to cause anaethesia is called anaesthetic pressure of the gas.
- For example, the tables below shows sub lethal partial pressures (dosage/anaesthetic pressures) of different gases in anaesthesia for mice, which is similar to that of man.

Gas	Anaesthetic pressure
Nitrogen	33
Argon	15
Sulphur hexafluoride	6.1
Dinitrogen monoxide/laughing gas	1.5
Xenon	0.95
Ether	0.03
Chloroform	0.008

Graham's law of gaseous diffusion and effusion:

- Effusion is the jetting out of a gas through a small aperture. It is basically not a different process from diffusion.

The statement of the law:

The rate of a diffusion/effusion of a gas at a constant temperature and pressure is inversely proportional to the square root of its density.

- Consider a gas 'A' with rate of diffusion 'R_a' and density ρ_a

From graham's law of gaseous diffusion,

$$R_a \alpha \frac{1}{\sqrt{\rho_a}}$$

Introducing a constant of proportionality,

$$\Rightarrow R_a = K\frac{1}{\sqrt{\rho_a}} \quad \text{.....1.21}$$

- If under the same conditions of temperature and pressure as in the case above, a gas 'B' of density ρ_b diffuses at a rate of 'R_b'

$$R_b \alpha \frac{1}{\sqrt{\rho_b}}$$

The constant of proportionality is the same as the one for gas 'A'

$$\Rightarrow R_b = K\frac{1}{\sqrt{\rho_b}} \quad \text{.....1.22}$$

- Dividing equation 1.22 by equation 1.23;

$$\Rightarrow \frac{R_a}{R_b} = \sqrt{\frac{\rho_b}{\rho_a}} \quad \text{.....1.23}$$

- The quantity $\frac{R_a}{R_b}$ in equation 1.23 above is called relative rate of diffusion.
- Hence Graham's law of diffusion can be restated as "The relative rate of diffusion of two gases is inversely proportional to the square root of their densities.

- The density of a gas is directly proportional to it molar mass. So that density of a gas can be substituted for by the molar mass of the gas.
- Hence the equation 1.23 in terms of molar masses becomes:
- $\frac{R_a}{R_b} = \sqrt{\frac{Mr_b}{Mr_a}}$ 1.24

Ways of expressing rate of gaseous diffusion:

- Distance moved/diffused by a gas per unit time.
- Volume diffused per unit time.
- Mass diffused per unit time.
- Decrease in pressure per unit time.

Worked example:1.10

The rate of diffusion of gas X is four times slower than that of gas Y of molar mass 2, under similar conditions. Calculate the molar mass of X.

Solution:

From,

$$\frac{R_x}{R_y} = \frac{\sqrt{M_y}}{\sqrt{M_x}}$$

$$\Rightarrow \frac{R_x}{4R_x} = \frac{\sqrt{2}}{\sqrt{M_x}}$$

$$M_x = 32$$

Task:1.12

$20cm^3$ of carbon dioxide diffused through a porous diaphragm in 32 seconds. The same volume of a gas Z took 46.3 seconds to diffuse under similar conditions. Calculate the formula mass of Z.

Worked example:1.11

a. What is rate of diffusion?
b. Calculate the rate at which carbon monoxide diffuses faster than carbon dioxide under similar conditions.

Solution:

a. Amount of a gas diffused per unit time.
b. RMM of CO =(12x1)+(16x1) =28
RMM of CO_2 = (12x1) + (16x2) =44

From $\frac{R_{CO}}{R_{CO_2}} = \frac{\sqrt{M_{CO_2}}}{\sqrt{M_{CO}}}$

$$\Rightarrow \frac{R_{CO}}{R_{CO_2}} = \frac{\sqrt{44}}{\sqrt{28}}$$

$$R_{CO} = 1.25 R_{CO_2}$$

Hence, carbon monoxide diffuses 1.25 times faster than carbon dioxide.

Task:1.13

An oxide of nitrogen diffuses at the same rate as vapour of ethanol, under similar conditions. Identify this oxide.

Task:1.14

Cotton wool soaked in ammonia and a second cotton wool soaked in concentrated hydrochloric acid were placed at the ends of a hollow tube of unknown length. If a white disc was formed 30cm away from the cotton wool soaked in ammonia solution;

a. Write the equation for the formation of the disc.
b. To the nearest whole number, how long is the hollow tube?

Task:1.15

When a certain volume of a gas P diffused through a porous plug, the decrease in its pressure was 1700Pa. while under similar conditions, the decrease in the pressure of ammonia within the same time was 27500Pa. calculate the formula mass of P.

Task:1.16

An observer at the end of a hollow tube, to which the opposite end is placed cotton wool soaked in hydrogen sulphide gets the smell of a rotten egg after 15 seconds. The same observer at the end of the same tube, to which the opposite end is placed cotton wool soaked in amine, $C_nH_{n+1}NH_2$ gets fishy smell after 17 seconds.

a. Calculate the value of n in the amine.
b. Write the molecular formula of the amine.

Task1.17

a. What is the difference between diffusion and effusion?
b. i. State Graham's law of gaseous diffusion.
   ii. 25g of ozone diffused through a porous membrane in 20 minutes. Calculate the time that would be taken for 30g of helium to diffuse through the same membrane under the same conditions.

Task1.18

At the ends of a 50cm long tube were placed cotton wool soaked in ammonia solution and the other end cotton wool soaked in hydrogen chloride containing an isotope of chlorine. A white ring was formed 30cm from ammonia solution.

a. Name the isotopes of chlorine.
b. Identify the isotope of chlorine in the hydrogen chloride.

Factors that affect rate of diffusion:

- Diffusion medium
- Temperature (directly proportional)
- Surface area (directly proportional to)
- Distance (indirectly proportional to)
- Pressure/concentration (directly proportional to)

Gay – lusaac's law/principle:

- This law governs reacting gases and gaseous products of the reaction, under constant conditions of temperature and pressure.
- It states that:
  "When gases react, they do so in their volumes which bear a simple ratio to one another and to the volume of the gaseous products, at constant temperature and pressure".
- The simple ratios are ratios like: 1:2, 1:2:3, 1:1:1:1, 1:5, 2:3, etc.
- These simple ratios are the mole/stoichiometric ratios of the reacting gases and the gaseous products.
- The implication of this law is that; the mole ratios for gaseous reactions can be replaced by volume ratios, for as long as the reaction takes place at constant temperature and pressure.
- Examples:

1. $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$
   1mol 3mol 2mol
   1vol 3vol 2vol
   Simple ratio: 1:3:2
2. $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$
   2mol 1mol 2mol
   2vol 1vol 2vol
   Simple ratio: 2:1:2

3. $C_xH_y(g) + \left(x + \frac{y}{4}\right) O_2(g) \longrightarrow xCO_2(g) + \frac{y}{2} H_2O(l)$

1mol	$\left(x + \frac{y}{4}\right)$ mol	xmol	$\frac{y}{2}$
1vol	$\left(x + \frac{y}{4}\right)$ vol	xvol	

Simple ratio: $1 : \left(x + \frac{y}{4}\right) : x$

Avogadro's law/hypothesis:

- Since mole ratio can be replaced by volume ratio for gaseous reactions (Gay–Lusaac's principle), Avogadro therefore stated that:
  Equal volumes of all gases measured under the same conditions of temperature and pressure contain equal number of moles/molecules.
- Implication of the law:
- $10cm^3$ of carbon dioxide at 20^0C and 1atm pressure contain the same number of moles as $10cm^3$ of ammonia, $10cm^3$ of sulphur dioxide, $10cm^3$ of methane and $10cm^3$ of any gas at 20^0C and 1atm pressure.

1.5 Non ideal/real gases:

- These are practical gases. They do not obey the ideal gas laws.
- From the ideal gas equation, $PV = nRT$,
  Dividing both sides by nRT;

$$\Rightarrow \frac{PV}{nRT} = \frac{nRT}{nRT}$$

$$\frac{PV}{nRT} = 1 \quad \text{.....1.25}$$

- The quantity $\frac{PV}{nRT}$, symbolized Z, is called compressibility factor/compression factor.
- For the ideal gas, the compression factor, Z=1. However, for real gases compression factor varies with pressure and temperature.
- The cause of deviation from ideality comes from two major assumptions of the kinetic theory of gases, which don not apply to real gases:

1. The assumption that there are no intermolecular forces is wrong for real gases. There is a considerable intermolecular force of attraction and repulsion. The forces get stronger at lower temperature and higher pressure.
2. The assumption that the gas molecules do not occupy any volume of space is wrong. The molecules occupy a definite volume known as covolume. This reduces the effective compressible volume of the gas, since the molecules are incompressible.

- Therefore, the causes of deviation of real gases from ideal behaviours are:

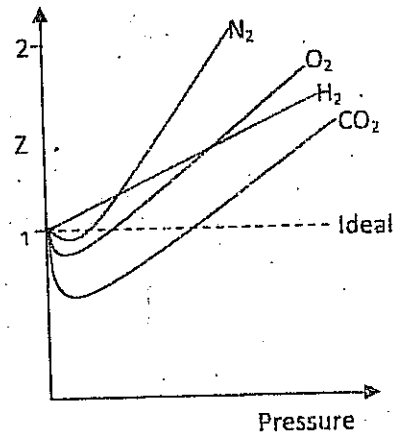
i. Intermolecular forces.
ii. Covolume.

Nature of the intermolecular forces:

- The intermolecular forces are both repulsive and attractive.
- The repulsive forces are due to the repulsion between outermost electron shells of closely approaching molecules.
- The attractive forces are due to the van der Waal's forces between the molecules.
- At very low pressure, the particles are far apart so that both the attractive and repulsive forces are negligible, hence real gases very closely approximate to ideal gas behavior.

- At moderate pressure, both attractive and repulsive forces are considerable, and hence deviation from ideality (easy liquefaction).
- At high pressure, the particles are very close to one another, hence the repulsive forces are more pronounced. This makes a real gas hard to liquefy (compressibility factor greater than one).

Variation of compression factor, Z with pressure for different gases at constant temperature (273K):

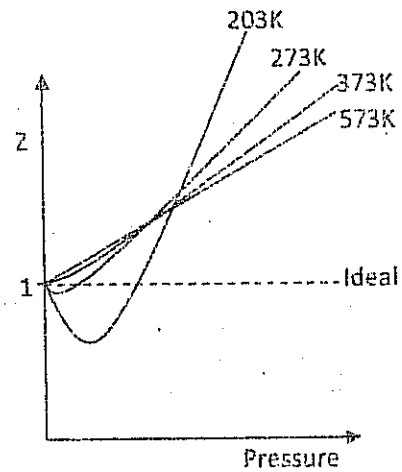


- All the gases approximate ideal gas behaviours at very low pressures (pressures less than one atmosphere). This is because at low pressures, the molecules are far apart, reducing the effect of covolume and the strength of intermolecular forces.
- However, all the gases deviate from ideality, with the extent of deviation decreasing from that shown by carbon dioxide, followed by oxygen then nitrogen, with hydrogen being the least deviating.
- This is because the extent of deviation depends on the size of the molecule. Carbon dioxide with the biggest molecule has a bigger covolume compared to all the other gases. As well

experience the strongest intermolecular attraction. Hence the above order of deviation.
- Apart from hydrogen, the compressility factors for all the other gases first decrease with pressure to a minimum, then increase with increase in pressure.
- However, this does not mean that for hydrogen there is no minimum. The minimum exists, but at a lower temperature than 273K.

❖ For all the gases, the minimum value of the compressibility factor can be made to lie on the line, Z=1, by adjusting the temperature.
- At this temperature, the real gas behaves as the ideal gas over a wide range of pressure.
- This unique temperature is called the Boyle's temperature of the gas, which is characteristic for the gas (every gas has its own Boyle's temperature).

Variation of compression factor, Z with pressure for a gas at different temperatures:



- Whatsoever low temperature, if the pressure is very low, the real gas approximates ideal behaviours.
- A real gas deviates more from ideal gas behaviours at low temperatures than at high temperatures. This is because at low temperatures, the molecules can experience intermolecular forces easily.
- Therefore, a real gas behaves ideally over a wider range of pressure at higher temperature than at lower temperature.
- Hence the following are the conditions under which a real gas approximates ideal gas behaviours:

i. High temperature.
ii. Low pressure.

The real gas equation:

- This is the modification of the ideal gas equation where:

a. The volume of a real gas (volume occupied by molecules of real gases or covoume) is not negligible. So the compressible volume of a gas is less by the covolume.
I.e effective volume is given by: $(V - nb)$

b. The intermolecular forces in a real gas are not negligible especially at high pressure and low temperature.

i. A particle about to collide with the wall of the container is pulled backward by the rest of bulk of particles. This reduces the speed of the particle and hence total pressure and is proportional to the number of particles and inversely proportional to volume. i.e: pressure defect is proportional to $\frac{n}{V}$, n is the number of particles.

ii. Also, the frequency of collision with the wall of the container is reduced. This reduces the total pressure and the reduction is proportional to $\frac{n}{V}$

- The effective pressure is always less by a value proportional to $\frac{n^2}{V^2}$.
- Therefore for a real gas the actual pressure should be: $P + \frac{n^2}{V^2}$
- So that the real gas equation for n moles of a gas is given by:

$$\left(P + a\frac{n^2}{V^2}\right)(V - bn) = nRT \quad \text{.....1.26}$$

- For one mole of a real gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{.....1.27}$$

Where a and b are constants.

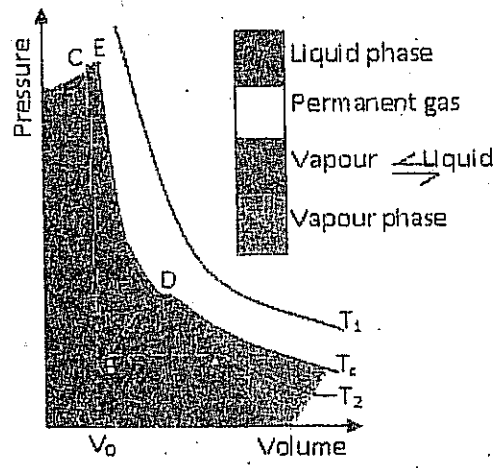
Liquefaction of real gases:

- When a real gas is compressed at a high pressure and pushed to a low temperature, the van der Waal's forces of attraction become progressively stronger and there will come a time when the gas changes to liquid.
- Such a point where a gas changes to a liquid is called a critical point. At a critical point, there are three constants, which are characteristic of a gas (i.e. every gas has its own critical point constants). These are:
- Critical volume, V_c
- Critical temperature, T_c
- Critical pressure, P_c

a. **Critical volume:** Is the volume of one mole of a gas when it changes from gaseous state to liquid state.
b. **Critical pressure:** Is the pressure which is just sufficient to liquefy a gas at its critical temperature.
c. **Critical temperature:** Is the temperature above which a gas cannot be liquefied by mere increase in pressure alone.

- The behaviour of real gases in the neighbourhood of their critical constants was first investigated by a scientist called Andrews (1869).
- Andrews compressed a fixed mass of carbon dioxide at different temperatures, some of which were above and below the critical temperature of carbon dioxide and one temperature was the critical temperature of carbon dioxide.
- On plotting the various values of pressures and volumes at their constant temperatures, he noted rectangular hyperbolae (ideal behaviours) at temperatures above the critical temperature of carbon dioxide. A slight deviation (shown as a point of inflexion) at the critical temperature, and massive deviation at temperatures below the critical temperature, with greatest deviation at the lowest temperature.

Andrews' curves of carbondioxide:



- The isothermal at T_1 is when the real gas approximates the ideal gas behaviours.

- Isothermal T_c, at D shows the conditions of pressure and volume when the real gas begins to deviate from the ideal gas behaviour.
- Point D is the critical point and the temperature T_c is the critical temperature beyond which no matter what pressure is applied at a constant temperature (T_c), the gas cannot turn into liquid.
- For isothermal T_2, before point 'A', the gas behaves ideally. Part 'AB' represents the conditions when there is drastic decrease in volume for almost no change in pressure.
- At 'A', the gas begins to liquefy and completes turning into liquid at point 'B'.
- Along 'BC', there is a very small change in volume for a large change in pressure indicating that there is no significant effect on volume of a liquid when pressure is increased.
- Check the key to the right of the diagram for the different phases in the system.

A gas may be liquefied if it is:

a. Compressed at temperatures below its critical temperature.
b. Compressed and simultaneously cooled.

1.6 Determination of RAM, RFM/RMM:

1.6.1 Determination of RAM:

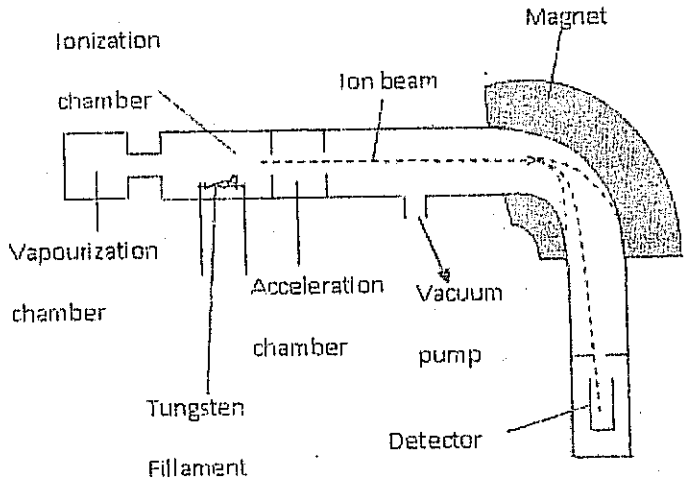
Relative atomic mass is the ratio of mass of one atom of an element to one twelfth the mass of one atom of carbon – 12 isotope.

- From the above definition therefore, the mass of one atom of carbon – 12 isotope is a reference scale on which the masses of other atoms are compared with.
- Hence, relative atomic mass is the mass of one atom of an element on a scale in which one atom of carbon – 12 isotope has a mass of 12g.

- Relative atomic mass has no unit since it is a ratio of quantities of the same unit, so the unit cancels out.
- The relative atomic masses are determined by a special apparatus known as the **mass spectrometer**.

The mass spectrometer (mass spectrometry)

i. *The structure:*



- From the above diagram therefore, the mass spectrometer is chambered, and these chambers are:
  a. Vapourization chamber
  b. Ionization chamber
  c. Acceleration chamber
  d. Deflection chamber (the magnetic field)
  e. Detection chamber
- In the vapourization chamber, the solid and liquid samples are first converted to their vapour form.
- The ionization chamber is made of a hot tungsten filament continuously emitting electrons by thermoionic emission. The emitted electrons knock electrons from the vapour/gas producing positive ions.

- The acceleration chamber is made of two negative electric plates the rear plate at a higher potential, together which, they accelerate the produced ions in a straight line towards the magnetic field.
- The deflection chamber is made of a magnet of a variable magnetic field. Here, the ions in the beam are deflected in a circular path, depending on the charge to mass ratio. Lighter and heavily charged ions are the most deflected compared to heavier and lightly charged ions.
- The detection chamber is made of a calibrated photographic plate (for that matter, the apparatus is called mass spectrograph) or an electrical analyzer, hence called the mass spectrometer. Here, the masses and proportions (abundancies) of the ions that have been sorted out by different extent of deflection are recorded.
- The outlet to a vacuum pump is to provide the ideal condition (partial vacuum/low pressure) for the operation of the spectrometer, by reducing the pressure.

Action of the mass spectrometer:

- If the sample is solid or a liquid, then it is first vapourised, after which, it is let into the ionization chamber. Here, the electrons emitted by thermoionic emission from the tungsten filament knock electrons from the vapour producing positively charged ions.

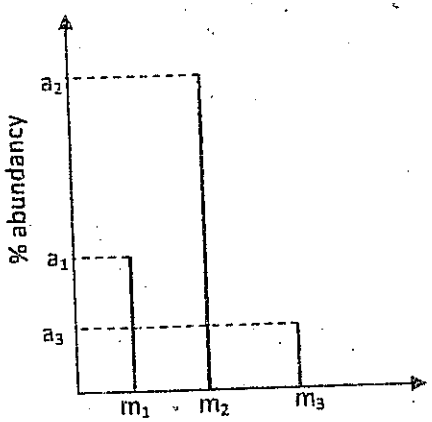
$$P(g) \longrightarrow P^{+}(g) + e$$

- Even electrons of the produced ions can also be knocked to produce doubly, triply, etc charged ions:

$$P^{+}(g) \longrightarrow P^{2+}(g) + e$$

- The positively charged ions are then attracted and hence accelerated by the electric field, segregating them according to their masses and charges.

- On reaching the magnetic field, they are deflected according to their charge to mass ratio (sorted into groups); focusing them on a detector which records the masses and abundancies of a particular isotope as peak.
- By adjusting the electric field and/or the magnetic field, another group of ions are focused on the detector and their masses and abundancies recorded.
- By repeating the adjustment of the fields, a mass spectrum showing all the isotopes of the element is obtained simplified by a stick diagram as shown below.



C – 12 scale of masses

- From the mass spectrum, the relative atomic mass is given by:

$$R.A.M = \sum_{n=1}^{n=n}\left(\frac{m \times \%abundancy}{100}\right)$$

Advantages of mass spectrometer:

i. Shows the proportions/abundancies of all the isotopes of an element
ii. Determines the masses of all the isotopes of the elements.

iii. Can also determine the relative molecular masses.
iv. Establishes the structures of some molecules.

Worked example:1.12

Magnesium is consists of three isotopes. The table below shows the mases and the abundancies of the isotopes.

Isotopic mass	Percentage abundancy
24	78.6
25	10.1
26	11.3

Calculate the relative atomic mass of magnesium.

Solution:

From, $$R.A.M = \sum \frac{mass \times \%abundancy}{100}$$

$$\Rightarrow R.A.M = \frac{(24 \times 78.6) + (25 \times 10.1) + (26 \times 11.3)}{100}$$

R.A.M =24.327.

Task:1.19:

A sample of chlorine contains 75.5% chlorine – 35 and 24.5% chlorine – 37. Calculate the relative atomic mass of chlorine.

Task:1.20

a. What is meant by:
   i. Isotopy
   ii. Isotopes
   iii. Isotopic abundancy
   iv. Mass spectrum
b. Below is a stick diagram showing the mass spectrum of an element P.

Definitions:

a. An orbital is the volume of space around the nucleus of an atom where the probability of finding an electron is highest.
b. A sub–shell is a group of orbitals of the same type within a given energy level.
c. A shell is a group of orbitals of different or the same types with the same principal quantum number.

- The shells are given principal quantum numbers: 1, 2, 3, 4, 5, etc outward from the nucleus. At times the letters:K,L,M,N, are used.
- The sub–shells are: the s,p,d,f sub–shells. The s sub–has one orbital, the p has three orbitals, the d has five orbital and the f has seven orbitals.
- Each orbital has a maximum capacity of only two electrons.
- The energy levels of the sub–shells increase in the order: s<p<d<f.
- Shell of quantum number 1 has only the s sub–shell; number 2 has the s and the p; number 3 has the s,p and d; number 4 has the s,p,d and f, and so on.

Quantum number	Sub shells
1	s
2	s,p
3	s,p,d
4	s,p,d,f

Writing the electronic configuration:

- The electronic configuration of an element describes how the electrons of its atoms are arranged in their shells, sub – shells and orbitals.

- Electronic configuration normally applies to atoms in their ground state, not the excited state.
- The electronic configuration of an atom with one or more electrons in an excited state is called an excited state configuration.
- There are three rules for writing the ground state electronic configuration of an element:
  a. **The aufbau principle:** It states that in their ground states, electrons occupy the orbitals of the lowest energy first.
  b. **Pauli's exclusion principle:** It states that an orbital cannot contain more than two electrons; pairing is only if the electrons have opposite spins.
  c. **Hund's rule:** This states that electrons occupy the orbital of a sub–shell singly and with parallel spin before pairing begins.
- Quantum numbers, sub–shell and number of electrons in an orbital, the sub–shell and hence the shell are shown in the electronic configuration.

Worked example:2.4

Write the electronic configurations of the following elements:

a. Lithium (atomic number 3)
b. Oxygen (atomic number 8)
c. Sodium (atomic number 11)
d. Argon (atomic number 18)

Solution:

a. $1s^2 2s^1$
b. $1s^2 2s^2 2p^4$

c. $1s^2 2s^2 2p^2 3s^1$
d. $1s^2 2s^2 2p^6 3s^2 3p^6$

Worked example:2.5
Write the electronic configuration of the following:
a. Vanadium (atomic number 23)
b. Chromium (atomic number 24)
c. Zinc (atomic number 30)
d. Copper (atomic number 29)

Solution:
a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$
c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Note the following:
a. There is overlap between 4s and 3d sub–shells, such that the 4s is nearer the nucleus than the 4s. However, the 3d sub–shell is of a lower energy than the 4s.
b. The electronic configuration of copper is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ and not $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$, because the half filled and completely filled orbitals are stable.
c. Therefore, the noble gasses with completely filled shells have stable electronic configurations.

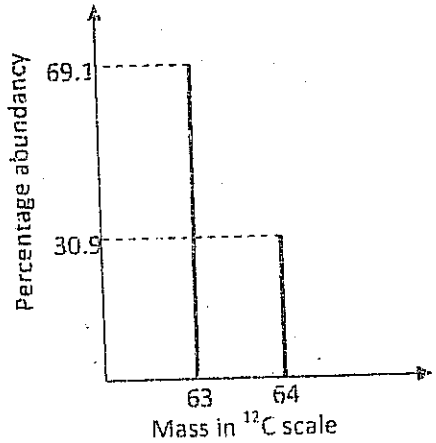
Task:2.5
Write the electronic configurations of the following:
a. Neon (atomic number 10)
b. Potassium ion (atomic number of potassium is 19)
c. Iron (atomic number 26)

d. Iron (III) ion.
e. Copper (atomic number 29)
f. Copper (II) ion

2.3: The nucleus of an atom, stability of the nucleus and radioactivity:

2.3.1: The nucleus:
- Except for hydrogen atom which contains only a proton, the nuclei of all atoms contain positively charged protons and neutral neutrons, which are collectively known as **nucleons**.
- The masses of protons and neutrons are taken to be the same; however, the neutrons are slightly heavier than the protons.
- The **atomic number** of an element is the number of protons in the nucleus. However, the nuclei of atoms of the same elements may contain different number of neutrons.
- This gives rise to **isotopes**, and account for the fact that most elements do not have integral relative atomic masses.
- Any nuclear species characterized by its atomic number and mass number is called a **nuclide**. A nuclide is conventionally written with the chemical symbol, together with an upper index denoting mass number (A) and a lower index denoting atomic number (Z), ${}^{A}_{Z}X$.

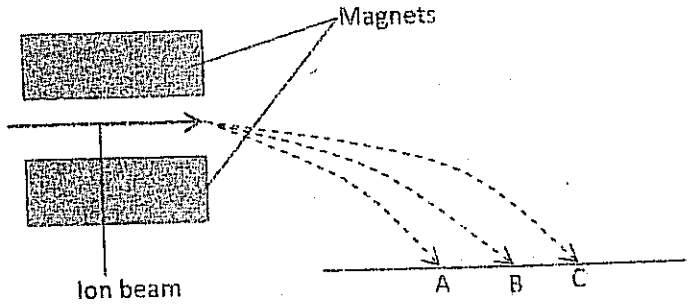
2.3.2: Radioactivity:
- Radioactivity is the spontaneous disintegration of heavier nuclei into lighter nuclei with emission of particles and energy. Radioactivity is also called **radioactive decay**.
- The particles emitted are alpha (α) and beta (β) particles, while the energy is given out in the form of gamma (γ) rays.



Calculate the relative atomic mass of the element.

Task:1.21

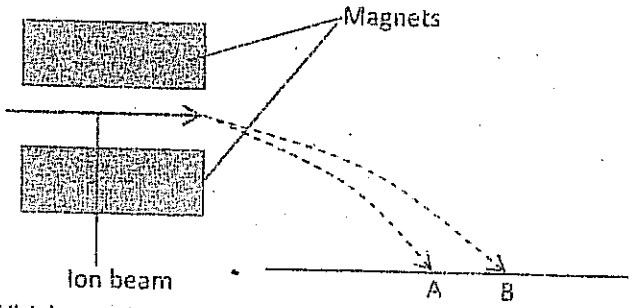
An element M is non isotopic. During its atomic mass determination using a mass spectrometer, the ionic species: M^{+}, M^{2+} and M^{3+} were obtained and emerged from the magnetic analyser as shown below.



Which species do A, B and C stand for? Give reason for your answer.

Task:1.22

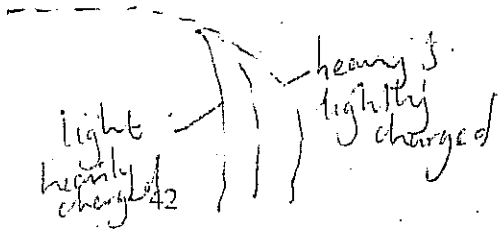
The diagram below shows the sorted – out – emerging ions from magnetic chamber when a sample of gallium was analysed by a mass spectrometer. Given that, gallium has two isotopes of masses 69 and 70 of respective abundancies of 60.4% and 39.6%.

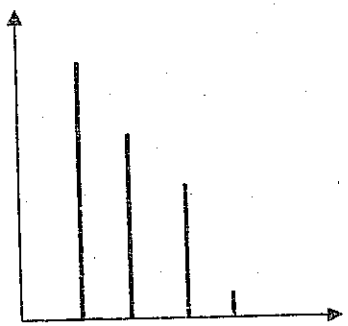


a. Which species is responsible for spot:
   i. A
   ii. B
   iii. Give a reason for your answer.
b. Calculate the relative atomic mass of gallium.

Task:1.23

a. Describe how the mass spectrometer can be used to determine the relative atomic mass of an element.
b. How does the mass spectrum of an element that is isotopic differ from that of an element that is non isotopic?
c. Below is a simplified mass spectrum of an element.





i. Label the axes of the spectrum.
ii. How many isotopes does the element have?

Task:1.24

The relative atomic mass of an element X is 10.8. The element has two isotopes of masses 10 and 11 respectively. Calculate the abundancies of the isotopes in:

a. Percentages.
b. Fractions.

Task:1.25

Bromine has two isotopes; bromine –79 and bromine –81. The abundancies of the two isotopes are 0.505 and 0.495 respectively.

a. calculate the average relative atomic mass of bromine
b. Bromine exists as diatomic molecules. The possible relative molecular masses are; 158, 160 and 162. Explain the occurrences of the three possible masses.

1.6.2 Determination of RMM/RFM:

- The relative molecular mass is the mass of one molecule of a compound on a scale in which one atom of carbon – 12 isotope has a mass of 12g.

- The relative molecular mass is therefore more associated to molecular substances – substances formed by covalent bonding, in which the particles that make them are molecules.
- However, after the postulation of the ionic theory of matter, relative molecular mass becomes unsatisfactory to describe the masses of ions, the particle that makes up ionic substances.
- Hence relative formula mass is adopted to cater for both ionic and covalent substances, without discarding the former since molecules and ions are both represented using formulae.
- Therefore, the relative formula mass and relative molecular mass are used interchangeably.

a. **Of gases:**

i. Victor – Meyer's method:

- This basically depends on the application of the ideal gas equation PV=nRT. Hence;
- The mass of an empty and completely evacuated container of known volume is determined by weighing and recorded as m_1.
- Some mass of a gas is then injected into the container and the mass of the container with the gas determined, m_2.
- The temperature and the pressure during the experimentation P and T respectively are recorded.

Treatment of the results:

Mass of the gas taken = $m_2 - m_1$

If M_r is the molar mass of the gas, the, it is given by:

$$M_r = (m_2 - m_1)\frac{RT}{PV}$$

ii. By limiting density method:

- The product of pressure and volume (PV) of a gas varies with pressure, at a constant temperature, and as mentioned earlier, a real gas approximates ideality at a very low pressure.
- In using limiting density to determine the relative molecular mass of a gas:
- The PV value of a fixed mass, 'm' of a gas is determined at 273K and various values of PV at reducing pressures are also determined.
- The different PV values are plotted graphically against the different values of the pressure at 273K.
- Then, the graph is extrapolated to zero pressure, and the PV value at this pressure, P_0V_0 recorded.
- If P_1V_1 is the PV value at one atmosphere,
- Relative molecular mass at one atmosphere is given by:

$$M_r^1 = \frac{mRT}{P_1V_1}$$

- The more accurate relative molecular mass at zero pressure is given by:

$$M_r = \frac{mRT}{P_0V_0}$$

$$M_r = M_r^1 \times \frac{P_1V_1}{P_0V_0}$$

- Since $\frac{M_r}{22.4}$ and $\frac{M_r^1}{22.4}$ are respectively the limiting and the normal density of the gas at 273K,

Limiting density = normal density $\times \frac{P_1V_1}{P_0V_0}$

iii. Eudiometry /gaseous explosion.

- Eudiometry literally means "gaseous explosion".
- It is a method mainly used to determine the formula and hence the formula mass of a gaseous hydrocarbon by exploding a known volume of the hydrocarbon in excess oxygen, determining the volume of carbon dioxide produced and applying Gay–Lusaac's principle and Avogadro's hypothesis in order to determine the formula and hence the formula mass of the hydrocarbon.
- In practice:
- A known volume of the gaseous hydrocarbon is exploded in excess oxygen in a eudiometer, according to the equation:

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g), \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$$

- The eudiometer is then cooled to room temperature, leading to contraction in volume due to condensation of steam.
- Caustic potash is then added to the remaining gaseous mixture to absorb carbon dioxide according to the equation:

$$2KOH(aq) + CO_2(g) \longrightarrow K_2CO_3(aq) + H_2O(l)$$

- This causes a reduction in volume of the mixture equal to volume of carbon dioxide produced.
- Then Gay – Lusaac's principle and Avogadro's hypothesis are applied on the gaseous species of the reaction in order to determine the formula and hence the formula mass of the hydrocarbon.

Worked example:1.13

$20cm^3$ of a gaseous hydrocarbonwas exploded with $50cm^3$ (an excess) of oxygen and cooled to room temperature. On exposing the mixture to caustic potash, the resultant volume contracted by $20cm^3$.

i. Identify the hydrocarbon.

ii. What volumes of oxygen reacted and remained unreacted?

Solution:

$$C_xH_y(g)+\left(x+\frac{y}{4}\right)O_2(g) \longrightarrow xCO_2(g)+\frac{y}{2}H_2O(l)$$

i. For C_xH_y and CO_2:

Volume of C_xH_y =20cm^3 and volume of CO_2 =20cm^3

1mole of C_xH_y reacts produces xmoles of CO_2

1volume of C_xH_y produces xvolume of CO_2

1:x=20:20

X=1

Since methane is the only hydrocarbon containing one carbon atom in its molecule, the hydrocarbon is therefore methane.

ii. Equation for complete combustion of methane:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

1volume of methane reacts with 2volumes of oxygen

20cm^3 will react with $\frac{20\times 2}{1} = 40cm^3$

Hence volume of oxygen reacted =40cm^3

Volume unreacted = (50 – 40) =10cm^3

Worked example1.14

When 15cm^3 of a hydrocarbon X was exploded with excess oxygen, 30cm^3 of carbon dioxide was produced. Given that, the vapour density of X is 15. Determine the formula of X.

Solution:

$$C_xH_y(g)+\left(x+\frac{y}{4}\right)O_2(g) \longrightarrow xCO_2(g)+\frac{y}{2}H_2O(l)$$

15cm^3 of X produce 30cm^3 of CO_2

1cm^3 of X will produce $\frac{1\times 30}{15} = 2cm^3$

Hence, x =2

Molar mass =2 x vapour density

Molar mass of X =2x15 =30

30=(12x2) + (1xy)

Y=6

Hence the formula of the hydrocarbon is C_2H_6

Task:1.26

30cm^3 of an alkane was exploded with 150cm^3 of oxygen and cooled to room temperature. The total volume was 105cm^3. On absorption with caustic potash, the volume reduced to 15cm^3.

i. Calculate the formula of the alkane.

ii. Identify the alkane.

Task:1.27

12.5cm^3 of a gaseous hydrocarbon Q requires exactly 81.25cm^3 of oxygen for complete combustion. When the eudiometer was cooled to an ambient temperature, addition of caustic potash caused a decrease in volume of 50cm^3.

i. Determine the formula of Q.

ii. Draw the structural formulae and name all the isomers of Q.

iii. Identify the isomer with the lowest boiling point and briefly explain why the isomer has the lowest boiling point.

Worked example1:15

11.5cm^3 of a gaseous hydrocarbon were exploded with excess oxygen and there was a diminution of 34.5cm^3. On adsorption with sodium hydroxide solution, there was a further diminution of 34.5cm^3. What is the molecular formula of the hydrocarbon?

Solution:

$$C_xH_y(g)+\left(x+\frac{y}{4}\right)O_2(g) \longrightarrow xCO_2(g)+\frac{y}{2}H_2O(l)$$

Let volume of reacted oxygen be p and volume of unreacted oxygen be q.

$11.5+(p+q) - 34.5 - 34.5 = q$

$P = 57.5cm^3$

$11.5cm^3$ of the hydrocarbon produce $34.5cm^3$ of CO_2

$1cm^3$ will produce $\frac{1 \times 34.5}{11.5} = 3cm^3$ of CO_2

Hence x = 3.

$11.4cm^3$ of the hydrocarbon react with $57.5cm^3$ of O_2

$1cm^3$ will react with $\frac{1 \times 57.5}{11.5} = 5cm^3$ of O_2

Hence moles of O_2 reacted = 5

$$\Rightarrow \left(\frac{4x+y}{4}\right) = 5$$

But x = 3.

$$\Rightarrow \left(\frac{4 \times 3 + y}{4}\right) = 5 \text{ Hence } y = 8$$

The formula of the hydrocarbon is C_3H_8

Task:1.28

When $10cm^3$ of a hydrocarbon Z were exploded with excess oxygen, there was a contraction in volume of $30cm^3$. When the product was treated with caustic soda, there was a further contraction in volume of $30cm^3$. Deduce the formula of the hydrocarbon.

Task:1.29

When $120cm^3$ of a gaseous hydrocarbon Q was exploded with excess oxygen and cooled to room temperature, the volume of the residual gas was $560cm^3$. After addition of sodium hydroxide solution, the volume decreases to $80cm^3$. Given that 0.29g of Q occupies $112cm^3$ at s.t.p. determine the formula of the hydrocarbon.

Task:1.30

$15cm^3$ of a gaseous hydrocarbon A was exploded with $105cm^3$ (an excess) of oxygen and cooled to room temperature, the total volume was $75cm^3$. On addition of caustic soda, there was a diminution in volume of $60cm^3$.

i. Calculate the formula of A.

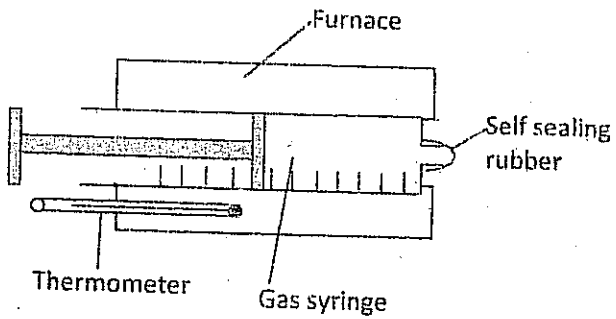
ii. Draw the structures and write the names of all the isomers of A.

iii. Two of the isomers do not undergo ozonolysis. Identify the isomers.

b. Of volatile solids and liquids:

- This is a slight modification of the Victor – Meyer's method, and it is done through the following procedures.
- A known mass, 'm' of the volatile sample is vapourised/volatilized in a syringe heated by a furnace, at a constant and known pressure, 'P'.
- The volume, 'V' and the temperature, 'T' of the produced vapour are then recorded.

The set up



- The formula mass is the given by:

$$M_r = \frac{mRT}{PV}$$

c. **Non volatile solids and liquids:**

- Those that easily form solutions are determined by colligative properties, discussed in the next chapter.
- Those that do not form solutions easily or no known solvent that dissolves them or soluble in solvents but not convenient to handle; their relative formula masses can be determined by mass spectrometry.

d. **For liquids immiscible with water:**

- Their formula masses are determined by steam distillation – discussed in chapter six.

Relationship between vapour density and molar mass:

- Vapour density is alternatively known as relative density of the vapour.
  It is the ratio of mass of a given volume of a gas to mass of an equal volume of hydrogen at a constant temperature and pressure.
- For one mole of a gas, the mass of one mole is molar mass, M_r and the mass of one mole of hydrogen is 2.

$$\Rightarrow V.D = \frac{M_r}{2}$$

Or,

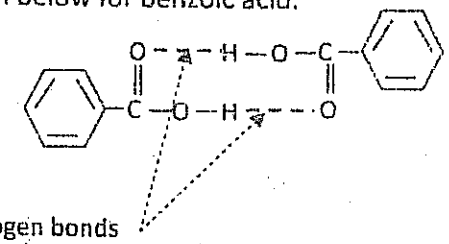
$$M_r = 2 \times V.D$$

Abnormal values of RMM:

- The molar masses of substances are always determined when the substance is beyond its boiling point (in gaseous phase) or in a convenient mixture with another substance.
- However, certain substances show abnormal molar masses in one or both of the cases above.

a. The molar masses of most carboxylic acids in an organic solvent are twice the expected values.

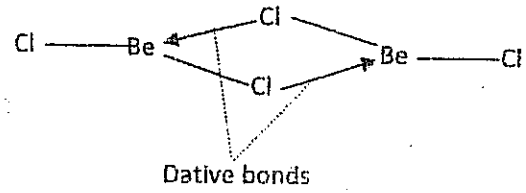
This is because in organic solvents like: benzene, ether and chloroform they dimerize through hydrogen bonding, as shown below for benzoic acid.



b. The molar masses of beryllium chloride, aluminium chloride and iron (III) chloride in the vapour phase are also twice the expected.

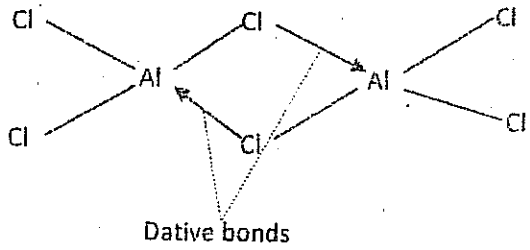
This because in vapour phase, they dimerise as shown below:

i. Beryllium chloride in vapour phase



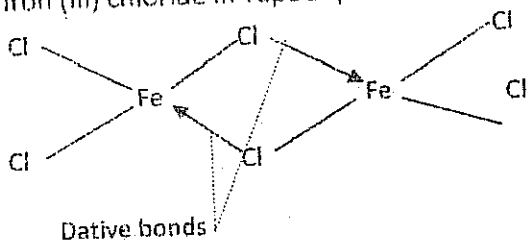
Molecular formula is given by: Be_2Cl_4

ii. Aluminium chloride in vapour phase:



Molecular formular is given by: Al_2Cl_6

iii. Iron (III) chloride in vapour phase:



Molecular formula given by: Fe_2Cl_6

Definitions:

a. **Dimerization** is the joining of two identical molecules through hydrogen or dative bonding to form a molecule whose formula mass is twice the joining molecule.
b. **A dimer** is a molecule formed by joining of two identical molecules through hydrogen or dative bonding.
c. As well, other substances do dissociate or ionize. Hence, the experimental formula mass is less than the expected. This experimental formula mass is the arithmetic average of masses of the produced species after complete ionization/dissociation, or is a function of degree of ionization or dissociation.

CHAPTER TWO: THE ATOMIC STRUCTURE:

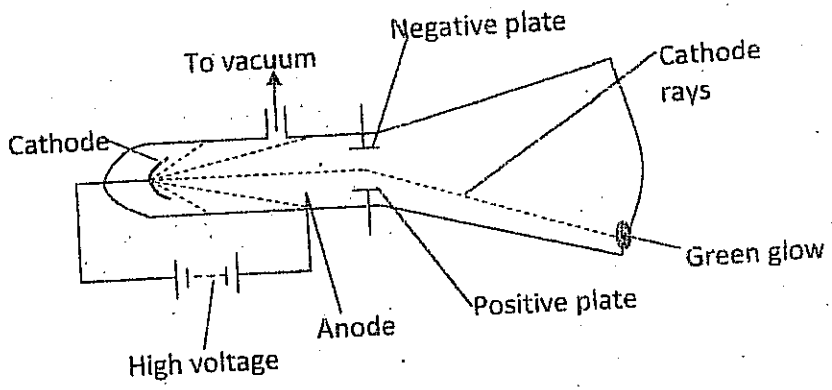
2.0: Introduction:

- John Dalton (1807) imagined what would finally remain when a piece of solid matter is divided continuously for several times.
- He argued that, finally a very tiny invisible and indivisible particle would remain. This particle was referred to 'atomos', a Greek adjective which means 'indivisible'.
- Then later, every matter was thought of as made up of tiny indivisible particles known as atoms. Hence the atomic theory of matter.
- So for long, an atom was viewed as a solid of unknown inside (probably like a ball bearing) with no particles inside as it was the smallest particle imagined.
- However, radioactivity and electrolysis have shown that an atom is made up of three basic particles, also known as sub atomic particles. These are: proton (p), neutron (n) and electrons (e).

2.1: Discovery of sub atomic particles:

a. **Electrons (Sir J.J. Thomson's experiments):**

- He connected a very high electric voltage across a discharge tube containing hydrogen at a very low pressure.
- He observed a green glow coming from the cathode. When he switched on the deflecting plate, the glow was deflected towards the positive plate.
- On directing the rays (glow) to a gold leaf electroscope, the rays gave the electroscope negative charge.
- When he replaced the hydrogen in the discharge tube with other gas, he obtained the same kind of glow (rays).



Conclusions:

- Since the rays were coming from the cathode, they were called cathode rays. Later named electrons.
- Being deflected towards the positively charged plate and imparting negative charge to an electroscope, the rays are negatively charged.
- Since the rays are produced by all gases, it is found in all atoms.
- Hence, all atoms contain negatively charged particles known as electrons.

b. Protons (Sir J.J. Thomson):

- Thomson modified the above experimental set up by using a central cathode with a hole at its centre.
- He observed that in addition to the green glow, there was a red glow on the side of the discharge tube.
- The red glow (rays) was directed away from the anode and was deflected towards the negative plate. However the rays required a stronger field to cause their deflection than the cathode rays.
- The rays were called positive rays. Later named protons.

Conclusions:

- An atom in addition to negatively charged particles called electrons also contains positively charged particles called proton.
- Protons are heavier than electrons as they required stronger field to cause their deflection than the electrons.

Explanation:

- The electric sparks in the tube breaks up the gas molecules at low concentration (pressure) into atoms and remove one or more electrons.
- This converts the atoms into positive ions, which are attracted towards the cathode, passes through the hole at the centre and causes the red glow in the tube.
- The electrons move in the opposite direction and cause the green glow in the opposite direction to the red glow.

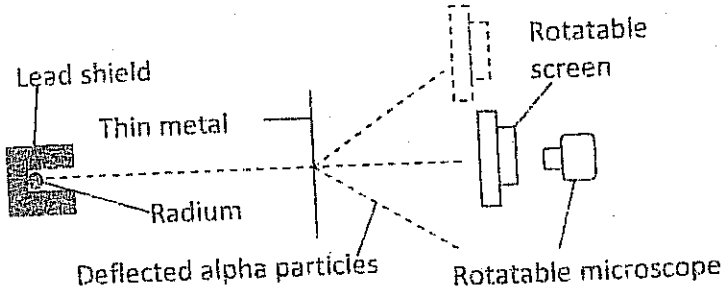
Thomson's atomic structure:

- An atom consists of negative electrons embedded in a sphere of positive charge. The negative and positive charges balanced so that an atom is electrically neutral.
- He believed wrongly that the mass of an atom was significantly contributed by the mass of electrons.

Work of Geiger and Marsden (alpha particle scattering experiment):

- The two placed radium (source of alpha particles) inside a protective lead shield with a narrow hole to allow the alpha particles travel only in one direction.
- The alpha particles were directed through a thin metal foil in an evacuated vessel, behind which fluorescent zinc sulphide screen is placed.

- A rotatable microscope was moved direction round the metal foil with the screen to detect alpha particles as pin flashes of light.



Observations:

Most of the alpha particles passed straight through the foil. When the screen and the microscope were rotated, away from the straight position, flashes were still seen. Even some particles were deflected to angles greater than 90^0 and others practically rebounded.

Explanation (By Rutherford):

- Since alpha particles are positively charged, the deflection is due to the alpha particles coming close to concentrated region of positive charge.
- As only a very small fraction of the alpha particles are deflected, the region of the positive charge, which caused the scattering, must occupy only a small part of the atom.

Rutherford's atomic structure:

- An atom is made up of small central positive nucleus. Outside which, electron(s) move round in the same way the planets move round the sun.
- However, the idea of small positively charged nucleus is accepted, the idea of charged electrons orbiting the charged

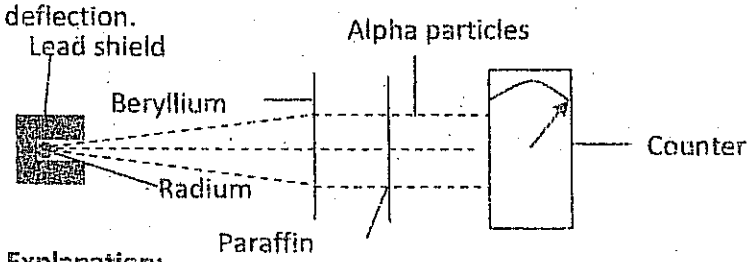
nucleus is rejected as the electron would thus spiral into the nucleus, and the atom would undergo self destruction.

c. **Neutrons:**

- The discovery of neutrons was aroused by the observation that: "hydrogen contains one proton and its mass is one unit. Helium contains two protons, but its mass is four units, and not two units."
- So, where does the extra mass of helium come from?

The work of Chadwick:

- He directed alpha particles to a charged particle counter, where the counter showed deflection.
- He the placed a thin foil of beryllium between the counter and the source of the alpha particles. The counter showed no deflection.
- Then, between the beryllium foil and the counter, he placed a sheet of paraffin wax. Here, the counter showed deflection.



Explanation:

- When beryllium foil was placed between the source of alpha particles and the counter, bombardment of the beryllium foil led to emission of neutral particles known as neutrons which have no effect on charged particles counter.
- When paraffin wax was placed behind the beryllium foil, the neutrons emitted bombarded the paraffin wax leading to emission of positively charged protons, hence deflection of the counter.

Conclusion

- An atom is made up of positively charged protons, negatively charged electrons and neutral neutrons.
- The mass of a neutron is the same as that of a proton. Hence a helium atom has a mass of four units because it has two neutrons and two protons. The mass of electrons are negligible.
- The electrons are found out side the nucleus in what is called electron shell.
- The neutrons and the protons are found in the nucleus.

Particle	Mass	Charge	Position
Proton	1	+1	Nucleus
Neutron	1	0	Nucleus
Electron	$\frac{1}{1840}$	−1	Shells

2.2: Electronic configuration:

Basic concepts and observations:

- When a beam of continuous radiation such as white light is passed through a gaseous sample of an element, the radiation that comes out of the element has some wavelengths missing.
- This is due to absorption of certain wavelengths of the light by the element.
- When the emerging radiation is resolved by a spectrometer, the missing wavelengths show up as discrete dark lines on the spectrum.
- The spectrum of this radiation is called **atomic absorption spectrum.**

- On the other hand, when an element in gaseous state is heated or subjected to electric sparks, and allowed to cool, radiation of a certain wavelength is emitted.
- When this radiation is resolved by a spectrometer, a spectrum of discrete lines is obtained.
- The spectrum of this radiation is called the **atomic emission spectrum.**
- The simplest emission spectrum was obtained when an electric spark was passed through hydrogen molecules at low pressure, as shown below.

Features of the spectrum:

a. Made up of several discrete lines.
b. Each line represents energy of a definite frequency.
c. The spacing between the lines is not constant. It decreases in one direction.
d. Finally the lines converge at one end of the spectrum.

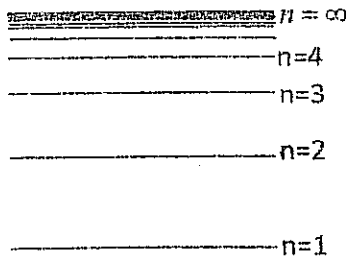
But, why do atoms of elements emit discontinuous or line spectra and not continuous?

Explanation by Niels Bohr:

- An atom contains electrons outside the nucleus in orbits called energy levels.
- Before sparks (excitation), the electrons are in the lowest energy level (ground/stable state).
- The spark causes the electron to absorb energy and hence is promoted to a higher energy level (excited).

- As the electron falls back to a lower energy level, it emits energy in the form of radiation.
- The radiation appeared as discrete lines because each energy level has a fixed (quantized) amount of energy.
- The spacing between the lines is not constant because the energy differences between the energy levels decrease away from the nucleus, until a point when they converge (form a continuum).
- Later, Bohr assigned each energy level a number known as principal quantum number; and numbered the energy levels 1,2,3,4,...,outwards from the nucleus.

The picture of energy levels:



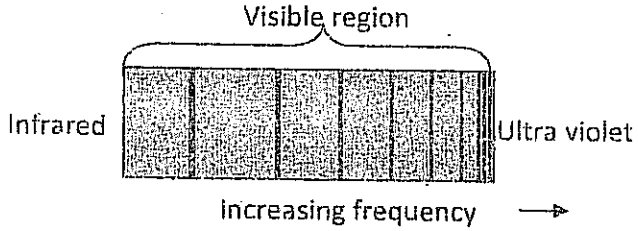
Note the following:

a. Decrease in the spacing between the energy levels.
b. Convergence of the energy levels at n=∞.
c. Energy level n=1 is the nearest to the nucleus and has the lowest energy.
d. When an electron is promoted beyond the energy level n=∞, the electron is lost from the atom; i.e: ionization.

The formation of hydrogen spectrum:

- Electric sparks break up the hydrogen molecules into hydrogen atoms.

- Each of the electrons of the hydrogen atoms absorbs energy and is promoted from energy level n=1 to a higher energy level (excited).
- As the electron falls back to a lower energy level, it releases energy in the form of radiation, which when resolved by a spectrometer, appears as series of both visible and invisible region of electromagnetic radiation; within the visible region, the lines have got different colours as shown below:



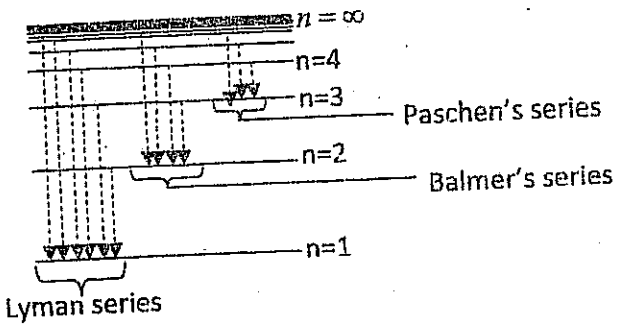
Take note:

- The convergent limit is the frequency of radiation due to an electron falling from n = ∞.

Evidences for existence of energy levels:

a. Formation of a series of lines yet there is only one electron.
b. Converging of the lines
c. Definite frequency and wavelength of the various lines.
d. Difference in the colours of the lines.
e. Increase in number of lines with the resolving power of the spectrometer.

- When the resolving power of the spectrometer was increased, the number of lines grouped into smaller bands (series) was observed, and later named after their discoverers as shown below



The mathematics in emission spectrum:

a. The wavelength of each line is given by:

$$\frac{1}{\lambda} = R_H\left\{\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right\} \quad \text{.....2.1}$$

Where:

R_H is Rydberg's constant = $10967800m^{-1}$

λ is the wave length

n_1 and n_2 are the quantum numbers for final and initial energy levels respectively.

Worked example:2.1

Calculate the wavelength of radiation emitted when an electron falls from:

i. n = 4 to n = 1

ii. n = 5 to n = 1

iii. n = 4 to n = 2

iv. n = ∞ to n =2

Solution:

i. from $\frac{1}{\lambda} = R_H\left\{\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right\}$

$$\Rightarrow \frac{1}{\lambda} = 10967800\left\{\frac{1}{1^2} - \frac{1}{4^2}\right\}$$

$$\lambda = 9.7x10^{-8}m$$

ii. from $\frac{1}{\lambda} = R_H\left\{\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right\}$

$$\Rightarrow \frac{1}{\lambda} = 10967800\left\{\frac{1}{1^2} - \frac{1}{5^2}\right\}$$

$$\lambda = 9.5x10^{-8}m$$

iii. from $\frac{1}{\lambda} = R_H\left\{\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right\}$

$$\Rightarrow \frac{1}{\lambda} = 10967800\left\{\frac{1}{2^2} - \frac{1}{4^2}\right\}$$

$$\lambda = 4.9x10^{-7}m$$

iv. from $\frac{1}{\lambda} = R_H\left\{\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right\}$

$$\Rightarrow \frac{1}{\lambda} = 10967800\left\{\frac{1}{\infty^2} - \frac{1}{4^2}\right\}$$

$$\lambda = 1.5x10^{-6}m$$

Task:2.1

Calculate the wavelengths of radiation emitted when an electron falls from:

i. n = ∞ to n = 1.

ii. n = ∞ to n =2

iii. n = ∞ to n =3

iv. n = 8 to n = 1

v. n = 8 to n = 2

vi. n = 8 to n = 3

b. The energy corresponding to each energy level is given by:

$$E = \frac{-R_H ch}{n^2} \quad \text{.....2.2}$$

Where:

c is the velocity of light = $3x10^8 ms^{-1}$

h is plank's constant = $6.63x10^{-34}$Js

Worked example:2.2

Calculate the energy corresponding to the following quantum numbers:

i. n = 1

ii. n = 2

iii. n = 3

iv. n = ∞

Solution:

i. From $E = \frac{-R_H ch}{n^2}$

$$\Rightarrow E = -\frac{10967800x3.0x10^8 x6.63x10^{-34}}{1^2}$$

E = 2.18 x 10^{-18}J/atom

Multiplying by Avogadro's constant (6.02 x 10^{23})

E = –1313.26kJ/mol.

ii. From $E = \frac{-R_H ch}{n^2}$

$$\Rightarrow E = -\frac{10967800x3.0x10^8 x6.63x10^{-34}}{2^2}$$

E = –5.45 x 10^{-18}J/atom

E = –328.32kJ/mol

iii. $E = \frac{-R_H ch}{n^2}$

$$\Rightarrow E = -\frac{10967800x3.0x10^8 x6.63x10^{-34}}{3^2}$$

E = –2.4 x 10^{-18}J/atom

E = –145.92kJ/mol

iv. $E = \frac{-R_H ch}{n^2}$

$$\Rightarrow E = -\frac{10967800x3.0x10^8 x6.63x10^{-34}}{\infty^2}$$

E = 0

An electron at n = ∞ does not have any energy. It is lost from the nuclear attraction.

Task:2.2

Calculate the energy per mole of the following energy levels:

i. n = 4

ii. n = 5

iii. n = 10

iv. n = 14

v. n = 100

vi. n = 1000

c. The energy given out when an electron falls to a lower energy level is given by:

$\Delta E = hf$, where f is the frequency of the radiation.

An electron falling from n_2 to n_1 emits energy of:

$$\Delta E = \frac{-R_H ch}{(n_2)^2} - \frac{-R_H ch}{(n_1)^2}$$

$$\Delta E = -R_H ch\left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right) \quad \text{.....2.3}$$

Worked example:2.3

Calculate the frequency of radiation emitted when electron falls from the following energy levels:

i. n = 4 to n = 1

ii. n = ∞ to n =2

Solution:

i. From $\Delta E = -R_H ch\left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right)$

$$\Delta E = -10967800x3.0x10^8 x6.63x10^{-34}\left\{\frac{1}{4^2} - \frac{1}{1^2}\right\}$$

$$\Delta E = 2.3x10^{-18}\ J/electron$$
$$\Delta E = 2.3x10^{-18}\ x6.02x10^{23}$$
$$\Delta E = 1384.6kJ/electron$$

From $\Delta E = hf$

$$\Rightarrow 1384600 = 6.63x10^{-34} f$$
$$f = 2.1x10^{39}\ Hz$$

ii. From $\Delta E = -R_H ch\left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2}\right)$

$$\Delta E = -10967800x3.0x10^8 x6.63x10^{-34}\left\{\frac{1}{\infty^2} - \frac{1}{1^2}\right\}$$

$$\Delta E = 2.2x10^{-18}\ J/electron$$
$$\Delta E = 2.2x10^{-18}\ x6.02x10^{23}$$
$$\Delta E = 1313kJmol^{-1}$$

From $\Delta E = hf$

$$\Rightarrow 1313260 = 6.63x10^{-34} f$$
$$f = 2.0x10^{39}\ Hz$$

(This is the value for convergent limit for the Lyman's series)

- Also note how close the frequencies are to one another. They are frequencies within a series.

Task: 2.3

Calculate the frequency of radiation emitted when electron falls from the following energy levels:

i. n = ∞ to n =2

ii. n = 8 to n =2

iii. n = 7 to n = 2

iv. n = 6 to n = 2

v. n = 5 to n =

Task: 2.4

Calculate the value of convergent limit for the Lyman's, Balmer's and Paschen's series. Comment on the differences between the values.

Applications of emission spectra:

a. The yellow street light is due to emission spectrum of sodium.

b. Highly coloured neon emission spectrum is used for adverts.

The nature of electron shells/energy levels:

- Evidences for the nature of the electron shells come from the emission spectrum and the gradation in the values of successive ionization energies.
- The electron shells are divided into sub--shells, which in turn are divided into orbitals, which are conveniently denoted by boxes.

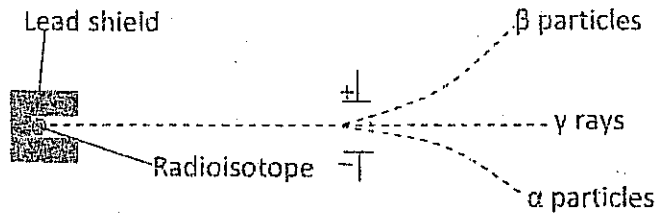
- The nucleus/isotope that undergoes radioactive decay is called **radioactive isotope/radioisotope**; while the particles and the energy emitted are called **radioactive emissions.**
- The properties of the radioactive emissions depend on their behaviours in magnetic and electric fields, and penetrative powers.
  a. Alpha particles are deflected towards the cathode (negative plate). Hence are positively charged. An alpha particle has a mass of four units and a charge of +2. Intuitively, alpha particles are helium nuclei. Because of that mass of an alpha particle and the charge, alpha particles only penetrate matter to a lesser extent.

     Definition:
     An alpha particle is a helium nucleus emitted during radioactive decay.
  b. Beta particles are deflected towards the anode (positive plate). Hence are negatively charged. A beta particle has no mass as per the available scale and has a charge of −1. Intuitively, a beta particle is an electron. Because of no mass and charge of just −1, beta particles are more penetrating than alpha particles.

     Definition:
     A beta particle is an intranuclear electron emitted when a neutron is converted to a proton.
     A beta particle is not the ordinary electrons of the atoms. This would give a deceptive picture that every element contains the number of beta particles equal to its atomic number. More so, ionization is therefore beta particle decay.

  c. Gamma rays are not deflected by any of the fields. They have no charge and mass. Gamma rays have the highest penetrating power.

     Definition:
     Gamma rays are the extra energies an isotope sheds out as it gains stability after decay.



Emission	Nature	Charge	Mass	penetration
α	Helium nucleus	+2(positive)	4	1 time
β	Electron	−1(negative)	0	100 times
γ	Radiation	0(neutral)	0	10,000 times

Effect of decay on the nucleus and atom generally:

a. ***Alpha particle decay:***
   The number of neutrons and protons (nucleons) decreases by four. The atomic number decreases by two. This makes the atom negatively charged. Hence two electrons are lost. The new element is then moved two steps to the left of the periodic table.
b. ***Beta particle decay:***
   Neutron is converted to proton; hence number of neutron decreases by one, number of protons increases

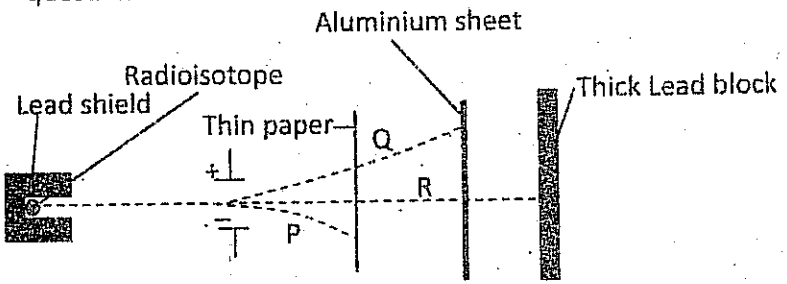
by one. This makes the new atom positively charged. So an electron is captured. Then it is placed one step to the right of the periodic table. The number of nucleons not affected.

c. ***Gamma rays decay:***

Only excess energy of the isotope given out. No effect on the nucleus and the placement of the atom.

Task:2.6

Study the diagram below and use it to answer the following questions:



a. Name the particles labeled P, Q and R.

b. Give two reasons for each of the namings.

Balancing radioactive decay equation:

In balancing the radioactive equation;

a. The sum of the mass numbers on the left must be equal to that on the right.

b. Also, the sum of atomic numbers on the left must be equal to that on the right.

c. Where periodic table is provided, the actual symbol of the nuclide in question must be used.

Worked example:2.6

Balance the following radioactive decay equations:

a. ${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{140}_{56}Ba + {}^{93}_{36}Kr + \ldots\ldots$

b. ${}^{14}_{7}N + \ldots\ldots \longrightarrow {}^{1}_{1}H + {}^{17}_{8}O$

c. ${}^{7}_{3}Li + {}^{1}_{1}P \longrightarrow \ldots\ldots$

d. ${}^{1}_{1}p \longrightarrow {}^{1}_{0}n + \ldots\ldots$

Solution:

a. Let the unknown mass number be A and the unknown atomic number be Z

235+1=143+90+A

A=3

92+0=56+36

Z=0

Since no element has atomic number of 0, the nuclide must be neutron.

Hence: ${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{140}_{56}Ba + {}^{93}_{36}Kr + 3{}^{1}_{0}n$

b. 14+A=17+1

A=4

7+Z=1+8

Z=2

The unknown nuclide is alpha particle.

Hence: ${}^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{1}_{1}H + {}^{17}_{8}O$

c. 7+1=A

A=8

3+1=Z

Z=4

Since beryllium with atomic number 4, does not have a mass number of 8, the unknown nuclides are two alpha particles.

Hence: ${}^{7}_{3}Li + {}^{1}_{1}P \longrightarrow 2{}^{4}_{2}He$

d. 1=1+A

A=0

1=0+Z

Z=1

Since beta particle has a mass of 0 but a charge of −1 the unknown particle is not a beta particle. It is called **positron.**

Hence: ${}^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}^{0}_{+1}e$

A popsitron is the positively charged particle emitted when a proton is converted to a neutron.

Task:2.7

Balance the following radioactive decay equations:

a. ${}^{24}_{11}Na + {}^{1}_{1}p \longrightarrow ..... + {}^{1}_{0}n$

b. ${}^{59}_{27}Co + {}^{1}_{0}n \longrightarrow {}^{60}_{27}Co + ...$

c. ${}^{23}_{11}Na \longrightarrow \beta + ...$

d. ${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{95}_{42}Mo + 2{}^{1}_{0}n + 7\beta$

e. ${}^{56}_{26}Fe + \alpha \longrightarrow {}^{1}_{1}H + ...$

Artificial radioactivity:

- This is about breakdown of the nuclei as a result of action of man. It is always achieved by bombarding the nuclei of the target element by fast particles.
- This leads to the change of the target element into a new element (mutation). Hence it is referred to as **artificial transmutation of elements.**
- The bombarding particles are: alpha particles, protons and neutrons.

a. Bombardment by alpha particles:

- It is more effective in transmuting lighter elements. Heavier elements have a large number of positively charged protons which repel the positively charged alpha particles. However, when accelerated to a high speed, it can effect the transmutation.

${}^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{1}_{1}H + {}^{17}_{8}O$

b. Bombardment by protons:

- It is more effective (attacking) than alpha particle as it is lighter and has a charge of +1 only. So it only experiences a smaller force of repulsion from the nucleus.

${}^{7}_{3}Li + {}^{1}_{1}P \longrightarrow 2{}^{4}_{2}He$

c. Bombardment by neutrons:

- More effective than both the alpha particles and protons since neutrons are not charged so do not experience any repulsion from the nucleus. More so, neutrons are produced in large numbers in nuclear reactions, so they are in plenty.
- Slow moving neutrons combine with the target elements to produce an isotope of the element, accompanied by emission of gamma rays.

${}^{31}_{15}P + {}^{1}_{0}n \longrightarrow {}^{32}_{15}P + \gamma$

- Fast moving neutrons eject out a proton from the nucleus of the target element.

${}^{14}_{7}N + {}^{1}_{0}n \qquad {}^{14}_{6}C + {}^{1}_{1}p$

Nuclear fission and nuclear fusion:

- Nuclear fission is the breaking of a heavy nucleus to lighter nuclei. It can be spontaneous (natural radioactivity) or induced (artificial radioactivity)

$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{140}_{56}Ba + ^{93}_{36}Kr + 3^{1}_{0}n$

- Nuclear fusion is the joining of light nuclei to form a heavier nucleus. As formation of a nucleus is accompanied by a decrease in mass, energy is therefore given out in a nuclear fusion according to Einstein equation.
- Nuclear fusion always takes place at extremely high temperatures in the order of 15,000,000^{0}C.

$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n + energy$

Radioactive decay law and quantitative treatment:

- The law states that the rate of radioactive decay is directly proportional to the number of the undecayed atoms.
- Like any decay law, the rate of decay decreases as the number of the decaying atoms decreases. Hence, the rate gets slower as the decay goes on.
- If N is the number of the decaying atoms:

Rate $\propto$ N

$$\frac{-dN}{dt} \propto N$$

$\frac{-dN}{dt} = \lambda N$, where λ is the constant of proportionality.

Separating variables and integrating,

$$\int \frac{dN}{N} = -\int \lambda dt$$

$\Rightarrow InN = -\lambda t + c$, where c is the constant of integration.

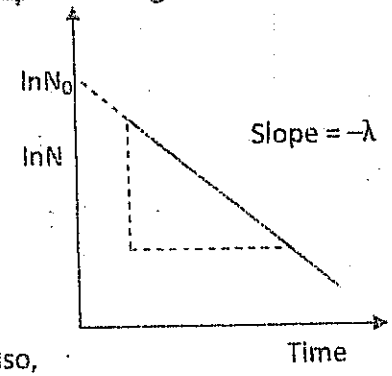
When t = 0, N = N_0,

$$InN_0 = -\lambda(0) + c$$

$$c = InN_0$$

Hence, $InN = -\lambda t + InN_0$ 2.4

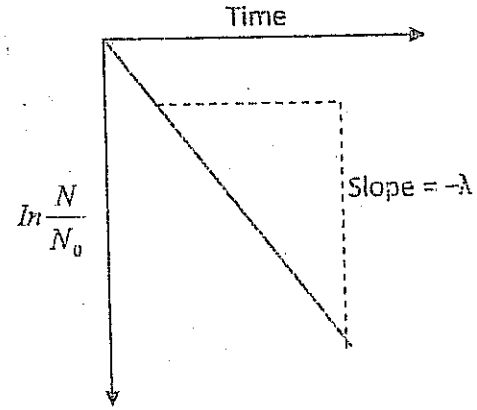
Graph of InN against time:



Also,

$$In\left(\frac{N}{N_0}\right) = -\lambda t \text{.....} 2.5$$

Graph of $In\frac{N}{N_0}$ against time:

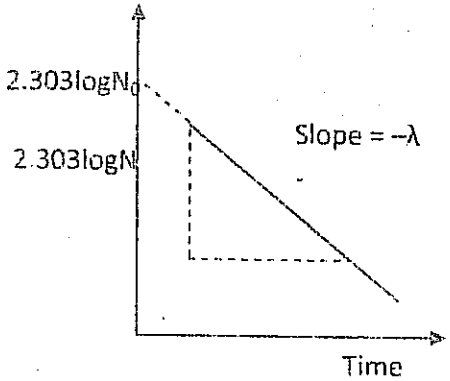


$$N = N_0 e^{-\lambda t}$$

Converting natural log to log_{10}:

$2.303 \log N = -\lambda t + \log N_0$ 2.6

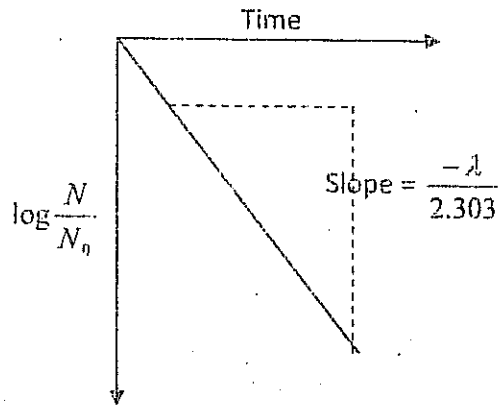
Graph of logN against time:



$$2.303\log\left(\frac{N}{N_0}\right) = -\lambda t \quad \text{.....2.7}$$

$$N = N_0 10^{\frac{-\lambda t}{2.303}} \quad \text{.....2.8}$$

Graph of $\log\frac{N}{N_0}$ against tme:



The half life of radioactive decay:

- This is the time taken for half the original number of the isotope to disintegrate.
- For each radioactive decay, the half life remains constant. For example, the half life of radioactive bismuth is 19.7 minutes. This starting with 8g means: after 19.7 minutes, 4g remains; after another 19.7 minutes, 2g remains; after another 19.7 minutes, 1g remains; after another 19.7 minutes, 0.5g remains, and so on.
- The half life is an indicator of the stability of radioisotopes. The longer the half life, the more stable the isotope and the shorter the half life, the less stable the isotope.
- The table below shows the half lives of some isotopes:

Isotope	Half life
Lawrencium – 257	8seconds
Nobelium – 253	10minutes
Molybdenium – 256	1.5hours
Phosphorus – 32	14.3days
Carbon – 14	5570years

- From equation 2.5;

When time is $t^1/_2$, $N = {}^{N_0}/_2$

$$\Rightarrow In\frac{\left(\frac{N_0}{2}\right)}{N_0} = -\lambda t_{\frac{1}{2}}$$

$$In\frac{1}{2} = -\lambda t_{\frac{1}{2}}$$

$$In2 = \lambda t_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{In2}{\lambda}$$

Or

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda} \quad \text{.....} 2.9$$

Worked example:2.7

If the half life of a radioisotope is 300 seconds. Determine its decay constant.

Solution:

From $t_{\frac{1}{2}} = \frac{0.693}{\lambda}$

$$\Rightarrow 300 = \frac{0.693}{\lambda}$$

$$\lambda = \frac{0.693}{300} = 2.31x10^{-3} s^{-1}$$

Worked example:2.8

A radioactive substance is known to retain $\frac{1}{16} th$ of its original activity in 64 days. Determine the half life of the isotope.

Solution:

Initial activity be A_0. After 64days, activity is $\frac{1}{16} N_0$

From $InN = -\lambda t + InN_0$

$$\Rightarrow In\frac{1}{16} N_0 = -\lambda(64) + InN_0$$

$$64\lambda = In\left(\frac{16N_0}{N_0}\right)$$

$$\lambda = \frac{In16}{64} = 0.043 day^{-1}$$

From $t_{\frac{1}{2}} = \frac{0.693}{\lambda}$

$$\Rightarrow t_{\frac{1}{2}} = \frac{0.693}{0.043} = 16 days.$$

Worked example:2.9

The half life of a radioisotope is 529 minute. After 30 minutes, the activity was found to be 285 counts per seconds. Calculate the initial activity of the sample.

Solution:

From $t_{\frac{1}{2}} = \frac{0.693}{\lambda}$

$$\Rightarrow 529 = \frac{0.693}{\lambda}$$

$$\lambda = \frac{0.693}{529} = 1.3x10^{-3} \min^{-1}$$

From $2.303 \log\left(\frac{N}{N_0}\right) = -\lambda t$

$$\Rightarrow 2.303 \log \frac{N}{N_0} = -\lambda t$$

$$2.303 \log \frac{285}{N_0} = (30x1.3x10^{-3})$$

$$\log \frac{285}{N_0} = 0.0176$$

$$\ln \frac{N}{N_0} = -\lambda t$$

$$\ln \frac{285}{N_0} = (30 \times 1.3 \times 10^{-3})$$

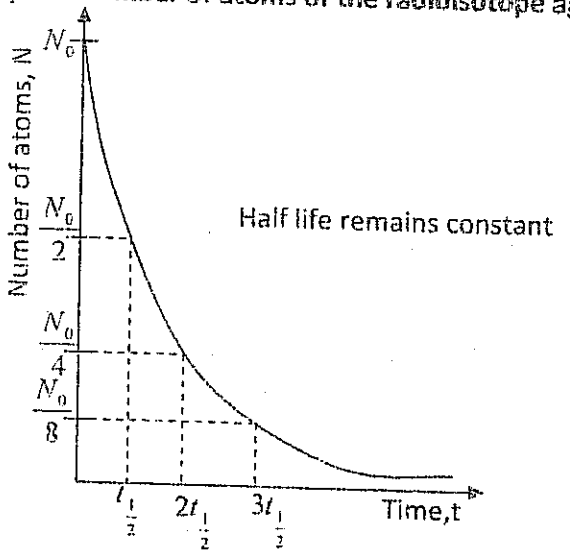
$$\frac{285}{N_0} = 1.03977$$

$$N_0 = 274 cps$$

$$\frac{285}{N_0} = anti\log 0.0176$$

$$N_0 = 274cps$$

Graph of number of atoms of the radioisotope against time:



Task:2.8

The results in the table below were obtained when a sample of a radioisotope was followed:

Activity/s^{-1}	11.3	8.3	6.0	4.4	2.35
Time/minutes	0	10	20	30	50

a. Plot a graph of activity against time and use it to determine the decay constant.

b. Plot a graph of log of activity against time and use it to determine the half life.

c. Plot a graph of ln(Activity) against time and use it to determine the decay constant and hence the half life of the radioisotope.

2.3.3: Stability of the nucleus:

- A nucleus is said to be stable if it does not easily undergo decay. This means that the nucleus has a very high tendency to resist separation, despite the fact that it contains positively charged protons which would repel each other and neutral neutrons.
- Except for hydrogen atom which contains only a proton, the nuclei of all atoms contain positively charged protons and electrically neutral neutrons.
- It therefore appears that the continuous repulsion between the positively charged protons would tear the nucleus apart.
- However, nuclei of most elements are quite stable, and a nuclear material is the heaviest known material of density $10^{17}kgm^{-1}$. So, what is that force that holds the nucleus, against inter–protons repulsion, making the nucleus so compact to such an enormous density???
- Proton–neutron interaction concept was put forward due to the release of energy, when a nucleus is formed from its constituent protons and neutrons, according to Einstein equation:

  $E = mc^2$

  Where E is the energy released, m is change in mass and c is the speed of light.
- Generally, the total mass of individual protons and neutrons is bigger than the mass of a nucleus formed by their combination.
- Therefore, formation of a nucleus from the individual protons and neutrons is accompanied by a decrease in mass, which releases energy according to the above Einstein equation.

- This energy released is called **binding energy** of the nucleus; and when the energy is divided by the total number of protons and neutrons (nucleons) in the nucleus, it is called **binding energy per nucleon.**
- Conversely, in order to separate a nucleus into its individual protons and neutrons, the same binding energy must be supplied.
- Therefore, stability of the nucleus depends on the binding energy, which in turn depends on the proton–neutron interaction.

Definition:

a. **Binding energy:** is the energy released when a nucleus is formed from individual protons and neutrons. Or the energy required to separate a nucleus into its individual protons and neutrons.
b. **Binding energy per nucleon:** is the ratio of binding energy to total number of protons and neutrons in the nucleus.
c. **Mass defect:** is the difference between the mass of a nucleus and the total mass of individual protons and neutrons.

Worked example:2.10

Given that the mass of individual protons and neutrons are respectively: 1.0078 and 1.0079. Calculate the binding energy of:

a. Carbon – 12, relative isotopic mass 12.0000.
b. Manganese – 55, relative isotopic mass 54.956.

Solution:

a. p=6 and n=6

Total mass of p =(6x1.0078)=6.0468

Total mass of n =(6x1.0079)=6.0474

Total mass of individual p and n = (6.0468+6.0474)=12.0942

Mass defect = (12.0942 – 12.0000) =0.0942g=9.42×10^{-5}kg

From $E=mc^2$

$E = 9.42\times10^{-5} \times (3.0\times10^{8})^2$

$E = 8.5\times10^{12}$Jmol^{-1}

b. p=25 and n=30

Total mass of p =(25x1.0078)=25.195

Total mass of n =(30x1.0079)=30.237

Total mass of individual p and n =(25.195+30.237)=55.432

Mass defect =(55.432 – 55.0000) =0.432g=4.32×10^{-4}kg

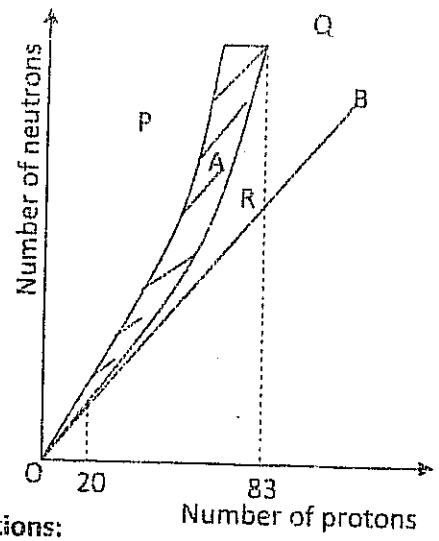
From $E=mc^2$

$E = 4.32\times10^{-4} \times (3.0\times10^{8})^2$

$E = 3.89\times10^{13}$Jmol^{-1}

Variation of number neutrons with number of protons:

- For light elements, the number of protons and neutrons are approximately equal. As the isotopic mass increases, the number of neutrons becomes gradually larger than the number of protons.
- When number of neutrons for all the isotopes are plotted against the number of protons, the elements are scattered on the graph page.
- However, a band/belt/area/zone is obtained on the graph where only the stable isotope lie, as shown below:



Definitions:

a. **Line OB:** Is where all isotopes would lie if they contained equal number of neutrons and protons.

The line is both imaginary and real. The real part is where we have elements like: helium, carbon–12, oxygen, calcium, etc.

b. **Area A:** It is the stability belt/band: it is the area where stable isotopes lie.

Within the stability belt, the neutron to proton ratio is in the range 1 – 1.5. Any isotope with neutron to proton ratio outside the range is outside the belt, and hence unstable.

The stability belt levels off at atomic number 83. This means all the elements with atomic numbers more than 83 are too heavy to be stable.

- Isotopes to the left of the belt, like P contain too many neutrons compared to protons. So they are unstable.
- Isotopes to the right of the belt, like R contain too many protons compared to neutrons. So they are unstable.

- Isotope Q is too heavy to be stable.

Gaining stability:

a. **Isotopes to the left of the belt:**

- Beta particle decay. This converts neutrons to protons hence decreasing the number of neutrons and increasing the number of protons.

$${}^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}e$$

- Neutron decay. This reduces the number of neutrons in the nucleus.
- Alpha particle decay. This reduces the mass number of the isotopes.

b. **Isotopes to the right of the belt:**

- Proton decay. This reduces the number of protons.
- Electron capture. This converts protons to neutrons.

$${}^{1}_{1}p + {}^{0}_{-1}e \longrightarrow {}^{1}_{0}n$$

- Alpha particle decay. This reduces the mass number of the isotopes.
- Positron decay. This converts protons to neutrons. Hence reduces the number of the protons and increases the number of neutrons.

$${}^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}^{0}_{+1}e$$

c. **Isotope Q:**

- Alpha particle decay.

Significance of the contact between line OB and A:

- It shows all the stable nuclei with equal number of neutrons and protons. The line OB emerges out of the belt at atomic

number 20. So calcium is the largest atom with equal number of neutrons and protons.

Factors that affect stability of the nucleus:

a. **Binding energy:** the higher the binding energy, the harder it is to separate the protons and neutrons. Hence the more stable the isotope

b. **Atomic number:** stability decreases with increase in atomic number. Isotopes with atomic number greater than 83 are too heavy to be stable.

c. **Neutrons to protons ratio:** very light nuclei (atomic number < or = 20) are stable if they have neutron to proton ratio of 1. Relatively light (atomic number 21 to<83) nuclei are stable if they have neutron to proton ratio of slightly greater than 1.

Applications/uses of radioactivity:

a. ***Detection of wear and tear on piston rings in industries.***

b. ***Cobalt – 60 is used to arrest growth of cancerous cells.***

c. ***Monitoring of mineral uptake in plants.***

d. ***Archeological dating like estimating the age of wood.***

Origin of carbon – 14 in life forms:

- The neutrons in the cosmic rays in the upper atmosphere continuously bombard the nitrogen atoms.
- This leads to formation of radioactive carbon – 14 according to the equation:

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}p$$

- The carbon – 14 combines with oxygen to form radioactive carbon dioxide.

- Photosynthesizers then use the carbon dioxide to produce food (complex organic compounds).
- Other consumers then obtain the carbon – 14 from the photosynthesizers through their feeding mechanisms.
- Hence all life forms contain a defined amount of carbon – 14.

Use of carbon – 14 to estimate the age of a dead wood:

- The activity of the dead wood A_t is determined using a scintillation counter.
- The activity of a life plant of the same species or any plant seemed to be closely related to it is determined, A_0.
- Since the half life of carbon – 14, a beta particle emitter is known, the decay constant, λ is calculated.
- The age of the dead wood, t is then calculated from:

$$A_t = A_0 10^{\frac{-\lambda t}{2.303}}$$

e. ***Elucidation of reaction mechanisms:***

Use of radioactivity to determine the mechanism for esterification:

- Alkanoic acid is reacted with an alkanol in which its oxygen atom is radioactive oxygen – 18.
- The ester produced is then purified and completely dried free from water.
- Using a radioactivity counter, the ester is then tested for radioactivity.
- Showing of radioactivity by the ester shows that the radioactive oxygen atom of the alkanol is incorporated into the ester. Hence in esterification, the O–H bonds of alkanols and the C–O bonds of alkanoic acids are broken.

- If the ester does not show radioactivity, then during esterification, the O–H bonds in alkanoic acids and the C–O bonds of alkanols are broken.

Differences between radioactivity and chemical reactions:

- Chemical reactions involve only the rearrangement of electrons; while radioactivity involves both the electrons and the nucleus.
- Rates of chemical reactions can be altered; wile rate of radioactivity is constant depending on the radioisotope.
- Chemical reactions produce relatively smaller amount of energy than radioactivity. For instance 1g of carbon produces only 34kJ; a radioactive change of 1g enormously produces 90,000,000,000kJ of heat.

CHAPTER THREE: BONDING AND STRUCTURE:

3.0: Introduction:

- In this sub topic the following questions are important and have to be answered:
  a. Why do atoms combine to form compounds?
  b. How do atoms combine to form compounds?
  c. What force holds the individual particles of a compound (molecules) to one another?
- Under electronic configurations, we said that the electronic configurations of the noble gases are the most stable configurations.
- From the observation that:
  i. Most natural processes occur in order to attain stability and
  ii. The electronic configurations of most bonded atoms are the same as that of a noble gas below or above it.
- Atoms therefore chemically get bonded so as to have the stable electronic configurations of the noble gases.
- There are six types of bonding:
  i. Covalent bonding,
  ii. Dative/coordinate bonding,
  iii. Electrovalent/ionic bonding,
  iv. Metallic bonding,
  v. Hydrogen bonding and
  vi. van der Waal's forces.
- However, the last two (hydrogen bonding and van der Waal's forces) are intermolecular forces–forces holding individual molecules to one another.

Illustration of bonding between atoms:

i. Only outer most (valency) electrons of the atoms are shown.

ii. To clearly show movements of electrons, the valency electrons of one atom is denoted by dots (•) and for the other atom by different symbol, say (ϕ).

iii. If one symbol is a dot and the other one a cross, it is known as the dot and cross illustration to show bonding between atoms.

3.1: Covalent bonding:

A covalent bond is a bond formed by sharing of valency electrons between two atoms in a molecule, with each atom contributing equal number of electrons in its atomic orbital to overlap and form molecular orbital.

Conditions for two atoms to form covalent bond:

i. The valency electrons to be shared must be unpaired and with opposite spins.

ii. The atoms must have either no or a small electronegativity difference.

- Therefore, a covalent bond is formed between atoms of non metals to form molecules (molecular compounds).

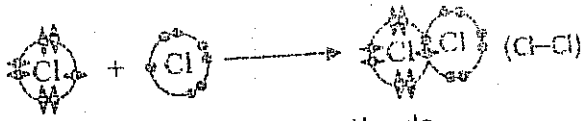
Formation of covalent bonds:

a. Between atoms of no electronegativity difference:

i. Formation of a chlorine molecule:

Electronic configuration of chlorine: $1s^2 2s^2 2p^6 3s^2 3p^5$

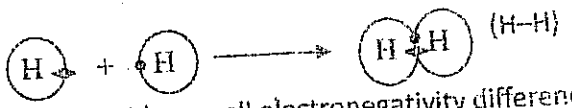
Outermost orbitals:



ii. Formation of a hydrogen molecule

Electronic configuration of hydrogen: $1s^1$

Outermost orbital:



b. Between atoms with a small electronegativity difference:

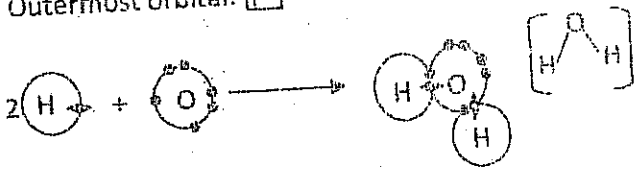
i. Formation of a water molecule.

Electronic configuration of oxygen: $1s^2 2s^2 2p^4$

Outermost orbital:

Electronic configuration of hydrogen: $1s^1$

Outermost orbital:



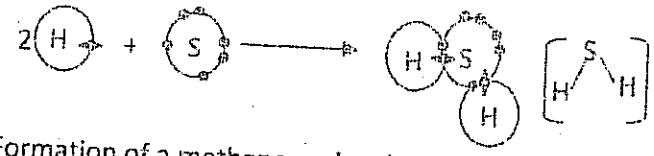
ii. Formation of a hydrogen sulphide molecule.

Electronic configuration of sulphur: $1s^2 2s^2 2p^6 3s^2 3p^4$

Outermost orbital:

Electronic configuration of hydrogen: $1s^1$

Outermost orbital:



iii. Formation of a methane molecule.

Ground state electronic configuration of carbon: $1s^2 2s^2 2p^2$

- Before carbon atom combines with other atoms, it absorbs energy. This energy promotes one of the 2s electrons to the vacant $2p_z$ orbital. The carbon atom in this case is in an excited state.

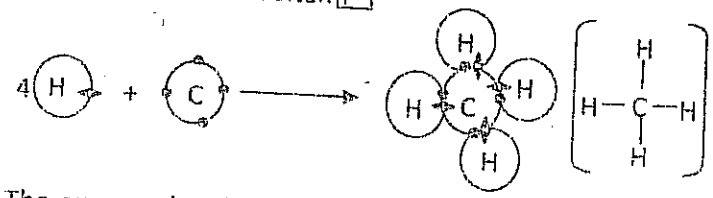
  Excited state electronic configuration of carbon: $1s^2 2s^1 2p^3$

- The 2s orbital then mixes with the three 2p orbitals to form four hybrid sp^3 orbitals of the same energy level with four unpaired electrons.

  Outermost orbitals: [↑|↑|↑|↑]

  Electronic configuration of hydrogen: $1s^1$

  Outermost orbital: [↑]



- The energy absorbed by carbon atom to cause excitation is released back during the formation of the covalent bonds.

iv. Formation of phosphorus trichloride and phosphorus pentachloride.

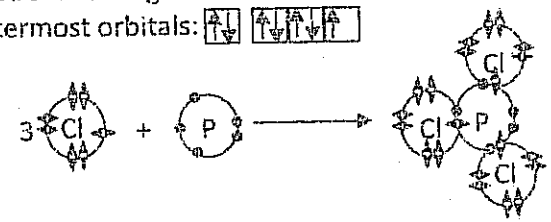
Formation of phosphorus trichloride:

Electronic configuration of phosphorus: $1s^2 2s^2 2p^6 3s^2 3p^3$

Outermost orbitals: [↑↓|↑|↑|↑]

Electronic configuration of chlorine: $1s^2 2s^2 2p^6 3s^2 3p^5$

Outermost orbitals: [↑↓|↑↓|↑↓|↑]



Formation of phosphorus pentachloride:

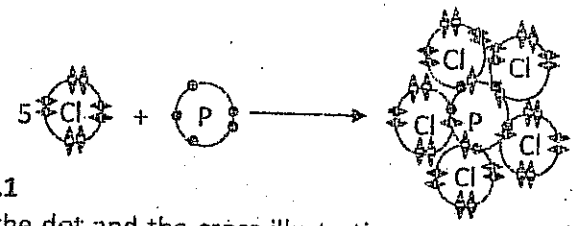
- In order for phosphorus to exhibit penta valency as in the formation of phosphorus pentachloride, the phosphorus atom absorbs energy. This leads to the promotion of one of the 3s orbital electrons to the empty 3d orbital. The phosphorus atom in this state is excited.

  Excited state electronic configuration of phosphorus: $1s^2 2s^2 2p^6 3s^1 3p^3 3d^1$

- The 3s, 3p and 3d orbital then undergo an sp^3d hybridization to form five hybrid orbitals of the same energy level with five unpaired electrons.

  Outermost orbitals: [↑|↑|↑|↑|↑]

- The five unpaired electrons are then shared with five chlorine atoms to form phosphorus (V) chloride.



Task:3.1

Using the dot and the cross illustration or any two different symbols, show the formation of covalent bonds in the following molecules:

a. Ammonia
b. Hydrogen chloride
c. Ethane
d. Silane
e. Trichloromethane

Task:3.2

Explain why nitrogen can show valencies of 3 and 5 in its compounds.

Types of covalent bonds:

- There are two main types of covalent bonds:

a. Single covalent bonds:

A covalent bond formed by sharing two electrons.

- The examples above are single covalent bonds. A single covalent bond is denoted by a dash (-).

b. Multiple covalent bonds:

A covalent bond formed by sharing of four or six electrons.
A covalent bond formed sharing of four electrons is called **double covalent bond**. It is denoted by (=).

- A covalent bond formed by sharing of six electrons is called **triple covalent bond**. A triple covalent bond is denoted by (≡).

Formation of double covalent bonds:

Formation of an oxygen molecule.

Electronic configuration of oxygen: $1s^2 2s^2 2p^4$

Outermost orbital: [↑↓][↑↓][↑][↑]

Task:3.3

Using the dot and cross illustration or any two different symbols, show the formation of double covalent bonds in:

a. A carbon dioxide molecule.
b. An ethene molecule.

Formation of triple covalent bonds:

Task:3.4

Using the dot and cross illustration or any two different symbols, show the formation of triple covalent bonds in:

a. Formation of a hydrogen cyanide molecule.
b. Formation of ethyne molecule.
c. Formation of a nitrogen molecule.

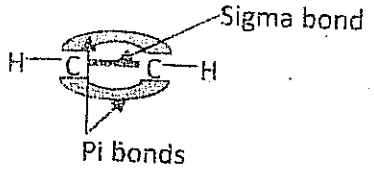
Pi bond, sigma bond and delocalization:

- In multiple bonds in ethene and ethyne, one of the bonds is formed by direct overlap between atomic orbitals of the hybrid orbitals to form a molecular orbital. This bond is called a **sigma (δ) bond**.
- The other bond in ethene and the other two bonds between the carbon atoms in ethyne are formed by side way (lateral) overlap of the unhybridized atomic orbitals to form molecular orbitals. This bonds are called **pi (π) bonds**.

- A sigma bond is stronger than a pi bond, and the electrons within a pi bond are not fixed (localized) to any of the carbon atoms. This is known as **delocalization.**

a. **Consider the formation of ethyne:**

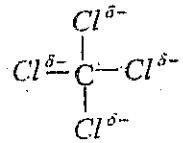
- In ethyne each carbon atom is sp hybridized, leaving the two 2p orbitals of each carbon atoms unhybridized.
- One of the hybrid orbitals forms a sigma bond with hydrogen and the other with the other carbon atom.
- The unhybridized 2p orbitals then laterally overlap to form two pi bonds as shown below.



Polarity of covalent bonds and molecules:

- In a covalent bond formed between two different atoms, the electrons are not equally shared by the two atoms.
- The more electronegative atom pulls the electrons towards its self. This makes it become partially negatively charged and the other atom partially positively charged.
- The molecule in this case is said to have electric dipole, quantified as electric dipole moment.
- Electric dipole moment is the product of magnitude of the partial charge and the distance of separation between the two atoms.
- Examples of these molecules include: hydrogen chloride, hydrogen bromide, water, phosphorus halides, ammonia, etc. These molecules have some ionic character.

- However, in some molecules, the individual covalent bonds are polar, while the molecule is non polar. This is due to the symmetrical distribution of the more electronegative atoms around the less electronegative atom, making the resultant dipole moment zero.



- Examples of such molecules include: tetrachloromethane, silane, tin (IV) chloride, carbon dioxide, etc.

Worked example:3.1

The individual bonds in tetrachloromethane are polar, but the molecule is neutral. Explain.

Solution:

The four polar carbon--chlorine bonds of tetrachloromethane are symmetrically distributed around the carbon atom. This makes the over all dipole moment of the partial charges zero. Hence the molecule is over all neutral.

Properties of covalent compounds:

- They are simple molecules held by weak van der Waal's forces. The magnitude of the van der Waal's forces increases with the formular mass/molecular weight.
- They have low melting and boiling points, since less energy is needed to overcome the weak van der Waal's forces.
- Mostly soluble in non polar solvents.
- Non conductors of electricity in the fused state.

- Covalent compounds react together slowly.

Abnormal/exceptional covalent compounds:

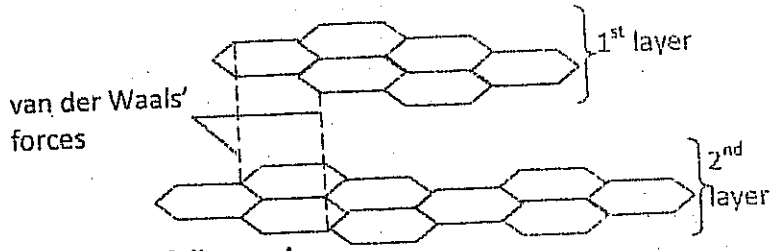
- Diamond, graphite, silicon and silicon dioxide (silicon (IV) oxide) are covalent compounds, but they have exceptionally high melting and boiling points as illustrated below:

Substance	Melting point/^{0}C	Boiling point/^{0}C
Graphite	3925 (sublimes)	Nil
Diamond	3823	5100
Silicon	1683	2628
Silicon dioxide	1880	2500

- The abnormally high melting and boiling points of these substances are due to the nature of bonding in themselves, which determines their structure and hence their melting and boiling points.

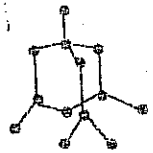
Structure of graphite:

- In graphite, each carbon atom is sp^2 hybridized and each carbon atom is covalently bonded to only three other carbon atoms to form layers of hexagons. The electrons of the unhybridized orbitals are set free within the layer, making graphite to conduct electricity along the layer (not across the layer).
- The layers are joined to one another by van der Waals' forces making graphite slippery and soft.
- This two dimensional net work of strong covalent bond requires a great deal of heat to break; hence graphite has an abnormally high melting point.



Structure of diamond:

- In diamond, each carbon atom is sp^3 hybridized and each carbon atom is bonded to four other carbon atoms by strong sigma covalent bonds. This gives diamond a repetitive unit of tetrahedron, which extends in three dimensions, making diamond exceptionally hard with high melting and boiling points.

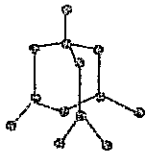


(Key:– a covalent bond; a carbon atom).

Structure of silicon:

- In silicon, each silicon atom is sp^3 hybridized and each carbon atom is bonded to four other carbon atoms by strong sigma covalent bonds. This gives silicon a repetitive unit of tetrahedron, which extends in three dimensions, making silicon exceptionally hard with high melting and boiling points.
- However, diamond is harder and has higher melting and boiling points than silicon due to the small size of carbon

atoms making them to experience stronger net nuclear–electronic attraction.

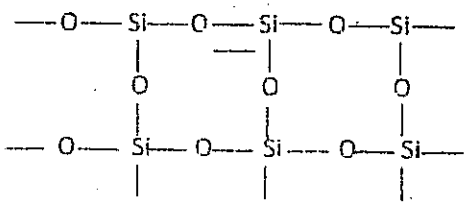


(Key:– a covalent bond; • a silicon atom).

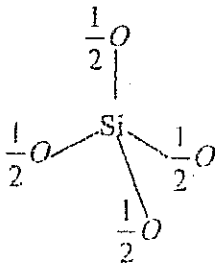
Structure of silicon dioxide:

- In silicon (IV) oxide, each silicon atom is bonded covalently to four oxygen atom, tetrahedrally; with each oxygen atoms linked to two silicon atoms. So each oxygen atom is shared equally between two silicon atoms, giving an empirical formula of SiO_2.
- This three dimensional net works of strong covalent bonds is hard to break, making silicon (IV) oxide to have an exceptionally high melting and boiling points.

Two dimensional structure:



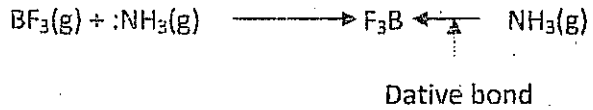
Three dimensional structure:



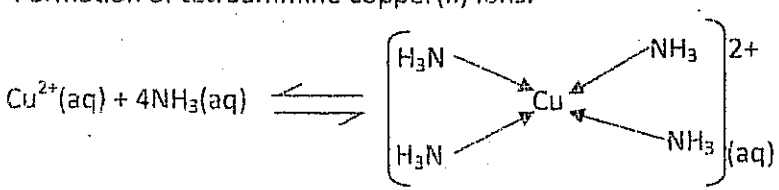
3.2: Dative/coordinate bonds:

- A weak covalent bond formed between an electron rich atom and an electron deficient atom.
- In this bonding, the shared electrons are contributed by only one atom, for that matter, it is called **donor atom**. The other atom that receives the electrons for dative bonding is called **recipient atom**.
- A donor atom has lone pair(s) of electrons. While the recipient atom is either a positively charged ion or a neutral atom with a vacant orbital of the right energy level.
- A dative covalent bond is represented by a straight arrow(→), with the tail coming from the donor atom and the head pointing at the recipient atom/ion.

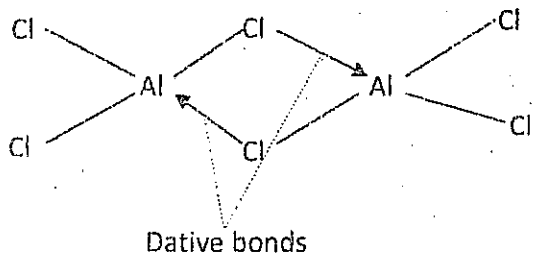
a. Formation of ammonia boron triflouride.



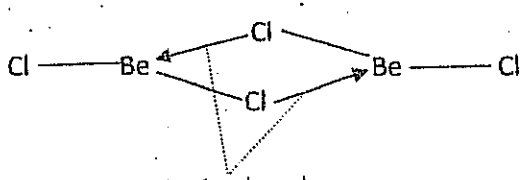
b. Formation of tetraammine copper(II) ions.



c. Dimerization of aluminium chloride in vapour phase.



d. Dimerization of beryllium chloride in vapour phase.



Task:3.5

Show the dative bond formation in the following species:

a. Ammonium ion,
b. Hydroxonium ion.

3.3: Ionic/electrovalent bonding:

- An ionic bond is formed by complete transfer of electron(s) from an electropositive atom to an electronegative atom.
- The electropositive atom, by so transferring electron(s) becomes positively charged; while the electronegative atom, by so gaining the transferred electron(s) becomes negatively charged.
- The electrostatic attraction between the oppositely charged ions constitutes the ionic bond.
- The attraction between the cation and the anion extends in three dimensions resulting into formation a **giant ionic lattice.**

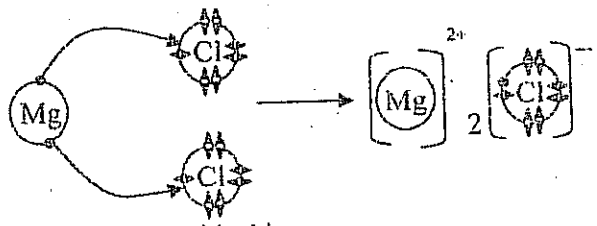
a. Formation ofmagnesium chloride.

Electronic configuration of magnesium: $1s^2 2s^2 2p^6 3s^2$

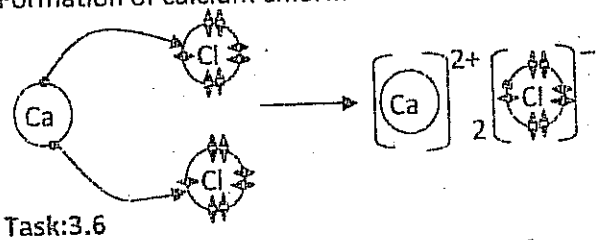
Outermost shell: [↑↓]

Electronic configuration of chlorine: $1s^2 2s^2 2p^6 3s^2 3p^5$

Outermost shell: [↑↓ | ↑↓ | ↑]



b. Formation of calcium chloride.



Task:3.6

Show how the following ionic compounds are formed.

a. Calcium oxide.
b. Sodium oxide.
c. Aluminium oxide
d. Sodium hydride.

Factors that determine the strength of ionic bonds:

- The stronger the ionic bond, the higher the melting and boiling points of the ionic compounds.
- Hence, these factors as well determine the melting and boiling points of ionic compounds.

i. **Ionic charge.**

- The strength of electrostatic force of attraction in ionic lattice increases with increase in ionic charge and hence the melting and boiling point. increase

ii. **Ionic radius.**

- The smaller the ionic radius, the stronger the electrostatic force of attraction in the ionic lattice. Hence, the higher the

melting and boiling points. Conversely, the bigger the ionic radius, the weaker the electrostatic attraction. Hence the lower the melting and boiling points.

Task:3.7

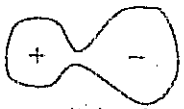
Explain why the melting points of oxides of period three metals increase in the order: $Na_2O<MgO<Al_2O_3$.

Task:3.8

Explain why the decomposition temperature of sodium carbonate is higher than that of magnesium carbonate.

Covalent character in ionic bonds:

- In an ionic bond, the positive charge of the cation attracts the electrons of the anion. This can lead to distortion of the electron shell of the anion i.e the symmetrical arrangement of the cell is distorted such that the shell is pulled towards the cation.



- This distortion causes slight sharing of electrons between the cation and the anion, hence covalency.
- This phenomenon is known as **ionic polarization**. The ability of a cation to cause ionic polarization is its **polarizing power**; while the tendency of an anion to ber polarized is called its **polarisability**.

Factors that affect polarizing power/polarisability:

a. **Charge on the ion:**

- The greater the charge on a cation, the greater is its polarizing power; the polarizing power increases in the order: $Na^{+}<<Mg^{2+}<<Al^{3+}$.
- The greater the charge on anion, the more is its polarisability.

b. **Ionic radius:**

- Polarizing power decreases as the ionic radius increases. Polarisability increases as the ionic radius increases.

Effect of polarization of ionic bonds:

a. Aluminium chloride is essentially a covalent compound with a low melting point. Or sublimation of aluminium chloride and iron (III) chloride.
b. Diagonal relationship in the periodic table.
c. Hydrolysis of compounds.

Properties of ionic compounds:

- They are crystalline solids at room temperature.
- High boiling and melting points.
- Soluble in polar solvents like water (see essence of dissolution of sodium chloride under thermochemistry).
- Conduct electricity when molten or in aqueous solution.
- When oppositely charged ions react together in aqueous solution, they do so rapidly.

3.4: Metallic bonding:

- Within a sample of a metal, the valency electrons are set free (delocalized), leaving positively charged nucleus.

- The attraction between this positively charged nucleus and the delocalized negatively charged valency electrons constitutes the metallic bonding.
- In the metallic lattice, the valency electrons do not belong to any particular nucleus. But rather are free to spread within the lattice.

Factors that determine the strength of metallic bonds:

- The stronger the metallic bond, the higher the melting and boiling points of the metal.
- Hence these factors as well determine the melting and boiling points of metals.

a. Number of valency electrons.
b. Atomic radius of the metal.
c. Types of packing of the atoms of the metal.

3.5: Hydrogen bonding:

- When an electronegative element is covalently bonded to hydrogen, the element continuously pulls the bonded electrons towards itself.
- Thus there is partial separation of charges with the element becoming partially negatively charged and hydrogen partially positively charged (formation of dipoles), as shown below:

$$X^{\delta-}—H^{\delta+}$$

- When two of such molecules approach one another with an appropriate orientation, a hydrogen bond is formed between the element and the hydrogen atom as shown below:

$$X^{\delta-}—H^{\delta+} \cdots X^{\delta-}—H^{\delta+}$$

Hydrogen

- Element X can be: fluorine, chlorine, iodine, bromine. Oxygen, nitrogen, sulphur, etc.

Definition:

A hydrogen bond is a permanent bond formed by dipole – dipole attraction between the hydrogen atom bonded to an electronegative atom and another highly electronegative atom with at least a lone pair of electrons.

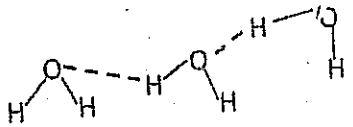
- Examples of hydrogen bonding include:

a. In hydrogen fluoride.

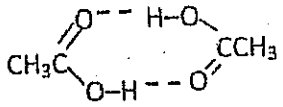
$$F^{\delta-}—H^{\delta+} \cdots F^{\delta-}—H^{\delta+}$$

Hydrogen

b. In water.



c. In ethanoic acid.



Types of hydrogen bonds:

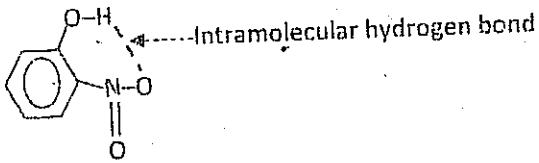
- There are two types of hydrogen bonds: intermolecular hydrogen bonds and intramolecular hydrogen bonds.

a. Intermolecular hydrogen bonds:

- These are hydrogen bonds formed between two different molecules. The molecules can be of the same substance or of different substances.
- The hydrogen bonds in water, hydrogen fluoride and ethanoic acid above are examples of intermolecular hydrogen bonds.

b. Intramolecular hydrogen bonds:

- These are hydrogen bonds within a single molecule of a substance. It is common in DNA molecules and 2 – nitrophenol, as illustrated below using 2 – nitrophenol.



Effects of hydrogen bonds:

a. Solubility in water:

- Organic compounds with polar functional groups such as: alkanols, carboxylic acids esters and amines dissolve in water due to formation of intermolecular hydrogen bonds.

Explain the following observations:

i. Both methanol and butan – 1 – ol are primary alcohols, but the solubility of butan – 1 – ol is very small while methanol is readily miscible with water.

ii. Methoxymethane is immiscible with water while propan – ol is soluble in water, yet they are isomeric.

b. Increase in boiling and melting points.

- The boiling points of water, ammonia, alcohols, amines and carboxylic acids are higher than comparable molecules because of hydrogen bonds.

Worked example:3.2

The boiling point of 4–nitrophenol is higher than the boiling point of 2–nitrophenol, yet the two are isomeric. Explain.

Solution:

In 2–nitrophenol, the nitro–group and the hydroxyl–group are close to one another. This leads to formation of intramolecular hydrogen bonds. However, in 4–nitrophenol, the nitro–group and the hydroxyl group are far from one another. This leads to formation of inter–molecular hydrogen bonds between the molecules. In order to boil 4–nitro phenol, more heat is required to break the inter–molecular hydrogen bonds. Hence it has a higher boiling point than 2–nitrophenol

Task:3.9

The boiling point of ethoxyethane is 22^0C, while the boiling point of butan–1–ol is 124^0C.

Task:3.10

The table below shows the boiling points of water, ammonia and hydrogen fluoride:

Water	Ammonia	Hydrogen flouride
100^0C	-10^0C	19^0C

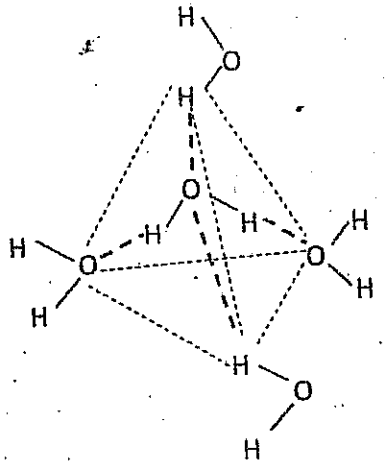
Explain the variation in boiling points.

c. ***Increase in volume and decrease in density of water.***

Explain why ice floats on water.

In ice, each water molecule is joined to four other water molecules by longer hydrogen bonds to form repetitive units of tetrahedron. This locks up a hollow space in ice. When ice melts, the hydrogen bonds collapse, which breaks up the tetrahedron structure and hence the hollow is lost. So more water molecules are packed in a smaller volume with increase in density of liquid water. Hence, ice being less dense than water, floats on liquid water.

Hydrogen bonding in ice:



Factors that determine the strength of intermolecular hydrogen bonds:

- The number of hydrogen bonds formed. The more the number, the stronger the bond.
- Electronegativity of the non metal bonded to the hydrogen atom. The more electronegative the element, the stronger the bond.

Importance of hydrogen bonds:

- Stability of biological molecules like DNA, RNA and proteins.
- Conservation of aquatic lives as ice floats on water.
- Enables solubility in water, hence separation of a compound.
- Grouping of compounds, especially organic compounds.

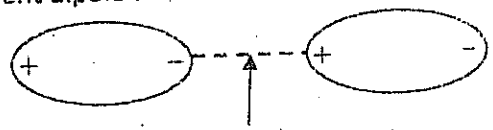
3.6: van der Waal's (bonds) forces:

These are forces of attraction between molecules or atoms (for monoatomic molecules).

Origin of van der Waal's forces:

a. ***Polar molecules:***

- These molecules contain negative polarity at one point and positive polarity at the other point.
- Proximal (close) approach between the opposite polarities of two molecules leads to attraction (van der Waal's bond).
- Such molecules (trichloromethane,propanone, nitrobenzene, etc) are said to have permanent dipole, and the van der Waal's force in this case is called permanent dipole – permanent dipole attraction.



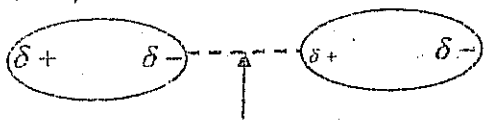
van der Waal's bond

b. ***Non polar molecules:***

- These are symmetrical molecules like: the noble gases, carbon dioxide, benzene, tetrachloromethane, etc. taking the case of the monoatomic noble gases:
- The electrons are not symmetrical in the molecules at all times. There is a certain time when electrons are dispersed from a point. This point therefore becomes partially

positively charged. The opposite end therefore gains partial negative charge.

- Two of such molecules approaching one another with opposite orientation therefore experience attraction (van der Waal's bond) due to the induced charge separation.



van der Waal's bond

Evidences for the existence of van der Waal's forces:

- Deviation of real gases from ideality.
- Increase in melting and boiling points of group seven elements down the group.
- Liquefaction and condensation of noble gases.

Shapes of simple molecules and ions:

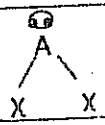
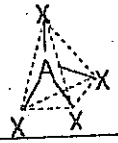
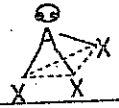
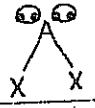
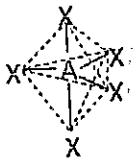
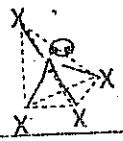
- A covalent molecule and simple ion take a two or three dimensional shape depending on the number of electrons in the valency shell of the central atom.
- The electrons on the valency shells are bonded electron pairs or lone (unbonded) electron pairs.
- The prediction of the shape of a molecule or an ion is based on: Valency Shell, Electron Pairs Repulsion theory (VSEPR), which outlines:
  a. Electron pairs repel one another and in a molecule they take up position of maximum separation.
  b. The repulsion increases in the order: Lone/lone>>lone/bonded>>bonded/bonded.
  c. Repulsion between the electron pairs increases with increase in the electronegativity of the central atom.

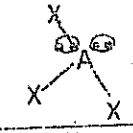
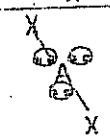
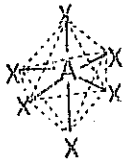
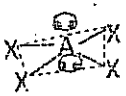
  d. Multiple bonds are treated as single bonds.

- So to predict the shape of a given molecule or ions, one has to:
  a. Identify the central atom.
  b. Identify the number of bonded and lone pairs of electrons.
  c. Arrange the electron pairs around the central atoms, taking into consideration three dimension where need be. A bonded pair of electrons is denoted by a dash (–).

General rule:

The table below gives a summary of the shapes, number of electron pairs (N), number of bonded pairs (BP), number of lone pairs (LP) and the bond angles (BA) for possible molecules and ions.

N	BP	LP	SHAPE	STRUCTURE	BA
2	2	0	Linear	X – A – X	180
3	3	0	Trigonal planar or triangular planar		120
3	2	1	Bent or V shaped		<120
4	4	0	Tetrahedral. **NOT tetrahedron!!!!**		$109^0 28^l$
4	3	1	Trigonal pyramidal		$<109^0 28^l$
4	2	2	Bent/V shaped		<<120
5	5	0	Trigonal bipyramidal		180, 120 and 90
5	4	1	Irregular tetrahedral		

N	BP	LP	SHAPE	STRUCTURE	BA
5	3	2	T shaped		
5	2	3	Linear		
6	6	0	Octahedral **NOT Octahedron!!!**		180 and 90
6	5	1	Square pyramidal		
6	4	2	Square planar		

Factors that determine bond angles:

a. Number of lone pairs of electrons.
b. Number of bonded pairs of electrons.
c. Electronegativity of the central atom.

Worked example:3.3

Draw the structures and name the shapes adopted by the following chemical species:

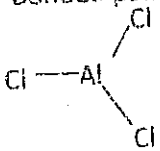
a. Beryllium chloride

b. Aluminium chloride
c. Carbonate ions
d. Sulphur dioxide
e. Ammonia

Solution:

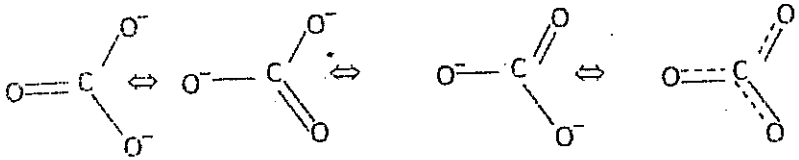
a. Bonded pairs=2; lone pairs=0
Cl–Be–Cl: Shape; Linear

b. Bonded pairs=3; lo0ne pairs=0



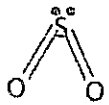
Shape: Trigonal planar

c. Bonded pairs=3; lone pairs=0



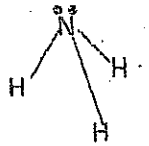
The structures above are known as resonance hybrid structures. The electrons in the pi bonds are delocalized. They don't belong to any oxygen atom.
Shape: Trigonal planar.

d. Bonded pairs=2; lone pairs=1



Shape: bent.

e. Bonded pairs=3; lone pairs=1



Shape: trigonal pyramidal

Task:3.11

Draw and name the shapes adopted by the following species:

a. Nitrate ions
b. Carbon dioxide
c. Nitrite ions
d. Ethyne
e. Sulphur hexafluoride
f. BrF_3
g. Nitronium ion (H_3O^+)
h. Trimethyl amine.

Task:3.12

Explain the following:

a. Both hydrogen sulphide and water adopt V–shape, but the bond angle in water is smaller than the bond angle in hydrogen sulphide.
b. Both hydrogen sulphide and nitrite ions adopt bent shape, but the bond angle in hydrogen sulphide is smaller than in nitrite ion.

electronegativity

CHAPTER FOUR: COLLIGATIVE PROPERTIES:

4.0: Introduction:

- When into a pure solvent is added some solute to form a dilute solution, the physical properties of the solvent containing a small amount of the solute are quite different from those of the pure solvents.
- These properties of the solvent are more consistent when:
  i. The solution is dilute,
  ii. And the solute is non volatile.
- The quantity/magnitude of any of these properties is directly proportional to the mass of a non–volatile solute dissolved and inversely proportional to the relative molecular mass of the solute.
- If Q is the magnitude of the property of a solvent containing mg of a non volatile solute of relative molecular mass M_r then;

$Q \alpha m$ and $Q \alpha \frac{1}{M_r}$

Combining the two proportionalities above,

$Q \alpha \frac{m}{M_r}$

But $\frac{m}{M_r}$ = number of moles.

Q α number of moles.....4.1

- From equation 4.1, the magnitude of any of the properties therefore only depends on the number of particles (moles) of the non volatile solute, but independent of the chemical identity (nature) of the non volatile solute.
- It therefore means that: 0.5 moles of sucrose, 0.5 moles of urea, 0.5 moles of starch, 0.5 moles of a carboxylic acid, and 0.5 moles of any non volatile solute cause the same value of the property.

- For that matter therefore, these properties are colligated (fastened together in general description/hypothesis) and are called **colligative properties.**
- The chemistry of colligative properties is important in determination of relative formula masses in solution.

Key definitions:

i. ***A solution:***
A uniform mixture of a solute and a solvent.

ii. ***A dilute solution:***
A solution that contains a very small amount of the solute compared to that of the solvent. Consider a teaspoonful of sugar dissolved in Lake Victoria!

iii. ***A non volatile solute:***
A solute that does not generate a significant vapour pressure compared to that of the solvent. Or a solute that has an abnormally high boiling point compared to that of the solvent.

iv. ***Colligative properties:***
These are physical properties of a dilute solution which depend only on the number of particles of non volatile solute dissolved in pure solvent but independent of the chemical nature of the solute.
These particles are: atoms, molecules or ions, and their numbers are expressed in moles.

v. ***The mole***
Is the amount of a substance that contains 6.02×10^{23} particles of that substance. This quantity of substance (6.02×10^{23}) was discovered by Avogadro and is known as Avogadro's constant, L. It is not Avogadro's number!

Limitations/conditions of colligative properties:

- The values of the colligative properties are only dependent on the number of particles and consistent on the following conditions or limited to the following conditions:
- The solution must be dilute
- The solute must be non volatile
- The solute and solvent must not chemically interact
- The particles of the solute must remain discrete i.e. no association and dissociation.

The colligative properties:

- There are only four colligative properties, and these are:

i. Lowering of vapour pressure of a solvent.
ii. Depression in freezing point of a solvent.
iii. Elevation of boiling point of a solvent.
iv. Osmotic pressure of a solution.

4.1 Lowering of vapour pressure of a solvent:

- At the surface of any liquid, the particles continuously escape to form vapour. If this vapour is restricted, say by closing the container of the liquid, the accumulated vapour generates pressure within the enclosure.
- This pressure is known as vapour pressure of the liquid. The pressure is a saturated vapour pressure, when in the above set up and at constant temperature, the rate at which the liquid particles escape into vapour is exactly matched with the rate at which the vapour condenses back to the liquid – a state of equilibrium.

Definition:

Saturated vapour pressure of a liquid is the pressure generated by the vapour above the liquid when they are in equilibrium in a closed container at a given temperature.

- Addition of a non volatile solute into a solvent reduces/lowers the vapour pressure of the solvent i.e. the vapour pressure of a solvent into which a small amount of a non volatile solute is added is lower than the vapour pressure of pure solvent at the same temperature.

Explanation:

- Introduction of non-volatile solute particles into a solvent reduces the surface area over which the liquid particles escape to form vapour; also some particles of the liquid are physically obstructed by the particles of the solute.
- These reduce the escaping tendency of the solvent molecules into vapour. Consequently a smaller amount of vapour is formed with a reduced vapour pressure.

Definitions:

a. ***Lowering of vapour pressure:***
The amount by which the vapour pressure of a solvent into which a non volatile solute is added is less than vapour pressure of pure solvent at a given temperature.

b. ***Relative lowering of vapour pressure:***
The ratio of lowering of vapour pressure of a solvent containing a non volatile solute to vapour pressure of pure solvent at the same temperature.

Raoult's law:

This law states that the relative lowering of vapour pressure of a pure solvent is equal to the mole fraction of the non volatile solute dissolved in that solvent at a given temperature.

- Consider a dilute solution containing m_1g of a non volatile solute of relative molecular mass M_1 dissolved in m_2g of a pure solvent of relative molecular mass M_2

- If the vapour pressure of pure solvent is P^0 and that of the the solvent in the above solution is P^1 at the same temperature.

The lowering of vapour pressure = $P^0 - P^1$

Relative lowering of vapour pressure = $\frac{P^0 - P^1}{P^0}$

Mole fraction of the solute, $X_1 = \left(\frac{\frac{m_1}{M_1}}{\left(\frac{m_2}{M_2} + \frac{m_1}{M_2}\right)}\right)$

Since the solution is very, very, very dilute, $\frac{m_2}{M_2} + \frac{m_1}{M_1} \approx \frac{m_2}{M_2}$

So, $X_1 = \frac{m_1}{M_1} \div \frac{m_2}{M_2} = \frac{m_1 \times M_2}{m_2 \times M_1}$

From the statement of Raoult's law:

$$\frac{P^0 - P^1}{P^0} = \frac{m_1 \times M_2}{m_2 \times M_1} \quad \text{.....4.2}$$

Or

$$\frac{P^0 - P^1}{P^0} = X_1 \quad \text{.....4.3}$$

Rearranging:

$P^1 = (1 - X_1)P^0$

But, $(1 - X_1) = X_2$, the mole fraction of the liquid.

$$\Rightarrow \frac{P^1}{P^0} = X_2 \quad \text{.....4.4}$$

From equation 4.4 above, the ratio of the vapour pressure of a solvent containing a non volatile solute to the vapour pressure of pure solvent at the same temperature is equal to the mole fraction of the solvent.

Worked example:4.1

The vapour pressure of water at 25^0C is 2170Nm^{-2}. A certain mass of urea ($CO(NH_2)_2$)when dissolved in 120g of water at 25^0C has a saturated vapour pressure of 2060Nm^{-2}. Calculate;

a. The lowering of vapour pressure
b. The mole fraction of urea in the solution
c. The mass of urea dissolved

Solution:

a. Lowering of vapour pressure =(2170 – 2060) =110Nm^{-2}

b. From $X_u = \frac{P^0 - P^1}{P^0}$

$$\Rightarrow X_u = \frac{2170 - 2060}{2170} = 0.05$$

c. RMM of water, M_w =(1x2)+(16x2) =18

RMM of urea, M_u = (12x1) + (16x1) + (14x2) + (1x4)=60

From, $\frac{P^0 - P^1}{P^0} = \frac{m_u \times M_w}{m_w \times M_u}$

$$\Rightarrow \frac{2170 - 2060}{2170} = \frac{m_u \times 18}{120 \times 60}$$

$m_u = 20.28g$

Task:4.1

The vapour pressure of water at 30^0C is 4240Nm^{-2}. The vapour pressure of 2g of solute X in 100g of water at the same temperature is 4028.5 Nm^{-2}. Calculate the relative formula mass of X.

Task:4.2

At a certain temperature, the saturated vapour pressure of ethoxyethane ($C_4H_{10}O$) is 35000Nm^{-2}. Calculate the mass of

camphor ($C_{10}H_{16}O$) that should be dissolved in 50g of ethoxyethane so that the solution has a vapour pressure of $34510Nm^{-2}$, at the same temperature.

Task:4.3

The vapour pressure of an organic solvent at 20^0C is $58.67kNm^{-2}$ and that of a solution of 9g of methyloctadecanoate in 100g of the organic solvent is $57.40kNm^{-2}$. Calculate the relative formula mass of the organic liquid.

Task:4.4

a) What is meant by:

i. Saturated vapour pressure of a liquid.

ii. Lowering of vapour pressure of a solution.

b) The table below shows the variation of vapour pressure of a solution of solute X in 160g of a solvent with number of moles of X in the solution at 298K.

V.P/Pa	3170	3120	3070	3020	2970	2920	2870
n_X	0.00	0.035	0.07	0.105	0.14	0.175	0.210

i. State how the vapour pressure of the solution varies with number of moles of X.

ii. With a reason, state the saturated vapour pressure of the solvent.

iii. Plot a suitable graph and use it to determine the molar mass of the solven.

4.2 Boiling point elevation of a solvent:

- When into a pure solvent is added a small amount of a non volatile solute, the boiling point of the solvent will be higher than the boiling point of the pure solvent at the same atmospheric pressure.

Why boiling point of a solvent containing a non volatile solute is higher than that of pure solvent at a given atmospheric pressure?

- Addition of non volatile solute into a solvent reduces the escaping tendency of the solvent particles into vapour; hence less vapour pressure at a given temperature.
- It therefore requires heating the ~~the~~ solvent containing the non volatile solute to a higher temperature in order to generate vapour pressure equals to external atmospheric pressure than for a pure solvent.
- Hence the boiling point of a solvent containing a non volatile solute is higher than the boiling point of pure solvent (is elevated) at a given pressure.

Definitions:

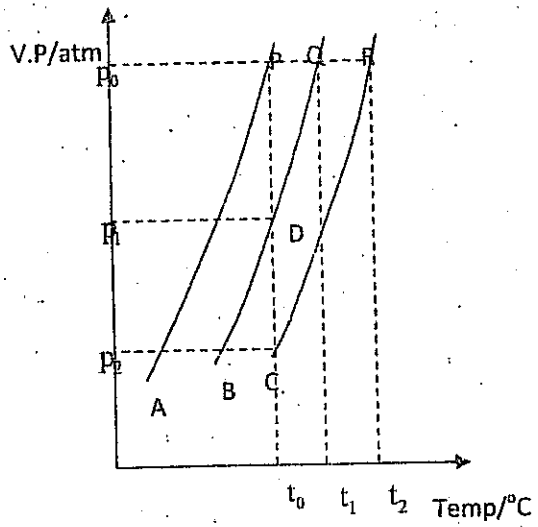
i. ***Boiling point:***

The boiling point of a liquid is the constant temperature at which the saturated vapour pressure of the liquid is equal to the external atmospheric pressure.

ii. ***Elevation in boiling point:***

The amount by which the boiling point of a solvent containing a dilute non volatile solute is higher than the boiling point of the pure solvent at a given pressure.

- The variation of vapour pressure of a liquid with temperature can be followed graphically.



Definitions:

i) Curves:

- AP shows the variation of vapour pressure of pure solvent with temperature.
- BQ and CR represent variations of vapour pressure of solutions 1 and 2 respectively with temperature. With curve CR displaced to the right implying that solution$_2$ is more concentrated than solution$_1$.

Note:

- BQ and CR are below AP at all points because the boiling points of the solutions (1&2) are raised by the presence and amount of the non volatile solute in the solution.

ii) Points:

- t_0 is the boiling point of pure solvent at 1 atmosphere (p_0)
- t_1 is the elevated boiling point of solution$_1$ at 1 atmosphere
- t_2 is the more elevated boiling point of more concentrated solution$_2$ at 1 atmosphere.

Derivations

- Lowering of vapour pressure of solution$_1$, $\Delta p_1 = p_0 - p_1$

- Lowering of vapour pressure of solution$_2$, $\Delta p_2 = p_0 - p_2$
- Elevation in boiling point of solution$_1$, $\Delta t_1 = t_1 - t_0$
- Elevation in boiling point of solution$_2$, $\Delta t_2 = t_2 - t_0$
- Assuming the vapour of pure solvent behaves as the ideal gas; then the curve AP approximates linearity (is almost a straight line).
- When solutions 1 and 2 are very, very, very dilute, then the curves BQ and CR approximate linearity (are almost straight lines) and are parallel to AP. Therefore triangles PRC and PQD are geometrically similar.

$$\Rightarrow \frac{PQ}{PR} = \frac{PD}{PC}$$

$$\frac{t_1 - t_0}{t_2 - t_0} = \frac{p_0 - p_1}{p_0 - p_2}$$

- Converting both numerator and denominator of the right quotient into relative lowering of vapour pressure:

$$\frac{t_1 - t_0}{t_2 - t_0} = \left(\frac{\frac{p_0 - p_1}{p_0}}{\frac{p_0 - p_2}{p_0}} \right)$$

But, $\left(\frac{p_0 - p_1}{p_0} \right) = \Delta p_1$, relative lowering of vapour pressure of solution$_1$ and $\left(\frac{p_0 - p_2}{p_0} \right) = \Delta p_2$, relative lowering of vapour pressure of solution$_2$.

$$\Rightarrow \frac{t_1 - t_0}{t_2 - t_0} = \left(\frac{\Delta p_1}{\Delta p_2} \right) \quad \text{.....4.5}$$

- This implies that the elevation of boiling point due to the presence of a non volatile solute is proportional to the relative lowering of vapour pressure of its dilute solution.

i.e: $\Delta t \alpha \frac{\Delta p}{p_0}$ 4.6

- If 'A' is the solute and 'B' is the solvent, then X_a is the mole fraction of the solute and X_b is the mole fraction of the solvent.
- From Raoult's law of relative lowering of vapour pressure,

$\Delta t \alpha \frac{\Delta p}{p_0} \alpha X_a$ 4.7

$\Rightarrow \Delta t \alpha X_a$ 4.8

Hence, $\Delta t = KX_a$ 4.9

- But, $X_a = \frac{n_a}{n_a + n_b}$, where: n_a is the number of moles of the solute in the solution, n_b is the number of moles of the solvent in the solution.

For the dilute solution of A in B, $\frac{n_a}{n_a + n_b} \approx \frac{n_a}{n_b}$

$\Rightarrow \Delta t = K\left(\frac{n_a}{n_b}\right)$ 4.10

- If m_a is the mass of solute of molar mass M_a, and m_b is the mass of solvent of molar mass M_b in the solution;

Then, $\frac{n_a}{n_b} = \frac{m_a \times M_b}{M_a \times m_b}$

$\Rightarrow \Delta t = K\frac{m_a \times M_b}{M_a \times m_b}$ 4.11

- Since molar mass of the solvent (M_b) is known and remains constant,

$\Delta t = K_b \frac{m_a}{M_a \times m_b}$ 4.12

Where, $K_b = K \times M_b$.

- The constant K_b is called the boiling point elevation constant or ebullioscopic constant.
- If one mole of non volatile solute is dissolved in 1000g of a solvent, then the constant is called **molal boiling point elevation** constant.
- In terms of 1000g of the solvent, the above equation becomes:

$\Delta t = K_b \times \frac{m_a}{M_a \times m_b} \times 1000$ 4.13

Definitions

i. ***Molality:***

Is the concentration of a solution expressed in moles of a solute per 1000g (1kg) of the solvent or solution.

ii. ***A molal solution:***

Is a solution which contains one mole of a solute in 1000g (1kg) of the solvent or solution.

iii. ***Molal boiling point constant/ebullioscopic constant:***

Is the elevation in boiling point of a dilute solution when one mole of a non – volatile solute is dissolved in 1000g of a pure solvent or the solution, at a given pressure.

iv. ***Ebullioscopy:***

Is the method of determining relative formula mass of a non volatile solute by measuring elevation in boiling point of its dilute solution with a pure solvent of known ebullioscopic constant at a given pressure.

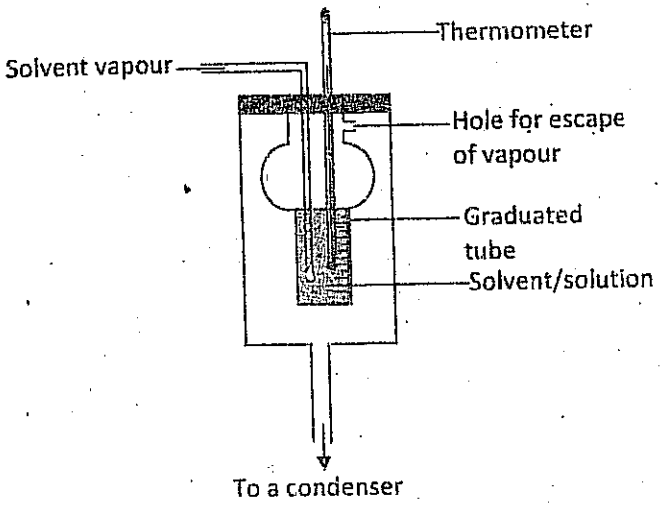
Determination of RMM by boiling point elevation method:

Procedures

- ag of a pure solvent of ebullioscopic constant $= K_b$ is put in the inner graduated or calibrated tube, which in turn is inserted in an air jacket tube.

- Some amount of the pure solvent is boiled in another flask and its vapour is bubbled into the solvent within the graduated tube until it boils. The boiling point of the pure solvent t_0 is recorded.
- A known mass of solute bg is added into the solvent and more solvent vapour is passed into this solution until it boils. The boiling point of the solution t_1, is recorded.
- The volume of the solution in the graduated tube is read off and since the solution is taken to be very dilute, its density can be taken to be the one of pure solvent; mass of solution is given as the product of the read volume of the solution and the density of the solvent.

Experimental setup:



Treatment of the results:

Elevation in boiling point $t_1 - t_0$

ag of the solvent dissolved bg of the solute

1000 g of the solvent would dissolve $\frac{b}{a} \times 1000$

$t_1 - t_0$ is the elevation caused by $\frac{b}{a} \times 1000$ of the solute in 1000 g of the solvent

K_b would be caused by $\frac{K_b}{t_1 - t_0} \times \frac{b}{a} \times 1000$ of the solute in 1000 g of the solvent.

But elevation equal to ebullioscopic constant is caused by RMM.

Hence the $RMM = \frac{K_b}{t_1 - t_0} \times \frac{b}{a} \times 1000$

Worked example:4.2

Pure ethanol boils at 78^{0}C at standard pressure. Calculate the elevation in boiling point of ethanol at the same pressure by dissolving 0.9g of ethanamide in 25g of ethanol. Boiling (point elevation constant of ethanol is 1.15^{0}C/mole/1000g of ethanol)

Solution:

25g of ethanol contains 0.9g of ethanamide

1000g will contain $\frac{1000 \times 0.9}{25}$ g of ethanamide.

$= 36$g

RMM of ethanamide (CH_3CONH_2)

= (12x2) + (1x5) + (14x1) =43g

43g of ethanamide in 1000g of ethanol caused 1.15^{0}C

3.6g in 1000g of ethanol would cause $\frac{3.6 \times 1.15}{43}{}^0C$

$= 0.096^0C$

Hence elevation in boiling point of ethanol $= 0.096^0C$

0.096°C

Task:4.5

One mole of urea in 1000g of water elevates boiling point of water by 0.52^0C. Calculate the mass of glucose ($C_6H_{12}O_6$) in 180g of water that would cause water to boil at 100.003^0C at standard pressure.

Task:4.6

The elevation in boiling point of propanone when 10g of a non volatile solute is dissolved in 100g of propanone is 1.2^0C. Given that the ebullioscopic constant of propanone is 1.71^0C/mole/kg. Calculate the molar mass of the solute.

Task:4.7

The table below shows the variation in boiling points (BPt) of pure benzene and a solution of tetrachloromethane in 80g of benzene with vapour pressure (V.P).

V.P/atm	0.50	0.74	0.90	1.20	1.44	1.60
BPt of benzene/^0C	78.2	79.2	79.7	80.5	81.1	81.6
BPt of solution/^0C	79.0	79.9	80.4	81.2	81.8	82.2

a. Plot a graph of boiling point of benzene and that of its solution of tetrachloromethane on the same pair of axes.

b. Use the graph to determine:

i. The elevation of boiling point

ii. The lowering of vapour pressure of pure benzene at the boiling point of pure benzene.

iii. The mass of tetrachloromethane dissolved (ebullioscopic constant is 6^0C/mole/1000g of benzene)

Task:4.8

a. Explain the following:

i. The vapour pressure of a solvent containing a non volatile solute is less than that of pure solvent at a constant temperature.

ii. Beans boiled with water to which sodium chloride is added gets more ready that beans boiled with pure water in the same time duration.

iii. The relative formula mass of potassium chloride determined by ebullioscopy is 37.25.

b. When 2g of a non volatile solute Z is dissolved in 10g of a solvent, then, the boiling point of the above solution is equal to the boiling point of4.5g of glucose ($C_6H_{12}O_6$) in 100g of the solvent, whose K_b=0.52^0C/mole/1000g of the solvent. Calculate the formula mass of Z.

Worked example:4.3

a. Describe an experimental determination of ebullioscopic constant of ethanol. Include treatment of results in your description

b. In such experiment, a student collected the following results:

- Mass of urea used=2g
- Mass of ethanol use=50g
- Boiling point of pure ethanol=78^0C
- Boiling point of its dilute solution above=78.77^0C, at the same pressure.

Calculate the ebulioscopic constant of ethanol;

i. Per 100g of ethanol

ii. Per 1000g of ethanol.

Solution:

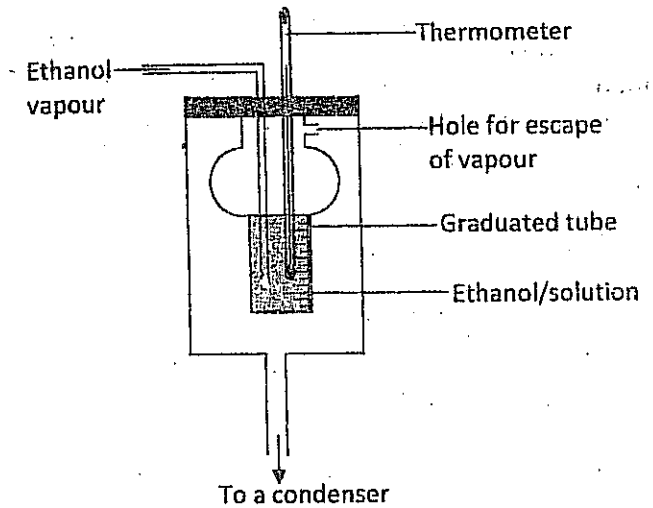
a. *Procedures:*

- *ag* of a pure ethanol is put in the inner graduated or calibrated tube, which in turn is inserted in an air jacket tube.
- Some amount of the pure ethanol is boiled in another flask and it vapour is bubbled into the ethanol within the

graduated tube until it boils. The boiling point of the pure ethanol t_0 is recorded.

- A known mass of ethanamide bg is added into the ethanol and more ethanol vapour is passed into this solution until it boils. The boiling point of the solution t_1, is recorded.
- The volume of the solution in the graduated tube is read off and since the solution is taken to be very dilute, its density can be taken to the one of pure ethanol; mass of solution is given as the product of the read volume of the solution and the density of the ethanol.

Experimental setup:



Treatment of the results

- Elevation in boiling point $t_1 - t_0$
- ag of the solvent dissolved bg of the solute
- 1000 g of the solvent would dissolve $\frac{b}{a} \times 1000$
- RMM of ethanamide (CH_3CONH_2)

$= (12x2) + (1x5) + (14x1) = 43g$

$\frac{b}{a} \times 1000g$ of ethanamide caused $t_1 - t_0$

43g of ethanamide would cause $\frac{a(t_1 - t_0)}{b} \times \frac{43}{1000}$

Hence ebullioscopic constant, K_b is given by:

$K_b = \frac{a}{b}(t_1 - t_0) \times \frac{43}{1000}\,^0C/mol/1000g$ of ethanol.

b. i. 50g of ethanol dissolved 2g of urea.

100g would dissolve $\frac{100 \times 2}{50} = 4g$ of urea

Elevation in boiling point $=(78.77 - 78) = 0.77^0C$

RMM of $CO(NH_2)_2 = (12x1) + (16x1) + (14x2) + (1x4) = 60$

4g of urea in 100g of ethanol caused 0.77^0C

60g of urea in 100g of ethanol would cause $\frac{60 \times 0.77}{4} = 11.55^0C$

Hence $K_b = 11.55^0C/mol/100g$ of ethanol.

ii. 50g of ethanol dissolved 2g of urea.

1000g would dissolve $\frac{1000 \times 2}{50} = 40g$ of urea.

40g of urea in 1000g of ethanol caused 0.77^0C

60g of urea in 1000g of ethanol would cause $\frac{60 \times 0.77}{40} = 1.155^0C$

Hence $K_b = 1.155^0C/mol/1000g$ of ethanol.

- Multiplying the volume of solvent by a factor, divides the ebullioscopic constant by that very factor.

Task:4.9

a. State what is meant by:
   i. Boiling point of a liquid
   ii. Boiling point elevation.

b. Boiling point elevation measurement can be used to determine the relative molecular mass of a compound.

i. State the conditions under which this method is most suitable.

ii. The following results were obtained from experiment involving boiling point elevation measurement:

- Boiling point of pure solvent at 760mmHg = t_1
- Boiling point of m_bg of solute X in m_ag of the solvent at 760mmHg = t_2.

Taking the boiling point constant of the solvent as K_b, show that the molar mass of X is given by: $\frac{-K_b}{t_1 - t_2}\left(\frac{m_b}{m_a}\right) \times 1000$

c. 20g of water containing 4g of cadmium (II) iodide boiled at 0.285^0C above the normal boiling point of water. If the K_b of water is 0.52^0C/mole/1000g of water;

i. Calculate the relative formula mass of cadmium (II) iodide, (Cd=112, I=127).

ii. Does aqueous solution of cadmium (II) iodide conduct electricity or not. Explain your answer.

2.2.3 Depression of freezing point of a solvent:

- When a pure liquid is cooled, its temperature and vapour pressure decrease almost in accordance to the pressure law. However a temperature will be reached when solid form separates out of the liquid.
- At this temperature, the vapour pressure of the liquid form is equal to the vapour pressure of the solid form. This is the freezing point of the liquid.
- Also when a dilute solution of a non volatile solute is cooled, a temperature is reached when the solid ***solvent*** separates out the solution.
- At this temperature, the vapour pressure of the solid ***solvent*** is equal to the vapour pressure of the liquid solvent

containing a non volatile solute. This is lowered freezing point of the solvent.

- Since presence of a non volatile solute lowers the vapour pressure of the solvent, the freezing point of the solvent containing a non volatile solute is therefore lower than that of the pure solvent i.e. depressed.

Definitions

i. **Freezing point of a pure solvent:**

Is the constant temperature at which the vapour pressure of solid form of a liquid is equal to the vapour pressure of the liquid form at constant external pressure.

ii. **Freezing point of a solvent containing a non volatile solute:**

Is the constant temperature at which the vapour pressure of the solid solvent is equal to the vapour pressure of the solvent containing a non volatile solute at constant external pressure.

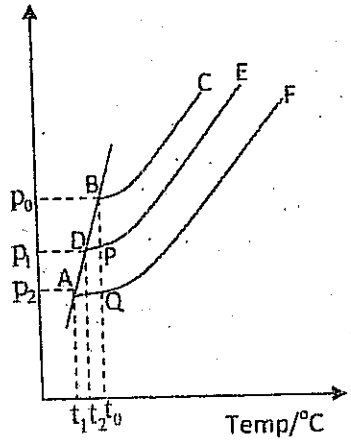
iii. **Depression in freezing point of a solvent:**

Is the amount by which the freezing point of a solvent containing a non volatile solute is lower than that of pure solvent at constant external pressure.

Causes of depression in freezing point of a solution

- Presence of a non volatile solute reduces the vapour pressure of a solvent. So the solvent has to be cooled to a lower temperature in order for its vapour pressure to be equal to the vapour pressure of solid solvent.
- Hence the freezing point of the solvent containing a non volatile solute is lower than that of pure solvent i.e. freezing point of the solvent is depressed.
- The variation of vapour pressure with temperature of a pure liquid solvent and that of the solvent containing a non –

volatile solute can be followed graphically as illustrated below:



Definitions

i. **Curves:**

- CB shows the variation of vapour pressure of pure liquid solvent with temperature.
- BA shows variation of vapour pressure of solid solvent with temperature.
- ED shows the variation of vapour pressure of solvent containing a less concentration of the solute, with temperature.
- FA shows the variation of vapour pressure of solvent containing more concentration of the solute, with temperature.

❖ ED and FA are below BC at all points because the freezing point of the solvent is depressed by the presence and amount of the non volatile solute in the solvent.

ii. **Points**

- B indicates the freezing point of pure solvent t_0 and the pressure of solid solvent/liquid, p_0

- D indicates the freezing point of solvent with a smaller amount of the solute t_1 and vapour pressure of solid solvent p_1.
- A indicates the freezing point t_2 of the solvent containing more of the solute and vapour pressure of solid solvent p_2.

Derivations:

- Lowering of vapour pressure $\Delta p_1 = p_0 - p_1$
- Lowering of vapour pressure $\Delta p_2 = p_0 - p_2$
- Depression in freezing point $\Delta t_1 = t_0 - t_1$
- Depression in freezing point $\Delta t_2 = t_0 - t_2$
- Assuming the vapour of pure solvent behaves as the ideal gas, and then the curve BC approximates linearity.
- For very small amounts of the solute, points D and A are very close to point B; the curves BC, DE and AF approximate straight lines and therefore triangles BDP and BAQ are geometrically similar.

$$\Rightarrow \frac{DP}{BP} = \frac{AQ}{BQ} \quad \text{.....4.14}$$

$$\frac{t_0 - t_1}{t_0 - t_2} = \frac{p_0 - p_1}{p_0 - p_2} \quad \text{.....4.15}$$

- Converting both numerator and denominator of the right quotient into relative lowering of vapour pressure:

$$\Rightarrow \frac{t_0 - t_1}{t_2 - t_0} = \left(\frac{\dfrac{p_0 - p_1}{p_0}}{\dfrac{p_0 - p_2}{p_0}} \right)$$

So that: $\dfrac{t_0 - t_1}{t_0 - t_1} = \dfrac{\Delta p_1}{\Delta p_2}$ 4.16

- Hence, the depression in freezing point of a solvent due to the presence of a non volatile solute is proportional to the relative lowering of vapour pressure of the solvent.

I.e: $\Delta t \alpha \frac{\Delta p}{p_0}$ 4.17

- If 'A' is the solute and 'B' is the solvent, then X_a is the mole fraction of the solute and X_b is the mole fraction of the solvent.
- From Raoult's law of relative lowering of vapour pressure,

$\Delta t \alpha \frac{\Delta p}{p_0} \alpha X_a$ 4.18

$\Rightarrow \Delta t \alpha X_a$ 4.19

Hence, $\Delta t = KX_a$ 4.20

- But, $X_a = \frac{n_a}{n_a + n_b}$, where: n_a is the number of moles of the solute in the solution, n_b is the number of moles of the solvent in the solution.

For the dilute solution; $\frac{n_a}{n_a + n_b} \approx \frac{n_a}{n_b}$

$\Rightarrow \Delta t = K\left(\frac{n_a}{n_b}\right)$ 4.21

- If m_a is the mass of solute of molar mass M_a, and m_b is the mass of solvent of molar mass M_b in the solution;

Then, $\frac{n_a}{n_b} = \frac{m_a \times M_b}{M_a \times m_b}$

$\Rightarrow \Delta t = K\frac{m_a \times M_b}{M_a \times m_b}$ 4.22

- Since molar mass of the solvent (M_b) is known and remains constant,

$\Delta t = K_f \frac{m_a}{M_a \times m_b}$ 4.23

Where, $K_b = K \times M_b$.

- The constant K_f is called the **freezing point depression constant.**
- If one mole of non volatile solute is dissolved in 1000g of a solvent, then the constant is called **molal freezing point depression constant or cryoscopic constant.**
- In terms of 1000g of the solvent, the above equation , 4.23 becomes:

$\Delta t = K_f \times \frac{m_a}{M_a \times m_b} \times 1000$

Definitions

i. ***Cryoscopic constant:***

Is the depression in freezing point of a solvent at a constant pressure when one mole of a non volatile solute is dissolved in 1000g (1kg) of the pure solvent.

ii. ***Cryoscopy:***

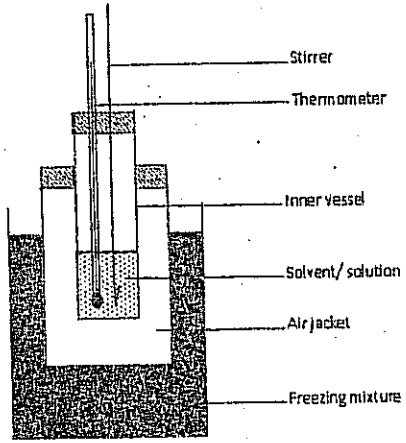
Is the method of determining relative formula mass of a non volatile solute by measuring depression in freezing point of a solvent caused by the solute in a solvent of known cryoscopic constant at a given atmospheric pressure.

Determination of RMM of a solute by the cryscopic method:

Procedure

- 'm_b' g of a solvent of known cryscopic constant K_f is placed in the inner test tube which has been fitted in a boiling tube to provide an air jacket.
- This is then placed in a freezing mixture; the solvent stirred and a steady temperature, t_1 when the solvent solidifies is noted.

- The tube containing the solvent is removed and warmed by hand to melt the solidified solvent.
- A known amount of solute 'm_a'g is then added to the solvent and stirred to dissolve it.
- The solution is then placed back in the freezing mixture and allowed to cool as before.
- A second steady temperature t_2, freezing point of the dilute solution is noted.



Quantitative treatment of the result:

Depression in freezing point of the solution $= t_1 - t_2$

Mass of the solvent used = m_b, let molar mass of the solvent be M_b

Mass of the solute = m_a, let the molar mass of the solute be M_a

Cryoscopic constant = K_f

m_b g of the solvent dissolve m_a g of the solute

1000g of the solvent will dissolve $\frac{m_a}{m_b} \times 1000g$

$t_1 - t_2$ is caused by $\frac{m_a}{m_b} \times 1000g$ of the solute in 1000g of the solvent

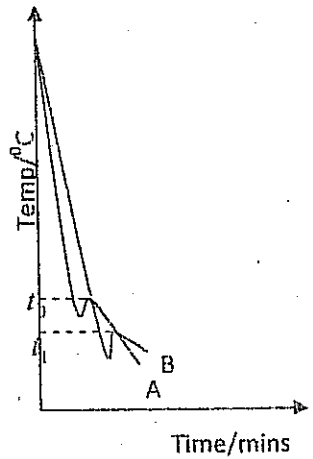
K_f would be caused by $\frac{m_a}{m_b} \times \left(\frac{K_f}{t_1 - t_2}\right) \times 1000g$ of the solute in 1000g of the solvent

Therefore, $M_a = \frac{m_a}{m_b} \times \left(\frac{K_f}{t_1 - t_2}\right) \times 1000g$

Take note:

- At times when a liquid is cooled, the freezing point is bypassed without the liquid solidifying. This is known as super cooling.
- Super cooling is the cooling of a liquid beyond its freezing point without the solid form of the liquid substance appearing.
- The liquid form of the substance that exists at a temperature below its freezing point is not in the standard state at that temperature. So it is metastable form of the liquid. It is so unstable that it can easily be converted to the solid state.

Cooling curves showing super – cooling



Definitions:

i. *Curves:*

- A – Cooling curve of pure solvent at constant temperature
- B – Cooling curve of the solvent cotaining a non – volatile solute at the same pressure.

ii. *Points:*

- t_0 –The freezing point of the pure solvent at the pressure; the part of the curve below this freezing point shows super – cooling of the pure solvent.
- t_1 – the freezing point of the solvent containing non volatile solute at the pressure; the part of the curve below this freezing point shows super – cooling.

Applications of depression in freezing point:

i. **In road construction:**

- In winter months of the cold countries, the atmosphere tends to become unnecessarily foggy.
- The fogs iand on roads and condense to form liquid water.
- When the temperature continuously decreases, the condensed liquid water solidifies, forming ice on the roads.
- A driver trying to cruise on the ice covered road fails to have enough frictional grips on the ice and therefore, the vehicle continuously skids and hence veers off the road.
- To reduce this, the tar for tarmacking the road is mixed with sodium chloride to depress the freezing point of water on the road (the condensed fogs).
- Hence making water to remain as liquid water for a wider range of decreasing temperature – its thermodynamic longevity as liquid extended!

ii. **In car radiators:**

- The car radiator is always fed with liquid water to provide a cooling effect to the engine.

- During the winter months of cold countries, the water in the radiator tends to solidify, forming ice.
- To reduce the possibility of this from occurring, the water in the car radiators is mixed with alkanols to depress the freezing point of the water in the radiator.
- Hence making water to remain as liquid water for a wider range of decreasing temperature – its thermodynamic longevity as liquid extended!

❖ Since the substances added to the tar of the tarmac and the water in the car radiator delay freezing (prevent freezing for a short while), they are therefore antifreeze.

Worked example:4.4

Calculate the molar mass of solute X, if 5.5g of X in 220g of ethanoic acid had a freezing point of 0.78^0C lower than that of pure ethanoic acid at the same pressure (K_f = 3.9^0Cper mole per 1000g of ethanoic acid)

Solution:

Depression in freezing point = 0.78^0C

220g of ethanoic acid dissolved 5.5g of X

1000g would dissolve $\frac{1000 \times 5.5}{220} = 25g$ of X

0.78^0C is caused by 25g of X in 1000g of ethanoic acid.

3.9^0C would be caused by $\frac{3.9 \times 25}{0.78} = 125g$ of X in 1000g of ethanoic acid.

Therefore, the relative formula mass of X is 125.

Task:4.10

20g of solute Z caused a depression in freezing point of 1000g of benzene by 5.5^0C. Calculate the mass of Z in 50g of

benzene that would cause a freezing point depression of 0.44^0C

Task:4.11

Calculate the freezing point constant of camphor if a solution of 15.4g of naphthalene ($C_{10}H_8$) in 180g of camphor has a freezing point depression of 2.67^0C.

Task:4.12

Methanol, ethanol, ethan–1,2–diol and propan–1,2,3–triol are substances that can be used as antifreeze in car radiators. The winter spell of a cold country can reduce the temperature to as low as -5^0C. (K_f =1.86^0C/mole/1000g of water)

a. Calculate the mass of ethan–1,2–diol that should be added to a car radiator of capacity $10000cm^3$ of water so that the water remains as liquid for 5^0C below the lowest temperature that can be attained in the cold country.
b. Calculate the masses of Methanol, ethanol and propan–1,2,3–triol (glycerol) required to cause the same depression as above.
c. Tabulate the required masses in a) and b) above against the relative formula masses of the above antifreeze substances. Comment on the values in your table.
d. Using the mass of ethan–1,2–diol calculated in a) above, calculate the amount of freezing point depression that the same mass of the different antifreeze substances would cause in the car radiator.
e. Tabulate the freezing point depressions caused by equal mass of the different substances. Comment on the variation and state its significance

Task:4.13

a. Define the following:
   i. Saturated vapour pressure.
   ii. Lowering of vapour pressure.
   iii. Relative lowering of vapour pressure
   iv. Mole fraction.
b. Describe an experimental determination of cryoscopic costant of carbon disulphide.
c. Why is cryoscopy not suitable for determination of molar mass of a polymer?
d. At what temperature will a solution of 4.2g of solute Y (Mr=62) in 30g of water boil higher than normal boiling point of pure water (100^0C); K_b=0.52^0C/mole/1000g of water.
e. If the empirical formula of Y is CH_3O. Name Y.

Task:4.14

The table below shows the variation of temperature (T) with time when pure benzene and a solution of 0.32g of naphthalene ($C_{10}H_8$) in 25g of benzene are cooled.

Time/minutes	0	8	15	18	20	23	27
T – benzene/^0C	40	22.5	5	5	5	0.0	-
T – solution/^0C	40	25	10	4.5	4.5	4.5	0

a. On the same pair of axes, plot the cooling curves for pure benzene and the solution.
b. Determine the freezing points of pure benzene and of the solution and hence the depression in freezing point.
c. Calculate the molal freezing point depression constant of benzene.

Task:4.15

a. Define the following terms:
   i. Cryoscopic constant.
   ii. Ebullioscopic constant.

b. The table below shows the values of cryoscopic and ebullioscopic constants in ^0C/mole/1000g of some solvents.

Solvents	Cryoscopic constant	Ebullioscopic constant
Benzene	5.12	2.53
Camphor	40.00	6.00
Naphthalene	6.81	5.80
cycohexane	20.10	2.79
water	1.86	0.52

i. Comment on the values of cryoscopic and ebullioscopic constants for the different solvents.

ii. Explain the significance of your comments with respect to determination of relative formula mass.

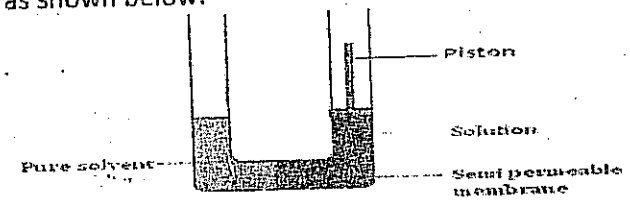
4.4 Osmotic pressure of a solution:

- Osmosis is the movement of solvent molecules from a region of high concentration to that of low concentration across a semi permeable membrane.
- Movement of molecules from a region of high concentration to that of low concentration is diffusion. Therefore osmosis is a special kind of diffusion in which:
- It is only the solvent molecules diffusing, and
- The diffusion requires a semi permeable membrane.
- A semi permeable membrane is a material or an interface which only allows a particular kind of particle/molecule to pass through, but retains the other.
- It is therefore selective in its permeability to molecules hence also described as selectively permeable membrane.
- For a solution, the membrane is always selectively permeable such that it only allows solvent molecules to pass through and not the solute.
- However, there is no ideal semi permeable membrane to hold solute particles because some solute particles generally

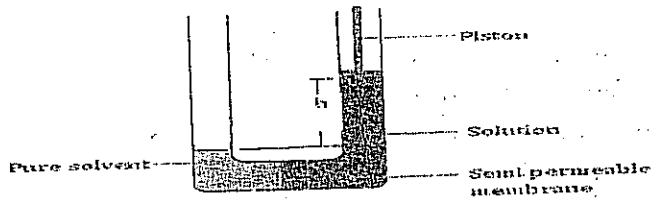
sneak through the tiny pores of the membrane; even; selective permeability depends on the sizes of the particle and the tiny pores of the membrane.

The osmotic pressure, Π

- Consider a pure solvent and its dilute solution of a non – volatile solute in the limbs of a manometer, separated by a semi permeable membrane, with a piston above the solution as shown below.



- After some time, pure solvent would pass through the semi permeable membrane and the piston will rise, as shown below:



- However, movement of the solvent and hence rise of the piston can be prevented by applying just the right external pressure on the piston.
- This right external pressure to be applied on the piston to stop the movement of solvent molecules to the solution side is called the ***osmotic pressure*** of the solution.

Definition:

i. ***Osmotic pressure of a solution:***
Is the pressure which must be applied on the solution to balance (stop) the tendency of the solvent to flow from the solvent side to the solution side across the semi permeable membrane.

ii. ***Osmometry:***
Is the method of determining formula mass of a non volatile solute by measuring the osmotic pressure of its dilute solution at a costant temperature.

Take note:

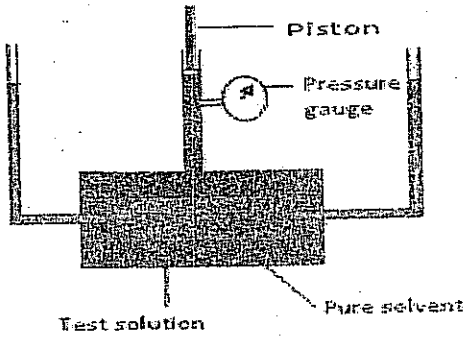
1. The pressure which is applied does not stop the diffusion of solvent molecules into the solution. It merely causes the solvent molecules to diffuse more rapidly through the membrane in the opposite direction. When the pressure is correctly adjusted a dynamic equilibrium will be established and solvent molecules diffuse in both directions at equal rates.
2. The osmotic pressure, Π can be calculated by using:
$\Pi = \rho hg$ 4.25
Where ρ is density of the solution, h is the difference in heights of the liquids in the two limbs of the manometer and g is acceleration due to gravity.
3. When the external pressure applied to stop the development of the osmotic pressure, is greater than the osmotic pressure itself, solvent molecules move generally from the solution side to pure solvent side across the semi permeable membrane. This phenomenon is known as ***reverse osmosis.***

Measurement of osmotic pressure.

- The osmotic pressure is measured by an apparatus known as the ***osmometer.***

- The osmometer widely used for measurement of osmotic pressure is that discovered by Hartley and Berkeley.
- It is made of a perforated horizontal tube, whose pores were sealed with copper (II) hexacyanoferrate (II) to provide the semi permeable membrane.
- The two ends of the tube are corked and then connected to two capillary tubes; water then filled in the tube until some rises in the capillary tubes.
- The horizontal tube is then enclosed in a metal jacket with a side arm containing a pressure gauge, from which an applied pressure can be read.
- The solution whose osmotic pressure is to be measured is then placed in the outer jacket and the whole apparatus thermostatted.

Illustration:



- As water osmotically enters the solution, the water level in the capillary tubes decreases.
- Pressure then applied on the piston of the side arm until the water levels in both capillary tubes remains constant.
- This applied pressure which arrests the fall in water level in the capillary tubes counterbalances the osmotic pressure and so is equal to the osmotic pressure of the dilute solution, and it is read from the gauge.

Factors that affect the value of osmotic pressure

1. **Concentration:**

- The osmotic pressure, Π of a solution is directly proportional to the concentration, at constant temperature i.e. the solution of higher solute concentration has a higher osmotic pressure and vice versa.

2. **Temperature:**

- Osmotic pressure of a solution increases with increase in thermodynamic temperature of the solution, if the concentration is constant.

Laws of osmotic pressure

1. The osmotic pressure of a solution is proportional to the concentration of the solution if temperature is constant.

   $\Pi \alpha C$

   But $C = \frac{n}{V}$

   $\Rightarrow \Pi \alpha \frac{n}{V}$ 4.26

   For one mole of a non volatile solute in a dilute solution,

   $n = 1$

   Hence, $\Pi \alpha \frac{1}{V}$ 4.27

   ⇒Osmotic pressure of a solution Π is inversely proportional to the volume of the dilute solution, at a constant temperature. (Analogous to Boyle's law).

2. The osmotic pressure of a solution is proportional to the Kelvin temperature if the concentration of solution is kept constant i.e.

   $\Pi \alpha T$ 4.28

   (Analogous to Pressure's law).

- From the two laws therefore, a dilute solution probably behaves as the ideal gas.
- Combining the two laws

  $\Pi V = nR^{I}T$ 4.29

  Where, R^{I} is molar ideal solution constant.
- R^{I} is approximately equal to the molar gas constant (8.31), at standard temperature of 298°K and a pressure of 760mmHg.
- The equation $\Pi V = nR^{I}T$, is called van't Hoff's equation for ideal solution, which can be rearranged to give:

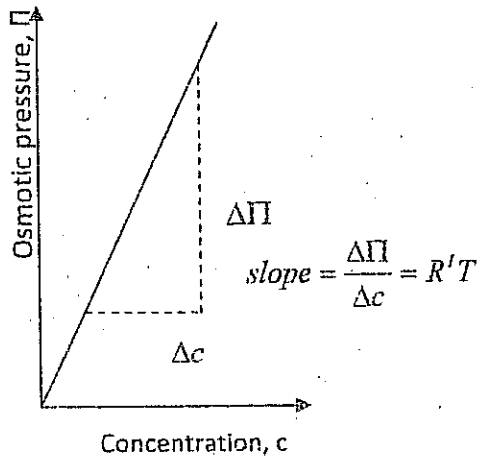
  $$\frac{\Pi_1 V_1}{T_1} = \frac{\Pi_2 V_2}{T_2} = ... = ... = \frac{\Pi_{(n-1)} V_{(n-1)}}{T_{(n-1)}} = \frac{\Pi_n V_n}{T_n} \text{ .....4.30}$$

  Dividing both sides of equation 4.29 by V;

  $\Rightarrow \Pi = \frac{n}{V} R^{I} T$, but $\frac{n}{V} = concentration, c$

  $\Pi = cR^{I}T$ 4.31
- A graph of osmotic pressure against concentration of the solute at a constant temperature gives a straight line with;

  Slope/gradient $= R^{I}T$



Applications/significance of osmosis:

- Osmosis is a physico – chemical process which majorly occurs in life forms. However, its model has been designed to enhance the understanding of the phenomenon.
- For the above reason therefore, apart from determination of relative molecular masses in solutions, the significance of osmosis is restricted to life forms:.
  - i. Support weak stems by turgor pressure.
  - ii. Passive uptake of minerals of finer particles dissolved in water.
  - iii. Osmoregulation and excretion.
  - iv. Stomatal opening and closure.

Worked example:4.5

Calculate the osmotic pressure of 0.1M sucrose ($C_{12}H_{22}O_{11}$) solution at 25^0C.

$V = 1000cm^3 = \frac{1000}{1000000}m^3$, n = 0.1moles, T = (273 + 25) = 298k, R = 8.31J/mol/K, Π=?

From, ΠV=nRT

$$\Rightarrow \Pi \times \frac{1000}{1{,}000{,}000} = 0.1 \times 8.31 \times 298$$

$$\Pi = 247{,}638 Nm^{-2}$$

Task:4.16

What mass of urea (M_r=60) must be dissolved in $500cm^3$ of water to make it dilute solution have an osmotic pressure of $5000\ Nm^{-2}$ at 30^0C?

Task:4.17

The osmotic pressure of 18g of glucose ($C_6H_{12}O_6$) in $240cm^3$ of water is equal to the osmotic pressure of 25g of a macromolecular compound solution in $100cm^3$ of water at

the same temperature. Calculate the formula mass of the compound.

Task:4.18

A sugar solution containing $2.5gdm^{-3}$ gave an osmotic pressure of $8.3x10^{-4}$atm at 30^0C. Calculate the mass of the same sugar that must be dissolved in $24dm^3$ of water at 25^0C to give an osmotic pressure of one atmosphere.

Task:4.19

$5gdm^{-3}$ of a polymer whose monomer has a mass of 25g has an osmotic pressure of 1.2kPa at 30^0C.

a. Calculate the molecular mass of the polymer.
b. The number of monomer units in the polymer.

Task:4.20

The table below gives the values of osmotic pressure (Π) at 25^0C for various concentrations (c) of solute X.

c/gdm^{-3}	1	3.8	6.2	9	11.2	13.2
Π/ kPa	3	11	18	26	32	38

a. Plot a graph of osmotic pressure against the concentration of the solute.
b. Use the graph to calculate the formula mass of the solute.

Task:4.21

The osmotic pressure of a dilute solution of a non volatile solute, π appears in the expression: πV=nRT.

a. Define all the terms in the expression.
b. Show that the molar mass of the non volatile solute is given by: $\frac{c}{\pi}RT$, where c is the concentration of the solute.

2.5g/dm³ of a s/n of substance has an osmotic pressure of 8.3×10⁻⁴ atm. at 25°C. Calculate the molar mass of the substance X.

Is used to determine substance that can decompose near their boiling points.

Task:4.22

a. With the aid of a labeled diagram, describe how osmotic pressure of a dilute aqueous solution of proptein can determined.

b. A 5% solution of a protein whose amino acid building block has a formula mass of 76 was found to have osmotic pressure of 1.63×10^{-3} Nm^{-2} at 25^0C. Calculate:

i. The formula mass of the protein

ii. How long is the protein?

Worked example:4.6

Explain why osmotic pressure measurement (osmometry) is preferred to cryoscopy and ebullioscopy when measuring the formula mass of a polymer.

Solution:

Osmotic pressure, depression in freezing point and elevation of boiling point are colligative properties and so their values inversely depend on relative molecular mass of the solute. Polymers have high molecular masses and so would give a very small depression in freezing point and elevation in boiling point, which are always immeasurable. Unlike their osmotic pressures which are always significant and easily measurable.

Alternatively:

Polymers tend to have stronger van der Waal's forces due to the big size of their molecules. Hence have higher melting and boiling points, difficult to determine in a laboratory set up.

Why is the relative molecular masses of polymers determined using osmotic pressure method rather than boiling point elevation / freezing depression

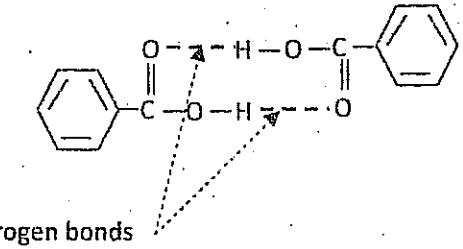
* The O.P is the method used 2 determine substance is higher molecular mass that gives

a measurable osmotic pressure yet they would give extremely small elevation & lowering of fp.

4.5 Correcting for association and dissociation/ ionization of solute particles:

a. Association:

- ***Association*** refers to the joining of solute particles (atoms, molecules or ions) to form bigger particles. This joining is majorly through hydrogen bonding or dative bonding. For example in benzene, two molecules of any carboxylic acid associate through hydrogen bonding to form a dimer (a bigger molecule), as shown below for benzoic acid;



- This has a net effect of reducing the number of solute particles. Since colligative properties depend on the number of particles, the value of the property is also reduced (smaller than expected without association). However, the experimental relative formula mass is greater than expected.

b. Dissociation and Ionization

- ***Dissociation*** is the production of free ions from ionic compounds i.e.

$NaCl(s) \xrightarrow{heat} Na^+(l) + Cl^-(l)$

- ***Ionization*** is the production of free ions from molecular substances often after dissolving in water.e.g.

$H_2SO_4(l) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$

- The two processes increase the number of solute particles and hence the value of a colligative property is bigger than expected. However, the experimental relative formula mass of the non volatile solute is smaller than expected. It is

always the arithmetic average of the masses of the produced particles.

- **Degree of association** refers to the fraction of one mole of a solute that has undergone association.
- **Degree of dissociation** refers to the fraction of one mole of a solute that has undergone dissociation.
- **Degree of ionization** refers to the fraction of one mole of a solute that has undergone ionization.
- **Observed colligative property:** This is the experimental or empirical or actual or apparent colligative property, taking into consideration association and dissociation.
- **Theoretical colligative property** is the expected value of colligative property assuming no association or dissociation.

Summary of effect of association and dissociation/ionization:

Quantity	Association/~~ionization~~ Ionisation	Dissociation
Number of particles	Decreases	Increases
Colligative properties	Decreases	Increases
RMM	Increases	Decreases

4.5.1 Correcting for dissociation:

- Consider 1 mole of a non volatile solute 'A' that undergoes dissociation in the solvent as shown below:

$$A \rightleftharpoons B + C + D + E$$

	A	B	C	D	E
Initially	1mole	0mol	0mol	0mol	0mol
Stoichiometrically;	1mol	1mol	1mol	1mol	1mol
At equilibrium;	(1−α)	α	α	α	α

Where α is the degree of dissociation

- Introduced number of particles (expected number of particles) =1mole
- Observed number of particles (practicle number of particles)

=(1−α)+α+α+α+α =1+3α

- Generally, it is given by; 1+(N−1)α

Where, N is the number of dissociated particles

- van't Hoff's factor, *i* is the ratio of observed colligative property to theoretical value.

$$i = \frac{CP_{observed}}{CP_{theoretical}},$$

where $CP_{observed}$ is the observed colligative property and $CP_{theoretical}$ is the expected colligative property.

Also, Also, $i = \frac{N_{observed}}{N_{theoretical}}$,

where $N_{observed}$ is the number of particles after dissociation and $N_{theoretical}$ is the number of particles assuming no dissociation.

$$\Rightarrow i = \frac{1+(N-1)\alpha}{1} \quad \text{.....4.32}$$

$$\text{So that, } \alpha = \left(\frac{i-1}{N-1}\right) \quad \text{.....4.33}$$

4.5.2: Correcting for association:

- Consider one mole of a non – volatile solute that undergoes association in a solvent as shown below.

$$A \rightleftharpoons \frac{1}{n}A_n$$

	A	$\frac{1}{n}A_n$
Initially;	1mol	0mol
Stoichiometrically;	1mol	$\frac{1}{n}mol$
At equilibrium;	$(1-\alpha)mol$	$\frac{\alpha}{n}mol$

- Introduced number of particles/expected number of particles =1

- Observed number of particles/practical number of particles =

$$(1-\alpha)+\frac{\alpha}{n}=\frac{n+(1-n)\alpha}{n}$$

- van't Hoff's factor, i is the ratio of observed colligative property to theoretical value.

$$i=\frac{CP_{observed}}{CP_{theoretical}},$$

where $CP_{observed}$ is the observed colligative property and $CP_{theoretical}$ is the expected colligative property.

Also, $i=\frac{N_{observed}}{N_{theoretical}}$, where $N_{observed}$ is the number of particles after association and $N_{theoretical}$ is the number of particles assuming no association.

$$\Rightarrow i=\left(\frac{\frac{n+(1-n)\alpha}{n}}{1}\right)=\frac{n+(1-n)\alpha}{n} \quad \text{.....4.34}$$

Making α subject;

$$\alpha=\left(\frac{(i-1)n}{1-n}\right) \quad \text{.....4.35}$$

When n=2, as in dimerization of carboxylic acids in benzene,

$$i=\frac{2+(1-2)\alpha}{2}$$

$$\Rightarrow i=2+\frac{\alpha}{2} \quad \text{.....4.36}$$

Worked example:4.7

The boiling point of pure water at 760mmHg is 100°C. At the same pressure a solution of 0.29g of sodium chloride in 11g of water boils at a temperature 0.443°C higher.

a. Calculate the boiling point of sodium chloride assuming it did not dissociate in water (K_b=0.52°C mole per 1000g of water).
b. Use your answer in a) above to calculate the apparent degree of dissociation of sodium chloride in water.

Solution:

a. 11g of water dissolved 0.29g of sodium chloride.

1000g of water would dissolve $\frac{1000\times 0.29}{11}=26.3636g$

RFM of NaCl = (23x1) + (35.5x1) = 58.5.

58.5g of sodium chloride in 1000g of water elevate by 0.52°C

26.3636g in 1000g of water will elevate by $\frac{26.3636\times 0.52}{58.5}=0.234$

Hence boiling point of the above solution is 100 + 0.234 = 100.234°C

b. Observed boiling point elevation = 0.443°C

Theoretical boiling point elevation = 0.234°C

Sodium chloride dissociates in water according to the equation:

$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$

From $i=\frac{C.P_{Observed}}{C.P_{Theoretical}}$,

$$\Rightarrow i=\frac{0.443}{0.234}=1.893$$

From $\alpha=\frac{i-1}{N-1}$, N = 2

$$\Rightarrow \alpha=\frac{1.893-1}{2-1}=0.893=89.3\%$$

Task:4.23

At certain pressure, pure water freezes at 0°C.

a. Calculate the freezing point of 0.1M solution of;

i. Potassium iron (III) sulphate and

ii. Potassium hexacyanoferrate (III), assuming no dissociation

b. Calculate their experimental freezing points, assuming they are 100% dissociated in solution. (K_f=1.86^{0}C/mol per 1000g of water)

Task:4.24

A certain organic acid was dissolved to form two of its solutions as follows:

- Solution X contains 1.45g of the acid in 10g of water.
- Solution Y contains 70.41g of the acid in 1000g of benzene.

The two solutions above had vapour pressures of 99.13kPa and 99.02kPa respectively at the boiling points of the pure solvents at 760mmHg.

a. Calculate the relative molecular mass of the acid in water and benzene.

b. Comment on the two values above and briefly explain the comment.

Task:4.25

When 3.6g of sulphur is dissolved into 240g of carbon disulphide the elevation of boiling point at the same pressure was 0.14^{0}C (K_b=2.35^{0}C/mol per 100g of carbon disulphide)

a. Calculate the formula mass of sulphur in carbon disulphide

b. Deduced the structure of sulphur in carbon disulphide.

Task:4.26

The saturated vapour pressure of water at a certain temperature is 4040Nm^{-2}. Calculate the lowering of vapour

pressure of water by dissolving 16.4g of calcium nitrate in 108g of water. Given that under these conditions, calcium nitrate is 95% dissociated.

By dissolving 8.5g of common salt in 125g of H_2O at a constant temperature, the vapour pressure was depressed from 2661Nm^{-2} to 2561Nm^{-2}. Calculate the degree of dissociation of common salt at this dilution and temp.

CHAPTER FIVE: THERMOCHEMISTRY:

5.0 Introduction:

- When some chemical reactions take place, the temperature of the reaction mixture increases. In this case, literally, chemical energy has been converted to heat energy.
- Examples include: burning of charcoal, paper, hydrocarbons, neutralization reactions, and so on.
- Conversely, when some chemical reactions take place, the temperature of the reaction mixture decreases. In this case, literally, heat energy has been converted to chemical energy.
- Examples include: dissolution of salts like ammonium nitrate, potassium iodide, hydrated copper (II) sulphate, and so on.
- All the above examples illustrate the inter–conversion between chemical and heat energies during chemical reactions.
- However, this inter–conversion is easily quantifiable in terms of the heat produced during a chemical reaction or heat absorbed during a chemical reaction **(heat changes).**

Key terms:

a. **Thermochemistry:**
This is the study of heat changes that accompany chemical reactions.

b. **Internal energy (U):**
This is the total amount of energy in a chemical substance.

- A chemical substance possesses energy as a result of:
  1. Translation and rotation about molecular axis; and vibration about mean positions of the particles i.e. kinetic energy.
  2. Chemical bond i.e. potential energy, as a result of net nuclear–electronic attraction.
- The combination of kinetic and potential energies gives the internal energy of a chemical substance.

c. **Enthalpy (H):**
This is the heat content of a chemical substance. It represents the total bond energy in a chemical substance.

d. **Enthalpy change (ΔH):**
This is the heat change that accompanies a chemical reaction.

- It is given by:
The bond energy (heat content) of products minus the bond energy (heat content) of the reactants.
Heat content of product(s) – Heat content of reactant(s)
- For example:
  a. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
  $\Delta H = (H_{2H_2O}) - (H_{2H_2} + H_{O_2})$
  b. $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$
  $\Delta H = (H_{NaCl} + H_{H_2O}) - (H_{NaOH} + H_{HCl})$

e. **Exothermic reactions:**
These are reactions which proceed with net evolution of heat energy to the surrounding.

- For exothermic reactions, the temperature of reaction mixture increases as reaction proceeds.
- Examples of exothermic reactions include: most neutralization reactions and all combustion reactions.
- For any exothermic reaction:
$H_{Products} < H_{Reactants}$, hence $\Delta H = -ve$
$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g); -393 kJmol^{-1}$

f. **Endothermic reactions:**

- These are reactions which proceed with net absorption of heat energy from the surrounding.
- For endothermic reactions, the temperature of the reaction mixture decreases as the reaction proceeds.

- Examples of endothermic reactions include formation of carbon disulphide from sulphur and carbon. dissolving NH_4NO_3 & anhydrous $CuSO_4$
- For any endothermic reactions:

  $H_{Products} > H_{Reactants}$, hence $\Delta H = +ve$

  $NH_4NO_3(s) + (aq) \longrightarrow NH_4NO_3(aq); +25.8kJmol^{-1}$

  Take note:

  In both exothermic and endothermic reactions, the temperature of the surrounding is changed but afterwards, the heat energy redistributes itself so that the temperature of the reaction system and the surrounding is the same.

5.1 Transition state theory of chemical reactions:

- According to this theory, for a chemical reaction to proceed/take place, the reactant particles must first acquire a certain minimum amount of energy.
- This minimum amount of energy required by reactant for the reaction to proceed is known as the **activation energy.**
- The moment this activation energy is just acquired, then the reactant is converted to a transition state known as **activated complex.**
- In this state, there is equal possibility of the complex forming product(s) and converting back to reactant(s).

Definitions

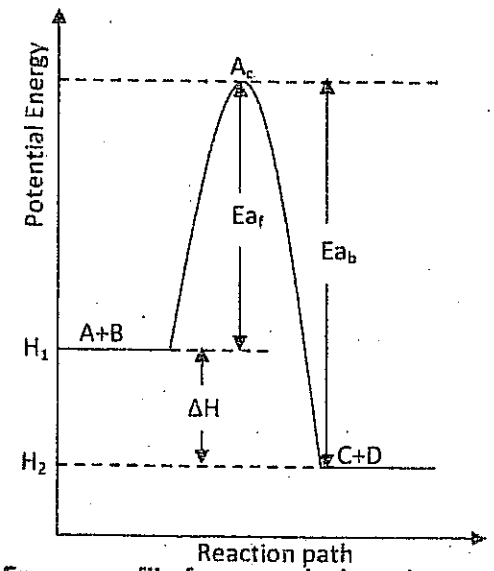
i. **Activation energy:**
This is the minimum amount of energy that the reactant(s) must acquire before conversion to product(s).

ii. **Activated complex:**
This is a short lived reaction intermediate characterized by highest potential energy, abnormal bond number and length in the reaction path.

iii. **Energy profile:**
Is a plot of variation in potential energy of reactant(s) against reaction path.

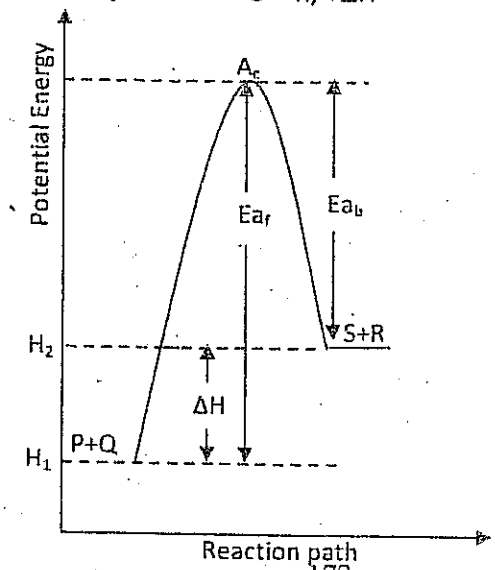
Energy profile for an exothermic reaction:

$A + B \longrightarrow C + D; -\Delta H$



Energy profile for an endothermic reaction:

$P + Q \longrightarrow S + R; +\Delta H$



Definitions:

- H_1: Heat content of reactants.
- H_2: Heat content of the products.
- A_c: Activated complex.
- Ea_f: Activation energy for forward reaction.
- Ea_b: Activation energy for backward reaction.
- ΔH: Enthalpy change for the reaction.

Take note:

$\Delta H = H_2 - H_1$

Or

$\Delta H = Ea_f - Ea_b$

ΔH is positive for endothermic reactions and negative for exothermic reactions.

Reaction path ≡reaction coordinate ≡extent of reaction ≡ reaction mechanism.

Task:5.1

- Before a chemical reaction can take place, the reactants must acquire activation energy then form a reaction intermediate known as activated complex.

a. what is:
   Activation energy?
   Activated complex?
b. State the purpose of the activation energy.
c. Give four characteristics of activated complex.

5.2 Laws of thermochemistry:

1. The enthalpy change of a reaction is directly proportional to the amount of reactant(s) used or product(s) formed i.e.

$$A + B \longrightarrow C + D;\ \Delta H = Q$$
$$2A + 2B \longrightarrow 2C + 2D;\ \Delta H = 2Q$$

2. *The law of Lavoisier and Laplace:*
   The enthalpy changes for forward and backward reactions are equal in magnitudes but opposite in signs.
   - From this law, it follows that for a reversible reaction, if the forward reaction is endothermic, then the backward reaction is exothermic.

$$A + B \longrightarrow C + D;\ +\Delta H$$
$$C + D \longrightarrow A + B;\ -\Delta H$$

3. *Hess' law:*
   The enthalpy change of a chemical reaction is independent of the number of pathways the reaction goes through but only depends on the heat contents of the reactants and final products.
   - Consider the formation of aqueous solution of ammonium chloride from solid ammonium chloride. This can be done by:

a. Directly dissolving solid ammonium chloride in water:
   $NH_4Cl(s) + aq \longrightarrow NH_4Cl(aq);\ \Delta H_1$
b. Indirectly through the following steps:
   i. Decomposing the solid ammonium chloride into gaseous ammonia and hydrogen chloride:
      $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g);\ \Delta H_2$
   ii. Dissolving ammonia gas in water to form aqueous ammonia:
      $NH_3(g) + aq \longrightarrow NH_3(aq);\ \Delta H_3$
   iii. Dissolving hydrogen chloride gas in water to form hydrochloric acid:
      $HCl(g) + aq \longrightarrow HCl(aq);\ \Delta H_4$
   iv. Reacting aqueous ammonia and the hydrochloric acid to form ammonium chloride solution:
      $NH_3(aq) + HCl(aq) \qquad NH_4Cl(aq);\ \Delta H_5$

- From Hess' law, reaction a) begins with solid ammonium chloride and produces ammonium chloride solution. Reaction b) with the four steps/pathways i), ii), iii) and iv)

$10cm^3$ of a base MOH was placed in five different but identical beakers at an initial temperature of 26^0C. To each beaker containing MOH of known concentration, was added $25cm^3$ of 1M hydrochloric acid. The mixture was stirred with a thermometer and the final temperature recorded as shown below:

Beaker number	1	2	3	4	5
Concentration of MOH/g/dm^3	2.0	4.0	8.0	16.0	64.0
Temperature rise	1.0	2.0	3.0	4.0	5.0

b. Plot a graph of temperature rise against the concentration of MOH.

c. Use your graph to determine the relative atomic mass of M.

d. Calculate the enthalpy of the above neutralization.

5. Enthalpy of displacement:

- Metals higher in the electrochemical series displace those lower in the series.
- For example, iron filings displace copper from its solutions according to the ionic equation:

  $Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$
- Also, more electronegative non metals displace less electronegative ones from their solutions.
- For example, when chlorine is bubbled into iodide ions solution, iodine is displaced according to the ionic equation:

  $Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq)$

of an element is displaced from its solution by another element.

Task:5.17

a. What is meant by enthalpy of displacement?

Copper (II) ions react with iron filings according to the equation:

$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq); -126\ kJmol^{-1}$

The table below shows the results obtained when 2g of iron filings were added to $40cm^{3+}$ of copper (II) sulphate solution.

Time/min	0	1	2	3	4	5	6	7
Temp/^0C	22.0	29.0	34.0	36.5	36.0	35.5	34.0	33.5

b. Plot a graph of temperature against time and use it to determine moles of copper (II) sulphate reacted and the concentration of copper (II) sulphate solution.

c. Plot a graph of temperature rise against time and use it to determine the moles of copper (II) sulphate reacted and hence it's molar concentration.

6. Enthalpy of precipitation:

- On mixing some two of more aqueous solutions, a precipitate is formed.
- For example:

i. When sodium hydroxide solution is mixed with copper (II) ions solutions, copper (II) hydroxide is precipitated according to the ionic equation:

pressure of 1 atmosphere (760mmHg).

ii. When a compound is formed endothermically i.e. an endothermic compound, it is thermodynamically less

stable compared to the elements from which it is formed.

iii. Standard enthalpy of formation of a pure element is conventionally taken to be 0 since it can not accurately be experimentally determined.

Indirect determination of enthalpy of formation:

- This is based on application of Hess' law of constant heat summation on given thermochemical data, always including enthalpy of combustion.

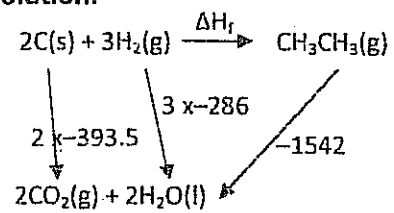
Worked example: 5.1

Given the following thermochemical data, calculate the standard enthalpy of formation of ethane:

- $C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H_c^0 = -393.5 kJmol^{-1}$ 1
- $H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(l);\ \Delta H_c^0 = -286 kJmol^{-1}$ 2

$CH_3CH_3(g) + {}^7/_2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);\ \Delta H_c^0 = -1542 kJmol^{-1}$ 3

Solution:



From Hess' law of constant heat summation,

$\Delta H_f + -1542 = (2 \times -393.5) + (3 \times -286)$

$\Delta H_f = -103 kJmol^{-1}$

Alternatively:

2x1st equation + 3x2nd equation:

$2C(s) + 2O_2(g) + 3H_2(g) + {}^3/_2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);$

$2C(s) + {}^7/_2O_2(g) + 3H_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); -1645$.....4

Equation 4 + the reverse of equation 3 and cancelling common species on both sides:

$2C(s) + 3H_2(g) \longrightarrow CH_3CH_3(g); -103\ kJmol^{-1}$

Take note:

a. Multiplying/dividing an equation by an integer multiplies/divides the enthalpy change by the same integer.

b. Reversing an equation reverses the sign of the enthalpy change.

Task: 5.2

Given the thermochemical data below.

- $C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H_c^0 = -393.5 kJmol^{-1}$ 1
- $H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(l);\ \Delta H_c^0 = -286 kJmol^{-1}$ 2
- $C_6H_{14}(l) + {}^{19}/_2O_2(g) \longrightarrow 6CO_2(g) + 7H_2O(l); -4141 kJmol^{-1}$ .3

Calculate the standard enthalpy of formation of hexane. Comment on the value of enthalpy of formation of hexane.

Task:5.3

The table below shows the standard enthalpy of combustion of some substances:

Substance	Enthalpy of combustion ($kJmol^{-1}$)
Sulphur	–296.9
Hydrogen	–285.8
Carbon disulphide	–1075
Propane	–2202
Carbon dioxide	–393

Calculate the standard enthalpy of formation of carbon disulphide and propane.

Take note:

Given standard enthalpies of formation of reactants and the products of a reaction, the heat of the reaction can be calculated using the formula:

$\Delta H = \sum\Delta H_f$ of products $- \sum\Delta_f$ of reactants.

Worked example:5.2

The table below shows the standard enthalpy of formation some substances:

Substance	ΔH_f kJmol^{-1}
Water	−285.8
Carbon disulphide	+87
Propene	+20.4
Methylbenzene	+12.1
2,2 – dimethylpropane	−189.8
Propan – 2 – ol	−327.4
Sulphur dioxide	−296.9
Carbon dioxide	−393.5

Calculate the enthalpy for the following reactions:

a. $CS_2(l) + 3O_2(g) \longrightarrow 2SO_2(g) + CO_2(g)$

b. $C_3H_8O(l) + {}^9/_2O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

Solution:

a. From $\Delta H = \sum\Delta H_f$ of products $- \sum\Delta_f$ of reactants.

$\Delta H = \{(2 \times -296.9) + (-393.5)\} - (+87 + 0)$

$\Delta H = -1074.3 kJmol^{-1}$

b. From $\Delta H = \sum\Delta H_f$ of products $- \sum\Delta_f$ of reactants.

$\Delta H = \{(4 \times -285.8) + (3 \times -393.5)\} - (-327.4 + (0 \times {}^9/_2)$

$\Delta H = -1996.3 kJmol^{-1}$

Task:5.4

Use the above table to calculate the enthalpy change for the following reactions:

a. Combustion of methylbenzene.

b. Combustion of 2,2 – dimethylpropane.

Task:5.5

Using the thermochemical data below:

Substance	$\Delta H_c^\theta (kJmol^{-1})$
Hydrogen	−285.8
Carbon	−393.5
Benzene	−3273
Ethyne	−1305

Calculate the standard enthalpy of formation of benzene and ethyne.

Task:5.6

Given the following reactions:

$2Al(s) + {}^3/_2O_2(g) \longrightarrow Al_2O_3(s)\ \Delta H_r^\theta = -1673.6 kJmol^{-1}$

$2Fe(s) + {}^3/_2O_2(g) \longrightarrow Fe_2O_3(s)\ \Delta H_r^\theta = -836.8 kJmol^{-1}$

a. Write the equation for the reaction between iron and aluminium oxide and calculate its enthalpy change.

b. Write the equation for the reaction between aluminium metal and iron (III) oxide and calculate the enthalpy change for the reaction.

c. Comment on the reactions in a) and b) above. Explain your comment.

Task:5.7

The table below shows the standard enthalpy of formation of some substances:

Substance	Standard enthalpy of formation
Steam	$-242\ kJmol^{-1}$
Nitric acid	$-176\ kJmol^{-1}$

a. Write the equation for the formation of one mole of nitric acid from nitrogen gas, steam and oxygen gas.
b. Calculate the enthalpy change for the above reaction.

Task:5.8

Using the thermochemical data below, calculate the enthalpy of formation of solid rubidium sulphate.

- $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$: $-57.3kJmol^{-1}$
- $RbOH(s) + aq \longrightarrow Rb^+(aq) + OH^-(aq)$: $-62.8kJmol^{-1}$
- $Rb_2SO_4(s) + aq \longrightarrow 2Rb^+(aq) + SO_4^{2-}(aq)$: $+24.3kJmol^{-1}$
- $H_2(g) + S(s) + 2O_2(g) + aq \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$: $-907.5kJmol^{-1}$
- $H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(l)$: $-285.0kJmol^{-1}$
- $Rb(s) + {}^1/_2O_2(g) + {}^1/_2H_2(g) \longrightarrow RbOH(s)$; $-414.0\ kJmol^{-1}$

Task:4.9

The data below is for the formation of sulphur dioxide at 298K from rhombic and monoclinic sulphur. Use the information to state which of the two allotropes of sulphur is stable at 298K.

$S_{(rhombic)}(s) + O_2(g) \longrightarrow SO_2(g)$: $-297.0kJmol^{-1}$

$S_{(monoclinic)}(s) + O_2(g) \longrightarrow SO_2(g)$: $-297.3kJmol^{-1}$

Task:5.10

Using the thermochemical data below:

- $H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(l)$: $-285.0kJmol^{-1}$
- $Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(s)$: $-205.0kJmol^{-1}$
- $Na(s) + H_2O(l) + aq \longrightarrow NaOH(aq) + {}^1/_2H_2(g)$: $-410.0kJmol^{-1}$

- $NaOH(s) + aq \longrightarrow NaOH(aq)$: $-56.5kJmol^{-1}$

a. Calculate the heat of formation of sodium ~~chloride~~ oxide
b. Comment of the enthalpy of formation above.

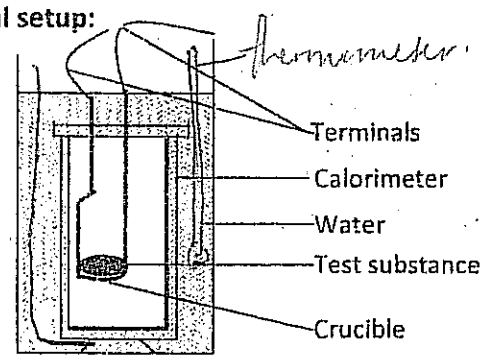
3. Standard Enthalpy of Combustion (ΔH_c^θ)

- Standard enthalpy of combustion is the heat given out when one mole of a substance in its standard state at 298K and 760mmHg pressure is completely burnt in oxygen.
- The phrase 'heat given out' is to refer to the fact that all combustion reactions are exothermic.

Experimental determination of enthalpy of combustion by direct method:

- A fixed mass 'w' of a substance whose enthalpy of combustion is to be determined is put in the crucible of a bomb calorimeterof mass 'm'.
- The calorimeter is then filled with oxygen at a high pressure.
- The calorimeter is then placed in water of known mass 'm_1' fitted with a thermometer and stirrer.
- The initial temperature of the water is then noted.
- The substance is then electrically fired to complete combustion and the highest temperature attained by water noted.

Experimental setup:



Treatment of the results:

Theory:

i. As the substance is burnt, the heat produced as a result of its combustion is in part absorbed by the calorimeter and in part goes to water hence temperature rise.

ii. The heat that is absorbed by the calorimeter and gained by water also comes from the heating effect of electric current on the wires, and let this heat be H

Let the heat capacity of the calorimeter be 'h', the molar mass of the substance be M and the temperature rise be't'.

Heat evolved = heat gained by calorimeter + heat absorbed by water

= (m x t x h) + (m_1 x t x c)

Heat energy produced by the substance alone = t(mh+m_1c)–H

wg of the substance produced t(mh + m_1c)–H

Mg of the substance would produce $\left(\frac{M}{w}\right)t(mh+m_1c)-H$

Therefore, $\Delta H_c = -\left(\frac{M}{w}\right)t(mh+m_1c)-HJmol^{-1}$

Determination of standard enthalpy of combustion by indirect method:

- This is based on application of Hess' law on given thermochemical data, always containing standard enthalpy of formation.

Worked example:5.3

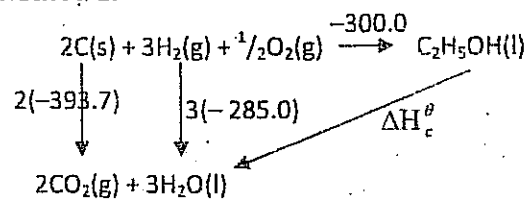
Write the equation for the complete combustion of ethanol. Using the information in the table below, calculate the standard enthalpy of combustion of ethanol.

Substance	$\Delta H_f^\theta kJmol^{-1}$
Carbon dioxide	–393.7
Ethanol	–300.0
Carbon monoxide	–111.7
Water	–285.0

Solution:

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

Method 1:



From Hess' law of constant heat summation;

$-300.0 + \Delta H_c^\theta = 3(-285.0) + 2(-393.7)$

$\Delta H_c^\theta = -1342.4kJmol^{-1}$

Method 2:

$H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(l)$: $-285.0kJmol^{-1}$.....1

$C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_c^\theta = -393.7kJmol^{-1}$.....2

$2C(s) + 3H_2(g) + {}^1/_2O_2(g) \longrightarrow C_2H_5OH(l)$: $-300.0kJmol^{-1}$....3

Reverse of equation 3 + 3 x equation 1 + 2 x equation 2, and cancelling common species on both side:

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$: 3(–285.0) + 2(–393.7) + 300.0 = –1342.4

Therefore, $\Delta H_c^\theta = -1342.4kJmol^{-}$

Task:5.11

Given the enthalpy of formation of the substances in the table:

Substance	$\Delta H_f^\theta kJmol^{-1}$
Octane	−250.0
Cyclohexane	−156.2
Propan – 1 – ol	−300.0
Ethylbenzene	−13.1
Methanol	−239.0
Carbon dioxide	−393.7
Water	−285.0

Calculate the enthalpy of combustion of:

a. Cyclohexane.
b. Ethylbenzene.
c. Propan – 1 – ol
d. Octane.
e. Methanol.

Task:5.12

The data below shows thermochemical information about some substances:

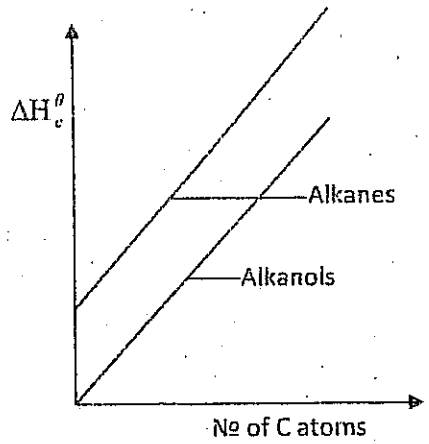
- $H_2(g) + {}^1/_2O_2(g) \longrightarrow H_2O(l)$: $-285.0kJmol^{-1}$
- $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_c^0 = -393.5kJmol^{-1}$

Calculate the heat energy obtained by burning $100cm^3$ of octane if its density is $0.73kgm^{-1}$ and standard enthalpy of formation is $-268.4kJmol^{-1}$

Task:5.13

a. What is meant by enthalpy of combustion?
b. With the aid of a diagram, describe an experiment to determine the enthalpy of combustion of sulphur.

The enthalpies of combustion of straight chain alkanes and alkanols vary with the nuber of carbon atoms as shown below:



c. State the similarities and differences between the two graphs.
d. Explain the similarities and the differences in c) above.

Task:5.14

a. State Hess, law.

Given the data in the table below:

Substance	$\Delta H_c^\theta kJmol^{-1}$
Benzene	−3268
Cyclohexane	−3920
Cyclohexene	−3754
Hydrogen	−286

b. Explain the trend in the variation of standard enthalpy of combustion of cyclohexane, cyclohexene and benzene.
c. Calculate the enthalpy of hydrogenation of cyclohexene and benzene.
d. Comment and explain your comment on the two enthalpies of hydrogenation.

Importance of enthalpy of combustion

a. **In the recommendation of dietary intake:**
Nutritionists first examine the extent a patient is malnourished then recommend a food supplement/formula depending on the calorific value of the food.

b. **Pricing of fuels.**
Expensive fuels have higher calorific values than less expensive fuels.

c. **Grouping of chemical substances and hence elucidation of reaction mechanisms.**
Substances within the same group (i.e. homologues) have similar enthalpies of combustion and hence show similar reactions.

4. Standard Enthalpy of Neutralization (ΔH_n^θ)

This is the heat give out when one mole of aqueous hydrogen ions reacts with one mole of aqueous hydroxyl ions to form one mole of water at 298K and 760mmHg.

Alternatively;

It's the heat given out when one mole of water at 298K and 760mmHg is formed from aqueous solutions of an acid and a base.

- The enthalpy of neutralizations of strong acids by strong bases are constant and higher as shown in the table below:

Acid	alkali	$\Delta H_n^\theta kJmol^{-1}$
Nitric acid	Sodium hydroxide	−57.1
Sulphuric acid	Sodium hydroxide	−66.5
Hydrochloric acid	Potassium hydroxide	−57.3
Nitric acid	Potassium hydroxide	−57.3

- The heats of neutralization of strong acids and bases are high and because they are completely ionized producing many

hydroxyl and hydrogen ions which readily react producing a lot of energy.

- The heats of neutralization are fairly constant because the basic reaction is the combination between aqueous hydrogen ions and aqueous hydroxyl ions to form water, according to the ionic equation:
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); -\Delta H$
- Heats of neutralization of weak acids or bases are not constant and are lower as shown in the table below:

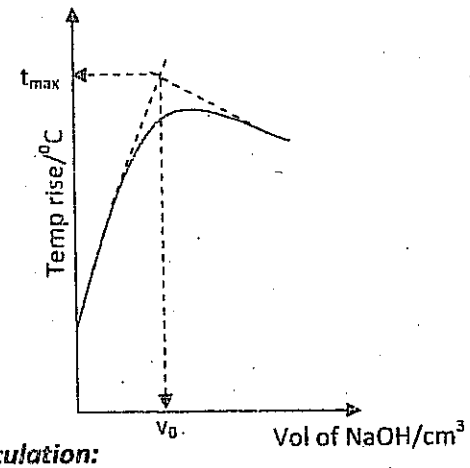
Acid	alkali	$\Delta H_n^\theta kJmol^{-1}$
Hydrogen sulphide	Sodium hydroxide	−16.0
Hydrocyanic acid	Sodium hydroxide	−12.0

- The heats of neutralization of weak acids and bases are low and not constant because the acids or bases are only slightly ionized producing a few hydroxyl or hydrogen ions which react to produce only a small amount of heat. Moreso, some of the heat produced is often used up to drive the ionization process which further reduces the enthalpy value. The enthalpies are not constant because the different weak bases and acids are ionized to a different degree.

Experimental determination of enthalpy of neutralization for example sodium hydroxide solution and hydrochloric acid:

- Record the room temperature and into eight plastic beakers labeled 1 – 8, add each 15cm^3 of 2M hydrochloric acid.
- Then add 40cm^3, 35cm^3, 30cm^3, 25cm^3, 20cm^3, 15cm^3, 10cm^3 and 5cm^3 of distilled water respectively to the beakers.
- To the first beaker, add 5cm^3 of 2M sodium hydroxide solution; stir with a thermometer and record the highest temperature attained.

- Repeat the above procedure with the remaining beakers, adding $10cm^3$, $15cm^3$, $20cm^3$, $25cm^3$, $30cm^3$, $35cm^3$ and $40cm^3$ of the 2M hydrochloric acid respectively.
- Tabulate the results showing highest temperature attained and volume of sodium hydroxide added.
- Then a graph of highest temperature attained against volume of sodium hydroxide added is plotted.



Calculation:

- To obtain maximum temperature rise and volume of sodium hydroxide at the end point, tangents are drawn as shown above.
- Assuming the solution is so dilute, then, specific heat capacity = 4.2J/g/^{0}C, and density = $1gcm^{-3}$
- Total volume of the solution at the end point is give by (v_0 + volume of distilled water added + 15) = V
- Mass of the solution = 1 x V = Vg
- Heat gained by the solution = V x 4.2 x t_{max}

$1000cm^3$ of NaOH contained 2 moles

v_0cm^3 would contain $\frac{2v_0}{1000} = \frac{v_0}{500} mol$

$\frac{v_0}{500} mol$ liberated $4.2Vt_{max}$

1mol would liberate $\frac{4.2Vt_{max} \times 500}{v_0} J$

Hence $\Delta H_n = -\frac{4.2Vt_{max} \times 500}{v_0} Jmol^{-1}$

Task:5.15

a. Write the equation for the neutralization of oxalic acid by sodium hydroxide solution.

b. In an experiment to determine the enthalpy of neutralization of oxalic acid by sodium hydroxide solution, the following results were obtained:

Vol of NaOH/cm^3	0	5	10	15	20	25	30	35
Vol of oxalic acid +vol of NaOH/cm^3	20	25	30	35	40	45	50	55
Temperature/^{0}C)	20	22	23	24	25	25	24	23

c. Plot a graph of temperature rise against volume of sodium hydroxide solution.

d. Use the graph to determine the standard enthalpy of neutralization of oxalic acid by sodium hydroxide solution. [molarity of sodium hydroxide is 1M, molarity of oxalic acid is 0.5M, density of the solution is $1gcm^{-1}$ and specific heat capacity of the solution is $4.2Jg^{-1}\,{}^0C^{-1}$]

e. Would you expect the standard enthalpy of neutralization to be greater, smaller or equal to the above value if ethanoic acid was used instead of oxalic acid? Explain.

Task:5.16

a. Explain what is meant by:

- Standard enthalpy of neutralization.
- Enthalpy of solution.

$10cm^3$ of a base MOH was placed in five different but identical beakers at an initial temperature of 26^0C. To each beaker containing MOH of known concentration, was added $25cm^3$ of 1M hydrochloric acid. The mixture was stirred with a thermometer and the final temperature recorded as shown below:

Beaker number	1	2	3	4	5
Concentration of MOH/g/dm^3	2.0	4.0	8.0	16.0	64.0
Temperature rise	1.0	2.0	3.0	4.0	5.0

b. Plot a graph of temperature rise against the concentration of MOH.

c. Use your graph to determine the relative atomic mass of M.

d. Calculate the enthalpy of the above neutralization.

5. Enthalpy of displacement:

- Metals higher in the electrochemical series displace those lower in the series.
- For example, iron filings displace copper from its solutions according to the ionic equation:

$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$

- Also, more electronegative non metals displace less electronegative ones from their solutions.
- For example, when chlorine is bubbled into iodide ions solution, iodine is displaced according to the ionic equation:

$Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq)$

- These displacement reactions lead to evolution/absorption of heat energy; and the enthalpy term is referred to as enthalpy of displacement.

Definition:

Enthalpy of displacement is the heat change when one mole of an element is displaced from its solution by another element.

Task:5.17

a. What is meant by enthalpy of displacement?

Copper (II) ions react with iron filings according to the equation:

$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq); -126\ kJmol^{-1}$

The table below shows the results obtained when 2g of iron filings were added to $40cm^{3+}$ of copper (II) sulphate solution.

Time/min	0	1	2	3	4	5	6	7
Temp/^{0}C	22.0	29.0	34.0	36.5	36.0	35.5	34.0	33.5

b. Plot a graph of temperature against time and use it to determine moles of copper (II) sulphate reacted and the concentration of copper (II) sulphate solution.

c. Plot a graph of temperature rise against time and use it to determine the moles of copper (II) sulphate reacted and hence it's molar concentration.

6. Enthalpy of precipitation:

- On mixing some two of more aqueous solutions, a precipitate is formed.
- For example:

i. When sodium hydroxide solution is mixed with copper (II) ions solutions, copper (II) hydroxide is precipitated according to the ionic equation:

$Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$

ii. When silver nitrate solution is mixed with sodium chloride solution, silver chloride is precipitated according to the ionic equation:

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

- These precipitation reactions lead to evolution/absorption of heat; and the enthalpy term is called enthalpy of precipitation.

Definition:

Enthalpy of precipitation is the enthalpy change when one mole of a solid is precipitated out from a mixture of solutions.

Task:5.18

$25.0cm^3$ of 0.5M silver nitrate was added to $25.0cm^3$ of 0.5M sodium chloride solution in an insulated container. The temperature of the resulting mixture rose by 3^0C. Assuming that the container has negligible heat capacity and the heat capacity of the resulting solution is $4.23g^{-1}c^{-1}$, calculate the heat of precipitation of silver chloride.

7. **Bond dissociation energy:**

- This enthalpy change is concerned with covalent compounds (molecules). Bond dissociation energy involves covalent bond formation and bond breaking.
- A chemical reaction involves bond breaking in the reactants and bond formation in products.
- Bond breakage (cleavage) requires heat input i.e. endothermic; while bond formation releases heat energy i.e. exothermic.

$\Delta H_{atomisation} = \frac{1}{2}$ Bond dissociation energy

Definition

Bond dissociation energy is the amount of energy required to break one mole of the same kind of covalent bonds into its constituent atoms in gaseous state.

Alternatively:

The energy released when one mole of covalent bonds of the same kind is formed from its constituent atoms in gaseous state.

- The table below shows different covalent bonds and their corresponding bond dissociation energies.
- From the bond dissociation energies of the different bonds, the heat content of a covalent compound (a molecule) is the sum of the bond dissociation energies of the different bonds at 298K.
- Enthalpy of a reaction ~~to~~ is the sum of bond energies of bond broken minus the sum of bond energies of bonds formed.

$\Delta H_{reaction} = \sum$of B.E of bonds broken $- \sum$of B.E of bonds formed

Bond	B.D.E/$kJmol^{-1}$	Bond	B.D.E/$kJmol^{-1}$
H–H	436	Si–H	318
C–C	348	P–H	322
C=C	612	O–H	436
C≡C	837	S–H	338
Si–Si	176	F–H	562
N≡N	944	Cl–H	431
O=O	496	I–H	299
S–S	264	C=O	743
F–F	158	C≡N	890
Cl–Cl	242	C–F	484
Br–Br	193	C–Cl	338
I–I	151	C–Br	276
C–H	412	C–I	238
C–O	358		

Worked example:5.4

Using the values of bond dissociation energies above, calculate the heat contents (bond energies) of the following substances.

a. Ethane.
b. Propanoic acid.
c. Cyclohexan – 1 – ol
d. Oxalic acid

Solution:

a. In ethane; 1C – C, 6C – H
BE =(348) + (6x412) = +2820 $kJmol^{-1}$

b. In propanoic acid; 5C – H, 3C – C, 1C = O, 1C – O and 1O – H
BE=(5x412) + (3x348) +743 + 358 + 436.
=+4641 $kJmol^{-1}$

Work out the bond energies for the remaining compounds.

Worked example:5.5

Using the bond energies in the table above, calculate the enthalpy change for the following reactions:

a. $2HI(g) \longrightarrow I_2(g) + H_2(g)$
b. $CH_3CH_3 + Cl_2(g) \longrightarrow CH_3CHCl_2(l)$

Solution

a. $\Delta H = \sum BE$ of bonds broken$-\sum BE$ of bonds formed.
ΔH=2x299 – (151 + 436) = –11$kJmol^{-1}$

b. (2x412) + 242–(2x338) = +390 $kJmol^{-1}$

Task:5.19

The table below shows the bond energies for hydrides of some elements, and the electronegativity values of the elements.

Hydride bond of	Electronegativity	Bond energy/kJ
Fluorine	4.0	568
Oxygen	3.5	463
Chlorine	3.2	428
Nitrogen	3.0	391
Bromine	2.8	366

a. Plot a graph of bond dissociation energy against the electronegativity of the elements.
b. How is bond dissociation energy related to the electronegativity of the elements bonded to hydrogen? Explain your answer.

Task:5.20

a. Define the term bond enthalpy.
b. Write the equation for complete chlorination of methane in the presence of sun light.
c. Given that the bond enthalpies for: Cl – Cl, C – Cl, H – C, and H – Cl are 242, 435, 431 and 339$kJmol^{-1}$ respectively. Calculate the enthalpy change for the complete chlorination of methane.

Task:5.21

a. Write the equation for the formation of one mole of ammonia.
b. Using the bond dissociation energies below, calculate the enthalpy change for the reaction.

Bond	Energy/kJ/mol
N≡N	945
H – H	432
N – H	391

c. Comment on your answer in b) above.

d. Draw the energy cycle and the energy profile for the formation of one mole of ammonia.

Task:5.22

a. State four factors that determine the magnitude of bond dissociation energy.
b. The bond enthalpy of P – Cl in phosphorus trichloride is +319kJ/mol, while in phosphorus pentachloride is +258kJ/mol. Explain.

8. Atomization energy, Ionization energy and Electron affinity:

- These enthalpies concern pure elements, their gaseous atoms and gaseous ions.

a. **Atomization energy:**

Is the energy required to convert one mole of an element into its gaseous atoms.

$Na(s) \longrightarrow Na(g); \Delta H_{atm}$

$H_2(g) \longrightarrow 2H(g); \Delta H_{atm}$

$C(s) \longrightarrow C(g); \Delta H_{atm}$

- The conversion of a solid direct to gas without appearance of liquid form of the substance is known as **sublimation**. Hence, for elements in solid state (sodium, carbon, etc) the atomization energy is also referred to as **sublimation** energy.
- For covalent elements (hydrogen, chlorine, and others), atomization energy is equal to bond dissociation energy.

b. **Ionization energy/ionization potential:**

This is the minimum amount of energy required to remove one mole of electrons from one mole of isolated gaseous atoms or ions.

$M(g) \longrightarrow M^+(g) + e$; I.E. ($1^{st}$ I.E)

$M^+(g) \longrightarrow M^{2+}(g) + e$; I.E ($2^{nd}$ I.E)

$M^{2+}(g) \longrightarrow M^{3+}(g) + e$; I.E ($3^{rd}$ I.E)

First ionization energy:

Is the minimum amount of energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions.

$M(g) \longrightarrow M^+(g) + e$; 1st I.E

c. **Electron affinity (E.A)**

First electron affinity refers to the energy released when one mole of electrons is gained by one mole of isolated neutral gaseous atoms to form one mole of uninegatively charged gaseous ions.

$X(g) + e \longrightarrow X^-(g)$; –E.A

9. Lattice energy, Hydration energy and Enthalpy of solution:

- These enthalpies are concerned with energy changes involving ionic compounds (ions). Ions in ionic compounds are regularly assembled into repetitive units known as crystal lattice.

a. **Lattice energy:**

Is the amount of energy required to break one mole of an ionic crystal lattice into its constituent ions in gaseous state.

$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$; +L.E.

Or:

Lattice energy is the amount of energy given out when one mole of an ionic crystal lattice is formed from its constituent ion in gaseous state.

$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$;–L.E.

Factors that determine the magnitude of lattice energy:

- The stronger the electrostatic force of attraction between the oppositely charged ions in a crystal lattice, the bigger the magnitude of lattice energy of the crystal.

- The following factors therefore affect the magnitudes of lattice energies of ionic crystal lattices

i. **Ionic charge:**

- Highly charged ions strongly attract the opposite ions, hence have stronger electrostatic forces. Therefore, they have bigger magnitude of lattice energy.

Task:5.23

Explain why Lattice energy of sodium chloride is smaller than that of magnesium chloride.

ii. **Ionic size:**

- Large cations have a weak attraction for small anions because of reduced effective nuclear charge and easy polarisability. As well, large anions have a weak attraction for small cations because of reduced effective nuclear charge and easy polarisability. This weakens the electrostatic attraction between the cation and the anion, hence the smaller the magnitude of the lattice energy.
- Conversely, small cations tend to have a strong attraction for the anion because of high effective nuclear attraction. As well, small cations tend to have a strong attraction for the anion because of high effective nuclear attraction. This strengthens the electrostatic attraction between the cation and the anion. Hence the bigger the magnitude of the lattice energy.

Task5.24

Consider the table below;

Compounds	NaF	NaCl	NaBr	NaI
L.E/Klmol^{-1}	−915	−776	−742	−699

Mention and explain the variation in Lattice energy.

b. Enthalpy of solution

Enthalpy of solution of a substance is the heat change when one mole of substance is dissolved in a specified amount of water.

- Formation of a solution of a substance (dissolution) can be exothermic or endothermic depending on the substance.
- For example sodium hydroxide, hydrogen chloride gas, sulphuric acid dissolve exothermically; while ammonium nitrate, potassium iodide and hydrated copper (II) sulphate dissolve endothermically.
- When on dissolution of a substance and then extra water is added, then, some heat change accompanies the dissolution, that heat change is called **enthalpy of dilution.**

The essence of dissolution of an ionic salt: sodium chloride:

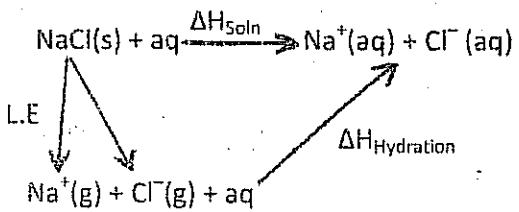
- This about what takes place at microscopic level when an ionic substance dissolves in water.
- First water molecules through their partially charged oxygen and hydrogen atoms attract the surface ions and draw them away from their neighbours sufficiently for water molecules to penetrate between them.
- Then because of the high relative permittivity of water, sodium ions and chloride ions are separated by input of energy at least equal to its lattice energy.
- Each sodium ion then attracts an envelope/sheath of water molecules which are orientated such that the oxygen atoms are directed (through their lone pairs of electrons) towards the metal ion and hydrogen atoms away from it.
- The chloride ion also becomes surrounded by an envelope of water molecules, but in this case, the attraction is between the lone pairs of electrons of the negatively charged chloride ion and the hydrogen atoms of water with their partial negative charges.

- Owing to the inductive effects of the ions attracting water molecules, the O–H bond polarization is increased and more water molecules are attracted by dipole–dipole attraction. Thus envelopes of water molecules round each ion may actually be two or three.
- This surrounding of ions by sheaths/envelopes of water without ionizing water into hydrogen and hydroxyl ions is called **hydration** or **salvation** and it is exothermic.
- The moment this energy is evolved, some will be expended to break the sodium chloride crystal lattice hence dissolution is continued.

c. **Hydration/salvation energy:**

Hydration/solvation energy is the heat given out when one mole of an ion in gaseous state is surrounded completely by water molecules without ionizing the water molecules.

- The moment water molecules are ionized, the pH of the solution changes, and the enthalpy term is not hydration energy.
- Hence, hydration energy also defined as: the heat given out when one mole of an ion in gaseous state is completely surrounded by water molecules without a change is pH.
- The, dissolution of an ionic salt is an interplay of two enthalpy terms:
  i. Lattice energy, which is ~~exothermic~~ endothermic
  ii. Hydration energy, which is ~~endothermic~~. exothermic
- The difference between hydration energy and lattice energy gives the enthalpy of solution of the salt, clearly illustrated in the thermochemical cycle below:



- From Hess' law of constant heat summation:
  Enthalpy of solution =Lattice Energy + Hydration Energy.
  ΔH_{Soln}=Lattice Energy + $\Delta H_{Hydration}$
- If magnitude of:

1. Lattice Energy > Hydration energy, then the salt dissolves endothermically. A non spontaneous process!
2. Lattice Energy < Hydration energy, then the salt dissolves exothermically. A spontaneous process!

The essence of hydration of an ion in gaseous state:
Explain why all hydration energies of ions are negative or all hydration processes are exothermic.

- The gaseous ions of the same charge experience only inter–ionic repulsion, while water molecules are held together by hydrogen bonds.
- During hydration, the weaker hydrogen bonds in between water molecules are broken and are replaced by stronger ion – dipole attraction between water molecules and the ion.
- Hence, during hydration, a small amount of energy is spent to break hydrogen bonds, while a bigger amount of energy is released in formation of ion – dipole attraction. Hence all hydration processes are exothermic.

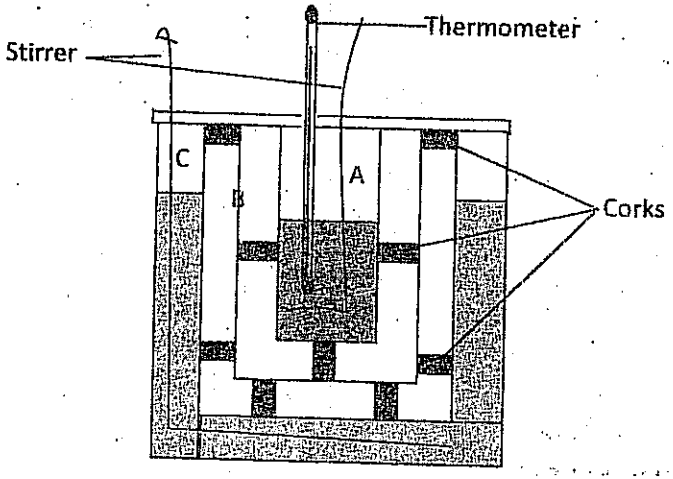
Experiment to determine the enthalpy of solution of a salt: a case of sodium chloride:

Procedure

- A known mass of water m_1 is placed in a copper calorimeter 'A' fitted with a stirrer and a thermometer; and its temperature't' noted.
- The calorimeter is surrounded by an empty cylinder 'B' which in turn is surrounded by a double walled copper vessel 'C' containing water.

- The vessels are prevented from touching each other by corks and the purpose of the outer vessel 'C' is to prevent gain or loss of heat by radiation.
- Finely powdered and known amount of the sodium chloride w_1 contained in a sealed bulb is then added to the water in A.
- The bulb is broken in the water by means of a thermometer and the solution stirred until there is no further change in temperature and temperature t_1 noted.

Experimental setup:



Treatment of the results:

Temperature change $(t_1 - t)$

Heat of dissolution=Heat gained by water

$=m_1c(t_1 - t)$

RFM of NaCl=(23x1) + (35.5x1) =58.5

W1g of NaCl absorbed/released $m_1c(t_1 - t)$

58.5g would absorb/release $\frac{58.5}{w_1} \times m_1c(t_1 - t)J$

Enthalpy of dissolution of sodium chloride is $\pm\frac{58.5}{w_1} \times m_1c(t_1 - t)J$ per m_1g of water.

RMM of H_2O =(1x2) + (16x1)=18

Enthalpy of dissolution of sodium chloride is $\pm\frac{58.5}{w_1} \times m_1c(t_1 - t)J$ per $\frac{m_1}{18}$ *moles* of water.

Assumptions in the experiment

i. The stirrer, the thermometer and the pieces of bulb have negligible heat capacity (don't absorb or lose any heat).
ii. The calorimeter is well lagged.
iii. The solution is so dilute that the specific heat capacity can be taken to be that of pure water.

Task:5.25

From the following data:

Hydroxide of	Lattice energy	Hydration energy
Magnesium	–2834kJ/mol	–1920kJ/mol
Barium	–2228kJ/mol	–1360kJ/mol

a. Calculate the enthalpies of solution of the hydroxides.
b. With a reason, which hydroxide is more soluble in water?

Task:5.26

a. Define the following terms:
- Salvation energy
- lattice energy
- Enthalpy of solution.

b. From the data below, with values in kJ/mol, determine the enthalpy of salvation of $Mg^{2+}(g)$ ions .
- Atomization energy of magnesium +167.2
- Dissociation energy of chlorine +241.6
- Enthalpy of formation of magnesium chloride –639.5

- Enthalpy of solution of magnesium chloride –150.5
- Salvation energy of chloride –383.7
- Electron affinity of chlorine –364.1
- 1st ionization energy of magnesium +738.1
- 2nd ionization energy of magnesium +1450.1

Task:5.27

a. What is meant by the term lattice energy?
b. Draw a thermochemical cycle to show the relationship between: lattice energy, hydration energy and enthalpy of solution for an ionic salt MX_3.
c. Explain why hydration of any gaseous ion is exothermic.

Task:5.28

In an experiment to determine the heat of hydration of copper (II) sulphate, the following experiments were carried out:

- When 8g of anhydrous copper (II) sulphate was dissolved in $50cm^3$ of water, there was a temperature rise of 12.0^0C.
- When 12.5g of hydrated salt was dissolved in $50cm^3$, there was a temperature drop of 2.0^0C.

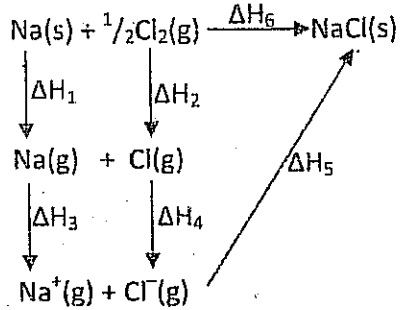
Calculate the hydration energy of copper (II) sulphate.

Born – Haber cycles and energy level diagrams:

A Born – Haber cycle is the splitting up of the overall energy terms of an ionic crystal into several stages some of which are hypothetical (not in practice).

- The energy terms for the formation of sodium chloride crystals can be interpreted as follows:
- Stage one: atomization of sodium
  $Na(s) \longrightarrow Na(g)$; $\Delta H_1=+108.4kJmol^{-1}$
- Stage two: atomization of chlorine
  $^1/_2Cl_2(g) \longrightarrow Cl(g)$; $\Delta H_2=+121.1kJmol^{-1}$

- Stage three: ionization of sodium atoms
  $Na(g) \longrightarrow Na^+(g) + e$; $\Delta H_3=+493kJmol^{-1}$
- Stage four: electron affinity of chlorine
  $Cl(g) + e \longrightarrow Cl^-(g)$; $\Delta H_4=-348kJmol^{-1}$
  Stage five: combination of the gaseous ions
  $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$; ΔH_5 ? (Lattice energy)
- Stage six: standard enthalpy of formation of sodium chloride
  $Na(s) + {}^1/_2Cl_2(g) \longrightarrow NaCl(s)$; $\Delta H_6=-411kJmol^{-1}$
- The Born – Haber cycle for the formation of sodium chloride crystals is drawn as shown below.



From Hess' law of constant heat summation;

$\Delta H_1+\Delta H_2+\Delta H_3+\Delta H_4+\Delta H_5=\Delta H_6$

$\Rightarrow 108.4+121.1+493+-384+\Delta H_5=-411$

$\Delta H_5= -785.5kJmol^{-1}$

- A Born – haber cycle is therefore a thermochemical cycle specifically for ionic crystals.

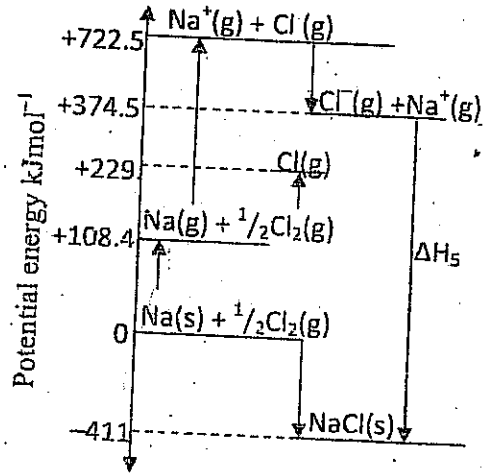
Energy level diagrams:

An energy level diagram is the diagrammatic illustration of energy levels of substances in a given reaction. It is also called **enthalpy diagram.**

- In drawing an energy level diagram;

i. Elements in their standard states are assigned a zero level,
ii. The positive area indicates decreasing stability and
iii. The negative area indicates increasing stability with respect to the elements.

- The energy level diagram for the formation of sodium chloride crystals is as shown below:



From the energy level diagram:
$\Delta H_5 = -375.5 + -411$
$= -785.5 kJmol^{-1}$

Task:5.29

Sketch the born – Haber cycle for the formation of:

a. Magnesium chloride
b. Calcium oxide
c. Aluminium oxide.

Task:5.30

a. Using the information in the table below, calculate the lattice energy of potassium bromide.

- Enthalpy of formation of potassium bromide $-392\ kJmol^{-1}$
- Atomization enthalpy of potassium $+90\ kJmol^{-1}$
- Ionization energy of potassium $+420\ kJmol^{-1}$
- Bond enthalpy of bromine $+112\ kJmol^{-1}$
- Electron affinity of bromine $-342\ kJmol^{-1}$

b. Do you expect the lattice energy of sodium bromide to be smaller, greater than or equal to the one of potassium chloride. Give a reason for your answer.

Task:5.31

a. Draw a Born – Haber cycle for the formation of rubidium chloride from its elements.
b. Using the following data, calculate the electron affinity of chlorine:

- Lattice energy of rubidium chloride 665
- Bond enthalpy of chlorine +226
- Atomization enthalpy of rubidium +84
- Enthalpy of formation of rubidium chloride −439
- Ionization energy of rubidium +403

All values are in kilo Joules for every mole.

c. Using the above information and the calculated value, draw the enthalpy cycle for the formation of rubidium chloride.

5.5 Free energy (G), Entropy (S) and Enthalpy (H)

- This sub topic attempts to answer two important philosophical questions in Chemistry:

1. Why do chemical reactions occur?
2. Why do some chemical reactions occur spontaneously while others do not?

- On mixing hydrochloric acid with sodium hydroxide solution at room temperature, they react immediately (spontaneously): while at room temperature calcium carbonate is not found to decompose freely!

Notion 1: All spontaneous natural processes occur in order to reduce the potential energy of the system.

a. Water spontaneously flows down hill and never uphill.
b. A stone spontaneously falls down and never spontaneously begins to fly vertically upwards.

- Hence any process that leads to a decrease in energy content of a system is spontaneous.
- A chemical reaction therefore takes place in order to reduce the potential energy of the system; i.e weaker bonds are broken and stronger ones are formed; so as to release much more heat than absorbed.
- This leads to evolution of energy to the surrounding hence any exothermic process is spontaneous/feasible/probable.
- However some reactions that are endothermic also occur spontaneously. For example ammonium nitrate dissolves endothermically, but spontaneously.
- From the above example therefore, decrease in potential energy is not enough to account for the spontaneity/feasibility of chemical reactions.

Notion 2: Chemical reactions occur in order to increase the entropy of the system; therefore a reaction that results into increase in the entropy of the system is spontaneous.

- Entropy is the measure of disorderliness/mixed–upness of the system.

$$NH_4NO_3(s) + aq \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$

$$KCl(s) + aq \longrightarrow K^+(aq) + Cl^-(aq)$$

$$CoCl_2.6H_2O(s) + 6SOCl_2(l) \longrightarrow CoCl_2(s) + 6SO_2(g) + 12HCl(g)$$

- The above endothermic processes occur spontaneously because of the increase in the entropy of the system.

- Entropy of solid<entropy of liquid<entropy of gas
- Changes that lead to increase in entropy are:

a. Changing a solid to a liquid.
b. Changing a liquid to a gas.
c. Increase in number of moles of gas/gases.

- However, a solid does not spontaneously change into a liquid; also, a liquid does not spontaneously change into a gas. Yet the two processes are accompanied by increase in entropy.
- Therefore, increase in entropy alone is not enough criterion for spontaneity of chemical reactions.

Notion 3: spontaneity depends on; entropy change, Kelvin temperature and enthalpy change for the system, which determines the free energy change of the system.

- Free energy change (ΔG) is the maximum amount of work done by a chemical reaction. It is also that work that must be done on a compound in order to get it back again to its original state (constituent elements).
- The free energy change (ΔG), the entropy change (ΔS), the enthalpy change (ΔH) and the Kelvin temperature (T) of a system are related according to **Gibb's equation:**

$\Delta G = \Delta H - T\Delta S$

- Under standard conditions, the above equation becomes:

$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$

- For a process to be spontaneous standard free energy change (ΔG^θ) must reduce i.e. become negative. This can be achieved when:

a. ΔH^θ is negative (exothermic reactions).
b. ΔS^θ is positive (an increase in entropy).
c. Temperature (T) must be high.
d. When both ΔH^θ and ΔS^θ are negative, then ΔG^θ will be negative at low temperatures and positive at higher temperatures.

e. If both ΔH^{θ} and ΔS^{θ} are positive, then ΔG^{θ} will be positive at low temperatures and negative at higher temperatures.
f. If is ΔH^{θ} negative and ΔS^{θ} is positive then ΔG^{θ} will be negative.
g. If is ΔH^{θ} positive and is ΔS^{θ} negative then ΔG^{θ} will be positive.

Task:5.32

Explain the following observations:

a. Ammonium nitrate dissolves spontaneously, but endothermically.
b. Enthalpy of neutralization of hydrochloric acid by sodium hydroxoide solution is higher than the enthalpy of neutralization by ammonium hydroxide solution.
c. The enthalpy change for the formation of one mole of liquid water is less negative than the enthalpy change for the formation of one mole steam.
d. The enthalpy of neutralization of aqueous solution of hydrochloric acid and sodium hydroxide solution releases less heat than when hydrogen chloride gas is bubbled into aqueous sodium hydroxide solution.

CHAPTER SIX: PHYSICAL EQUILIBRIA:

6.0 Introduction

- Upto now, substances are grouped into solids, liquids and gases depending on the strength of forces holding the particles of the substances which in turn determines the degree of compactness of the particles.
- Solids have the strongest forces followed by liquids and gases with the weakest intermolecular forces of attraction
- Whatsoever the strength of the forces, the particles of solids and liquids at their surfaces always gain enough energy to escape to form vapour – the gas produced from a solid or a liquid.
- As the particles of the solid or the liquid escape to form vapour, some of the vapours also condense back to form the solid or the liquid.
- As time goes on, the rate at which the solid or the liquid vapourises becomes equal to the rate at which the vapour condenses, i.e a state of dynamic equilibrium.

  Solid $\rightleftharpoons$ Vapour and Liquid $\rightleftharpoons$ Vapour
- These are physical equilibria because the components of the equilibria; solid, liquid and gas are chemically indistinguishable. They are mere physical state of a substance!

Disturbance of the equilibria:

- The moment the rate of any of: vapourization/condensation, melting/freezing or sublimation is altered, the equilibrium is said to have been disturbed/perturbed. The factors that disturb a physical equilibrium are: temperature, pressure and amount of the component.

a. **Temperature**

- The effect of temperature on an equilibrium system is summarised by van't Hoff's law of mobile equilibrium which is an extract of le Chatelier's principle, and it states:
  When a system is in equilibrium, increase in temperature favours the endothermic process and decrease in temperature favours the exothermic process.
- Melting, vapourization/evaporation and sublimation/vapourization of solids are endothermic processes. Increase in temperature increases their rates. The equilibrium is disturbed such that more of the solid melts, liquid vapourises and the solid sublimes. Decrease in temperature decreases their rates. The equilibrium is disturbed such that more of the vapour condenses to solid and liquid and more of the liquid freezes.
- Freezing, condensation and sublimation/ condensation of a vapour to solid are exothermic processes. Decrease in temperature increases their rates. The equilibrium is disturbed such that more of the vapour condenses to solid and liquid and more of the liquid freezes. Increase in temperature decreases their rates. The equilibrium is disturbed such that more of the solid melts, liquid vapourises and the solid sublimes.

b. **Pressure**

- The effect of pressure on an equilibrium system depends on whether the equilibrium is attained with an increase in volume (decrease in pressure) or a decrease in volume (increase in pressure). This is summarized by an extract of le Chatelier's principle, which states:
  In an equilibrium system, increase in pressure favours the direction in which there is a decrease in volume and decrease in pressure favours the direction in which there is increase in volume.

- Pressure has a negligible effect on the liquid states and a very negligible effect on the solid states. This is because the two states have their particles so close that compression or expansion at a constant temperature can not significantly bring their particles closer or pull them apart.
- On this account, they are referred to as the condensed systems.

a. Solid $\rightleftharpoons$ Liquid

- Solids that melt with increase in volume produce liquids that are lighter than them (the solids). Decrease in pressure favours melting; increase in pressure favours freezing. Most solids are examples; carbon dioxide, iodine, sulphur, phosphorus, naphthalene are just a few examples.
- Solids that melt with decrease in volume produce liquids that are denser than them (the solids). Increase in pressure favours melting; decrease in pressure favours freezing. Water is the only known example!

b. Solid $\rightleftharpoons$ Vapour and Liquid $\rightleftharpoons$ Vapour

- The vapour form is less dense than both the solid and the liquid form, so the vapours are produced by increase in volume. Increase in pressure causes the vapour to condense back to the liquid form and the solid form. The equilibrium is disturbed to form more solid and liquid respectively. Decrease in pressure increases the rate of vapourization. The equilibrium is disturbed to form more vapour.

c. **Amount of a component**

- The perturbation of an equilibrium system by varying the amounts of the components is summarized by an extract of le Chatelier's principle, which states:
  In an equilibrium system, decrease in the amount of a component leads to the system readjusting to replace the component, and increase in the amount of the component

leads to the system readjusting to remove some of the component.

a. Solid $\rightleftharpoons$ Liquid

- Increase in the amount solid makes the solid to melt; decrease causes the liquid to freeze.
- Increase in the amount of the liquid causes freezing, but decrease in the amount of the liquid causes the melting.

b. Solid $\rightleftharpoons$ vapour

- Increase in the amount of solid makes the solid to vapourise; decrease causes the vapour to condense into solid.
- Increase in the amount of the vapour causes condensation to form solid, but decrease in the amount of the vapour causes the vapourization/sublimation.

c. Liquid $\rightleftharpoons$ vapour

- Increase in the amount of liquid makes the liquid to vapourise; decrease causes the vapour to condense.
- Increase in the amount of the vapour causes condensation, but decrease in the amount of the vapour causes vapourization.

- The existence of equilibrium and its disturbance/perturbation can take place in a pure single substance or a mixture of pure substances involving the different states of matter, i.e: solid, liquid and gas.
- Since the solid state is uniform in itself, physically distinct and more so bounded by a boundary from the liquid and gaseous states, and the vice versa, they therefore constitute phases. Hence physical equilibria are also referred to as **phase equilibria**.

Definitions:

i. ***Phase:***

A phase is that part of a system having uniform properties and physically demarcated by a boundary from others.

ii. ***Phase boundary:***

A phase boundary is that physical part of a system demarcating the different phases.

iii. ***Component:***

The smallest number of chemical species that can be used to describe a phase system.

Examples to illustrate phase, phase boundary and component:

a. A system of ice, liquid water and water vapour.

- Contains one component – water; three phases – solid, liquid and gas/vapour. The solid – liquid interface, solid – vapour interface and liquid – vapour interface are the phase boundaries.

b. An aqueous solution of sodium chloride.

- Contains two components – water and sodium chloride; one phase since the solution is uniform. No phase boundary within the system.

c. An immiscible mixture of water and carbon tetrachloride.

- Contains two components – water and carbon tetrachloride; has two phases – pure water and carbon tetrachloride; has one phase boundary – the liquid junction.

d. An immiscible mixture of water and carbon tetrachloride in which iodine has been dissolved.

- Contains three components – water, carbon tetrachloride and iodine; two phases; iodine solution in water and iodine solution in carbon tetrachloride; and one phase boundary – aqueous solution of iodine and organic solution of iodine interface.

e. A gaseous mixture of carbon dioxide, nitrogen, neon, hydrogen, chlorine, sulphur dioxide, ammonia, water vapour, oxygen and argon

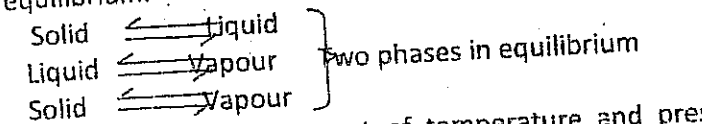
- Contains ten components – carbon dioxide, nitrogen, neon, hydrogen, chlorine, sulphur dioxide, ammonia, water vapour, oxygen and argon; one phase – the gaseous phase since all

gases are completely miscible; no boundary within the system.

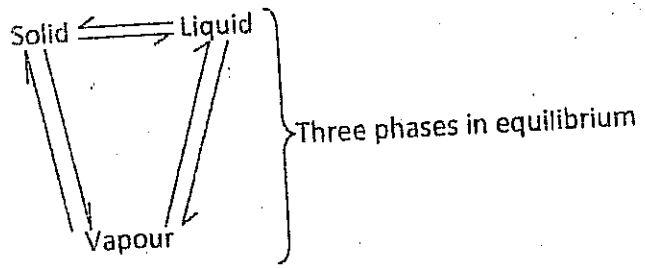
6.1 Single substance equilibria:

Introduction:

- A single substance equilibrium is the equilibrium between/among the states of a pure substance (a substance made of only one kind of particles and with uniform properties), in a closed system.
- When temperature and pressure surrounding a pure substance (say carbondioxide water and sulphur) in a closed system are altered, it is possible to convert the substance to all the three states, sequentially.
- As the substance converts from one state to another, there is a suitable set of conditions in which the two states are in equilibrium.



- Then, there is a unique set of temperature and pressure when all the three states are in equilibrium i.e; solid form, liquid form and vapour form co-exist in equilibrium.



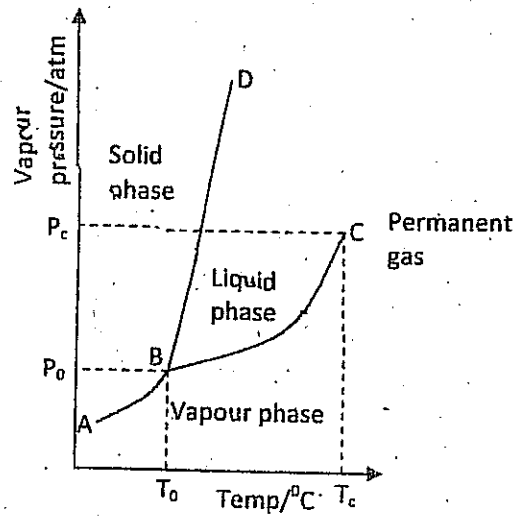
- At this point, the solid form and liquid form are in equilibrium with only one vapour and hence; the solid form and liquid form have the same vapour pressure.
- This is the triple point of the substance.

Definition:

The triple point of a substance is that one temperature and one pressure in which the solid, liquid and gaseous forms of the substance co-exist in equilibrium and have equal vapour pressures.

- The inter – conversion of states of a pure substance can be followed graphically to give a plot of various temperatures and pressures in which given states co – exist in equilibrium called a **phase diagram.**
- In following interconversion of states using a phase diagram, the solid form of a pure substance is heated below its melting/freezing point.
- As the temperature is increased, the solid is converted into vapour without passing through the liquid form i.e. sublimes.
- The produced vapour generates pressure of the solid form, known as sublimation pressure, which increases with temperature (almost in accordance to Pressure's law) until the liquid form begins to appear.
- However some solids, notably iodine and carbondioxide generate sublimation pressure equal to atmospheric pressure without appearance of liquid form.
- Such solids therefore boil and are referred to as **volatile solids** i.e. solids with boiling points and more so of low values.
- Some particles of the produced liquid escape to produce vapour which generates vapour pressure.
- When the vapour pressure of the liquid form is equal to the sublimation pressure (vapour pressure of solid form), with the total of the two pressures equal to or not the external atmospheric pressure, then the three states co – exist in equilibrium.

- When the value of this total pressure is equal to external pressure, then the triple point coincides with the melting/freezing point of the substance.
- Beyond the triple point, some solid form exists in equilibrium with some of the formed liquid form; also some of the formed liquid is converted to vapour and exists in equilibrium with the formed vapour as shown below.



Definitions:

a. Curves:

i. AB – sublimation curve.

Along AB, the solid form and vapour form are in equilibrium at different temperatures and pressures. It shows that sublimation pressure increases with increase in temperature.

ii. BD – melting curve.

Along BD, the solid form is in equilibrium with the liquid form, at different temperatures and pressures. By sloping away from the pressure axis, it shows that melting point of the solid increases with increase in pressure; i.e. it is more

difficult to convert the solid to liquid when pressure is high than when it is low.

- The curve BD does not have any known point it ends, probably because increase in temperature tends to convert the two states (solid and liquid) into vapour and so would disappear.

iii. AC – boiling curve (liquid vapourization curve)

Along AC, the liquid form is in equilibrium with the gaseous form at different temperatures and pressure. It shows increase in vapour pressure of the liquid with increase in temperature.

- The increase in vapour pressure of the liquid with temperature ends at point C, the critical point of the liquid, corresponding to the critical temperature, T_c and critical pressure P_c.
- At this point the liquid form and the vapour form are indistinguishable and the vapour is converted into permanent gas

b. Points:

i. Point B – triple point:

- Point B, the triple point indicates the one temperature T_0 and pressure P_0 in which all the three states are in equilibrium
- P_0 is the total value for sublimation pressure and the vapour pressure of the liquid form.
- Since at triple point, Sublimation pressure = vapour pressure of the liquid form

  $\Rightarrow$ Sublimation pressure = vapour pressure of liquid = $\frac{1}{2}P_0$

ii. Point C – the critical point:

- Point C indicates the critical temperature T_c and the critical pressure P_c at which the vapour and liquid forms are indistinguishable. Here, the vapour is converted into a permanent gas.

- The critical point is the maximum point at which a gas can be liquefied by mere increase in pressure at the critical temperature/constant temperature.
- Or is the point beyond which a gas can not be liquefied by mere increase in pressure at constant temperature.
- Critical pressure is the minimum pressure sufficient to liquefy a gas at its critical temperature.
- The critical temperature of a substance is the temperature above which the gaseous form of the substance cannot be converted into liquid form by mere increase in pressure alone.
- Liquefaction beyond the critical temperature by mere increase in pressure alone is impracticable because, the particles already have high speeds hence kinetic energies that pressure alone cannot bring them close enough for liquefaction.
- A gas beyond the critical point is known as the permanent gas, and to an excellent extent, behaves as the ideal gas.

c. **Areas/phases:**

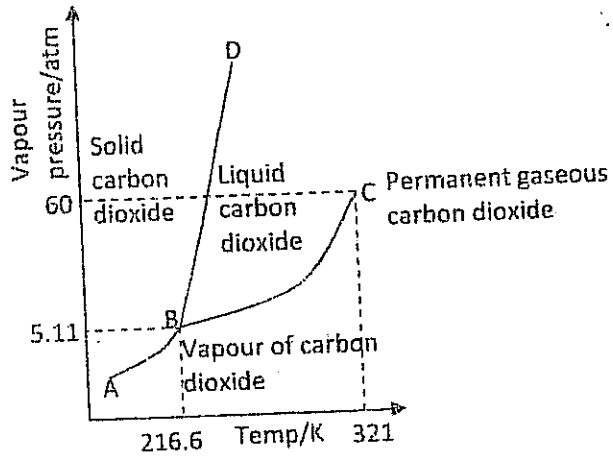
i. Left of ABD – the solid phase

ii. Below ABC – the gaseous/vapour phase

iii. DBC minor – liquid phase

iv. Right of T_c produced upwards – permanent gas

6.1.1 Phase diagram for carbondioxide:

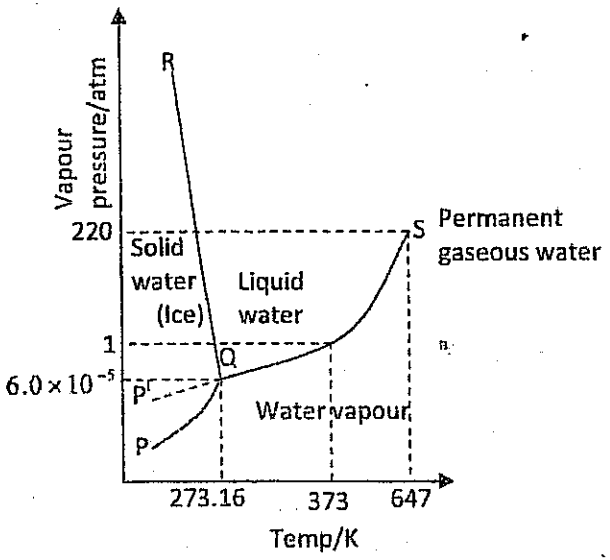


Description of the diagram

- Curve AB is the sublimation curve for carbondioxide. It indicates the various temperatures and pressures in which solid carbondioxide is in equilibrium with gaseous carbondioxide.
- At point B (temperature of 216.6K and pressure 5.11atm) the vapour pressure of the solid carbondioxide is equal to the vapour pressure of the liquid carbondioxide i.e. B is the triple point of carbondioxide.
- Since pressure at B is greater than 1atm, solid carbondioxide therefore boils without passing through the liquid state (sublimes) i.e. solid carbod dioxide (dry ice) is volatile.
- BC shows variation in vapour pressure of liquid carbondioxide with temperature and all the possible conditions of temperatures and pressures in which liquid carbondioxide is in equilibrium with gaseous carbondioxide. The curve ends at point C, the critical point of carbondioxide (temperature of 321K and pressure of 60atm).

- Curve BD shows the variation in melting point of carbondioxide with pressure. It shows that melting temperature increases with pressure (the curve sloping away from the pressure axis).It also shows the sets of pressures and temperatures in which solid carbondioxide and liquid carbondioxide co-exist in equilibrium.

6.1.2 Phase diagram for water:



Description of the diagram:

- PQ is the sublimation curve of water; showing the various temperatures and pressures in which ice is in equilibrium with water vapour.
- At point Q (temperature of 273.16K and pressure of 6.03×10^{-5} atm) ice and liquid water have equal vapour pressure. Q is therefore the triple point of water.
- Again the triple point, though has the same temperature as that of freezing point, it is not equal to freezing point

because the vapour pressure is not equal to the external atmospheric pressure (1 atm), which is generated when the temperature of the system is 373k, see the diagram.

- Curve QS shows the variation in vapour pressure of liquid water with temperature. The curve passes through possible conditions of temperature and pressures in which liquid water is in equilibrium with water vapour.
- The curve ends in point S, the critical point of water with temperature of 647K and pressure of 220atm.
- Curve QR shows variation in freezing point of water with temperature. By the curve sloping towards the pressure axis, it implies melting point of water decreases with increase in pressure, which is an anomalous behavior.
- Along the same curve, QR possible conditions of temperatures and pressures in which ice is in equilibrium with liquid water.
- The dotted curve, QP' represents variation in vapour pressure of liquid water below its freezing point. it is called super cooling curve and the liquid water existing below its freezing point is metastable water, which swiftly solidifies by seeding – addition of a small amount of ice.

Take note:

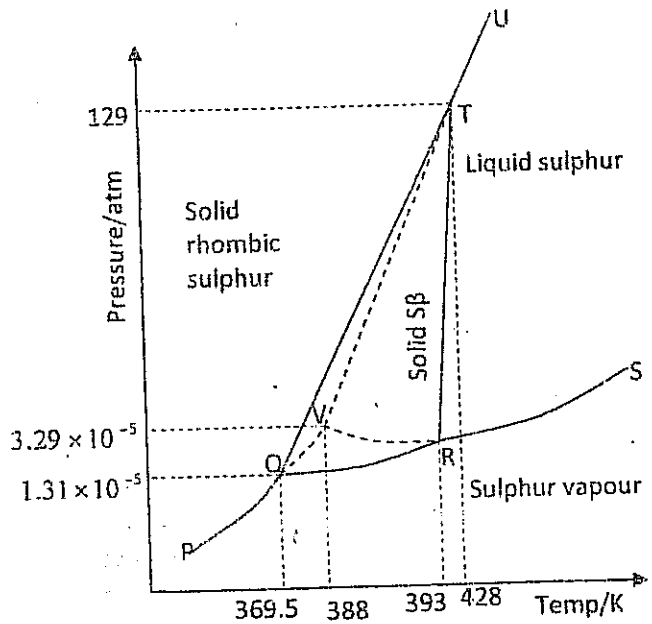
- Melting of a substance involves the equilibrium;

  Solid $\rightleftharpoons$ Liquid
- When a substance melts with an increase in volume i.e. the volume of the produced liquid is greater than the volume of the producing solid, high pressure favours formation of the solid; – direction of the change in which volume decreases.
- So it becomes more difficult to melt the substance at higher pressures as in the case of carbon dioxide.
- For water, freezing leads to decrease in volume, i.e. liquid water is denser than ice (solid water), an anomally!

- Therefore melting of ice is favoured by high pressure, and hence ice has progressively lower melting point at lower pressures.
- The above explanations are in accordance to le Chatelier's principle (ref: perturbation of equilibria).

6.1.3 Phase diagram for sulphur /carbon.

- Sulphur is selected to illustrate the equilibrium of a pure substance that is allotropic.
- Allotropy is the existence of a substance in more than one structural form within one physical state; allotropes are the various structural forms of a substance within the same physical state.
- Sulphur has two allotropes, rhombic sulphur or alpha sulphur (Sα) and monoclinic or beta sulphur (Sβ) which are stable below and above 96.5^{0}C (369.5K) respectively.
- So when a solid sample of sulphur is heated below 369.5k (transition temperature), the sublimation pressure of Sα varies with temperature until 369.5k at which Sβ appears.
- When heating is continued, equilibrium is established between Sα and Sβ until transformation is complete. At the same time equilibrium is established between the formed solid Sβ and its vapour, until the triple point when liquid sulphur appears.
- Rhombic sulphur can only be in equilibrium with liquid sulphur if super– heated to a metastable rhombic sulphur beyond the transition temperature, as illustrated below.



Description of the diagram

- Curve PQ shows variation of sublimation pressure of solid rhombic sulphur (Sα) with temperature.
- Point Q, corresponding to temperature 369.5K and pressure of 1.31x10^{-5}atm is the triple point of Sα, Sβ and their vapours.
- QR shows variation of sublimation pressure of Sβ with temperature
- R is the triple point of solid Sβ, its vapour and liquid sulphur.
- Solid Sβ is enclosed within the area QTR
- Since the rate at which one solid allotrope changes to another at its transition temperature is very slow (a high activation energy opposes solid transformation), rapid heating of solid Sα will allow the vapour pressure to rise as indicated by dotted line QV.
- When it liquefies at V, the vapour pressure of the liquid sulphur then varies with temperature along curve VR.

- Infact the dotted lines show the metastable equilibrium, QV is metastable sublimation curve Sα.
  VR shows metastable equilibrium between metastable liquid Sα and its vapour.
  VT shows variation of transition temperature of metastable Sα to Sβ, with pressure
- V is the metastable triple point of metastable solid, liquid and gaseous Sα at a temperature of 388K and a pressure of 3.29×10^{-5} atm.

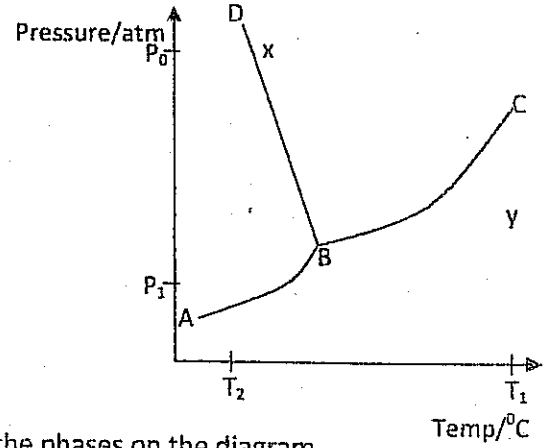
Take note:

i. When liquid sulphur is cooled at any pressure excess of 1290atm, it only forms rhombic sulphur and not monoclinic sulphur (see the diagram above).

ii. There is a very small increase in pressure of solid sulphur as it is heated. This is because of the very strong force of attraction between the particles of solid sulphur.

Worked example:6.1

The phase diagram below is for a water system; use it to answer the following questions.



a. Label the phases on the diagram.

b. What do lines AB, BC and BD represent?

c. Explain the significance/implications of line BD sloping towards pressure axis.

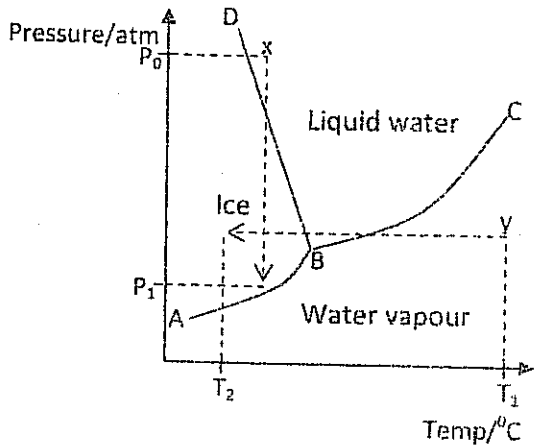
d. Explain what happens when;

   i. Substance at y is cooled from T_1 to T_2 at constant pressure.

   ii. The pressure on substance at x is reduced from P_0 to P_1 at a constant temperature.

Solution:

a.



b. AB represents variation of sublimation pressure of ice with temperature.
   BC represents the variation of vapour pressure of liquid water with temperature.
   BD represents the variation in the melting point of ice with temperature.

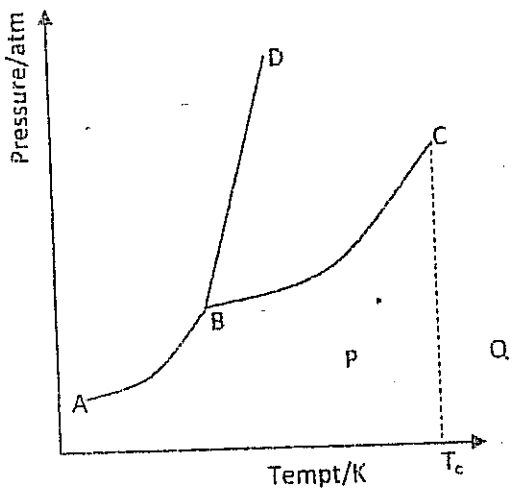
c. Implies that the melting point of ice decreases with increase in pressure. This is because ice melts with increase in volume. Hence it's melting favoured by high pressure.

d. i. The temperature of the vapour decreases at the constant pressure. On meeting the curve BC, the temperature remains constant as the vapour fully condenses into liquid. When the liquefaction is complete, the temperature of the liquid decreases at constant pressure until it meets the curve BD. Here, the temperature remains constant as the liquid water freezes into ice. On completion of the solidification, the temperature of ice the decreases to T_2 at the constant pressure.

ii. The pressure of ice decreases at constant temperature until it meets the curve BD. At this point, ice melts to form liquid water at a constant pressure and temperature. After which, the pressure of the liquid decreases at constant temperature to P_1.

Worked example:6.2

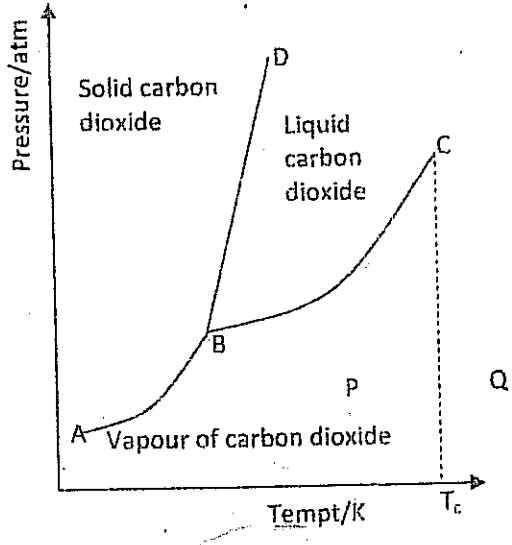
Below is a sketch phase diagram for carbon dioxide. T_c is the critical temperature of carbon dioxide.



a. Label the phases of carbon dioxide in the diagram
b. Describe and explain the curve BD
c. How would you expect the curve BD to change if the above was a phase diagram of water? Explain your answer.
d. Sketch on the same pair of axes, pressure – volume curves for carbon dioxide at points P and Q. Describe and explain the shape for the curve at point Q.
e. State dalton's law of partial pressure
f. For carbon dioxide at points P and Q.
   i. State the differences between them
   ii. $500cm^3$ of carbon dioxide at Q at a pressure of $2.05x10^5Pa$ and $30cm^3$ of carbon monoxide at a pressure of $6.05x10^6Pa$ were mixed into a $50cm^3$ vessel, under similar conditions. Calculate the total pressure of the mixture.

Solution:

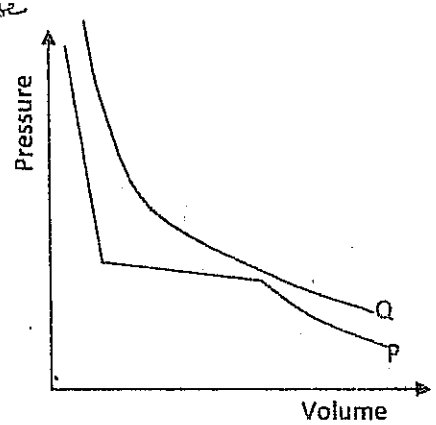
a.



b. Curve BD is the melting curve of carbon dioxide. Along the curve are various sets of conditions of temperature and pressure in which solid and liquid carbon dioxide are in equilibrium. By sloping away from the pressure axis, it shows that melting point of carbon dioxide increases with increase in pressure. This is because, carbon dioxide melts with increase in volume, and so is favoured at a low pressure.

c. The curve BD would slope towards the pressure axis. This is because water melts with a ~~decrease~~ increase in volume. So its melting is favoured at ~~higher~~ lower pressures, hence sloping of BD towards pressure axis to show ~~decrease~~ increase in melting point with ~~increase~~ decrease in pressure.

d.



The curve Q is a rectangular hyperbola. Because carbon dioxide at Q is beyond the critical temperature and so obeys Boyle's under at all conditions of pressure – approximates ideality to an excellent extent.

e. Under constant conditions of temperature and pressure, the total pressure of a mixture of gases that do not chemically react is the sum of the partial pressures of the gasese in the mixture.

f. i.

At P	At Q
Vapour of carbon dioxide	Permanent gaseous carbon dioxide
Can be liquefied by mere increase in pressure alone at its temperature.	Can not be liquefied at its temperature by mere in crease in pressure.

ii. Carbon dioxide contracts from $500cm^3$ into $50cm^3$ in accordance to Boyle's law:

$P_1V_1=P_2V_2$

$500x2.05x10^5=P_2x50$

$P_2=2.05x10^6Pa$

Carbon monoxide expands from $30cm^3$ to $50cm^3$ in accordance to Boyle's law:

$P_1V_1=P_2V_2$

$6.05x10^6x30=P_2x50$

$P_2=3.63x10^6Pa$

Total pressure of the mixture

$=2.05x10^6Pa+3.63x10^6Pa$

$=5.68x10^6Pa$

6.2 Phase equilibria involving two substances (eutectic mixtures):

Introduction:

- When a liquid form of a pure substance is cooled, a certain temperature is reached when the liquid is converted to its solid form at a constant temperature and constant pressure.
- This constant temperature is the freezing point of the liquid and takes a very narrow range of values.
- However, when a liquid mixture of two pure substances is cooled, freezing takes on a range of temperatures depending on the proportions of the components in the mixture.

- The spreading of freezing points to a range of values is due to depression in freezing point of one component (in this case it is a solvent) by the other component (in this case it is a solute).
- However, there comes a unique mole fraction and temperature when the two substances completely solidify at a constant temperature and pressure to give a solid of constant composition.
- This solid, solidified from the liquid mixture is what is called an "Eutectic mixture", from a Greek word "euteckos" which means "can easily be melted."
- There are two possibilities when forming a eutectic mixture from a liquid mixture:

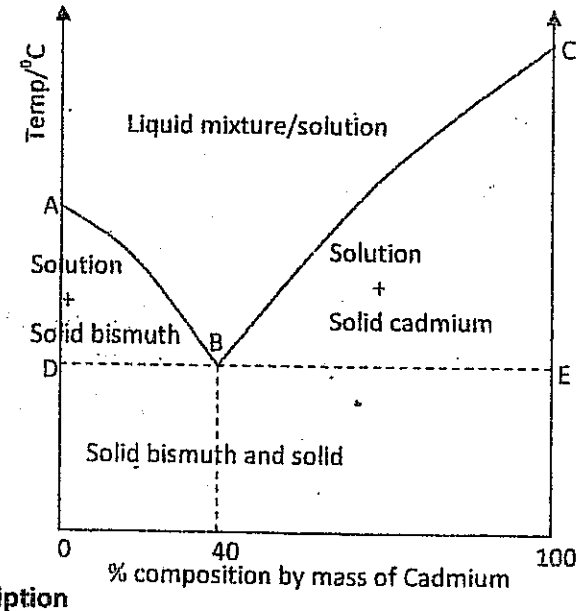
a. The solid forms of either the pure components only separate out or.
b. A compound of the two components and pure components separate out.

6.2.1 Only pure solid components separate out:

a. Liquid Bismuth – Cadmium mixture

- When a liquid mixture of Bismuth and Cadmium is cooled at a constant pressure, a temperature is reached when solid Bismuth separates out of the mixture.
- The temperature at which this separation begins is lower than the actual freezing point of bismuth (the freezing point is depressed due to the presence of cadmium – a solute)
- This depends on the proportion of cadmium in the mixture i.e. freezing point more depressed with bigger amount of cadmium.
- As cooling is continued, the crystallization of bismuth continues making the mixture less rich in bismuth, until a certain mole fraction of bismuth in the mixture, at which the mixture solidifies completely at a constant temperature.

- Likewise in the process of cooling the same solution, a temperature is reached when solid cadmium begins to separate out of the mixture.
- This freezing point is again depressed due to the presence of bismuth – a solute and the extent of the depression depends on the amount of bismuth in the mixture.
- As cooling is continued, the crystallization of cadmium continues making the mixture less rich in cadmium, until a certain mole fraction of cadmium (corresponding to the mole fraction of bismuth above) in the mixture, at which the mixture solidifies completely at a constant temperature.
- This constant point at which solidification, at a constant pressure of cadmium – bismuth system completes, corresponds to a temperature of 145^0C and composition 40% cadmium.
- This constant point at which solidification of cadmium, bismuth system completes is called eutectic point of bismuth – cadmium, with eutectic temperature of 145^0C and eutectic mixture of 60% bismuth and 40% cadmium.
- These are represented graphically into a phase diagram shown below.



Description

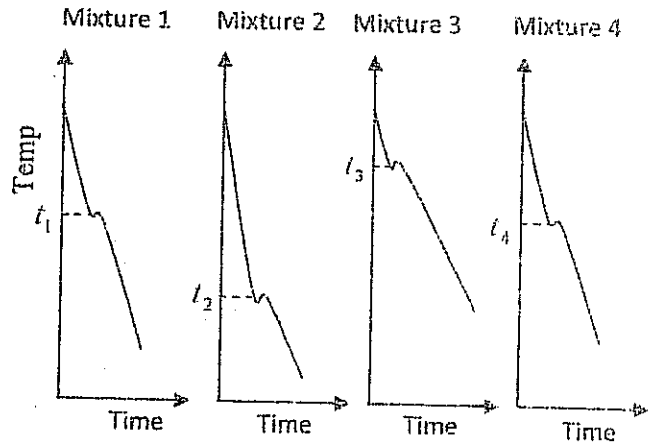
- Point A is the freezing/melting point of pure bismuth and the line AB represents the depression in melting point of bismuth due to increasing amount of cadmium.
- In area ABD solid bismuth is in equilibrium with the mixture/solution.
- Point C is the melting point of pure cadmium; and the line CB represents the depression in melting point of pure cadmium due to increasing amount of bismuth.
- In the area CBE, the solid cadmium and the mixture are in equilibrium.
- At point B, both solid cadmium and solid bismuth are in equilibrium with the solution; the solidification of the mixture is complete.
- Below the line DBE, it is only solid mixture (eutectic mixture) existing and further decrease in temperature does not affect the composition of the mixture.

Definitions:

1. ***Eutectic temperature:***
   Is the constant lowest possible temperature at which a liquid mixture solidifies completely, at a constant pressure and composition.
2. ***Eutectic mixture:***
   Is the solid mixture of constant composition obtained when a liquid mixture solidifies completely at a constant pressure and temperature.
3. ***Eutectic point:***
   - Is a point on eutectic phase diagram representing the fixed temperature and constant composition at which there is complete solidification at a constant pressure.

How to obtain a phase diagram for a eutectic mixture:

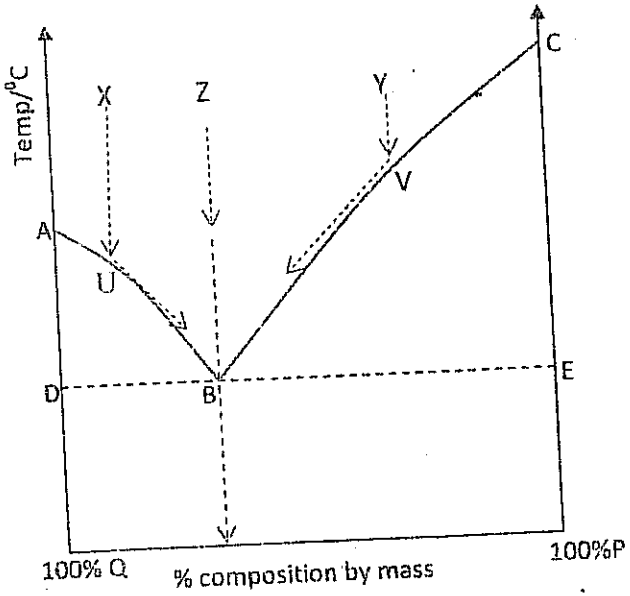
- The complete phase diagram may be obtained by taking a number of different liquid mixtures – mixtures of different compositions.
- The mixtures are then cooled and their cooling curves plotted. The freezing point of the mixture is indicated by a change in the slope of the cooling curve, as shown below:



- t_1, t_2, t_3 and t_4 are the freezing points of mixtures 1, 2, 3 and 4 respectively. Many of such say for ten different mixtures are obtained.
- Then to obtain the complete phase diagram, the different freezing points are plotted against the compositions of the different mixtures.

Cooling different mixtures and phase changes:

- Consider the general eutectic phase diagram below:



- The phases in the diagram are:

i. The unsaturated solution/liquid mixture above ABC
ii. Equilibrium between saturated solution and solid Q in the area ADB.
iii. Equilibrium between saturated solution and solid P in the area CEB.
iv. Solid phase (eutectic mixture) below the line DBE.

a. ***Cooling of mixture X:***
Temperature decreases at constant composition until point U. At point U, solid Q precipitates out of the mixture. As cooling is continued, more Q precipitates out and its freezing point is depressed along UB causing the composition of Q in the liquid mixture to decrease with temperature along UB. This makes the mixture richer in component P. On reaching point B, both Q and P precipitate out at once and the mixture completely solidifies. Any cooling beyond point B does not change the composition and the phase.

b. ***Cooling mixture Z:***
Temperature decreases at constant composition along ZB. At B, the mixture solidifies completely to a solid mixture of the same composition as Z. Any cooling beyond point B does not change the composition and the phase.

c. ***Cooling of mixture Y:***
Temperature decreases at constant composition until point V. At point V, solid P precipitates out of the mixture. As cooling is continued, more P precipitates out and its freezing point is depressed along VB causing the composition of P decrease with temperature along VB. This makes the mixture richer in component Q. On reaching point B, both P and Q precipitate out at once and the mixture completely solidifies. Any cooling beyond point B does not change the composition and the phase.

Task:6.1

The table below shows the freezing points of various mixtures of tin and lead.

% by mass of lead	0	25	45	63	81	100
FPt/^{0}C	327	275	229	183	211	232

a. i) Plot a graph showing variation of freezing points with compositions, on it label;

- The phases
- Eutectic point, U
- ii) Record the ordinates of the eutectic point.

b. i) Describe the phase changes that occur when the following mixtures are cooled from 350^0C to 175^0C
- 10% lead,
- 100% tin
- And 85% lead

ii) Sketch their cooling curves, indicating the differences between them

c. 40g of a mixture made of 5% lead was cooled from 350^0C to 225^0C. Calculate the mass of lead present in the mixrure at:
- 350^0C
- 225^0C, (Pb = 207, Sn = 119)

Explain the variation in the two values above.

Solution:

Task:6.2

Bismuth (melting point, 280^0C) and cadmium (melting point 240^0C) form a eutectic mixture of 60% bismuth by mass at a temperature of 145^0C.

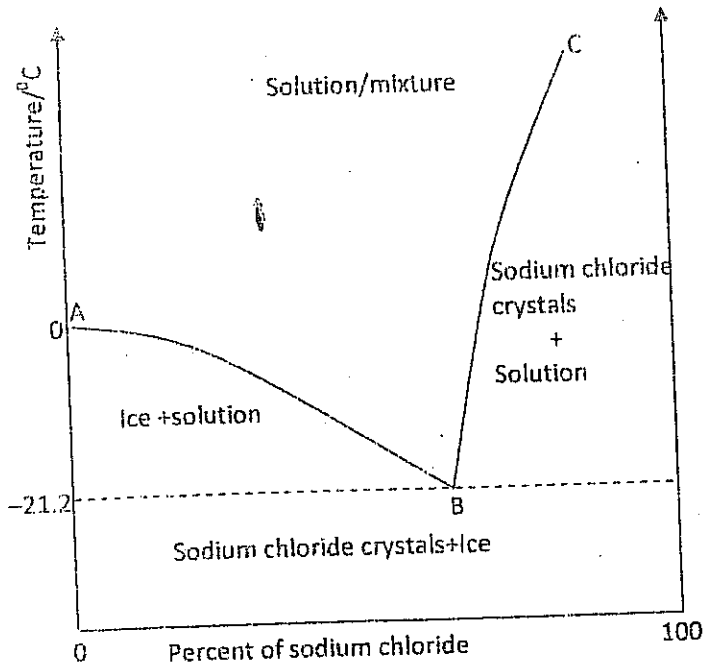
a. Sketch a well labeled phase diagram for bismuth – cadmium system

b. Four samples of the liquid mixture A, B C and D of composition 0%, 20%, 40% and 70% Bismuth respectively were cooled from a temperature of 400^0C separately to 100^0C at constant pressure. Indicate them on the sketch phase diagram and describe what happens to the four liquids during cooling.

c. Given that the freezing points of the liquids are 240^0C, 205^0C, 145^0C and 225^0C respectively, sketch their separate cooling curves. Label the phases on the cooling curves.

6.1.4 Salt- water system

- Inorganic salts like sodium nitrate and potassium iodide also form eutectic mixtures with water when their solutions are cooled at a constant pressure.
- Here;
- Because of the very strong electrostatic forces of attraction in the bonds of the ionic salts, the melting point is always unproportionately too high to be indicated on the phase diagram. Infact their melting points are higher than the critical temperature of water.
- Instead of depression freezing point of the salt with dilution (depression due to increasing amounts of water), we refer to increase in solubility of the salt with temperature.
- The extent to which the solubility increases with temperature is indicated by the steepness of the solubility curve, the steeper the slope of the curve, the slower the increase in solubility with temperature.
- Below is a sketch phase diagram for sodium chloride solution (sodium chloride – water system)



Description

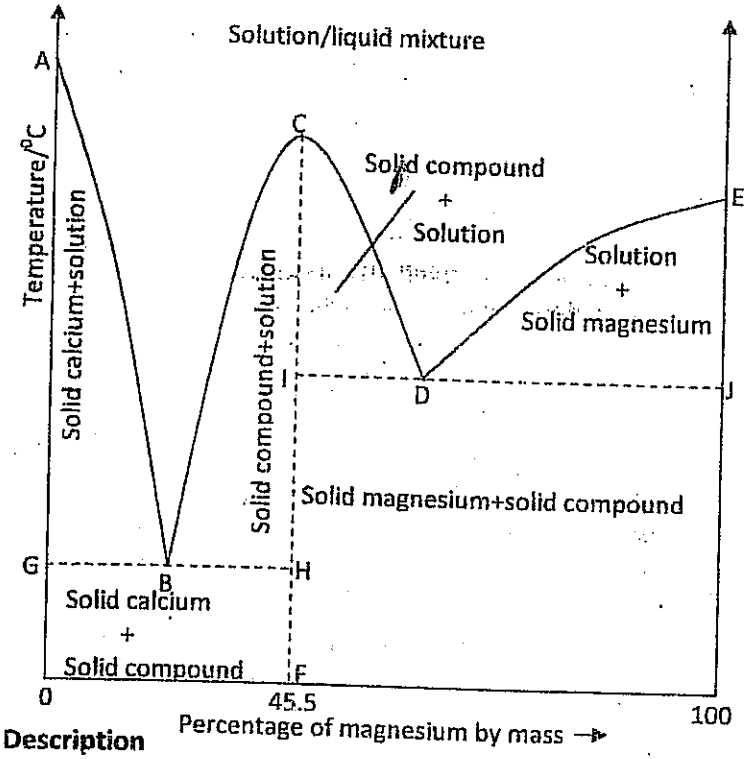
- Point A, temperature of 0^0C is the freezing point of water and the line AB represents the lowering freezing point of water by addition of sodium chloride.
- The line BC represents the increase in solubility of sodium chloride with temperature, with the sharp steepness of the line; it shows only slight increase in solubility of sodium chloride with temperature.
- Point B (a temperature of -21.2^0C and a composition of around 70% sodium chloride by mass) is the eutectic point, also called the cryohydric point sodium chloride solution.
- The eutectic mixture is called cryohydrate to imply hydrated frozen salt.

6.2.2: A compound of the two components and pure components separate out:

- Here when the liquid mixture is formed, some of the pure components form a compound and when it is cooled, a unique fixed temperature and a fixed composition are reached when a solid compound of the two pure components separates out at constant pressure.
- This unique point can be above the freezing point of either the pure components or in between the freezing points of the pure components, depending on the mixture.
- In most cases the formed compound freezes at a sharp constant temperature at a given pressure, to give a solid compound whose composition is equal to the producing liquid compound.
- This compound is known as congruent compound and the fixed melting point and the fixed composition of the compound is known as the congruent point.
- The congruent point on a phase diagram is indicated as a maximum in between (above or below) the curves indicating the depression in freezing points of the two pure components, as shown below for magnesium – calcium mixture.

Definition:

A congruent compound is that compound with a sharp melting point at a constant temperature and constant pressure to give a solid compound whose composition is equal to the producing liquid or producing solid.



Description

- Point A is the melting point of pure calcium and the line AB shows the lowering of the freezing point of calcium by addition of increasing amounts of magnesium.
- Similarly, point E is the melting point of pure magnesium and the line ED shows the lowering of freezing point of magnesium by addition of increasing amount of calcium.
- The maximum at point C corresponds to the formation of a compound of composition 55.5% calcium and 44.5% magnesium (mole ratio of Ca:Mg= 3:4). The empirical formular of the compound is therefore Ca_3Mg_4, a perplexing stoichiometry!

- The lines CB and CD represent the effect of increasing amounts of calcium and magnesium respectively on the melting point of this compound.
- The whole phase diagram is best visualized interms of two separate systems.

i. To the left of the vertical line CF the diagram refers to the system Ca/Ca_3Mg_4

ii. To the right the corresponding system is Mg/Ca_3Mg_4.

- Below the line GH the system is completely solid and consists of a mixture of calcium and the compound. Similarly, solid magnesium and solid compound exist below the line IJ.

- Eutectic mixtures can also be formed from organic solids like;
  - Naphthalene and benzene,
  - Naphthalene and biphenyl and
  - Benzene and chloromethane;
- Other metals pairs that can form eutectic mixtures include;
  - Gold and thallium
  - Tin and Zinc
  - Antimony and lead
  - Cadmium and zinc
  - Tin and silver
  - Bismuth and lead

Tests to show that eutectic mixture is not a compound:

i. Microscopic examination shows it to be heterogenous mixture of crystals that make up the eutectic mixture.

ii. Changing pressure which changes the composition of the mixture

iii. X-ray diffraction pattern which doesn't conform to that of compounds.

iv. Determining its composition which presents a perplexing stoichiometry, not corresponding to any known compound, a case of Calcium – Magnesium system above.

Similarities between a eutectic mixture and compound:

i. Both have constant compositions at constant pressure
ii. Both have a constant melting point at a constant external atmospheric pressure.

Applications of eutectic mixtures:

i. Formation of alloys of more valuable qualities than pure metals
ii. Soldering using tin – lead mixtures
iii. Determination of identity of unknown organic compound.

- Here, the unknown organic compound in the solid state is mixed with another organic compound, suspected to be similar to.
- The melting point of mixture is then determined. Should the mixture have a sharp melting point, then the unknown and the known organic compounds are in the same homologous series. If the melting takes a wide range or temperatures, then they are of different homologous series.

6.3 Miscible liquids:

Basic concepts:

- From kinetic theory of matter, a substance exists in liquid state because of relatively closer pack of its particles and stronger intermolecular forces of attraction.
- These forces of attraction are chiefly; hydrogen bonds and van der Waal's forces.
- van der Waal's forces include: dipole – dipole (orientation forces), dipole – induced dipole (induction forces) and dispersion forces.
- During mixing of a pair a more of liquids, the intermolecular forces of pure liquids (cohesive forces) are broken with consumption (absorption) of energy.

- This is closely followed by formation of intermolecular forces between the particles of the different liquids (adhesive forces) which releases heat.
- The difference between the energy of the two forces (weak bonds breaking and formation) indicates whether a liquid dissolves in or mixes with the other, either endothermically or exothermically.
- When the energy absorbed in breaking cohesive forces is greater than the energy released during the formation of adhesive forces, then the mixing of the liquids is endothermic and when energy absorbed in breaking cohesive forces in less than the energy released during the formation of adhesive forces, then the mixing of the liquids is exothermic.
- When liquids mix endothermically, temperature of the surrounding decreases and the total volume of the mixture is greater than the arithmetic sum of the volumes of the pure components.
- When liquids mix exothermically, temperature of the surrounding increases and the total volume of the mixture is less than the arithmetic sum of the volumes of the pure components.
- However, there are pairs of liquids which mix with no enthalpy change and volume change.
- A pair of liquids that mixes with no enthalpy change or volume change gives an ideal solution whereas a pair of liquids that mixes with enthalpy change or volume change forms a non ideal/imperfect/real solution.

Variables of a liquid – liquid solution:

- There are three important variables (quantities that do vary) of a liquid – liquid solution when in a closed system, whether it be ideal or non ideal. These are:

a. Composition i.e. proportion of each liquid in the mixture always expressed in terms of mole fraction.
b. Vapour pressure of the vapour above the solution.
c. Boiling point of the solution.

- The vapour above the solution varies in composition and the value of its pressure with the composition of the liquid – liquid mixture and can be plotted on a graph to give a curve known as vapour pressure – composition curve.
- Since the boiling point of the solution occurs when the pressure of the vapour above it is equal to external atmospheric pressure and the vapour pressure in turn depends on composition, boiling point of the solution varies also with composition and gives a plot called boiling point – composition curve.

6.3.1 Ideal liquid – liquid solutions:

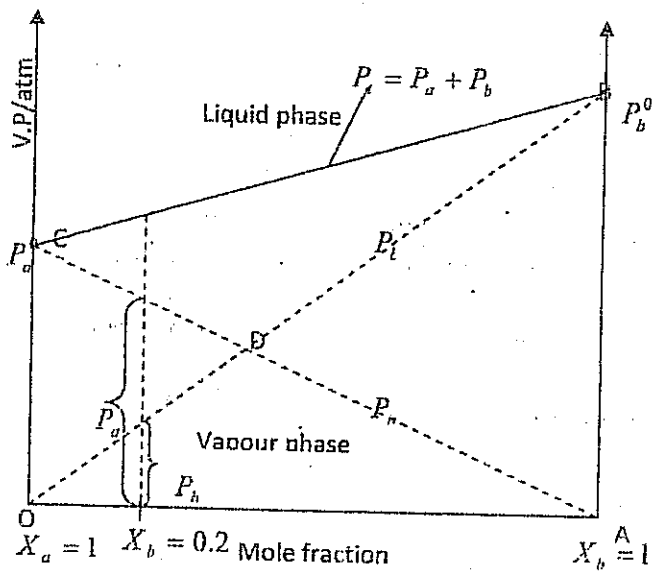
Definition:

A liquid – liquid solution formed by a pair of liquids in which the intermolecular (cohesive forces of attraction) of the pure liquids are equal to the intermolecular (adhesive forces), with zero enthalpy and volume changes and obeys Raoult's law.

- Consider an ideal liquid mixture made of pure components A and B. From the definition of an ideal solution, the A – A and B – B forces of attraction (cohesive forces) are therefore equal in magnitude to the A – B forces of attraction (adhesive forces).
- If P_a^0 and P_b^0 respectively are the vapour pressures of pure A and B above the solution of A and B and P_a and P_b are the partial vapour pressures of components A and B respectively, at the same temperature.
- The total vapour pressure P_t is given by Dalton's law of partial pressure.

$$P_t = P_a + P_b \quad \text{.....6.1}$$

- This is diagrammatically illustrated below in a vapour pressure – composition diagram for an ideal solution of components A and B.



Definitions

i) ***Curves (lines):***

- OB shows variation of partial vapour pressure of component B with its composition.
- AC shows variation of partial vapour pressure of component A with its composition.
- CB shows the variation in total vapour pressure with composition.

ii) ***Points:***

- P_a^0 indicates the saturated vapour pressure of pure component A at the given temperature.

- B indicates the saturated vapour pressure of pure component B at the given temperature.
- This phase diagram does not indicate the phase in which liquid and vapour are in equilibrium, i.e:

  Liquid $\rightleftharpoons$ Vapour
- The total vapour pressure at any composition is given by the sum of partial vapour pressures of the components at that composition.
- The more volatile component has a higher pressure at a given temperature, if the composition is the same.
- For the above case therefore component B is more volatile since its saturated vapour pressure is higher than that of pure A (mole fraction of each is one) at a given temperature. The same inference can be argued out by taking mole fraction of each equal to 0.5.
- Taking a composition of mole fraction of A, $X_a = 0.8$, the partial vapour pressure of A, a less volatile component is more than the partial vapour pressure of B, a more volatile component.
- This implies that the partial vapour pressure of a component in the mixture depends on the mole fraction of the component which is stated as Raoult's law.

The statement of Raoult's law:

The partial vapour pressure of any volatile component of a liquid in liquid solution is equal to the saturated vapour pressure of the pure component at the same temperature multiplied by the mole fraction of the component.

- This law can as well be stated: as the partial vapour pressure of any volatile component of a liquid in liquid solution is proportional the mole fraction of the component in the solution at the same temperature.
- For the above mixture of A and B, applying Raoult's law:

The partial vapour pressure of an volatile component of any ideal soln is the product of mole fraction & vp of the pure component.

$P_a = X_a P_a^0$ 6.2

$P_b = X_b P_b^0$ 6.3

- From Dalton's law of partial pressure

$P_t = P_a + P_b$

$\Rightarrow P_t = X_a P_a^0 + X_b P_b^0$ 6.4

But, $X_a + X_b = 1$, $X_a = X_b - 1$

Putting into equation 6.4,

$\Rightarrow P_t = (X_b - 1)P_a^0 + X_b P_b^0$

So that, $P_t = (P_a^0 + P_b^0)X_b - P_a^0$ 6.5

Also, $X_b = 1 - X_a$

Putting into equation 6.4,

$\Rightarrow P_t = X_a P_a^0 + (1 - X_a)P_b^0$

So that, $P_t = P_b^0 + (P_a^0 - P_b^0)X_a$ 6.6

- Since the vapour above the solution is assumed to behave as the ideal gas, and hence obeys Dalton's law of partial pressure, the compositions of each of the components in terms of mole fraction in the vapour is given by:

$$Y_a = \frac{P_a}{P_t} \quad \text{.....6.7}$$

From equation 6.5 or 6.6,

$$Y_a = \frac{P_a}{(P_a^0 + P_b^0)X_b - P_a^0} \quad \text{.....6.8}$$

Or

$$Y_a = \frac{P_a}{(P_a^0 - P_b^0)X_a + P_b^0} \quad \text{.....6.9}$$

$$Y_b = \frac{P_b}{P_t}$$

From equation 6.5 or 6.6,

$$Y_b = \frac{P_b}{(P_a^0 + P_b^0)X_b - P_a^0} \quad \text{.....6.10}$$

Or

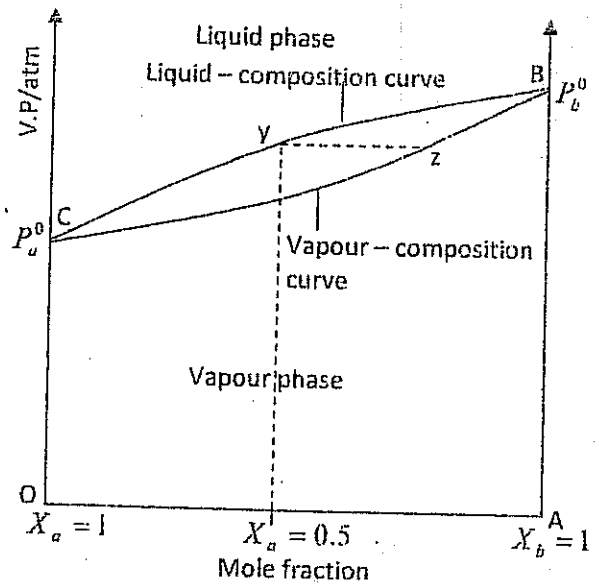
$$Y_b = \frac{P_b}{(P_a^0 - P_b^0)X_a + P_b^0} \quad \text{.....6.11}$$

Pairs of liquids that form ideal solutions:

- Ideal solutions are not practical solutions but there are pairs of liquids that form nearly ideal solutions and therefore their solutions are taken to be ideal. This is due to the similarity of their intermolecular forces.
- These pairs include:
- Water – methanol,
- Methylbenzene – benzene,
- Carbon tetrachloride – silicon tetrachloride,
- 2 – methylpropan – 1 – ol – propan – 1 – ol

Vapour/liquid composition diagram of an ideal liquid-liquid solution

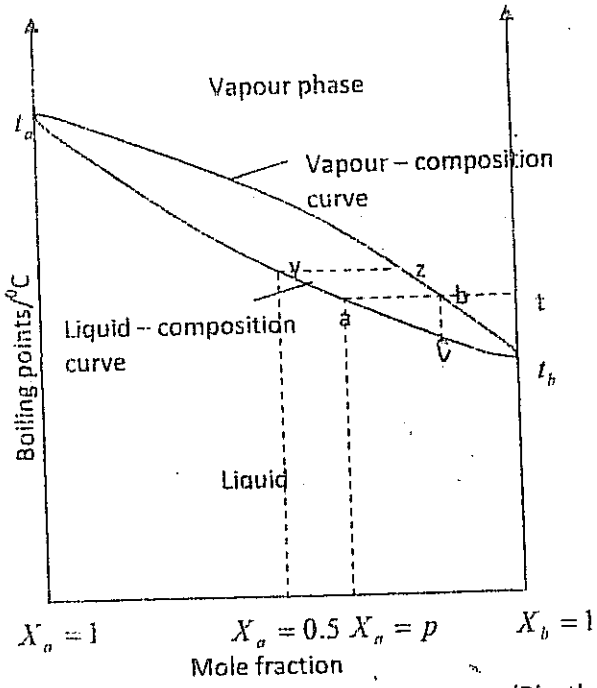
- The variation in the composition of the liquid – liquid solution and that of the of vapour can be plotted against composition to give a vapour pressure/liquid composition curve, as shown below:



- The upper curve shows variation in the composition of the liquid.
- The lower curve shows variation in composition of vapour.
- The horizontal line yz is called a tie line (a line joining a liquid and vapour it is in equilibrium with.
- Such a tie line is important to identify a liquid curve and a vapour curve
- If the composition of the liquid is constant/the same, the vapour in equilibrium with the liquid must be richer in the volatile component.
- The vapour phase is below the two curves while the liquid phase is above the two curves. In between the two curves, the liquid and vapour are in equilibrium; i.e Liquid Vapour.

Boiling point – composition diagram for an ideal solution

- Since a more volatile liquid has a lower boiling point than a less volatile liquid at a fixed external pressure, the boiling point – composition diagram of a pair of liquid that forms an ideal solution is the inverse of vapour pressure composition diagram.



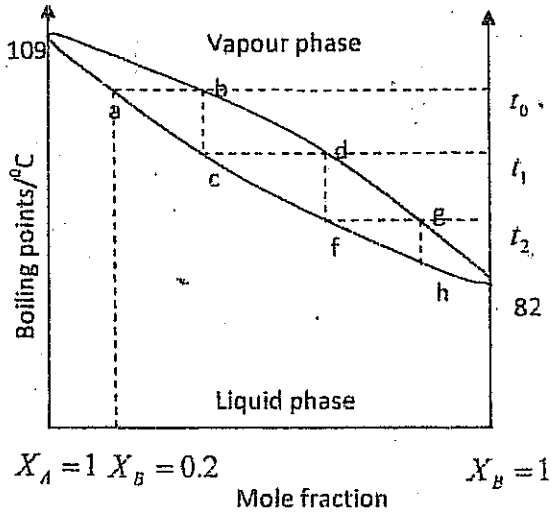
- t_b is the boiling point of pure component 'B', the more volatile liquid and t_a is the boiling point of pure component 'A' a less volatile liquid.
- Considering when the mole fraction of component "A" is equal to the mole fraction of component "B" i.e. $X_a = X_b = 0.5$, drawing a tie line 'yz' between the lower and upper curves.

- Since the composition of 'B', the more volatile component in vapour is richer at point 'z' than at 'y', the upper curve indicates vapour composition while the lower curve indicates liquid composition.
- The vapour phase is above the two curves while the liquid phase is below the two curves. In between the two curves, the liquid and vapour are in equilibrium; i.e Liquid Vapour.
- When a liquid in the mixture of composition $X_a = p$ is boiled (heated), its temperature increases along the dotted line to point 'a' on the diagram, with the composition remaining constant.
- At point 'a', it boils at temperature't' to give vapour 'b' richer in the more volatile component 'B'. If the vapour is cooled, it then condenses to give liquid 'c' of the same composition as the vapour.
- The fact that vapour of a mixture of miscible liquids is richer in the more volatile component with which it is in equilibrium is employed in fractional distillation.

Fractional distillation of an ideal liquid – liquid solution:

- Fractional distillation is a method of separating a mixture of miscible liquids with marked difference in boiling points. It uses the fact that the vapour of an ideal liquid in liquid solution is richer in the more volatile component than the solution/liquid with which it is in equilibrium.
- In practice:
- The liquid mixture is heated to its boiling point:
- This gives 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.

- The liquid obtained is then heated to give vapour still richer in the more volatile component; vapour condensed to give liquid of the same composition as the condensed vapour.
- By repeating heating and condensation a number of times reasonably pure sample of the more volatile compon be obtained as the distillate and the less volatile as the residue.
- Since an ideal liquid – liquid solution can be separ fractional distillation, it is also known as a **zeotropic** mix
- A boiling point – composition phase diagram satisfact illustrates fractional distillation.
- Consider an ideal liquid mixture of 2 – methylpropan – 1 – ol (boiling point=109^{0}C) and propan – 1 – ol (boiling point=82^{0}C) of mole fraction propan – 1 – ol is 0.2, shown in the diagram below:



$A \equiv 2-$methylpropan$-1-$ol , $B \equiv$ propan$-1-$ol

- When the mixture of the two liquids in which the mole fraction of propan – 1 – ol is 0.2 is heated, it boils at temperature t_0 giving vapour b richer in propan – 1 – ol.

MEMBERSHIP DETAILS
HOLDER'S NAME
CLASS
HOLDER'S SIGNATURE
PRESIDENT'S SIGNATURE
P.O. BOX
KISUBI SEMINARY

oiling to give liquid c of the same

ils at temperature t_1 lower than liquid to produce vapour d nponent (propan – 1 – ol). ng to give liquid f of the same

of heating the condensed vapour and vapour is continued several times, a distillate opan – 1 – ol is obtained, while the residue es richer in 2 – methylpropan – ol.

actional distillation can be done in two different ways: i.e discontinuous and continuous methods.

a. Discontinuous method:

- Here after heating a mixture of a given composition to its boiling point, the vapour produced is removed and condensed. The liquid obtained from the condensation of the vapour is then heated to its boiling point. The produced vapour is again removed and condensed.
- When the process of heating the mixture to its boiling point, removing the produced vapour and condensing the vapour is continued, a fraction (portion) of distillate of pure the more volatile component is obtained

b. Continuous method:

- The discontinuous method is quite tedious. Instead in practice, continuous method is employed in a fractionating column.
- A fractionating column is a glass column fitted or packed with small trays, glass or stainless steel coils or beads.
- This packing provides a large surface area for the condensation of the vapour produced from the mixture.
- In the continuous method of fractional distillation;

- When the mixture is heated in a boiler or a distillation
the vapour produced is then condensed in the fr
column into a liquid, richer in the more volatil
- Because of reduction of the proportion of the
component in the distillation flask/boiler, the tem
the residual mixture increases. The vapour produ
the otherwisely continuously heated boiler is at a
temperature and boils the condensed liquid i
fractionating column, producing a vapour which ascends
condenses in the upper part of the column.
- With continuous heating of the mixture, the residual liquid i
the flask/boiler becomes richer in the less volatile
component, while a distillate of pure the more volatile liquid
is obtained.
- Up the fractionating column, the mixture is progressively richer in the more volatile component and the boiling points and therefore temperature progressively decrease. Hence down the fractionating column, the mixture is progressively richer in the less volatile component and the boiling points and therefore temperature progressively increase.

Industrial applications of fractional distillation:

i. Manufacture of nitrogen and oxygen from liquid air.
ii. Purification/refining of crude oil/petroleum.
iii. Concentrating alcohol in breweries.

Worked example:6.3

1. The saturated vapour pressures of components A and B are 50,000Nm^{-2} and 10,000 Nm^{-2} respectively at a given temperature. Calculate the partial vapour pressures and hence total vapour pressure of the ideal mixture of A and B at the given temperature, if 0.1 moles of A was mixed with 0.3 moles of B.

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$=0.4$

$= \frac{3}{4}$

0.4

$10,000$

$= \frac{1}{4} \times 50,000 = 12,500 Nm^{-2}$

$P_b = X_b P_b^0$

$P_b = \frac{3}{4} \times 10,000 = 7,500 Nm^{-2}$

$P_t = P_a + P_b$

$\Rightarrow P_t = 12,500 + 7,500 = 20,000 Nm^{-2}$

Worked example:6.4

2. Ethanol and methanol solutions are ideal. The saturated vapour pressures at 355K of pure ethanol and methanol are 4.5x10^{4}Nm^{-2} and 8.1x10^{4}Nm^{-2} respectively.
a. Why is a liquid mixture of ethanol and methanol ideal?
b. Calculate the partial vapour pressures of ethanol and methanol over the mixture of 64g of methanol and 46g of ethanol.
c. What is the total vapour pressure above the mixture if the mixture contained a total of only 2 moles after one mole of methanol is removed at the temperature?

Solution:

a. In both pure methanol and ethanol, the molecules are bonded by van der Waal's forces and hydrogen bonds respectively. When they are mixed, the two forces of cohesion are broken and replaced by hydrogen bonds and van der Waal's forces between molecules of ethanol and

– the substance mix with no increase in volume and no enthalpy change.

methanol (adhesive forces). The methyl group of methanol and the ethyl group of ethanol do not significantly affect the magnitude of the adhesive forces. Hence the magnitudes of cohesive and adhesive forces are about the same, hence ideality.

b. RMM of CH_3OH =(12x1)+(1x4)+(16x1) =32

Number of moles of methanol, $= \frac{64}{32} = 2$

RMM of CH_3CH_2OH =(12x2)+(16x1)+(1x6) =46

Number of moles of ethanol, $\frac{46}{46} = 1$

Total moles =(2+1) =3

Mole fraction of methanol, $X_m = \frac{2}{3}$

Mole fraction of ethanol, $X_e = \frac{1}{3}$

$P_m^0 = 8.1 \times 10^4 Nm^{-2}$ and $P_e^0 = 4.5 \times 10^4 Nm^{-2}$

$P_m = X_m P_m^0$

$\Rightarrow P_m = \frac{2}{3} \times 8.1 \times 10^4 = 54{,}000 Nm^{-2}$

$P_e = X_e P_e^0$

$\Rightarrow P_e = \frac{1}{3} \times 4.5 \times 10^4 = 15{,}000 Nm^{-2}$

c. $X_m = \frac{1}{2}$ and $X_e = \frac{1}{2}$

$P_m = X_m P_m^0$

$\Rightarrow P_m = \frac{1}{2} \times 81{,}000 = 40{,}500 Nm^{-2}$

$P_e = \frac{1}{2} \times 45{,}000 Nm^{-2} = 22{,}500 Nm^{-2}$

$P_t = P_m + P_e$

= (40,500+22,500)

63,000Nm^{-2}

Task:6.3

Liquids W (molar mass 18) and M (molar mass 32) form an ideal solution. When 9g of W was mixed with 3.2g of M at a given temperature, the total vapour pressure of the mixture was 1217Nm^{-2}. When 19.2g of M was added, the total vapour pressure at the temperature was 3855 Nm^{-2}. Calculate at the temperature;

a. The saturated vapour pressures of W and M.
b. The mole composition of the vapour, before more M was added.
c. The composition of the mixture that will make W and M to have the same partial vapour pressure.

Task:6.4

Tetrachloromethane (boiling point =77^{0}C) and tin (IV) chloride (boiling point =114^{0}C) form an ideal liquid solution. Below are the boiling points (BPt) of different mixtures of tetrachloromethane and tin(IV) chloride at a constant external atmospheric pressure:

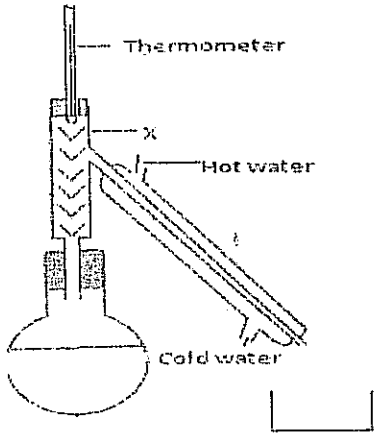
Boiling point/^{0}C	114	100	90	83	77
X_{CCl4}	0.00	0.25	0.50	0.75	1.00

a. i. State Raoult's law
   ii. What is meant by ideal solution?
b. i. Draw on a pair of axes a graph to show variation in boiling point of the mixture with mole fraction
   ii. What other name is given to the graph you have drawn.
   iii. Describe the shape of the graph.
   iv. Descibe generally what takes place during fractional distillation of the mixture.

Task:6.5

Benzene (boiling point = 80^0C) and methylbenzene (boiling point = 110^0C) form a solution that can be separated by fractional distillation.

a. What is meant by fractional distillation?
b. Explain why a mixture of Benzene and methylbenzene can be separated by fractional distillation
c. Sketch;
   i. Boiling point – liquid/ vapour composition diagram
   ii. Vapour pressure – liquid/ vapour composition diagram for the system and on it, label;
      - The curves
      - The phases
d. The above mixture containing mole fraction of benzene less than 0.5 was heated in the experimental setup below.



Describe using the sketch in c.i) above what happens

e. How do you expect the following to vary in the apparatus labeled X
   i. Temperature
   ii. Composition

Task:6.6

The table below shows how the various vapour pressure (V.P atm) of mixture of liquids A and B varies with mole fraction of A (X_a) at a certain temperature.

Mole fraction of A	0.0	0.2	0.4	0.6	0.8	1.0
Vapour pressure/atm	308	318	328	338	348	358

a. State the saturated vapour pressures of A and B.
b. Plot the graph of vapour pressures of the mixture against mole fraction of A.
c. Using the graph, determine the partial vapour pressures of A and B when the mole fraction of B is 0.3.
d. Calculate the partial vapour pressures of A and B when the mole fraction of B is 0.3.
e. Calculate the mole fraction of A at which the partial vapour pressures of A and B are the same.
f. Describe the fractional distillation of the mixture in e) above.

6.3.2 Non ideal liquid – liquid solutions

- These are real/practical or imperfect liquid – liquid solutions. In real solutions, the intermolecular forces of attraction i.e. cohesive forces are not equal in magnitude/strenght to adhesive forces.
- Therefore, on formation of the solution, there are
  a. Change in volume
  b. Enthalpy change
- Therefore real/non ideal ideal liquid – liquid solutions deviate from Raoult's law. The deviations can be negative or positive.

a. **Negative deviation:**
- This occurs when the vapour pressure of the solution is smaller than expected from Raoult's law.

- On mixing pure liquid components A and B, the A---B (force of attraction between A and B i.e. adhesive forces) are stronger than the A---A and B---B (cohesive forces). This leads to decrease in volume and evolution of heat on mixing
- The decrease in volume and evolution of heat when the solution is formed reduce the escaping tendency of the particles of the pure components in the solution to form vapour hence reduced vapour pressure at a given temperature.

Summary of causes of negative deviation:

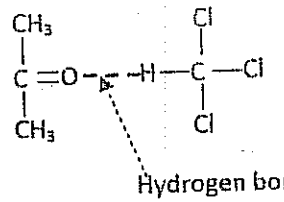
a. Stronger adhesive forces than cohesive forces.
b. Decrease in volume on mixing of the liquids.
c. Heat given out on mixing the liquid.

Pairs of liquids whose mixtures deviate negatively:

- These are generally liquid pairs with different polarities. In this case, one liquid can have a negative polarity at one end or point, while the other has a positive polarity at one end or point.
- These lead to formation of ion – dipole forces or dipole – dipole forces between the particles of the different components, which are stronger than the intermolecular forces in the pure liquids.
- Examples include the following:

a. *Propanone and trichloromethane.*

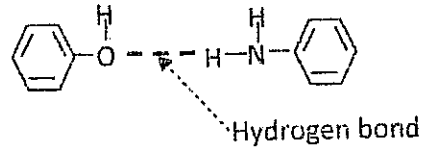
- Propanone has a negative polarity on the oxygen atom; while trichloromethane has a positive polarity on the hydrogen atom. This leads to formation of hydrogen bond between propanone and trichloromethane, which is stronger than the van der Waal's forces between pure propanone and pure trichloromethane respectively.



- Consequently, heat energy is given out on mixing them and hence volume decrease. These reduce the escaping tendency of the liquids to form vapour at a given temperature. Hence negative deviation.

b. *Phenol and phenylamine*

- Phenol has a positive polarity on its hydrogen atom of the phenolic group and a negative polarity on the oxygen atom. Phenylamine has positive polarities on the hydrogen atoms of its amino group. A hydrogen bond is formed between phenol and phenyl amine, which is stonger than the cohesive forces in phenol and phenyl amine.



- This leads to evolution of heat energy and volume decrease on mixing the two. These reduce the escaping tendency of the liquids to form vapour at a given temperature. Hence negative deviation.

c. *Nitric acid and water*

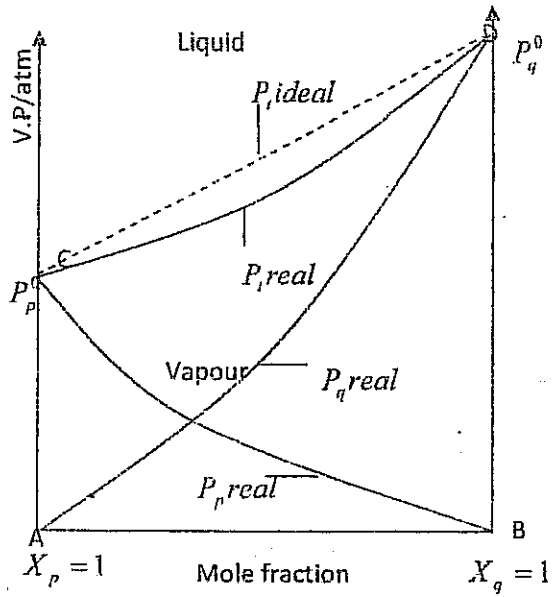
- Nitric acid ionizes in water to produce hydrogen ions and nitrate ions.
- As ions are hydrated, strong ions – dipole attractions are formed compared to the van der Waal's forces in nitric acid and hydrogen bonds in water.

$$HNO_3(l) + H_2O(l) \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$

- Thus heat is released on mixing with a subsequent decrease in volume. These reduce the escaping tendency of nitric acid and water to form vapour at a given temperature. Hence negative deviation.
- All other mineral acids like sulphuric acid and hydrogen halides like: hydrochloric acid, hydroiodic acid and hydrobromic acid, their aqueous solutions show negative deviation from ideality because of similar explanations to the one of nitric acid.

Vapour pressure – composition diagram, at a constant temperature

- The adhesive forces which are stronger than the cohesive forces, responsible for negative deviation get progressively strong with mole fraction of the mixture.
- However, there is a certain unique mole fraction, where the adhesive forces are strongest, making the mixture to have the most reduced escaping tendency to form vapour and hence a minimum vapour pressure.
- Hence, the partial vapour curves and total vapour curve sag (show pseudo – minima), as shown below.



Definitions:

i. ***Curves/ lines:***

- AD shows increase in partial pressure of component Q with incease in its mole fraction in the mixture.
- BC shows increase in partial pressure of component P with incease in its mole fraction in the mixture.
- CD (the solid line) shows variation of real/observed total vapour pressure with mole fractions of the components in the mixture.
- CD (the broken line) shows how the total vapour pressure would vary with the mole fractions of the component, if the solution was ideal.
- Also, straight broken lines can be drawn from A to D and from B to C to show the partial pressures of Q and P respectively vary with their mole fractions in the mixture.

ii. ***Points:***

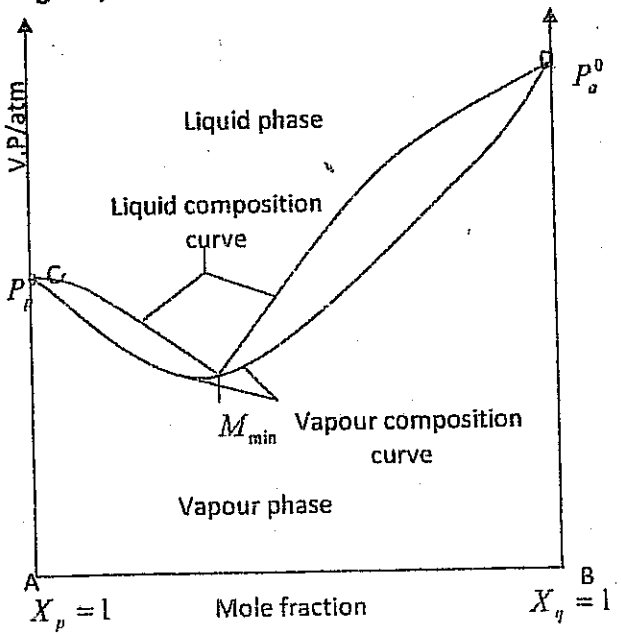
- C is saturated vapour pressure of pure component P, P_p^0 at the given temperature.

- D is the saturated vapour pressure of component Q, at the given temperature.

The shape of total vapour pressure curve:

P_p^0 is the saturated vapour pressure of pure component P. The total vapour pressure increases along CD with increase in mole fraction of Q. The variation is not linear because of strongest attraction between P and Q at a certain mole fraction, causing the mixture to have the smallest vapour pressure, hence the curve sags greatest at that composition. P_q^0 is the saturated vapour pressure of pure component Q at the temperature.

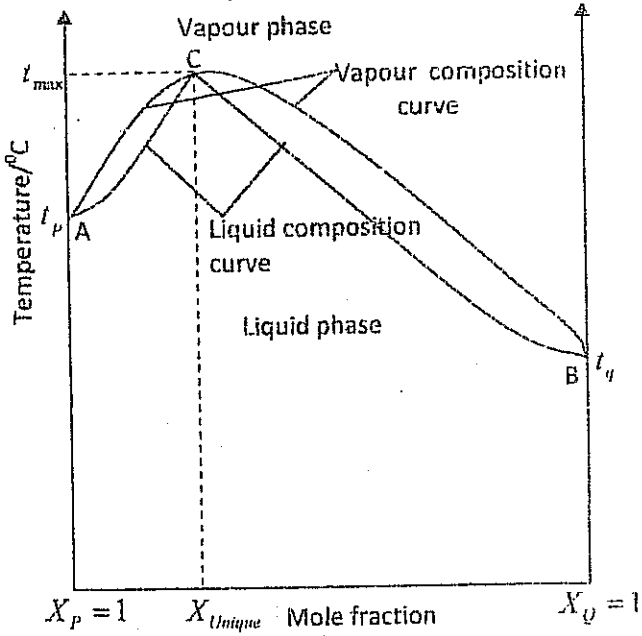
Vapour pressure – liquid and vapour compositions diagram, at constant temperature:



- Point M_{min} is point where the adhesive forces are stongest with minimum vapour pressure. This shows the mole fraction at which the escaping tendency of P and Q to form vapour is most reduced.
- In between point C and M_{min} and between points M_{min} and D, the vapour and liquid are in equilibrium

Boiling point – composition diagram at constant pressure

- Since the vapour pressure composition diagram has a minimum at a certain composition, the boiling point composition diagram therefore will have a maximum at that point.
- This is because, at that composition, the mixture has to be heated to a higher temperature in order for it to generate vapour pressure equal to external atmospheric pressure.
- Hence it has the highest boiling point compared to all the other mole fractions (compositions), as shown below.



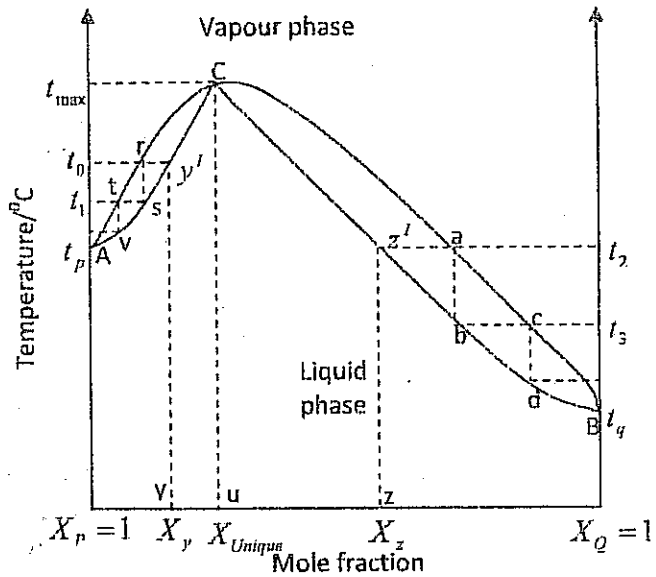
- Point A, t_p is the boiling point of pure component P and point B, t_q is the boiling poit of pure component Q, at the given pressure.
- Point C, given by the co – ordinates (X_{unique},t_{max}) shows the unique mole fraction (X_{unique}) at which the boiling point of the mixture is maximum, t_{max} at a given pressure.
- The mole fraction X_{unique} is called the ***azeotropic miuxture*** of P and Q at that external pressure, and the temperature, t_{max} is the ***boiling point of the azeotropic mixture*** at the same pressure.
- In the areas between points A and C and between points C and B, the liquid mixture and the vapour are in equilibrium.

The shape of the graph:

Pure P boils at a temperature of t_p. As Q is added to the mixture, the boiling point of the mixture increases upto a maximum value at t_{max}. This is because the strength of the adhesive forces increases with mole fraction of Q in the mixture, and is strongest at X_{unique}, corresponding to point C, making the mixture to generate the lowest vapour pressure hence the highest boiling point. Beyond C, as mole fraction of Q increases, the boiling point decreases. This is due to decrease in the strength of the adhesive forces, making the mixture to generate higher vapour pressure, hence lower boiling point. Pure Q boils at t_q.

Fractional distillation of a mixture that deviates negatively:

- The fractional distillation can be done using different mixtures, represented as mixtures: "y", "u" and "z", which give different products on distillation.



Fractional distillation of mixture "u"

- When mixture "u" is heated at a constant pressure, its temperature increases along uC, while its mole fraction remains constant at x_{unique}.
- At C, the mixture boils at the temperature t_{max} to give vapour of the same composition x_{unique} as mixture "u".
- On cooling, this vapour condenses to give mixture "u"
- When the process is repeated, the composition of the mixture x_{unique} and the boiling point t_{max} do not change, and so the mixture is inseperable by fractional distillation.
- Such a unique mixture in a liquid – liquid solution behaves as if it were a third other component in the otherwise binary system, in that:
    1. Its composition remains constant at a constant pressure

2. Its boiling point remains constant at constant pressure.

- Such a mixture in a liquid in liquid solution, which is a pseudo – component in the mixture is known as a **constant boiling mixture** or an **azeotropic mixture.**
- It is a constant boiling mixture because of the constancy of its composition and boling point during distillation; and an azeotropic mixture because of its inseparability by fractional distillation.
- Since the boiling point of this azeotropic mixture is always higher than the boiling points of each of the pure components in the mixture (shown as a maximum on the diagram), at a given pressure, it is referred to as: a **maximum constant boiling point mixture** or a **maximum boiling point azeotrope.**

Definitions:

1. ***An azeotropic mixture or a constant boiling mixture:***

A liquid – liquid mixture that boils at constant temperature to give vapour of the same composition as the mixture, at a constant external pressure.

2. ***A maximum boiling point azeotrope or a maximum constant boiling point mixture:***

- A liquid – liquid mixture that boils at constant temperature always higher than the boiling point of each of the pure component in the mixture to give vapour of the same composition as the mixture, at a constant external pressure.

Distillation of mixture "y".

- When heated at constant external pressure, its temperature increases along yy^{l} until point y^{l} where it boils at temperature, t_0 to give vapour r, richer in component P than

the mixture. The residual liquid in the boiler becomes richer in component Q. On cooling, vapour r condenses to give liquid s of the same composition as vapour r.

- Liquid s boils at temperature t_1 to give vapour t much richer in component P. on cooling vapour t, it condenses to form liquid v or the same composition as vapour t. The residual liquid in the boiler also gets much richer in component Q, tending towards azeotropic mole fraction, X_{unique}.
- When the process of heating the liquid to produce vapour and condensing the produced vapour (distillation) is continued, a pure sample of component P is obtained as the distillate and, the residual liquid on reaching azeotropic composition distils unchanged, and azeotropic mixture is obtained as the residue.
  - ❖ Mixtures like y, to the left of the azeotropic mixture in the diagram are referred to as *below* the azeotropic mixture.

Distillation of mixture z:

- When heated at constant external pressure, its temperature increases along zz^{l} until point z^{l} where it boils at temperature, t_2 to give vapour a, richer in component Q than the mixture. The residual liquid in the boiler becomes richer in component P. On cooling, vapour a condenses to give liquid b of the same composition as vapour a.
- Liquid b boils at temperature t_2 to give vapour c much richer in component Q. On cooling vapour c, it condenses to form liquid d of the same composition as vapour c. The residual liquid in the boiler also gets much richer in component P, tending towards azeotropic mole fraction, x_{unique}.

- When the process of heating the liquid to produce vapour and condensing the produced vapour (distillation) is continued, a pure sample of component Q is obtained as the distillate and, the residual liquid on reaching azeotropic composition distils unchanged, and azeotropic mixture is obtained as the residue.
  - Mixtures like z, to the right of the azeotropic mixture in the diagram are referred to as *above* the azeotropic mixture.
  - Therefore a liquid – liquid mixture of any mole fraction that deviates negatively from Raoult's law can not be completely into the pure components simple fractional distillation. A maximum boiling point azeotrope (an inseparable mixture) is always obtained.

Worked example:6.5

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

a. State the types of deviation from Raoult's law and briefly explain them.
b. How does the mixture of propanone and trichloromethane deviate from Raoult's law? Show your reasoning.
c. What is/are observed when propanone is mixed with trichloromethane? Explain your observation(s)

Solution:

a. Negative deviation: occurs when the total vapour pressure of the mixture is less than expected from Raoult's law.

Positive deviation: occurs when the total vapour pressure of the mixture is more than as expected from Raoult's law.

b. RMM of $CHCl_3$ =(12x1)+(1x1)+(35.5x3) =119.5

Number of moles of $CHCl_3$, $\frac{11.95}{119.5} = 0.1$

RMM of C_3H_6O = (12x3) + (1x6) + (16x1) =58

Number of moles of C_3H_6O, $\frac{14.5}{58} = 0.25$

Total number of moles =0.1 + 0.25 = 0.35

Mole fraction of chloroform (trichloromethane), $X_c = \frac{0.1}{0.35} = \frac{2}{7}$

Mole fraction of propanone, $X_p = \frac{0.25}{0.35} = \frac{5}{7}$

Expected partial vapour pressure of $CHCl_3$ is given by:

$$P_c = X_c P_{tr}^0$$

$$P_c = \frac{2}{7} \times 300 = 85.7143 mmHg$$

Expected partial vapour pressure of propanone is given by:

$$P_p = X_p P_p^0$$

$$P_p = \frac{5}{7} \times 380 = 271.4286 mmHg$$

Expected total vapour pressure is given by:

$$P_t = P_c + P_p$$

$$\Rightarrow P_t = 85.7143 + 271.4286 = 357.1429 mmHg$$

Since the observed total vapour pressure (300mmHg) is less tha the expected total vapour pressure (357.1429mmHg), a mixture of propanone and trichloromethane deviates negatively from Raoult's law.

c. Temperature rise
Volume decrease

As propanone mixes with trichloromethane, van der Waal's forces between their molecules are broken and are replaced by stronger hydrogen bonds between propanone and trichloromethane. This releases heat, hence rise in temperature. The stronger hydrogen bonds compact the molecules closer, hence decrease in volume.

Task:6.7

Nitric acid (boiling point =86^{0}C) and water (boiling point=100^{0}C) are completely miscible and yet their mixtures can not be completely separated by a single fractional distillation.

a. Explain why a mixture of nitric acid and water which are miscible, even with marked difference in boiling points (14^{0}C) can not be separated by fractional distillation.

b. The table below shows a composition of nitric acid in the liquid mixture and vapour above it at various temperature

Temperature/^{0}C	86	100	120	111	103	100
% HNO_3 in liquid	100	81	68	50	20	0
%HNO_3 in vapour	100	87	68	30	06	0

i. Plot a graph of temperature against vapour / liquid compositions. Label the phases.

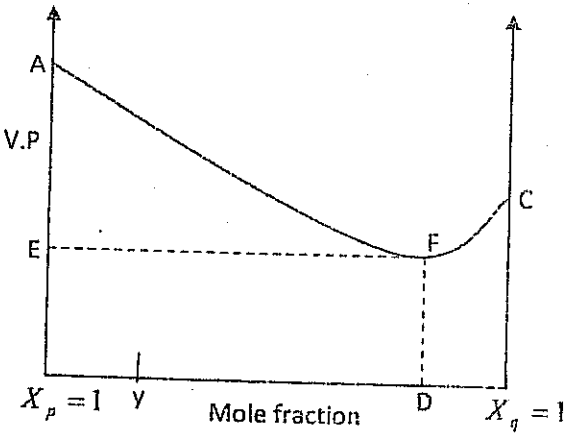
ii. Write the co-ordinates pf the azeotropic point and on the graph mark it U.

iii. How many distillations are needed to obtain a distillate of boiling point equal to 100^{0}C from a mixture of 50% nitric acid by mass? Identify the distillate.

iv. Calculate the volume of the residue of fractional distillation of any of the mixture that would react completely with marble chip to produce 448dm^3 of carbon dioxide at s.t.p (density of the solution is 1.86gcm^{-3}).

Worked example:6.6

The graph below shows variation in total vapour pressure of a liquid – liquid solution that deviates from Raoult's law.



a. i. On the graph indicate how the total vapor pressure would vary if the solution were ideal

ii. What type of deviation is exhibited by the mixture?

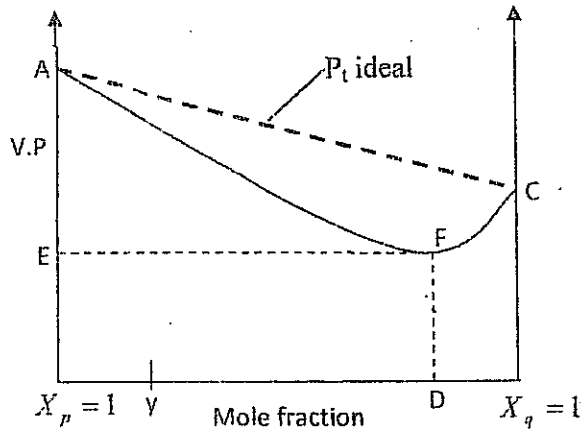
b. Identify the points; A, C, D, E and F.

c. Explain the shape of the curve ACF.

d. Describe the fractional distillation of the mixture y without using a boiling point – composition diagram

Solution:

a. i.



ii. Negative deviation.

b. A – saturated vapour pressure of pure component P
C – Saturated vapour pressure of pure component Q.
D – Azeotropic mixture of Q and P.
E – Vapour pressure of the azeotropic mixture.
F – Azeotropic point.

c. A is the saturated vapour pressure of pure component P. as mole fraction of Q increases in the mixture, the total vapour pressure of the mixture decreases along AF. Due to increase in the strength of the adhesive forces reducing the escaping tendency of the components to form vapour. At F, corresponding to mole fraction at D, the adhesive forces are strongest; with greatest reduced escaping tendency to form vapour, hence the smallest vapour pressure. Beyond F, the strength of adhesive forces decreases. This increases the escaping tendency of the components to form vapour. Hence vapour pressure

increases along FC. C is the saturated vapour pressure of pure component Q.

d. Boils to give a vapour richer in component P. the vapour condenses to give a liquid of the same composition as the vapour. This liquid then boils to give a vapour much richer in component P, which condenses to give a liquid of the same composition as itself. When the process is repeated several times, a distillate of pure P is obtained and a residue of composition represented as D is obtained.

b. Positive deviation from ideality

- This occurs when the vapour pressure of the solution is greater than expected from Raoult's law.
- On mixing pure liquid components A and B, the A---B (force of attraction between A and B i.e. adhesive forces) are weaker than the A---A and B---B (cohesive forces). This leads to increase in volume and absorption of heat on mixing.
- The increase in volume and absorption of heat when the solution is formed increases the escaping tendency of the particles of the pure components in the solution to form vapour hence increased vapour pressure at a given temperature.

Summary of causes of positive deviation:

1. Weaker adhesive forces than cohesive forces.
2. In crease in volume on mixing of the liquids.
3. Absorption of heat on mixing the liquid.

Liquid pairs whose solutions positively deviate:

- These liquids generally have similar polarities causing repulsion between the different particles. Or one component has hydrogen bonds and the other only van der Waal's forces such that on mixing the hydrogen bonds are broken and only

rplaced by van der Waal's forces between the different components.

- Hence on mixing, there is a weaker adhesive force of attraction than cohesive force between the pure components.
- Therefore, stronger cohesive forces (bonds) are broken and weaker adhesive forces (bonds) are formed.
- This leads to net absorption of energy and volume increase, which increases the escaping tendency of the particles in the solution to form vapour making vapour pressure of the solution higher than expected from Raoult's law – positive deviation.
- Examples include:

a) *Water and ethanol*

Both ethanol and water have hydrogen bonds in their molecules. On mixing, the hydrogen bonds (stronger cohesive forces) are broken and replaced by hydrogen bonds between water and ethanol molecules whose formation is hindered by the water hating ethyl group in the molecule of ethanol (weaker adhesive forces). This leads to net absorption of heat and increase in volume, hence positive deviation.

b) *Benzene and cyclohexene*

Both benzene and cyclohexene have a region of high electron density due to pi – bonds. On mixing, van der Waal's forces in between the molecules are broken and the pi – electrons of the different molecules continuously repel one another leading to formation of weaker adhesive forces than cohesive forces. Hence a net absorption of heat and increase in volume which leads to positive deviation.

c) *Acetone and carbon disulphide*

The oxygen atom of propanone (acetone) has negative polarity; also the sulphur atoms of carbon disulphide have

negative polarity. On mixing therefore there is repulsion between the molecules of propanone and that of carbon disulphide leading to absorption of heat and increase in volume, hence positive deviation.

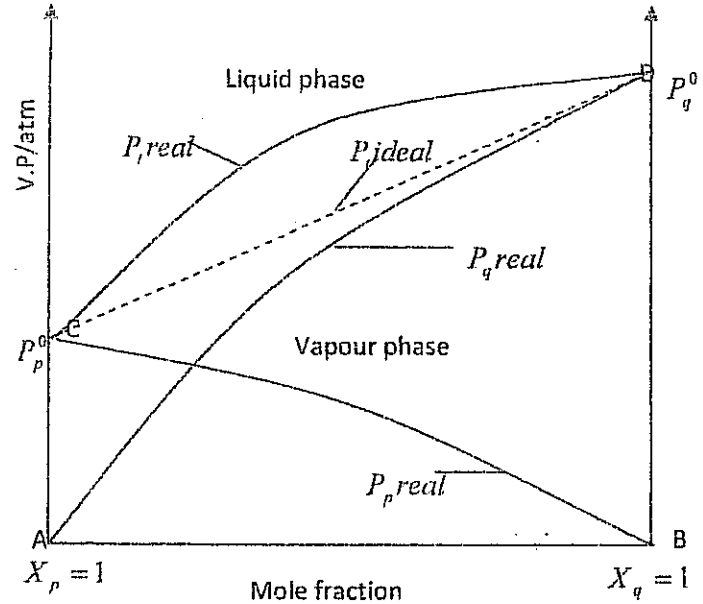
d) *Benzene and ethanol*

The stronger hydrogen bond between ethanol molecules are broken on mixing, but only replaced by weaker van de Waal's forces between ethanol and benzene. This increases the escaping tendency of the molecules in the mixture to form vapour hence positive deviation from ideality.

- Other pairs of liquids whose mixtures deviate positively from Raoult's law include:
- Chloroform and ethanol
- Acetic acid and water
- Tetrachloromethane and ethanol
- Propan – 1 – ol and water

Vapour pressure – composition diagram, at a constant temperature:

- The adhesive forces which are weaker than the cohesive forces, responsible for positive deviation get progressively weaker with mole fraction of the mixture.
- However, there is a certain unique mole fraction, where the adhesive forces are weakest, making the mixture to have a maximum vapour pressure at that mole fraction.
- Hence, the partial vapour pressure curves and total vapour curve bulge somewhat upwards (show pseudo – maxima), as shown below.



Definitions:

i. ***Curves/ lines:***

- AD shows increase in partial vapour pressure of component Q with incease in its mole fraction in the mixture.
- BC shows increase in partial vapour pressure of component P with incease in its mole fraction in the mixture.
- CD (the solid line) shows variation of real/observed total vapour pressure with mole fractions of the components in the mixture.
- CD (the broken line) shows how the total vapour pressure would vary with the mole fractions of the component, if the solution were ideal.
- Also, straight broken lines can be drawn from A to D and from B to C to show the partial vapour pressures of Q and P respectively vary with their mole fractions in the mixture. If they are ideal.

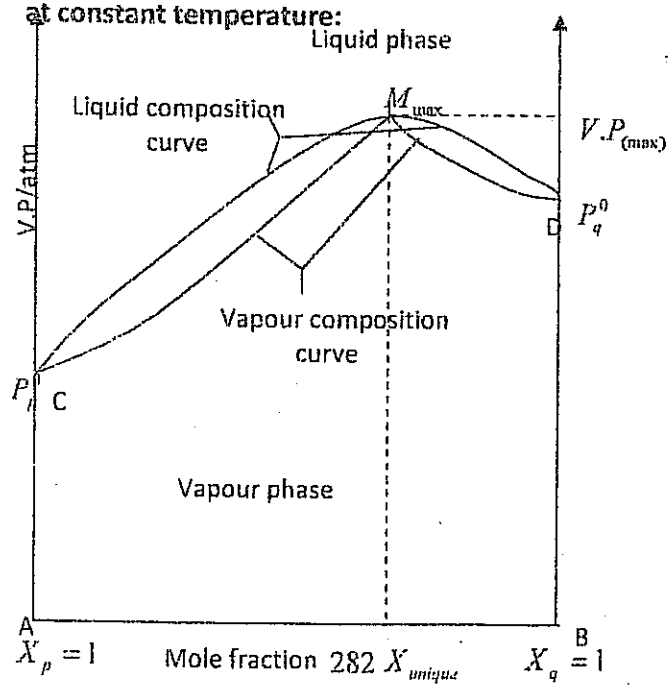
ii. ***Points:***

- C is saturated vapour pressure of pure component P, P_p^0 at the given temperature.
- D is the saturated vapour pressure of component Q, Q_q^0 at the given temperature.

The shape of the total vapour pressure curve:

P_p^0 is the saturated vapour pressure of pure component P. The total vapour pressure increases along CD with increase in mole fraction of Q. The variation is not linear because of weakest attraction between P and Q at a certain mole fraction, causing the mixture to have the biggest vapour pressure, hence the curve bulges greatest at that composition. P_q^0 is the saturated vapour pressure of pure component Q at the temperature.

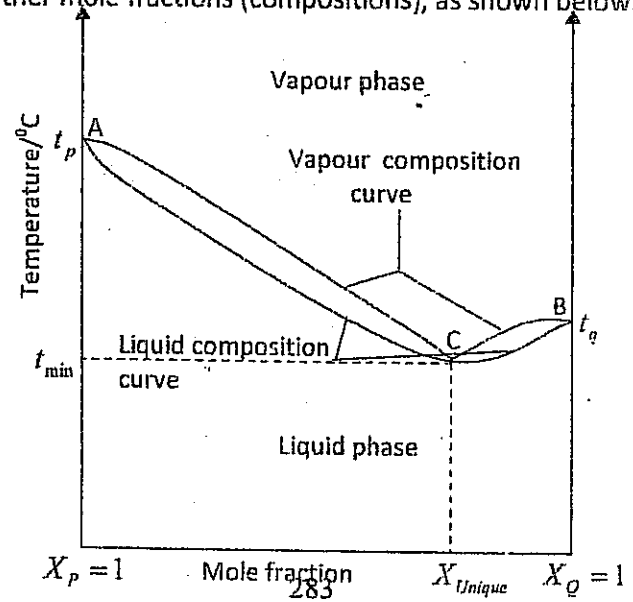
Vapour pressure – liquid and vapour compositions diagram, at constant temperature:



- Point m_{max} corresponding to the co – ordinates (x_{unique}, m_{max}) is the point where the adhesive forces are ~~strongest~~ weakest at the mole fraction, x_{unique} with a maximum vapour pressure. This shows the mole fraction at which the escaping tendency of P and Q to form vapour is most increased.
- In the area between point C and m_{max} and between point m_{max} and D, the vapour and liquid are in equilibrium.

Boiling point – composition diagram at constant pressure

- Since the vapour pressure – composition diagram has a maximum at a certain composition, the boiling point – composition diagram therefore will have a minimum at that point.
- This is because, at that composition, the mixture is just heated to even a lower temperature in order for it to generate vapour pressure equal to external atmospheric pressure.
- Hence it has the lowest boiling point compared to all the other mole fractions (compositions), as shown below.



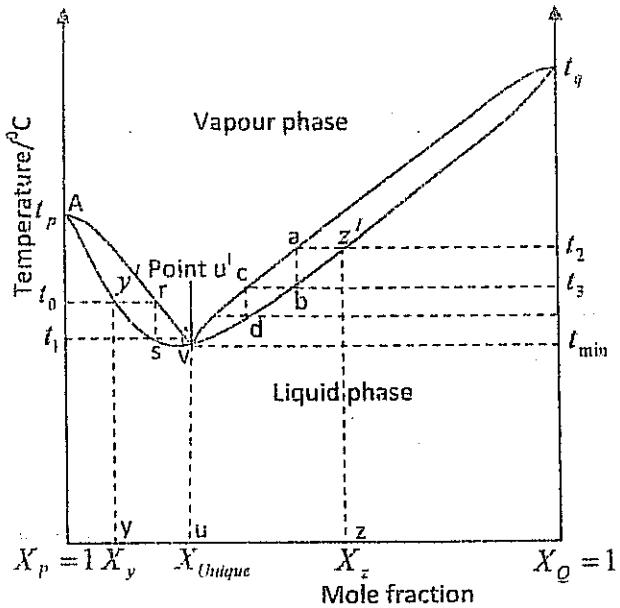
- Point A t_p is the boiling point of pure component P and point B t_q is the boiling point of pure component Q, at the given pressure.
- Point C, given by the co – ordinates (x_{unique}, t_{min}) shows the unique mole fraction x_{unique} at which the boiling point of the mixture is minimum, t_{min} at a given pressure.
- The mole fraction x_{unique} is called the ***azeotropic miuxture*** of P and Q at that external pressure, and the temperature, t_{min} is the ***boiling point of the azeotropic mixture*** at the same pressure.
- In the areas between points A and C and between points C and B, the liquid mixture and the vapour are in equilibrium.

The shape of the graph:

Pure P boils at a temperature of t_p. As Q is added to the mixture, the boiling point of the mixture decreases upto a minimum value at t_{min}. This is because the strength of the adhesive forces decreases with mole fraction of Q in the mixture, and is weakest at C, making the mixture to generate the highest vapour pressure hence the lowest boiling point. Beyond C, as mole fraction of Q increases, the boiling point increases. This is due to increase in the strength of the adhesive forces, making the mixture to generate lower vapour pressure, hence higher boiling point. Pure Q boils at t_q.

Fractional distillation of a mixture that deviates positively:

- The fractional distillation can also be done using different mixtures, represented as mixtures: "y", "u" and "z", which give different products on distillation.



Fractional distillation of mixture "u"

- When mixture "u" is heated at a constant pressure, its temperature increases along uu', while its mole fraction remains constant at X_{unique}.
- At u', the mixture boils at the temperature (t_{min}) to give vapour of the same composition (X_{unique}) as mixture "u". On cooling, this vapour condenses to give mixture "u"
- When the process is repeated, the composition of the mixture (X_{unique}) and the boiling point (t_{min}) do not change, and so the mixture is inseperable by fractional distillation.
- Again, such a unique mixture in a liquid – liquid solution behaves as if it were a third other component in the otherwise binary system, in that:

a. Its composition remains constant at a constant pressure.

b. Its boiling point remains constant at constant pressure.

- It is the pseudo – component in the mixture known as a **constant boiling mixture** or an **azeotropic mixture**.
- As in the fractional distillation of a mixture that negatively deviates from Raoult's law, it is a constant boiling mixture because of the constancy of its composition and boiling point during distillation; and an azeotropic mixture because of its inseparability by fractional distillation.
- Since the boiling point of this azeotropic mixture is always lower than the boiling points of each of the pure components in the mixture (shown as a minimum on the diagram), at a given pressure, it is referred to as: **a minimum constant boiling point mixture** or **a minimum boiling point azeotrope.**

Definitions:

A minimum boiling point azeotrope or a minimum constant boiling point mixture:

- A liquid – liquid mixture that boils at constant temperature always lower than the boiling point of each of the pure component in the mixture to give vapour of the same composition as the mixture, at a constant external pressure.

Distillation of mixture "y".

- When heated at constant external pressure, its temperature increases along yy' until point y' where it boils at temperature, t_0 to give vapour r, richer in component Q than the mixture. The residual liquid in the boiler becomes richer in component P. On cooling, vapour r condenses to give liquid s of the same composition as vapour r.
- Liquid s boils at temperature t_1 to give vapour t much richer in component Q, tending towards azeotropic mole fraction,

X_{unique}. On cooling vapour t, it condenses to form liquid v or the same composition as vapour t. The residual liquid in the boiler also gets much richer in component P,

- When the process of heating the liquid to produce vapour and condensing the produced vapour (distillation) is continued, a sample of the azeotropic mixture is obtained as the distillate and, the residual liquid obtained as pure Q.
  - ❖ Mixtures like y, to the left of the azeotropic mixture are referred as a mixture *below* azeotropic mixture.

Distillation of mixture z:

- When heated at constant external pressure, its temperature increases along zz^{l} until point z^{l} where it boils at temperature, t_2 to give vapour a, richer in component P than the mixture. The residual liquid in the boiler becomes richer in component Q. On cooling, vapour a condenses to give liquid b of the same composition as vapour a.
- Liquid b boils at temperature t_2 to give vapour c much richer in component P, tending towards azeotropic mole fraction, X_{unique}. On cooling vapour c, it condenses to form liquid d of the same composition as vapour c. The residual liquid in the boiler also gets much richer in component Q,
- When the process of heating the liquid to produce vapour and condensing the produced vapour (distillation) is continued, a sample of the azeotropic mixtue (X_{unique}) is obtained as the distillate and component Q is obtained as the residue.
  - ❖ Mixtures like z, to the right of the azeotropic mixture are referred to as *above* the azeotropic mixture.
  - ❖ Therefore a liquid – liquid mixture of any mole fraction that deviates positively from Raoult's law can not be

completely separated into the pure components by single fractional distillation. A minimum boiling point azeotrope (an inseparable mixture) is always obtained.

- From the fractional distillation of mixtures that deviate negatively and positively from Raoult's law, there are two types of azeotropic mixtures:

1. Maximum boiling point azeotrope
2. Minimum boiling point azeotrope.

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 always higher than the boiling points of each of the pure components.	Its boiling point is always lower than the boiling points of each of the pure components.
Obtained as residue during fractional distillation.	Obtained as distillate during fractional distillation.

Azeotropic mixtures and pure substances:

- Azeotropic mixtures to a certain degree behave as pure compounds in that:

i. Their compositions are constant at constant pressures.

ii. They have sharp and constant boiling points.

- However, on close examination, they contrast to pure compounds in:

Azeotropic mixtures	Pure compounds
Composition varies with pressure	Composition remains constant
Freezing takes a wide range of temperature	Freezing takes a narrow range of temperature
Components easily seperable	Components separated by complex processes.

Task:6.8

The table below shows some data about two immiscible liquids A and B.

Liquid	Saturated V.P	RMM
A	400mmHg	106.5
B	600mmHg	58

When 10.6g of A was mixed with 2.9g of B at 20^0C, the total vapour pressure of the mixture was 500mmHg.

a. Show that the mixture of A and B deviates positively from Raoult's law.

b. Sketch the vapour pressure – liquid/vapour composition diagram for the mixture of A and B. label the phases and the curves.

c. Explain the shape of vapour pressure curve

d. Describe the fractional distillation of the mixture.

Task:6.9

A mixture of methanol and water is ideal, while a mixture of propan – 1 – ol and water deviates positively from Raoult's law.

a. Explain why the mixture of water with;

i. Methanol is ideal

ii. Propan – 1 – ol deviates positively

b. Propan – 1 – ol (boiling point=97^0C) and water(boiling point =100^0C) form a minimum boiling point azeotrope of composition 72% propan – 1 – ol and boils at 88^0C.

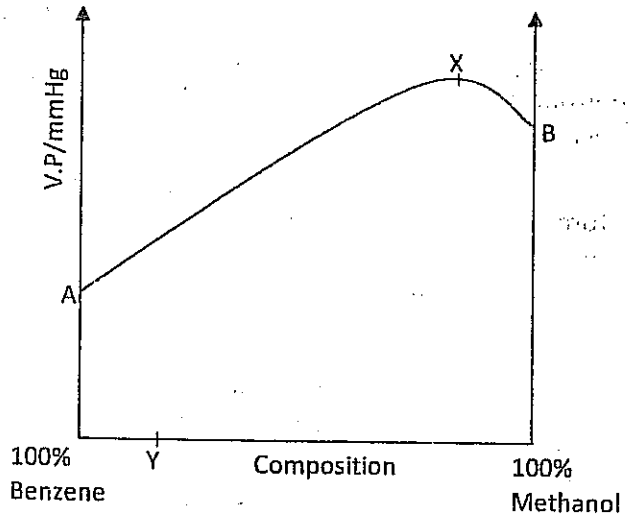
i. What is meant by the term minimum boiling point azeotrope

ii. Sketh the boiling point – composition diagram for the mixture.

iii. Describe how a distillate of pure propan – 1 – ol can be obtained from a mixture containing 50% water.

Task:6.10

The vapour pressure – composition diagram below is for benzene methanol system.



a. Label the phases

b. What is the significance of the curve AXB, and state what point X represents?

c. The boiling points of benzene and methanol are 80^0C and 65^0C respectively

   i. What do points A and B represent?

   ii. Will mixture X boil at a temperature above or below 65^0C?

d. Suggest a reason why benzene – methanol mixtures deviate from Raoult's law.

e. The mixture of composition Y was fractionally distilled.

   i. What will be the composition of the distillate?

   ii. What will be the composition of the liquid residue in the flask?

Separation of azeotropic mixtures:

- Despite their miscibility in all proportions, coupled with even marked difference in boiling points, mixtures of liquids that deviate from Raoult's law (mixtures that form azeotropic mixtures) can not be separated by one fractional distillation.
- The following methods are used to separate azeotropic mixtures, it be form a positively or a negatively deviating mixture.

i. Chemical method

- An azeotropic mixture of ethanol and water is separated by adding quick lime (calcium oxide) which removes water leaving ethanol.

ii. Distillation by use of a third component

- An azeotropic mixture of ethanol and water may be separated by addition of benzene and then distilling the mixture of the three components.

- Here first distillation yields an azeotropic mixture of the three components, a ternary azeotrope and the second distillation produces a mixture of ethanol and benzene (a binary azeotrope), pure water isolated.
- On fractionally distilling the mixture of ethanol and benzene, pure ethanol is obtained.

iii. Separation by absorption

- Always effected by addition of charcoal or silica gel which absorbs one component.

iv. Solvent extraction.

6.4 Immiscible liquids:

Introduction

- Immicible liquids are liquids which do not mix in any proportion; instead they segregate to form layers of pure components.
- Immiscibility of liquids is an extreme case of positive deviation from ideality. In the case of immiscibility, the repulsion between the molecules of the different liquids is extreme to the extent that the particles are segregated to form layers according to their densities.
- However it should be noted that:

a. However much the segregation of the pure liquid molecules, at the junction (liquid –liquid interface), there is virtual miscibility.

b. Due to immiscibility, volume increase and heat absorption on mixing, molecules of immiscible liquids have a much more increased escaping tendency to form vapour compared to each of the separate pure liquids and a mixture that deviates positively from Raoult's law.

- Therefore at a given temperature the total vapour pressure of the mixture of immiscible liquids is higher than that of

- Also the boiling point of the mixture remains constant irrespective of the composition as long as both liquids are present.

6.4.1 Steam distillation

Steam distillation is a technique of separating a volatile substance that is immiscible with water from its mixture with a non-volatile component at a temperature below its boiling point by passing steam through the mixture, condensing the immiscible distillate and separating to obtain a pure sample.

- In practice:
  - Steam is passed through the mixture (instead of boiling the mixture with water).
  - The steam on meeting the cold mixture condenses releasing a lot of latent heat of condensation.
  - The latent heat of condensation boils the mixture at a temperature lower than the boiling temperature of water since each liquid vapourises independently making the total vapour pressure to equal to external pressure at a lower temperature.
  - The vapour is condensed to give an immiscible distillate of the substance and water.
  - The immiscible mixture of the distillate is then separated by using a separating funnel, and the substance dried using a suitable drying agent.
- Steam is preferred to liquid water because it keeps the mixture agitated and equilibrium between the vapour and the liquid is attained rapidly.

Applications of steam distillation

- Purification of organic solvents that would decompose close to their boiling points.

- It is used to determine relative formular mass relative formula masses.

Advantages of steam distillation

- Can distill organic solvents near to their boiling points.

Conditions under which steam distillation can be conducted satisfactorily:

- The compound being separated should have a considerable vapour pressure at the temperature near to the usual boiling point of water.
- The compound should have a fairly high relative formular mass, to obtain a good quantity.

Worked example:6.6

A certain hydrocarbon was found to distill freely in steam at a temperature of 95^{0}C when the atmospheric pressure was 744mmHg. The vapour pressure of pure water at this temperature is 634mmHg. The distillate contained 55% by weight of the hydrocarbon. Calculate its molecular weight.

Solution:

Saturated vapour pressure of water, $P_w^0 = 634$

Saturated vapour pressure of the hydrocarbon, $P_t^0 = 744 - 634 = 110$

Percentage of water, m_w= (100 – 55) =45

Percentage of the hydrocarbon, m_t=55

RMM of H_2O, M_w= (1x2) + (16x1) =18

Let RMM of terpinene be M_t

From, $\frac{P_w^0}{P_t^0} = \frac{m_w \times M_t}{m_t \times M_w}$

$\Rightarrow \frac{634}{110} = \frac{45 \times M_t}{55 \times 18}$

$M_t = 126.8 \approx 127$

Conditions
- Compound must have high Molar mass
- must exert an high vapour pressure.

Worked example:6.7

An organic liquid which is immiscible with water is steam distilled at 80^{0}C and at 751mmHg. The distillate is found to contain 71% by weight of the organic liquid. The vapour pressure of water at 80^{0}C is 355mmHg. Calculate the molecular weight of the organic liquid.

Solution:

Saturated vapour pressure of water, $P_w^0 = 355$

Saturated vapour pressure of the organic liquid, $P_{or}^0 = 751 - 355 = 396$

Percentage by mass of the organic liquid, $m_{or} = 71$

Percentage by mass of water, $m_w = 100 - 71 = 29$

RMM of H_2O, M_w=(1x2)+(16x1)=18

Let RMM of of the organic liquid be M_{or}

From $\frac{P_{or}^0}{P_w^0} = \frac{m_{or} \times M_w}{m_w \times M_{or}}$

$$\Rightarrow \frac{396}{355} = \frac{71 \times 18}{29 \times M_{or}}$$

$$M_{or} = 39.506 \approx 40$$

Task:6.11

1. An aromatic compound freely distils in steam at 98.2^{0}C under a pressure of 732mmHg. The distillate was found to contain 15.8% by mass water. Calculate the formula mass of the aromatic compound if the saturated vapour pressure of water at the distillation temperature is 713.5mmHg.

Task:6.12

2. Chlorobenzene and water are immiscible and their mixtures boil at 91^{0}C under atmospheric pressure of 101kPa. A

distillate of a mixture of the two substances contained 2.37g of chlorobenzene and 19 of water. Calculate the saturated vapour pressures of water and chlorobenzene at 91^{0}C.

Task:6.13

3. The table below shows the vapour pressures of pure water and phenylamine at different temperatures.

Temperature/^{0}C	85	90	95	100	105
V.P of water/mmHg	434	526	634	760	906
V.P of phenylamine /mmHg	22.9	29.2	36.5	45.7	55.0

a. Work out the total vapour pressure of the mixture
b. On the same pair of axes, plot graphs showing the variation of total vapour pressure and vapour pressures of pure water and phenylamine with temperature.
c. Use the graph to determine the boiling points of the mixture at:
   i) Sea level of standard pressure of 760mmHg
   ii) On a mountain peak of pressure 720mmHg
d. Calculate the mass of steam required to produce 20g of phenylamine;
   i) At the sea level
   ii) On top of the mountain

6.4.2 Partition/distribution of a solute between a pair of immiscible liquids in contact

- When a pair of immiscible liquids is in contact and a solute soluble in both of them is introduced to the system, then the solute will dissolve/ partition/distribute itself in both liquids in a definite concentration ratio and establishes equilibrium at a constant temperature.

- Therefore there is a quantitative relationship between the concentrations of the solute in the solvents and is stated into partition/distribution law.

Partition/distribution law:

"A solute soluble in two immiscible liquids in contact, will distribute itself between the two solvents in a definite ratio of the concentrations of the solute when in equilibrium between the two liquids at a constant temperature.

- This ratio is called the partition/distribution co-efficient.

Definition:

Partition/distribution coefficient is the ratio of the concentrations of a solute soluble in two immiscible liquids in contact and in equilibrium in the liquid at a given temperature.

- Suppose a solute A is dissolved in solvent$_1$ and a less dense immiscible liquid$_2$ is added or placed on top of this solution.
- The solute A particles then move upward across the interface between the two liquids and dissolve in solvent$_2$
- Because of the random motion of the dissolved solute molecules, some will pass back into the lower solvent and as time passes the rate of this downward movement increases. As if the solvents are competing for the solutes!
- Then a certain time is reached when the rate of upward movement of the solute particles is exactly matched with the rate of downward movement of the solute particles hence a state of dynamic equilibrium is achieved between two liquids at the temperature. As if the solvents have agreed on the portion of the solute each one should take!
- If the molar concentrations of solute A in immiscible solvent$_1$ and solvent$_2$ in contact and in equilibrium at a given temperature are $[A]_{solv1}$ and $[A]_{solv2}$ respectively.
- Then from the partition law:

$$K_{d1} = \frac{[A]_{solv1}}{[A]_{solv2}} \quad \text{.....6.18}$$

Or

$$K_{d2} = \frac{[A]_{solv2}}{[A]_{solv1}} \quad \text{.....6.19}$$

Where, K_{d1} is partition coefficient of solute A between solvent$_1$ and solvent$_2$ at the temperature; and K_{d2} is the partition coefficient of solute A between solvent$_2$ and solvent$_1$

$$\Rightarrow K_{d1} = \frac{1}{K_{d2}} \quad \text{.....6.20}$$

- When:

1. $K_{d1}=1$, then the solute is equally soluble in the two solvents (equal competition!)
2. $K_{d1}<1$, then the solute is less soluble in solvent$_1$ than solvent$_2$ (solvent$_2$ more competitive than solvent$_1$)
3. $K_{d1}>1$, then the solute is more soluble in solvent$_1$ than solvent$_2$ (solvent$_1$ more competitive than solvent$_2$)

Worked example:6.7

When 5g of a solute Z in 50cm^3 of water was shaken with 75cm^3 of benzene, 3.5g of Z was absorbed in the benzene layer. Calculate the partition coefficient of Z at the temperature, between:

i. Water and benzene
ii. Benzene and water.
iii. Comment on the nature of Z.

Solution:

i. Concentration of Z in aqueous layer $= \frac{5-3.5}{50} = \frac{1.5}{50}$

Concentration of Z in organic layer $= \frac{3.5}{75}$

$$K_d = \frac{1.5}{50} \times \frac{75}{3.5} = 0.6429$$

Hence the partition coefficient of Z between water and benzene is 0.4269.

ii. The partition coefficient of Z between benzene and water is the reciprocal of the partition coefficient of Z between water and benzene.

$$\Rightarrow K_d = \frac{1}{0.6429} = 1.5556$$

iii. Being more soluble in benzene than water, Z is possibly and organic substance.

Worked example:6.8

At a certain temperature, excess aqueous ammonia was shaken with chloroform. After attainment of equilibrium, 20cm^3 of the aqueous layer required 30cm^3 of 0.5M hydrochloric acid for end point neutralization, while, 10cm^3 of the organic layer required 15cm^3 of 0.05M hydrochloric acid for end point neutralization.

i. Calculate the partition constant of ammonia between chloroform and water

ii. Comment on the solubility of ammonia in chloroform and water.

Solution:

i. Aqueous layer

Moles of hydrochloric acid reacted $= \frac{30 \times 0.5}{1000} = 0.015$

So moles of ammonia reacted = 0.015

Concentration of ammonia $= \frac{0.015 \times 1000}{20} = 0.75M$

Organic layer:

Moles of hydrochloric acid reacted $= \frac{15 \times 0.05}{1000} = 0.00075$

So, moles of ammonia reacted = 0.00075

Concentration of ammonia $= \frac{0.00075 \times 1000}{10} = 0.075$

$$K_d = \frac{0.075}{0.75} = 0.1$$

ii. Ammonia is more soluble in water than in chloroform.

Task:6.14

When 1g of iodine in 50cm^3 of water was mixed with 75cm^3 of tetrachloromethane and equilibrated, 25cm^3 of the aqueous layer required 5cm^3 of 0.01M sodium thiosulphate solution for end point neutralization.

a. Calculate the molar concentration of iodine in the:
   i. Aqueous layer
   ii. Organic layer
b. Calculate the partition coefficient of iodine between:
   i. Water and tetrachloromethane
   ii. Tetrachloromethane and water
c. Comment on the solubility of iodine in water and tetrachloromethane. Explain your comment

Task:6.15

10g of butanoic acid was added to 100cm^3 of water and was shaken with 100cm^3 of ether at a certain temperature and 3.6g of the acid remained in the aqueous layer.

a. Calculate the distribution coefficient of butanoic acid between:
   i. Water and ether
   ii. Ether and water
b. Explain why butanoic acid is:
   i. Soluble in water

ii. Soluble in ether
iii. More soluble in ether

Limitations of the partition law

- The solutions of the solute in the two liquids must be dilute.
- The solute must remain in the same molecular state in both the liquids/solvents i.e. no association or dissociation.
- Temperature must remain constant
- There should be no chemical interaction between the solute and the solvent.

Determination of distribution coefficient (K_d)

- It involves 2 steps:

1. Making solutions of a solute in the two immiscible liquids in contact and allowing equilibrium to be established, at a constant temperature.
2. Determination of the concentrations of the solute is the two layers.

- Determination of the concentration of the solute in the two layers is always by titration/titrimetric technique.
- The standard solution selected to titrate the solutions of the solute in the two layers depends on the nature of the solute itself.

Nature of solute	*Usable standard solution*
Acidic e.g ethanoic acid	Alkalis e.g sodium hydroxide
Alkaline e.g ammonia	Acids e.g hydrochloric acid
Iodine	Sodium thiosulphate

- In titrimetry, the end point is detected by indicators, which are selected depending on the titrant/titrand itself. However, in titrations of iodine solutions, the indicator is starch solution.

- For others, choice of indicators under acid – alkali titrations under ionic equilibria gives a detailed guide. However, below is a general summary.

Reactants	*Suitable indicator*
Strong acid – strong base	Any indicator
Weak acid – strong base	Methyl orange
Strong acid – weak base	phenolphthalein

Case 1: K_d for iodine between water and tetrachloromethane

Procedure

- A known volume of water vcm^3 is added to a separating funnel and xg of iodine is then added to the water.
- vcm^3 of tetrachloromethane is added to the solution of iodine in water, the mixture is shaken vigorously for some time to ensure dissolution of iodine in both the liquids.
- The mixture is then thermostatted and allowed to segregate in layers and attain equilibrium.
- The equilibrated layers are then separated in different beakers out of the funnel.
- Then a fixed volume of aqueous layer is pipetted and titrated with standard sodium thiosulphate solution using starch indicator until consistent titre values in order to determine the concentration of iodine in the aqueous layer.
- From the total amount of iodine introduced and the amount of iodine in aqueous layer, the amount of iodine in tetrachloromethane layer (organic layer) is determined and hence its concentration.
- Hence K_d calculated from, $K_d = \frac{[I]_{aqueous}}{[I]_{organic}}$

❖ Assumptions;

1. Equilibrium not disturbed during separation of the mixture

2. Equilibrium not disturbed during titration
3. The iodine used was pure enough. If purity doubted, then both the organic and the aqueous layers be seperately pipetted and titrated.

Case II: K_d for succinic acid or butanedioic between water and ethoxyethane:

- An aqueous solution of butanedioic acid is prepared, the mixture shaken with ethoxyethane and transferred into a separating funnel.
- The mixture is allowed to stand in order to equilibrate at a constant temperature.
- The layers are separated and fixed volumes of both the organic and the aqueous layers pipetted and titrated with standard sodium hydroxide solution, using methyl orange indicator until consistent titre values.
- From the volume and hence the amount of standard sodium hydroxide solution reacted, the amount of butanedioic acid reacted and hence its concentration in the two solvents are determined.
- Hence $sK_d = \frac{[C_4H_6O_4]aqueous}{[C_4H_6O_4]organic}$

Case III: K_d of ammonia between water and chloroform:

- Aqueous solution of ammonia of known molarity is prepared and vcm^3 of the solution is transferred into a beaker.
- The solution is then shaken with trichloromethane at a constant temperature and allowed to equilibrate.
- Then both aqueous layer and the organic layers are pipetted and titrated with standard hydrochloric acid solution using phenolphthalein indicator until consistent titre values.
- From the end – point volume of hydrochloric acid, the molarities of ammonia in both the aqueous and organic

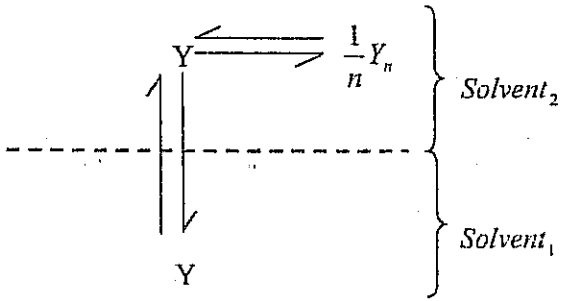
layers are determined and the distribution coefficient at the temperature calculated as:

$$K_d = \frac{[Ammonia]_{water}}{[Ammonia]_{chloroform}}$$

Correcting for association/dissociation of a solute in Kb expression:

a. **Correcting for association**

- Consider a solute Y soluble and remains discrete in a denser solvent$_1$.
- When a solution of this solute with solvent$_1$ is shaken with solvent$_2$, a less dense solvent in which the solute strongly associates to form molecules of formula mass 'n' times the formula mass of the unassociated molecules, then the following equilibria are established.



- If c_1 and c_2 are the respective molar concentrations of solute Y in solvent$_1$ and solvent$_2$ and α is the degree of association.

The equilibrium in solvent$_2$:

	$Y \rightleftharpoons \frac{1}{n}Y_n$	
Before association (initially)	c_2	0
At equilibrium for one mole	(1−α)	$\frac{\alpha}{n}$
At equilibrium for c_2 moles	$c_2(1-\alpha)$	$\frac{\alpha}{n}c_2$

$\Rightarrow [Y] = c_2(1-\alpha)$ and $[Y_n] = \frac{\alpha}{n} c_2$

From the law of mass action/ the equilibrium law,

$$K_c = \frac{[Y_n]^{\frac{1}{n}}}{Y}$$

$$\Rightarrow K_c = \frac{\left(\frac{\alpha}{n} c_2\right)^{\frac{1}{n}}}{c_2(1-\alpha)} \quad \text{.....6.21}$$

For the partition system:

- From the partition law for the partition of Y between solvent$_2$ and solvent$_1$

$$K_d = \frac{[Y]_{solvent2}}{[Y]_{solvent1}}$$

$$\Rightarrow K_d = \frac{c_2(1-\alpha)}{c_1} \quad \text{.....6.22}$$

- Combining equations 6.21 and 6.22, so as to eliminate $c_2(1-\alpha)$;

$$\Rightarrow K_c = \frac{\left(\frac{\alpha}{n} c_2\right)^{\frac{1}{n}}}{K_d c_1} \quad \text{.....6.23}$$

Rearranging:

$$\frac{K_c K_d}{\left(\frac{1}{n}\right)^{\frac{1}{n}}} = \frac{(\alpha c_2)^{\frac{1}{n}}}{c_1}$$

But $\frac{K_c K_d}{\left(\frac{1}{n}\right)^{\frac{1}{n}}} = K^{II}$, a new constant and since the solute is strongly associated in solvent$_2$ $\alpha^{\frac{1}{n}} \approx 1$.

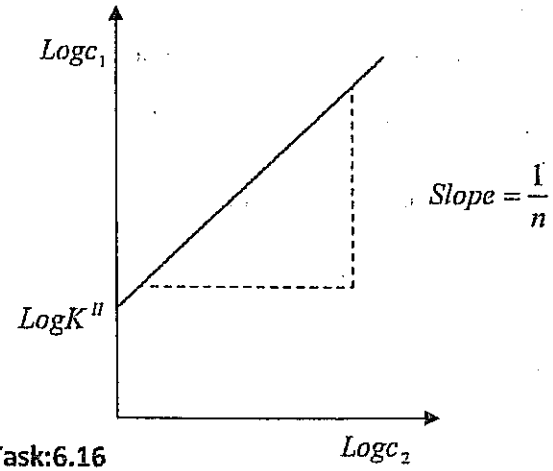
$$\Rightarrow K^{II} = \frac{c_2^{\frac{1}{n}}}{c_1} \quad \text{.....6.24}$$

- Taking $\log_{10}$ of both sides,

$$\log K^{II} = \frac{1}{n}\log c_2 - \log c_1$$

So that,

$$\log c_1 = \frac{1}{n}\log c_2 + \log K^{II} \quad \text{.....6.25}$$



Task:6.16

Ethanoic acid when dissolved in benzene strongly associate according to the equation;

$$nCH_3COOH \rightleftharpoons (CH_3COOH)_n$$

When an aqueous solution of ethanoic acid was shaken with benzene and equilibrated at a constant temperature, the data in the table below was obtained.

$[CH_3COOH]$ in water/moldm^{-3}	4.90	5.70	8.25	9.82	10.63
$[CH_3COOH]$ in benzene/moldm^{-3}	0.30	0.40	0.90	1.20	1.40

a) Comment on the concentration of ethanoic acid in water and in benzene and briefly explain your comment.

b) Plot a suitable graph using the data above and use it to;

   i. Determine the partition coefficient of ethanoic acid between water and benzene.

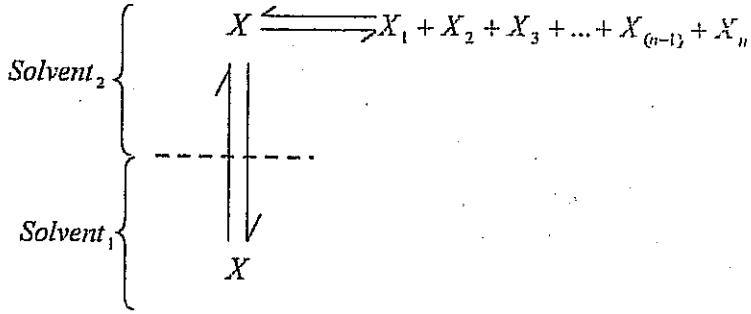
   ii. The value of n in the association equation of ethanoic acid

c) Name the force responsible for the strong association of ethanoic acid.

d) Draw the structure of associated ethanoic acid; label the force responsible for the strong association of ethanoic acid.

b. Dissociation:

- Consider a solute x soluble and remains discrete in a denser solvent$_1$
- When this solution is shaken with solvent$_2$, a less dense solvent and immiscible with solvent$_1$ and the solute strongly dissociates in solvent$_2$ to form "n" particles.
- The following equilibria are established at a constant temperature;



- If c_1 and c_2 are the respective molar concentrations of solute X in solvent$_1$ and solvent$_2$ and α is the degree of dissociation.

The equilibrium in solvent$_2$

	$X \rightleftharpoons$	X_1	$+ X_2 ... +$	$X_{(n-1)}$	$+ X_n$
Before dissociation	c_2	0	0	0	0
At eq=m for one mole	$1-\alpha$	α	α	α	α
At eq=m for c_2 moles	$c_2(1-\alpha)$	αc_2	αc_2	αc_2	αc_2

- From the law of mass action, the equilibrium law;

$$K_c = \frac{[X_1][X_2][X_{(n-1)}][X_n]}{[X]}$$

$$\Rightarrow K_c = \frac{(\alpha c_2)(\alpha c_2)(\alpha c_2)(\alpha c_2)(\alpha c_2)}{c_2(1-\alpha)}$$

$$K_c = \frac{(\alpha c_2)^n}{c_2(1-\alpha)} \quad \text{.....6.26}$$

The partition equilibrium

- From the partition law of distribution of X between solvent$_1$ and solvent$_2$,

$$K_d = \frac{[X]_{solvent1}}{[X]_{solvent2}}$$

$$\Rightarrow K_d = \frac{c_1}{c_2(1-\alpha)} \quad \text{.....6.27}$$

Combining equation 6.26 and 6.27 so as to eliminate $c_2(1-\alpha)$

$$\Rightarrow \frac{K_c}{K_d} = \frac{(\alpha c_2)^n}{c_1} \quad \text{.....6.28}$$

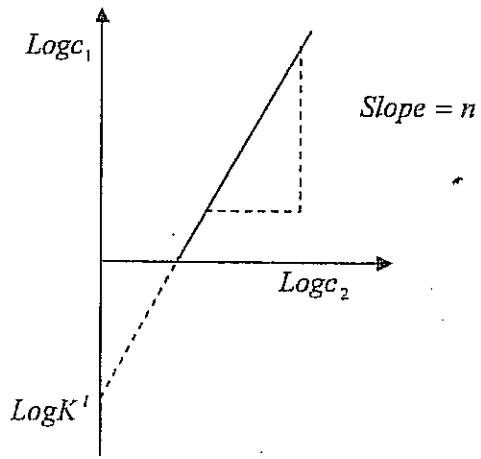
But $\frac{K_c}{K_d}$ is a new constant K^I and since the solute is strongly dissociated, $\alpha^n \approx 1$

$$K^I = \frac{(c_2)^n}{c_1} \quad \text{.....6.29}$$

Taking $\log_{10}$ of both sides,

$$\log K^I = n \log c_2 - \log c_1$$

$$\log c_1 = n \log c_2 - \log K^I \quad \text{.....6.30}$$



Applications of the partition law:

- Solvent extraction

- Investigation of the structure of complexes
- Determination of equilibrium costants (stability constants of complexes)
- Chromatography
- Ion exchange
- Extraction of metals like silver.

1. Solvent extraction:

- This is partial removal of a solute from a solvent by introducing a second solvent immiscible with, in which the solute is also soluble.
- Solvent extraction is always applied in the purification of organic acids present in aqueous solution together with ionic impurities.
- In practice:
- The mixture of the organic acid and the ions is shaken with a suitable organic solvent immiscible with water (e.g ether, benzene, etc) in a separating funnel.
- The layers are allowed to separate (according to their densities) and separated using the separating funnel.
- The organic layer is then dried using a solid drying agents for example quick lime, anhydrous calcium chloride etc; after which it is distilled by simple or fractional distillation to remove the ether or benzene.

❖ The ionic impurities being insoluble in organic solvents remain in the aqueous layer (does not dissolve in non polar solvent)

❖ Ether is the preferred organic solvent because;

i. It dissolves a wide range of organic substances (the universal organic solvent).

ii. It is very volatile.

Worked example:6.9

The partition coefficient of solute Z between two immiscible solvents A and B at a certain temperature is 5. 100cm^3 of A contains 15g of Z. calculate the mass of Z that would be extracted by shaking the above solution of Z by:

a. One 100cm^3 of B.
b. 100cm^3 of B in 50cm^3 portions
c. 100cm^3 of B of 25cm^3 portions
d. What comment can you draw from the three extractions?

Solution:

a. Let mass of Z extracted by 100cm^3 of B be xg
Mass of Z remaining in A =(15 – x)

From $K_d = \frac{[z]_A}{[Z]_B}$

Concentration = mass / volume

$$\Rightarrow 5 = \frac{\left(\frac{15-x}{100}\right)}{\left(\frac{x}{100}\right)}$$

$x = 2.5g$

b. Let mass of Z extracted by the first 50cm^3 portion of B be ag
Mass of Z remaining in A =(15 – a)

From $K_d = \frac{[z]_A}{[Z]_B}$

$$\Rightarrow 5 = \frac{\left(\frac{15-a}{100}\right)}{\left(\frac{a}{50}\right)}$$

$a = 1.3636g$

Mass of Z remaining in A after the first extraction =(15 – 1.3636)=13.6364g
Let the mass of Z extracted by the second 50cm^3 portion be bg
Mass of Z remaining in A =(13.6364 – b)

From $K_d = \frac{[z]_A}{[Z]_B}$

$$\Rightarrow 5 = \frac{\left(\frac{13.6364-b}{100}\right)}{\left(\frac{b}{50}\right)}$$

$b = 1.2397g$

Total mass of Z extracted by the two successive 50cm^3 portions of B
=(1.3636 + 1.2397) = 2.6033g

c. Let mass of Z extracted by the first 25cm^3 portion be cg
Mass of Z remaining in A = (15 – c)

From $K_d = \frac{[z]_A}{[Z]_B}$

$$\Rightarrow 5 = \frac{\left(\frac{15-c}{100}\right)}{\left(\frac{c}{25}\right)}$$

$c = 0.7143g$

Mass of Z remaining in A after the first extraction = 14.2857
Let mass of Z extracted by the second 25cm^3 portion of B be d
Mass of Z remaining in A = (14.2857 – d)

From $K_d = \frac{[z]_A}{[Z]_B}$

$$\Rightarrow 5 = \frac{\left(\frac{14.2857 - d}{100}\right)}{\left(\frac{d}{25}\right)}$$

$d = 0.6803g$

Mass of Z remaining in A after the second extraction = (14.2857 – 0.6803) = 13.6054g

Let mass of Z extracted by the third 25cm^3 portion of B be eg

Mass of Z remaining in A = (13.6054 – e)

From $K_d = \frac{[z]_A}{[Z]_B}$

$$\Rightarrow 5 = \frac{\left(\frac{13.6054 - e}{100}\right)}{\left(\frac{e}{25}\right)}$$

$e = 0.6479g$

Mass of Z remaining in A after the third extraction = (13.6054 – 0.6479) = 12.9575

Let mass of Z extracted by the fourth 25cm^3 portion of B be fg

Mass of Z remaining in A = (12.9575 – f)

From $K_d = \frac{[z]_A}{[Z]_B}$

$$\Rightarrow 5 = \frac{\left(\frac{12.9575 - f}{100}\right)}{\left(\frac{f}{25}\right)}$$

$f = 0.6170g$

Total mass of Z extracted by the four 25cm^3 portions of B =(0.6170 + 0.6479 + 0.6803 + 0.7143)

= 2.6595g

d. More of the solute is extracted when many smaller amount of the extracting solvent is used than a bigger portion.

Task:6.17

20g of iodine was dissolved in 150cm^3 of water. Calculate the mass of iodine that remains in water if the above solution is shaken with;

a. 150cm^3 of carbon disulphide
b. Three 50cm^3 portions of carbon disulphide
c. What conclusion can you draw from the two values in a) and b) above? Given that K_d=585, iodine is more soluble in carbon disulphide than water.

Task:6.18

When 100cm^3 of water containing 10g of butanoic acid was shaken with two separate 100cm^3 of ether, 9.50g of butanoic acid was extracted. Calculate at the temperature:

a. The partition coefficient of butanoic acid between water and ether if the second extraction yielded 1.5g.
b. The mass of butanoic acid that would be extracted by using one 200cm^3 portion of ether.

Task:6.19

A compound X is soluble in both water and benzene. Calculate:

a. The mass of X that would remain in the organic layer when 50cm^3 of the organic layer containing 11g of X is shaken with 75cm^3 of water at a constant temperature, partition coefficient of X between benzene and water is 12.2.

b. The mass of X that remains in the organic layer when $150cm^3$ portion is used instead of $75cm^3$ of water at the same temperature.

2. Investigation of complex ions.

- Many ions undergo complexation when a ligand substance is added to their aqueous solutions.
- The formular of the formed complex and hence the number of ligand molecules coordinated to the ions can be determined by the application of partition law.
- The investigation of complex ions is done as follows:

- A known amount of ligand substance is partitioned between water and a selected organic solvent, at a given temperature.
- The concentration of the ligand substance either in aqueous layer/organic layer is determined, from which partition coefficient K_d, at the temperature is determined.
- Then the ligand substance is partitioned between an aqueous solution of the ion of known concentration and the organic solvent.
- The concentrations of the ligand substance are then determined in both the organic layer and aqueous layer containing the ions.
- The concentration of the ligand substance in the aqueous layer in this case gives the total of free ligand substance and the complexed (fixed) ligand substance.

Assumptions

(i) Free ligand substance partitions itself between the organic solvent and aqueous solution of the ions in the same ratio as it does between pure water and organic solvents.

(ii) During titration (the always technique) the equilibrium is not disturbed.

a. Determination of the number of ammonia molecules that complexes with a copper (II) ion:

- A known volume of aqueous solution of ammonia of known concentration is shaken with equal volume of trichloromethane, at a costant temperature and allowed to equilibrate.
- The aqueous layers and the chloroform layers are pipetted and titrated with standard hydrochloric acid using ~~metyl orange indicator~~, until consistent titres.
- From the end point volumes of hydrochloric acid, the molar concentrations of the ammonia in the two solvents are determined, from which the distribution coefficient at the temperature is determined.
- Then at the same temperature, a known volume of excess ammonia solution is added into a known volume of an aqueous solution of a copper (II) salt of known concentration.
- Then the mixture is shaken with a known volume of trichloromethane and allowed to equilibrate.
- The aqueous and the organic layers are pipetted and titrated with a standard hydrochloric acid using methyl orange indicator, until consistent titre values.
- The molar concentration of ammonia in the organic layer is determined from the end point volume of hydrochloric acid during the titration of the organic layer.
- The total molar concentration of ammonia (free and complexed) is calculated from the end point volume during the titration of the aqueous layer.
- The molar concentration of free/uncomplexed/unfixed ammonia is calculated from its molar concentration in the organic layer and the just determined distribution coefficient.

- Molar concentration of fixed/complexed/unfree ammonia is determined from the total molar concentration of ammonia in the aqueous layer and the just determined molar concentration of free ammonia.
- Then, the coordination number of copper (II) ions, 'n' in the complex is given by:

$$n = \frac{[Ammonia]_{complexed}}{[Cu^{2+}]}$$

Worked example:6.10

4. 0.04 moles of a cation X, which in aqueous solution complexes with ammonia was shaken excess concentrated ammonia and the solution made upto 1l. The resultant solution was shaken with trichloromethane and left to settle. $50cm^3$ of the organic layer required $25cm^3$ of the 0.05M hydrochloric acid for end point neutralization; and $20cm^3$ of the aqueous layer was neutralized by $34.4cm^3$ of 0.5M hydrochloric acid. (K_d at the temperature is 0.04, ammonia more soluble in water than trichloromethane).

a. Explain why ammonia is more soluble in water than in trichloromethane
b. Determine the coordination number of the cation.
c. Name any three cations X could be, and in each case, state the colour of the aqueous layer.
d. Draw the structural formula of the complex and name the shape adopted by the complex.

Solution:

a) The nitrogen atom of ammonia is more electronegative than the hydrogen atoms. Therefore, the nitrogen atom becomes partially negatively charged and the hydrogen atoms partially positively charged. The oxygen atom of water is more electronegative than the hydrogen atoms. Therefore, the

oxygen atom becomes partially negatively charged and the hydrogen atoms partially positively charged. This leads to formation of hydrogen bonds between water and ammonia, which is facilitated by dative bond formation between nitrogen and hydrogen of water. Whereas in trichloromethane, the dissolution is only due to hydrogen bonding between the hydrogen of trichloromethane and the oxygen of water. Hence ammonia has a higher solubility in water than in trichloromethane.

b) For organic layer

Moles of hydrochloric acid reacted is given by:

$$\frac{25 \times 0.05}{1000} = 1.25 \times 10^{-3} moles$$

Reaction ratio between ammonia and hydrochloric acid is 1:1

$$[NH_3] = \frac{1.25 \times 10^{-3} \times 1000}{50} = 0.025M$$

For aqueous layer:

From $K_d = \frac{[NH_3]_{Or}}{[NH_3]_{Aq}}$

$$\Rightarrow 0.04 = \frac{0.025}{[NH_3]_{Aq}}$$

$[NH_3]_{Aq} = 0.625M$ (For free ammonia)

Moles of hydrochloric acid reacted is given by:

$$\frac{34.4 \times 0.5}{1000} = 0.0172 moles$$

Since reaction ratio between ammonia and hydrochloric acid is 1:1,

Total molar concentration of ammonia is given by:

$$[NH_3] = \frac{0.0172 \times 1000}{20} = 0.86M$$

Molar concentration of fixed ammonia is given by:

$$0.86 - 0.625 = 0.235M$$

Equation for complexation with ammonia is given by:

$$X^{y+}(aq) + nNH_3(aq) \rightleftharpoons [X(NH_3)_n]^{y+}(aq)$$

0.04mole of X complexed with 0.235 moles of ammonia

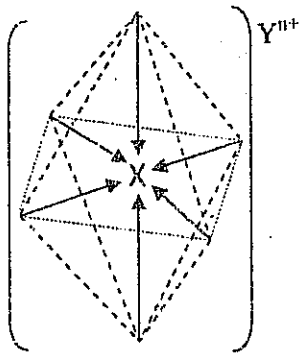
1mole of complexes with $\frac{1 \times 0.235}{0.04} = 5.875 \approx 6$

Hence the coordination number of the cation is 6.

c)

Possible cation	Colour
Nickel (II) ion	Blue
Cobalt (II) ion	Pink
Chromium (III) ion	green

d)



Shape: Octahedral.

Task:6.20

The table below shows the various concentrations of ammonia in 7.5×10^{-3} aqueous solution of copper (II) chloride and chloroform at equilibrium.

$[NH_3]_{water}$	0.035	0.045	0.055	0.065	0.075
$[NH_3]_{chloroform}$	2×10^{-4}	6×10^{-4}	10×10^{-4}	14×10^{-4}	18×10^{-4}

Plot a suitable graph and use it to determine;

a. The distribution coefficient of ammonia between water and chloroform.
b. The coordination number of copper in the complex, $[Cu(NH_3)_n]^{2+}$

Task:6.21

$25cm^3$ (an excess) of aqueous ammonia was added to $12.5cm^3$ of 7.5×10^{-4}M zinc nitrate solution and the resultant solution shaken with chloroform. After the layers had settled, $25cm^3$ of the organic layer required $13cm^3$ of 0.005M

hydrochloric acid for complete neutralization and $12.5cm^3$ of the aqueous layer required $17cm^3$ of 0.05M hydrochloric acid for end point neutralization. Given that the partition coefficient for ammonia between water and chloroform at the temperature is 25.

a. The molar concentration of ammonia in chloroform.
b. The molar concentration of free ammonia in water.
c. The total molar concentration of ammonia in water.
d. The molar concentration of fixed ammonia.
e. The formula mass of the complex, $[Zn(NH_3)_y]^{2+}$ (Zn=65, N=14, H=1)

3. **Determination of stability constants of complexes:**

- When iodine is added into aqueous solution of potassium iodide, the iodine complexes with iodide ions in the solution to form a complex known as triiodide ions.
- This leads to the attainment of the following equilibrium at a constant temperature.

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

- The equilibrium constant for this reaction (a complexation) is known as the stability constant for the complex, triiodide ions, and it is given by:

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

- This constant, at a constant temperature can be determined as follows;

- A known volume of aqueous solution of iodine of known concentration is shaken with equal volume of carbon disulphide, at a constant temperature and allowed to equilibrate.
- The aqueous layers and the carbon disulphide layers are pipetted and titrated with standard sodium thiosulphate solution using starch indicator, until consistent titres.

- From the end point volumes of sodium thiosulphate solution, the molar concentrations of the iodine in the two solvents are determined, from which the distribution coefficient of iodine between the two solvents at the temperature is determined.
- Then at the same temperature, a known volume of excess iodine solution is added into a known volume of an aqueous solution of potassium iodide of known concentration.
- Then the mixture is shaken with a known volume of carbon disulphide and allowed to equilibrate.
- The aqueous and the carbon disulphide layers are pipetted and titrated with a standard sodium thiosulphate solution using starch indicator, until consistent titre values.
- The molar concentration of iodine in the carbon disulphide layer is determined from the end point volume of sodium thiosulphate solution during the titration of the layer.
- The total molar concentration of iodine (free and complexed) is calculated from the end point volume during the titration of the aqueous layer.
- The molar concentration of free/uncomplexed/unfixed iodine is calculated from its molar concentration in the carbon disulphide layer and the just determined distribution coefficient.
- Molar concentration of fixed/complexed/unfree iodine is determined from the total molar concentration of iodine in the aqueous layer and the just determined molar concentration of free iodine.
- Since one mole of iodine reacts with one mole of iodie ions to produce one mole of triiodide ions in the solution, the mole of iodine, mole of iodide and mole of triiodide at equilibrium are determined from which the stability constant of the complex calculated from;

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

Task:6.22

A certain amount of iodine was shaken with carbon disulphide and an aqueous solution containing 0.3M potassium iodide. By titrating with thiosulphate solution, the carbon disulphide layer was found to contain $16.2gdm^{-3}$ and the aqueous layer was found to contain $0.77gdm^{-3}$. The distribution coefficient of iodine between carbon disulphide and water at the temperature was 585.

a. Comment on the solubility of iodine in carbon disulphide and water. Briefly explain your comment.
b. Write the equation for the complexation of iodine in the aqueous layer.
c. Calculate;
   i. Molar concentration of iodine in the carbon disulphide layer.
   ii. Molar concentration of free iodine in aqueous layer.
   iii. Molar concentration of fixed iodine.
   iv. The stability constant of the complex formed in equation b) above.

Task:6.23

Molten zinc and molten lead are immiscible. Calculate the amount of silver that would be absorbed into zinc layer if 0.005l of zinc is added to a liquid solution of 2g of silver contained in 0.1l of lead. (K_d of silver between zinc and lead is 300, at the temperature).

Task:6.24

a. State the partition law.
b. State the conditions under which the law is valid.

c. Define the term partition coefficient.
d. The following results were obtained in an experiment to determine the partition coefficient of ammonia between water and chloroform:

- $10.0cm^3$ of the aqueous layer required $21.6cm^3$ of 0.25M hydrochloric acid for end point neutralization.
- $25.0cm^3$ of the organic layer required $21.6cm^3$ of 0.05M hydrochloric acid for end point neutralization.

Calculate the partition coefficient of ammonia at the laboratory temperature.

Task:6.25

0.025M aqueous solution of a doubly charged cation that complexes with ammonia were allowed to reach equilibrium with excess ammonia and chloroform. The aqueous layer was found to have $0.4moldm^{-3}$ of ammonia and the organic layer was found to have $0.012moldm^{-3}$ of ammonia. Using the K_d for ammonia between water and chloroform as 25, calculate:

a. Concentration of fixed ammonia in the aqueous layer.
b. The coordination number of the cation of the complex.
c. Name three possible cations in the solution and state the colours of their aqueous solutions.
d. Draw and name the shape adopted by the complex above.

Task:6.26

a. What is meant by the term partition coefficient?
b. Give any five applications of distribution of a solute between two immiscible solvents in contact.
c. Some iodine dissolved in 1.75M aqueous solution of potassium iodide was shaken with carbon tetrachloride to equilibrium at 15^0C. By titrimetry, 0.089M iodine was found in organic layer and 0.7M iodide ion complexed.

i. How can the end point be detected?

ii. Write the equation for the reaction in the aqueous layer.

iii. Given that the distribution coefficient for iodine between carbon tetrachloride and water is 85. Calculate the equilibrium constant for the reaction in the aqueous layer.

An excess of NH_3 soln was add to a soln of 0.1M $CuSO_4$ soln. Ferrous and deep blue soln was shaken with trichloromethane and 0.1 molar $CuSO_4$ soln. A fixed vol of each layer was pipetted and titrated against a standard soln of HCl.

HCl	[illegible]	0.02	0.03	0.04	0.05	0.06
[illegible]	[illegible]	0.87	[illegible]	1.33	1.50	1.80

Plot a graph of the concentration of NH_3 in 0.1M $CuSO_4$ against concentration in $CHCl_3$

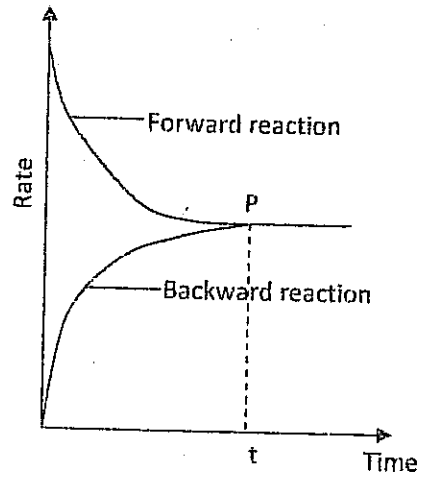
Determine the value of n in the complex below.

$Cu(NH_3)_n^+$

CHAPTER SEVEN: CHEMICAL EQUILIBRIA:

7.0: Introduction:

- Chemical equilibria are concerned with reversible reactions. In a reversible reaction as reactants combine to form products (forward reaction) the products also combine to form reactants (backward reaction).
- As time goes on, the rate of the forward reaction decreases while that of the backward reaction increases, until a certain point at which the two rates are equal at a constant temperature, as illustrated diagrammatically below:



- P, after time t is the point at which the rates of the forward and backward reactions are the same. At this point:

a. A dynamic equilibrium is attained.
b. None of the reactants is fully consumed.
c. The amounts of both reactants and products remain constant. Not necessarily the same!

Definition

A reversible reaction is a reaction which does not go to completion, instead reaches a state of dynamic equilibrium in which the rates of forward and backward reactions are equal.

7.1: Examples of reversible reactions:

1. Reduction of copper (II) ions by iron filings.

$$Cu^{2+}(aq) + Fe(s) \rightleftharpoons Cu(s) + Fe^{2+}(aq)$$

2. Oxidation of iron (II) ions by silver ions.

$$Ag^{+}(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$$

3. Synthesis of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

4. Esterification.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

7.2: Experiment to show reversibility of a reaction:

Case I: Oxidation of iron (II) ions by silver ions:

- Non radioactive silver ions are mixed with iron (II) ions in a beaker and allowed to stand in order to establish equilibrium at a constant temperature.
- A small amount of radioactive silver metal is added to the system and allowed to stand for sometime.
- Some silver ions in the system are then isolated by precipitation (adding sodium chloride or hydrochloric acid solution) and analyzed for radioactivity.
- Showing of radioactivity by the isolated sample shows that some of the radioactive silver metal was converted to silver ions (backward reaction) hence the reaction in reversible.

Case II: Esterification:

- A sample of ester is formed from a mixture of ethanoic acid and ethanol, which do not contain radioactive oxygen.

- The sample is then isolated and hydrolysed using water, whose oxygen is labeled with radioactive oxygen–18.
- Since from reaction mechanism, the oxygen atom, formerly in water is incorporated in ethanoic acid, and not ethanol, the produced ethanoic acid is then isolated, purified and tested for radioactivity.
- Showing of radioactivity in the ethanoic acid shows reaction of ester with water to form ethanol and ethanoic acid, hence reversibility of the reaction.

7.3: Characteristics of a chemical equilibrium:

b. Attained in a closed system
c. Attained at a constant temperature
d. The equilibrium is dynamic
e. Not all the reactants are used up
f. It is reversible.
g. The amounts of the reactants and the product in the equilibrium mixture remain constant.
h. Can be attained from both directions.

7.4: Factors that affect reversible reactions:

- There are three important variables of a reversible reaction

A. The position of the equilibrium: i.e is the equilibrium established when much of the reactants are converted to products or only a small amount converted.
B. The equilibrium constant (K_c)

- This refers to the quantitative connection between the amount (concentration) of the products and that of the reactants, when equilibrium is attained.
- For a reversible reaction in equilibrium, at a constant temperature there is a fixed relationship between the molar concentrations of the products and those of the reactants in the equilibrium mixture.

- This is stated as the law of mass action/the equilibrium law.

The law of mass action/the equilibrium law:

This law states that: "for any reversible reaction in a state of dynamic equilibrium at a constant temperature, the product of the molar concentrations of the products, each raised to their stoichiometric coefficient, divided by the product of molar concentrations of the reactants each also raised to the power of their stoichiometric coefficient, is a constant".

- The process of raising the molar concentration of intereacting species of a chemical reaction to their coefficient in the equation is called involution.
- So the law of mass action can as well be stated as: for any reversible reaction in a state of dynamic equilibrium at a constant temperature, the product of the molar concentrations of the products, each raised to its stoichiometric coefficient, divided by the product of molar concentrations of the reactants similarly involuted, is a constant.

Consider a reversible reaction of the general form,

$aA + bB \rightleftharpoons cC + dD$

at equilibrium and at a constant temperature.

Applying the law of mass action:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where: 'K_c' is the equilibrium constant, and '[ ]' is the molar equilibrium concentration.

The unit of the equilibrium constant:

From the K_c expression above,

The unit of K_c is given by: $\frac{(moldm^{-3})^c(moldm^{-3})^d}{(moldm^{-3})^a(moldm^{-3})^b}$

$$= \frac{(moldm^{-3})^{(c+d)}}{(moldm^{-3})^{(a+b)}}$$

$$= (moldm^{-3})^{[(c+d)-(a+b)]}$$

Worked example:7.1

Write the equilibrium constant expressions, K_c for the following reactions and work out their units:

$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$

b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Solution:

$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$

$$K_c = \frac{[CH_3COOCH_2CH_3]^1[H_2O]^1}{[CH_3COOH]^1[CH_3CH_2OH]^1}$$

$$\Rightarrow K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$\text{Unit} = \frac{(moldm^{-3})(moldm^{-3})}{(moldm^{-3})(moldm^{-3})} = 1$$

Hence K_c has no unit in this case (is a dimensionless constant)

b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$\text{Unit} = \frac{(moldm^{-3})^2}{(moldm^{-3})(moldm^{-3})^3}$$

$= mol^{-2}dm^6$

Task:7.1

Write the equilibrium constant expressions for the following and state its unit.

a. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

b. $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$

c. $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$

Deductions from K_c value

- The bigger the value of K_c, the more are the reactants converted to products and the smaller the K_c value the less are the reactants converted to products.
- K_c is an indicator of the position of the equilibrium i.e. if under certain conditions then, one calculates K_{c1} value; then conditions surrounding the reactions are varied and one calculates K_{c2} value then:

i. If K_{c1} is greater than K_{c2}, then the position of the equilibrium is shifted to the left direction (backward direction) i.e. less reactants under these conditions are converted to the product.

ii. If K_{c1} is less than K_{c2}, then the position of the equilibrium is shifted to the right i.e. more reactants under the second conditions are converted to products.

iii. When K_{c1} is equal to K_{c2}, then the position of the equilibrium is not affected.

C. The rate of attaining the equilibrium i.e. how fast a reversible reaction establishes equilibrium.

- The following factors affect the above variables of a reversible/equilibrium reaction:
  a. Temperature
  b. Catalysts
  c. Concentration
  d. Pressure

1. Catalyst

- A catalyst is an agent that alters the rate of a chemical reaction. A positive catalyst increases the rate of a chemical

reaction; while a negative catalyst decreases the rate of a chemical reaction.

- Since the catalyst alters the rates of forward and backward reactions alike, a catalyst therefore does not affect the equilibrium constant and hence the position of the equilibrium, it only alters the rate at which the equilibrium is attained.
- A positive catalyst increases the rate of attaining equilibrium; while a negative catalyst decreases the rate of attaining equilibrium.

2. Temperature

- The effect of temperature on an equilibrium reaction depends on whether the reaction is exothermic or endothermic. The summary of effect of temperature is stated as *van't Hoff's* law of mobile equilibrium, which states:

"If a system is in equilibrium, raising the temperature will favour that reaction which is accompanied by absorption of heat and lowering the temperature will favour that reaction which is accompanied by evolution of heat"

- This law is an extract from le *Chatelia's* principle which states: "If a system in equilibrium is subjected to a constraint, it readjusts itself so as to remove the constraint".
- Consider the reactions below in which the forward reactions are exothermic and backward reactions endothermic.

$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g);-\Delta H$

$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g);-\Delta H$

$H_2(g)+O_2(g) \rightleftharpoons 2H_2O(l);-\Delta H$

- Decrease in temperature favours the forward reactions i.e. more water, ammonia and sulphur trioxide are produced hence equilibrium constant K_c increases and the position of the equilibrium is shifted to the right. However, the rate at which the equilibrium is attained is reduced because of

reduced number of reactants' particles with at least activation energy and frequency of collision.

- Increase in temperature favours the backward reaction; i.e more water, ammonia or sulphur trioxide decomposes, equilibrium constant K_c decreases and the position of the equilibrium is shifted to the left. Equilibrium is attained in a shorter time because of increase in frequency of collision between the particles and the proportion of the reactant with just activation energy.

3. Concentration

- The effect of concentration on an equilibrium system takes place in accordance to le Chatelia's principle.
- Consider a reversible reaction below in equilibrium, in a closed system:

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

- When more nitrogen is introduced in the system, its concentration increases. Hydrogen then combines with excess nitrogen (the constraint) to form more ammonia. This reduces the molar concentration of nitrogen (removes the constraint) and hydrogen and the molar concentration of ammonia increases. The equilibrium constant, K_c remains constant, but the position of the equilibrium is shifted to the right. The equilibrium is attained in a shorter time i.e. the rate increases.
- Conversely, when some nitrogen is removed from the equilibrium mixture, some ammonia decomposes producing more nitrogen and hydrogen. The equilibrium constant, K_c remains constant, but the position of the equilibrium is shifted to the left. The equilibrium is attained in a longer time i.e. the rate decreases.

4. Pressure

- Pressure has a very negligible effect on condensed systems i.e. a system of solids or liquids. It greatly affects the gaseous

system. Its effect on a gaseous system depends on whether the equilibrium reaction occurs with a decrease in volume (literally compression), increase in volume (literally expansion) or at a constant volume.

a. ***An equilibrium where there is a decrease in volume (compression) i.e. ΔV is negative:***

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

1vol 3vols 2vols

Change in volume = 2 – (1+3) = –2

- An equilibrium system that establishes itself with a decrease in volume is favoured by high pressure. In the above system therefore increase in pressure shifts the equilibrium from left to right, K_c remains constant and the equilibrium is attained in a shorter time, since particles are brought closer to one another with higher frequency of collision.

b. ***An equilibrium where there is an increase in volume (expansion) i.e. ΔV is positive:***

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Change in volume = 2 – 1 = +1

- An equilibrium system that establishes itself with an increase in volume is favoured by low pressure, which shifts the equilibrium position to the right, the equilibrium constant, K_c remains constant, but rate of attaining equilibrium is reduced, since the particles are far apart with lower collisions per second.

c. ***An equilibrium where the volume remains constant i.e. ΔV is zero:***

$$2HI(g) \qquad H_2(g)+I_2(g)$$

$$N_2(g)+O_2(g) \qquad 2NO(g)$$

- Here, the position of the equilibrium and the equilibrium constant K_c remains constant. Increase in pressure increases

the rate of attaining the equilibrium; while decrease in pressure decreases the rate of attaining the equilibrium.

Task:7.2

Manganese (II) sulphide reacts with acids according to the equation:

$MnS(s) + 2H_3O^+(aq) \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l) + H_2S(g)$

a. Write the equilibrium constant K_c expression for the above reaction.

State with a reason, what would happen to the equilibrium, when:

b. Water is added to the equilibrium mixture.
c. Hydrogen sulphide gas is bubbled into the equilibrium mixture.
d. pH of the solution is increased.
e. pH of the solution is lowered.

7.5: Experimental determination of K_c

(a) *Esterification:*

- A known amount of ethanoic acid is mixed with a known amount of ethanol and the mixture is thermostated in a closed system.
- The set-up is allowed to stand in order to attain equilibrium.
- The mixture is then rapidly cooled so that the equilibrium is not shifted.
- Fixed volumes of the mixture are then pipetted and titrated with standard sodium hydroxide solution using phenolphthalein indicator to obtain consistent titre values.
- The amount of sodium hydroxide reacted is then used to obtain the amount of ethanoic acid in the mixture, hence the amount of ethanol, ethyl ethanoate and water in the mixture, from which the equilibrium constant, K_c is calculated.

Model results:

- If initially amoles of ethanoic acid and bmoles of ethanol were mixed to form equilibrium volume. If after titration with a standard sodium hydroxide solution it was found that x moles of ethanoic acid were used up.

$CH_3COOH\ (l) + CH_3CH_2OH\ (l) \rightleftharpoons CH_3COOCH_2CH_3\ (l) + H_2O\ (l)$

Initial moles	a	b	0	0
At equilibrium	(a–x)	(b–x)	x	x
Equilibrium conc	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

Applying the law of mass action:

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

$$\Rightarrow K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{(a-x)}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

Assumption:

- Equilibrium not shifted during the titration.

(b) Decomposition of hydrogen iodide:

- A fixed amount of hydrogen iodide is sealed in a thin glass bulb of a known volume, v.
- The bulb is heated, thermostatted and allowed to attain equilibrium.
- The bulb is then rapidly broken under potassium iodide solution.
- The iodine liberated (now liquefied) is then titrated with a standard sodium thiosulphate solution using starch indicator until consistent titre values.

- From the average titre value, the moles of sodium thiosulphate used, the equilibrium concentration of iodine, hydrogen and hydrogen iodide are calculated, from which equilibrium constant, K_c is calculated, from $K_c = \frac{[H_2][I_2]}{[HI]^2}$

Model results

- If n moles of hydrogen iodide were heated and on titration with standard sodium thiosulphate x moles of iodine where set free.

Treatment of the results

	$2HI(g)$	$\rightleftharpoons H_2(g)$	$+ I_2(g)$
Initial moles	nmoles	0mol	0mol
Equilibrium moles	(n − 2x)mol	xmol	xmol
Equilibrium concentration	$\left(\frac{n-2x}{v}\right)$	$\frac{x}{v}$	$\frac{x}{v}$

From $K_c = \frac{[H_2][I_2]}{[HI]^2}$

$$\Rightarrow K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{n-2x}{v}\right)^2}$$

$$K_c = \frac{x^2}{(n-2x)^2}$$

Assumption:

Equilibrium not shifted during the titration.

Interms of degree of dissociation:

- If n moles of hydrogen iodide in a glass bulb of capacity vdm^3 were heated, then α is the degree of dissociation;

	$2HI(g)$	$\rightleftharpoons H_2(g)$	$+ I_2(g)$
Initial moles	nmol	0mol	0mol
Stoichiometrically	2mol	1mol	1mol
Equilibrium moles	$n(1-\alpha)$	$n\alpha$	$n\alpha$
Equilibrium concn	$\frac{n(1-\alpha)}{v}$	$\frac{n\alpha}{v}$	$\frac{n\alpha}{v}$

From $K_c = \frac{[H_2][I_2]}{[HI]^2}$

$$\Rightarrow K_c = \frac{\left(\frac{n\alpha}{v}\right)\left(\frac{n\alpha}{v}\right)}{\left(\frac{n(1-\alpha)}{v}\right)^2}$$

$$K_c = \frac{\alpha^2}{(1-\alpha)^2}$$

Worked example:7.2

A mixture of 0.92g of ethanol and 1.2g of ethanoic acid were allowed to react at 363K until equilibrium was attained. Calculate the mass of ethylethanoate formed (K_c=3.6).

Solution:

RMM of C_2H_6O = (12x2) + (1x6) + (16x1) = 46

Moles initially = $\frac{0.92}{46} = 0.02mol$

RMM of $C_2H_4O_2$ = (12x2) + (1x4) + (16x2) = 60

Initial moles = $\frac{1.2}{60} = 0.02mol$

Let the moles of $CH_3COOCH_2CH_3$ formed be x; also for H_2O is x

Number of moles of C_2H_6O at equilibrium is (0.02 − x)

Number of moles of $C_2H_4O_2$ in equilibrium is (0.02 − x)

$$K_c = \frac{[CH_3COOCH_3CH_3][H_2O]}{CH_3CH_2OH][CH_3COOH\}}$$

$$\Rightarrow 3.6 = \frac{(x)(x)}{(0.02-x)(0.02-x)}$$

$$3.6(x-0.02)^2 = x^2$$

$$2.6x^2 - 0.144x + 0.00144 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.144 \pm \sqrt{(-0.144)^2 - 4x2.6x0.00144}}{2x2.6}$$

X = 0.043mole or x = 0.0125mol.

X = 0.043 is inadmissible since chemically, a reaction can not produce more product than the starting material.

RMM of $CH_3COOCH_2CH_3$ = (12x4) + (16x2) + (1x8) = 88

1 mol of the ester weighs 88g

0.0125g will weigh $\frac{0.0125x88}{1} = 1.1g$

Hence the mass of ethylethanoate produced is 1.1g.

Worked example:7.3

At a certain temperature, 6.4g of hydrogen iodide was heated. When equilibrium was attained, the degree of dissociation of hydrogen iodide was 45%. Calculate:

a. The number of moles of hydrogen iodide in the mixture.
b. The number of moles of iodine formed.
c. The number of moles of hydrogen formed.
d. The equilibrium constant, K_c for the reaction.

Solution:

RMM of HI = (127x1) (1x1) = 128

Number of moles of hydrogen iodide taken = $\frac{6.4}{128} = 0.05mol$

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	$+ I_2(g)$
Initially	0.05mol		0mol	0mol
Stoichiometrically	2mol		1mol	1mol
At equilibrium	0.05(1 – 0.45)		$(^{0.45}/_2)$	$0.05(^{0.45}/_2)$

a. Moles of hydrogen iodide in the mixture = 0.05(1 – 0.45) =0.0275mol
b. Number moles of iodine formed = $0.05x^{0.45}/_2$ =0.01125mol
c. Number of moles of hydrogen formed=$0.05x^{0.45}/_2$ =0.01125mol
d. $K_c = \frac{[I_2][H_2]}{[HI]^2}$

$$K_c = \frac{(0.01125)(0.01125)}{(0.0275)^2} = 0.167$$

Task:7.3

Hydrogen reacts with iodine according to the equation:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Stoichiometric amounts of hydrogen and iodine were reacted at 10atm and 500^0C. At equilibrium, 1.6 moles of hydrogen iodide were formed. Calculate the:

a. Partial pressure of each gas.
b. The value of K_p at 500^0C.

Task:7.4

At a temperature close to 400^0C, hydrogen iodide has a degree of dissociation of 20%.

a. Write the equation for the dissociation of hydrogen iodide.
b. Write the K_c expression for the above reaction.

c. If 1 mole of hydrogen was mixed with 2.1 moles of iodine, calculate the composition of the mixture.

Task:7.5

A mixture of 0.5 moles of ethanoic acid and 1.0 mole of ethanol was shaken for a long time to reach equilibrium. The whole equilibrium mixture required $80cm^3$ of 1M sodium hydroxide solution for complete neutralization.

a. Write the equation for the reaction between ethanoic acid and ethanol.
b. Calculate the number of moles of ethanoic acid that remained in the equilibrium.
c. Calculate the number of moles of ethanoic acid that reacted with ethanol.
d. Calculate the number of moles of ethanol left in the equilibrium mixture.
e. Hence calculate the equilibrium constant at the temperature.

Task:7.6

When 60g of ethanoic acid were heated with 46g of ethanol until equilibrium was reached, 12g of water and 58.7g of ethylethanoate were formed.

a. Calculate the equilibrium constant for the reaction between ethanoic acid and ethanol.
b. What mass of the ester would be formed under the same conditions, starting with 90g of ethanoic acid and 92g of ethanol.

Task:7.7

When 1 mole of ethanol reacts with 1 mole of ethanoic acid until equilibrium is attained, there is present in the mixture 0.333 moles of alcohol and acid and 0.666 moles of ester and

water. Calculate the amount of ester present at equilibrium when:

a. 1 mole of acid reacts with 3 moles of the alcohol.
b. 92g of ethanol reacts with 60g of ethanoic acid.
c. 1 mole of ethanol reacts with 1 mole of ethanoic acid in the presence of 1 mole of water.

Task:7.8

0.5 moles of hydrogen and 0.5 moles of iodine were allowed to reach equilibrium in an evacuated vessel of capacity $10dm^3$ at a temperature of 450^0C. If the equilibrium concentration constant at this temperature is 50.

a. Calculate the value of K_p.
b. The composition of the container.
c. The partial pressure of hydrogen in the container.

Task:7.9

a. Describe how the equilibrium constant for the reaction between iodine and hydrogen can be determined.
b. A mixture of 0.8 moles of hydrogen and 0.6 moles of iodine was allowed to reach equilibrium in a sealed tube at 450^0C. At equilibrium, 0.2 moles of iodine had reacted. Calculate the value of the equilibrium constant at the temperature.

Task:7.10

2 moles of ethanoic acid and 1 mole of ethanol were allowed to equilibrate at a certain temperature. If the equilibrium constant at this temperature is 4.0. Calculate the number moles of ethylethanoate formed.

Task:7.11

0.009 moles of hydrogen and 0.008 moles of iodine were mixed and equilibrated. The mixture was found to have 0.0134 moles of hydrogen iodide. Calculate the equilibrium concentration constant for the reaction.

Task:7.12

When 12.44cm^3 of hydrogen were heated with 11.42cm^3 of iodine in a sealed tube at a certain temperature, it was found that 19.2cm^3 of hydrogen iodide were present in the equilibrium mixture. Calculate:

a. The equilibrium constant.

b. The volume of hydrogen iodide in the equilibrium by heating 3.2cm^3 of hydrogen and 5.2cm^3 of iodine at the above temperature.

7.6: Chemical equilibria in homogeneous systems:

- A homogenous equilibrium is where both the reactants and the product are in the same phase. It is more common in gaseous systems.
- For gaseous system, the equilibrium constants can be expressed in terms of:
  - Concentration, denoted K_c
  - Partial pressure, K_p

Case 1: Number of moles of reactant is equal to number of moles of products, no change in volume ($\Delta V = 0$)

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

- **K_c expression:**
- If ^{a}moles of carbon monoxide were mixed with ^{b}moles of steam and at equilibrium ^{x}moles of carbon dioxide is obtained and total volume is vdm^3;

	$CO(g)$	$+H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	$+H_2(g)$
Initial moles	amol	bmol		0mol	0mol
Eqbrium mol	$(a-x)$	$(b-x)$		xmol	xmol
Eqbrium concn	$\frac{(a-x)}{v}$	$\frac{(b-x)}{v}$		$\frac{x}{v}$	$\frac{x}{v}$

From $K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

- Show that K_c remains constant when volume is doubled or halved.

K_p expression:

- If P is the total pressure of the system:
- Total moles at equilibrium = $(a - x + b - x + x + x) = (a + b)$

$P_{CO} = \frac{(a-x)}{(a+b)}P$, $P_{H_2O} = \frac{(b-x)}{(a+b)}P$, $P_{CO_2} = \frac{x}{(a+b)}P$ and $P_{H_2} = \frac{x}{(a+b)}P$

From $K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})}$

$$\Rightarrow K_p = \frac{\left(\frac{x}{(a+b)}P\right)\left(\frac{x}{(a+b)}P\right)}{\left(\frac{(a-x)}{(a+b)}P\right)\left(\frac{(b-x)}{a+b}P\right)}$$

$$K_p = \frac{x^2}{(a-x)(b-x)}$$

- Hence for reactions in gaseous phase, where there is no change in volume, $K_c = K_p$

Show that the K_p is constant when the total pressure is halved or doubled.

Case II: number of moles of reactants is greater than number of moles of the products, $n = -ve$ **or there is a decrease in volume** $(\Delta V = -ve)$.

- Examples:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

K_c expression:

- If a moles of nitrogen and b moles hydrogen were mixed and allowed to attain equilibrium. If at equilibrium, x moles ammonia was formed.

	$N_2(g)$	$+3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initially	amol	bmol		0mol
At equilibrium	$(a-\frac{x}{2})$	$\left(b-\frac{3}{2}x\right)$		x
Eqbrium conc	$\left(\frac{a-\frac{x}{2}}{v}\right)$	$\left(\frac{b-\frac{3}{2}x}{v}\right)$		$\frac{x}{v}$

From $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$$K_c = \left(\frac{\left(\frac{x}{v}\right)^2}{\left(\frac{a-\frac{x}{2}}{v}\right)\left(\frac{b-\frac{3}{2}x}{v}\right)^3}\right) = \left(\frac{x^2v^2}{\left(a-\frac{x}{2}\right)\left(b-\frac{3}{2}x\right)^3}\right)$$

$$\therefore K_c = \frac{x^2v^2}{\left(a-\frac{x}{2}\right)\left(b-\frac{3}{2}x\right)^3}$$

K_p expression:

- If P is the total pressure of the system;

- Total moles at equilibrium

$$= a - \frac{x}{2} + b - \frac{3}{2}x + x = (a+b-x)$$

$$pN_2 = \left(\frac{2a-x}{2(a+b-x)}\right)P,\ pH_2 = \left(\frac{2b-3x}{2(a+b-x)}\right)P \text{ and}$$

$$pNH_3 = \left(\frac{x}{a+b-x}\right)P$$

From $K_p = \frac{(pNH_3)^2}{(pN_2)(pH_2)^3}$

$$\Rightarrow K_p = \frac{\left(\frac{x}{a+b-x}P\right)^2}{\left(\frac{2a-x}{2(a+b-x)}P\right)\left(\frac{2b-3x}{2(a+b-x)}P\right)^3}$$

$$\therefore K_p = \frac{16x^2(a+b-x)^2}{(2a-x)(2b-3x)^3P^2}$$

Worked example:7.4

Nitrogen monoxide reacts with oxygen to form nitrogen dioxide according to the equation:

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

a. Write the expression for the equilibrium constant.

b. 3 moles of nitrogen monoxide and 1.5 moles of oxygen were mixed into a vessel and heated to 400^0C. At equilibrium, only 0.5 moles of oxygen were found. Calculate the K_c at this temperature.

c. When the temperature was raised to 500^0C, the mixture in b) was found to contain 25% of the initial nitrogen monoxide. Calculate the equilibrium constant at this temperature.

d. From your answers in b) and c) deduce whether the process is endothermic or exothermic. Explain.

Solution:

a. $$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

b. Moles of oxygen reacted = (1.5 – 0.50) = 1mol

From reaction ratio, moles of NO reacted = (2x1) =2 moles, and moles of NO_2 produced = (2x1) = 2 moles.

Moles of NO at equilibrium = (3 – 2) = 1mol.

From $$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$\Rightarrow K_c = \frac{2^2}{1^2 x1} = 4$$

c. Equilibrium moles of NO = 0.25x3 = 0.75mol;

Moles of NO reacted = (3 – 0.75) = 2.25mol;

Moles of NO_2 produced = 2.25 moles (from reaction ratio)

Moles of O_2 = ($^{2.25}/_2$)= 1.125mole (from reaction ratio)

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$\Rightarrow K = \frac{2.25^2}{0.75^2 x1.125} = 8$$

$$K = 8mol^{-1}$$

d. The process is endothermic since increase in temperature increases the value of equilibrium constant.

Case III: number of moles of reactants is smaller than number of moles of products: Δn = +ve or there is increase in volume (Δv = +ve)

- Examples include:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

K_c expression:

- If a moles of phosphorus (V) chloride were taken initially and x moles of chlorine were produced in the equilibrium volume, v;

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+ Cl_2(g)$
Initially	amol	0mol	0mol
At eqbrium	(a – x)mol	xmol	xmol
Eqbrium conc	$\frac{a-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

From $$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$\Rightarrow K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right)}$$

$$\therefore K_c = \frac{x^2}{(a-x)v}$$

- If P is the total pressure of the system at equilibrium;
- Total number of moles at equilibrium = (a – x + x + x) = a + x

$pPCl_5 = \frac{a-x}{a+x}P$, $pPCl_3 = \frac{x}{a+x}P$ and $pCl_2 = \frac{x}{a+x}P$

From $K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

$$\Rightarrow K_p = \frac{\left(\frac{x}{a+x}P\right)\left(\frac{x}{a+x}P\right)}{\frac{a-x}{a+x}P}$$

$$\therefore K_p = \frac{x^2P}{(a-x)(a+x)}$$

Relationship between K_p and K_c

- Consider the gaseous system of ammonia, hydrogen and nitrogen:

$$K_p = \frac{16x^2(a+b-x)^2}{(2a-x)(2b-3x)^3P^2}$$

$$K_c = \frac{x^2v^2}{\left(a-\frac{x}{2}\right)\left(b-\frac{3}{2}x\right)^3}$$

- Let $K_p = YK_c$

$$\Rightarrow \frac{16x^2(a+b-x)^2}{(2a-x)(2b-3x)^3P^2} = Y\frac{16x^2v^2}{(2a-x)(2b-3x)^3}$$

$$Y = \frac{(a+b-x)^2}{(Pv)^2}$$

$$Y = \frac{(Pv)^{-2}}{(a+b-x)^{-2}} = \left(\frac{Pv}{a+b-x}\right)^{-2}$$

But (a + b – x) = number of moles = n

$$\Rightarrow Y = \left(\frac{Pv}{n}\right)^{-2}$$

But $\frac{Pv}{n} = RT$ and –2 = Δn

$$\Rightarrow Y = (RT)^{\Delta n}$$

Hence, $K_p = K_c(RT)^{\Delta n}$

Task:7.13

Write the relationship between K_p and K_c for the following equilibrium reactions:

a. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

b. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

Task:7.14

At 18^0C, carbon monoxide and hydrogen reacts according to the equation:

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$; ΔH=–65kJ/mol

a. Write the connection between K_c and K_p.

b. When stoichiometric amounts of carbon monoxide and hydrogen were mixed, 15% of methanol vapour was

formed. Calculate the equilibrium composition of the mixture.

c. Calculate the K_c and hence the K_p for the reaction.

d. Calculate the total pressure of the system.

7.7: Addition of an inert gas to a gaseous system in equilibrium:

- Inert gases are chemically unreactive. They include; helium, neon, argon, krypton and xenon.
- Nitrogen is also an inert gas under ordinary condition because of the great deal of energy required to break the triple bonds in between the two nitrogen atoms in a nitrogen molecules.
- However, in a gaseous system where nitrogen is one of the components, it ceases to be an inert gas.
- An inert gas can be added at constant volume or constant pressure.

Casel: Addition of an inert gas to a system where number of moles of reactant is equal to number of moles of products, no change in volume ($\Delta V = 0$):

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

a. At a constant pressure:

- When an inert gas is added, the pressure of the system increases. To keep the pressure constant, the volume must increase.
- This spreads the molecules of hydrogen, iodine and hydrogen iodide farther apart, reducing the frequency of collision. Hence rate of attaining equilibrium decreases.
- The equilibrium constant and the position of the equilibrium are not disturbed since they are not affected by volume increase.

b. At constant volume:

- If the volume is constant, then the total pressure of the system increases.
- This increases the frequency of collision amongst hydrogen, iodine and hydrogen iodide. Hence rate of attaining the equilibrium increases.
- The equilibrium constant and the position of the equilibrium are not disturbed since they are not affected by pressure increase.

Summary:

Variable	Constant volume	Constant pressure
Equilibrium constant	Not affected	Not affected
Equilibrium position	Not affected	Not affected
Rate	Increases	Decreases

Case II: Addition of an inert gas to a gaseous system where number of moles of reactants is greater than number of moles of the products, $n = -ve$ or there is a decrease in volume ($\Delta V = -ve$).

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

a. At constant pressure:

- When an inert gas is added, the pressure of the system increases. To keep the pressure constant, the volume must increase.
- This spreads the molecules of hydrogen, nitrogen and ammonia farther apart, reducing the frequency of collision. Hence rate of attaining equilibrium decreases.
- Increase in volume favours the backward reaction hence the position of the equilibrium is shifted to the left. The equilibrium constant is not affected.

b. At constant volume:

- If the volume is constant, then the total pressure of the system increases.
- This increases the frequency of collision amongst hydrogen, nitrogen and ammonia. Hence rate of attaining the equilibrium increases.
- Since the equilibrium is attained with a decrease in volume, the forward reaction is favoured by pressure increase; hence the position of equilibrium is shifted to the right. The equilibrium constant is not affected.

Summary:

Variable	Constant volume	Constant pressure
Equilibrium constant	Not affected	Not affected
Equilibrium position	Shifted forward	Shifted backward
Rate	Increases	Decreases

Case III: Addition of an inert gas to a gaseous system where number of moles of reactants is smaller than number of moles of products: Δn=+ve or there is increase in volume (Δv=+ve)

$2SO_3(g) + O_2(g) \rightleftharpoons 2SO_2(g)$

a. At constant pressure:

- When an inert gas is added, the pressure of the system increases. To keep the pressure constant, the volume must increase.
- This spreads the molecules of sulphur dioxide, oxygen and sulphur trioxide farther apart, reducing the frequency of collisions. Hence rate of attaining equilibrium decreases.
- Increase in volume favours the forward reaction hence the position of the equilibrium is shifted to the right. The equilibrium constant is not affected.

b. At constant volume:

- If the volume is constant, then the total pressure of the system increases.
- This increases the frequency of collisions amongst sulphur dioxide, oxygen and sulphur trioxide. Hence rate of attaining the equilibrium increases.
- Since the equilibrium is attained with increase in pressure, the backward reaction is favoured by pressure increase; hence the position of equilibrium is shifted to the left. The equilibrium constant is not affected.

Summary:

Variable	Constant volume	Constant pressure
Equilibrium constant	Not affected	Not affected
Equilibrium position	Shifted backward	Shifted forward
Rate	Increases	Decreases

7.8: Heterogeneous equilibria:

- These are equilibria where the reactants and products have two or more different phases.
- Here:

a. Concentrations of the solid substances are taken to remain constant. So they do not appear in the K_c and K_p expressions.

b. When Water in the liquid phase is one of the reactants, it is assumed to be in large excess hence its concentration remains constant.

c. However, liquid water as a product can not be in large excess. So, its concentration appears in the equilibrium constant expression.

d. When writing K_p expression, the condensed states (solid, liquid and aqueous) do not appear as pressure has a very little effect on them.

Worked example:7.5

Write the equilibrium constant (K_c or K_p) for the following reactions.

a. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_c = [CO_2]$

$K_p = pCO_2$

Calcium carbonate and calcium oxide being solids, their concentrations are constant (their densities)

b. $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$$K_c = \frac{[H_2]^4}{[H_2O]^4}$$

Iron and triiron tetraoxide being solids, their concentrations are constant (their densities).

$$K_p = \frac{(pH_2)^4}{(pH_2O)^4}$$

Iron and triiron tetraoxide being solids do not generate significant partial pressures.

c. $NH_3(g) + H_2O(l) \rightleftharpoons NH_4OH(aq)$

$$K_c = \frac{[NH_4OH]}{[NH_3]}$$

Water is in large excess.

d. $CHOOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CH_2OOCH(l) + H_2O(l)$

$$K = \frac{[CH_3CH_2OOCH][H_2O]}{[CHOOH][CH_3CH_2OH]}$$

Task:7.15

Write the expression for the equilibrium constant K_c or K_p, as appropriate for the following reactions and indicate the units in each case.

$A + B \rightleftharpoons C + D$

a. If A, B, C and D are all gases.

b. A, B, C and D are all liquids.

c. A, B and C are all solids and only D a gas.

7.9: Multiple equilibria:

- An equilibrium reaction can go through several stages; each stage with its own equilibrium constant. Thus, there are a series of (a multiple of) equilibria.
- The over all equilibrium constant depends on the several constants.
- Consider the general case:

$P + Q \rightleftharpoons R + S$

$$K_{c1} = \frac{[R][S]}{[P][Q]}$$

$R + S \rightleftharpoons T + U$

$$K_{c2} = \frac{[T][U]}{[S][R]}$$

Over all:

$P + Q \rightleftharpoons T + U$

$$K_c = \frac{[T][U]}{[P][Q]}$$

But $K_c = \frac{[R][S]}{[P][Q]} \times \frac{[T][U]}{[R][S]} = K_{c1} \times K_{c2}$

- Hence $K_c = K_{c1} \times K_{c2}$

Task:7.16

Equations for some reactions are given below:

$AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq); K_1 = 1.7 \times 10^{-10}$

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq); K_2 = 1.7 \times 10^{-7}$

a. derive the equilibrium constant expression for the reaction below in terms of K_1 and K_2.

$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

CHAPTER EIGHT: IONIC EQUILIBRIA:

8.0 General introduction:

- Ionic equilibria are chemical equilibria in which at least one of the species in equilibrium is an ion. Types of ionic equilibria include:
  - Dissolution of a sparingly soluble electrolyte (solubility product).
  - Self ionization of water (ionic product of water).
  - Weak base ionization (base ionization constant).
  - Weak acid ionization (acid ionization constant).
  - Indicator ionization (indicator ionization constant).
  - Hydrolysis of salt (salt hydrolysis constant).
  - Buffers.
  - Complexation (stability constant of complex).

8.1: Solubility products:

8.1.0: Introduction:

- Solubility product is concerned with the equilibrium existing in a saturated solution of a sparingly soluble electrolyte at constant temperature.
- A sparingly soluble electrolyte is the one which dissolves just up to a certain point beyond which no more of it dissolves.
- At this point a dynamic equilibrium is established between the unionized solid and the ions produced.
- The sparingly soluble electrolytes are:

a. Salts like: calcium carbonate, barium sulphate, silver chloride, etc.–the salts described as insoluble in elementary Chemistry.

b. Bases like: copper (II) hydroxide, barium hydroxide. Magnesium hydroxide, zinc hydroxide, etc.–the bases described as insoluble in elementary Chemistry.

- Consider a saturated solution of barium carbonate in equilibrium with some undissolved barium carbonate.

$BaCO_3(s) + aq \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$ 8.1

- Applying the law of mass action:

$$K_c = \frac{[Ba^{2+}][CO_3^{2-}]}{[BaCO_3]} \quad \text{.....8.2}$$

Since barium carbonate is very sparingly soluble, $[BaCO_3]$, a solid remains constant (its density).

$\Rightarrow K.K_c = [Ba^{2+}][CO_3^{2-}]$, where K is the $[BaCO_3]$

But, $K.K_c = K_{sp}$, solubility product expression of barium carbonate.

$$\Rightarrow K_{sp} = [Ba^{2+}][CO_3^{2-}] \quad \text{.....8.3}$$

- The equation 8.1 is called solubility equation of barium carbonate.
  - The equation 8.3 is called solubility product expression of barium carbonate.
  - Consider the general cases below:

a. **Sparingly soluble electrolytes of the form MX**

Solubility equation is given by:

$MX(s) + aq \rightleftharpoons M^{n+}(aq) + X^{n-}(aq)$

Solubility product expression is given by:

$$K_{sp} = [M^{n+}][X^{n-}]$$

The unit of K_{sp} is $(moldm^{-3})(moldm^{-3}) = mol^2dm^{-6}$

- If MX is silver bromide:

Solubility equation is given by:

$AgBr(s) + aq \rightleftharpoons Ag^+(aq) + Br^-(aq)$

Solubility product expression is given by:

$$K_{sp} = [Ag^+][Br^-]$$

- If MX is copper (II) sulphide:

Solubility equation is given by:

$CuS(s) + aq \quad Cu^{2+}(aq) + S^{2-}(aq)$

Solubility product expression is given by:

$$K_{sp} = [Cu^{2+}][S^{2-}]$$

b. Sparingly soluble electrolytes of the form MX_2

Solubility equation is given by:

$MX_2(s) + aq \rightleftharpoons M^{2+}(aq) + 2X^-(aq)$

Solubility product expression is given by:

$$K_{sp} = [M^{2+}][X^-]^2$$

The unit of K_{sp} is $(moldm^{-3})(moldm^{-3})^2 = mol^3dm^{-9}$

- If MX_2 is lead(II) iodide:

  Solubility equation is given by:

  $PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

  Solubility product expression is given by:

  $$K_{sp} = [Pb^{2+}][I^-]^2$$

- If MX_2 is iron (II) hydroxide:

  Solubility equation is given by:

  $Fe(OH)_2(s) + aq \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$

  Solubility product expression is given by:

  $$K_{sp} = [Fe^{2+}][OH^-]^2$$

c. Sparingly soluble electrolytes of the form M_2X:

Solubility equation is given by:

$M_2X(s) + aq \rightleftharpoons 2M^+(aq) + X^{2-}(aq)$

Solubility product expression is given by:

$$K_{sp} = [M^+]^2[X^{2-}]$$

The unit of K_{sp} is $(moldm^{-3})^2(moldm^{-3}) = mol^3dm^{-9}$

- If M_2X is silver chromate (VI):

  Solubility equation is given by:

  $Ag_2CrO_4(s) + aq \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

  Solubility product expression is given by:

  $$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

d. Generally, for a sparingly soluble electrolyte M_aX_b where a and b are integers;

The solubility equation is given by;

$M_aX_b(s) + aq \rightleftharpoons aM^{b+}(aq) + bX^{a-}(aq)$

Solubility product expression is given by:

$$K_{sp} = [M^{b+}]^a[X^{a-}]^b$$

The unit of K_{sp} is $(moldm^{-3})^a(moldm^{-3})^b = (moldm^{-3})^{(a+b)}$

Definition:

Solubility product of a sparingly soluble electrolyte is the product of the concentrations of the ions raised to the power of their stoichiometric coefficients in a saturated solution of the electrolyte at a given temperature.

Solubility and solubility product:

- Solubility is the amount of a solute required to saturate 100g of water at a fixed temperature.
- The solubility can be expressed in terms of moles or grams of the solute per given volume or mass of water.
- It should be noted that solubility deals with only saturated solution. So concentration should not be used to mean solubility. However, for sparingly soluble electrolytes, their solutions are always saturated. So their concentrations at any temperature are the same as their solubilities at that temperature.

Calculation of solubility product given solubility:

Worked example:8.1

The solubility of barium sulphate in water is 0.00024g/100g of water at a certain temperature. Write down the;

a. Equation for the solubility of barium sulphate.
b. Expression for its solubility product.
c. Calculate the solubility product of barium sulphate.

Solution:

a. $BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$
b. $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
c. RFM of $BaSO_4$ = 137 + 32 + (16x4) = 233

Moles of barium sulphate dissolved = $\frac{0.00024}{233} = 1x10^{-6}$

$100cm^3$ contain $1x10^{-6}$ moles

$1000cm^3$ will contain $1000x1x10^{-6} x \frac{1}{100} = 1.0x10^{-5}\ moles$

$[BaSO_4] = 1.0x\ 10^{-5}$

Since one mole of $BaSO_4$ produces one mole of Ba^{2+} and one mole of SO_4^{2-} ions respectively;

$[BaSO_4]=[Ba^{2+}]=[SO_4^{2-}]=1.0x\ 10^{-5}$

From $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$K_{sp} = (1.0x10^{-5})(1.0x10^{-5})$

$K_{sp} = 1.0x10^{-10}\ mol^2 dm^{-6}$

Worked example:8.2

Lead (II) chloride is sparingly soluble in water.

a. Write down the expression for solubility product for lead (II) chloride.
b. Calculate the solubility product of lead (II) chloride at 20^0C if its solubility at 20^0C is 9.9g/1000g of water.

Solution:

a. $PbCl_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ $ksp = [Pb^{2+}][Cl^-]^{2}$
b. RFM of $PbCl_2$ = 207 + (35.5x2) = 278

$[PbCl_2] = \frac{9.9}{278} = 0.0356$

Since $PbCl_2$ produces one mole of Pb^{2+} and two moles of Cl^- ions;

$[Cl^-]=2x0.0356=0.0712M$, $[Pb^{2+}]=0.0356$

From $K_{sp}=[Pb^{2+}][Cl^-]^2$

$K_{sp}=0.0356(0.0712)^2$

$K_{sp}=1.8x10^{-4}mol^3dm^{-9}$

Worked example:8.3

Calculate the solubility of lead (II) sulphate in mole per litre if its solubility product at 298K is $1.6x10^{-8}mol^2dm^{-6}$

Solution:

$PbSO_4(s) + aq \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp}=[Pb^{2+}][SO_4^{2-}]$

Let the $[SO_4^{2-}]$ be x, $[Pb^{2+}]=x$

$1.6x10^{-8}=(x)(x)$

$x = \sqrt{1.6x10^{-8}} = 1.26x10^{-4} M$

Since one mole of lead (II) sulphate produces one mole of lead (II) ions;

Solubility of lead (II) sulphate is therefore $1.26x10^{-4}$mol/l

Task:8.1

Iron (III) hydroxide is sparingly soluble in water.

a. Write the equation for the solubility of iron (III) hydroxide.
b. Write down the solubility product expression for iron (III) hydroxide.
c. Calculate the solubility product of iron (III) hydroxide if its solubility is $3.6x10^{-5}$g/100g of water at 298K.

Task:8.2

a. Write the equation for the sparing solubility of magnesium carbonate.
b. Calculate the solubility constant of magnesium carbonate at 25^0C if its solubility at the temperature is 0.01g/100g of water.

Task:8.3

The solubility of silver chromate (VI) at 298K is 0.03g per 100g of water. Write down:

a. The equation for the solubility of silver chromate.
b. Expression for its solubility product.

c. Calculate the solubility product of silver chromate (VI) at the above temperature.

Task:8.4

The solubility of zinc carbonate is $8.0x10^{-4}$M, at a certain temperature.

a. Write the equation for the sparing solubility of zinc carbonate.
b. Give the solubility constant expression of zinc carbonate.
c. Calculate the above constant at the stated solubility temperature.

Task:8.5

Barium chromate (VI) is a sparingly soluble salt.

a. Write down its solubility constant expression.
b. Calculate the solubility product of barium chromate (VI) at 298K, given that its solubility at that temperature is $1.15x10^{-5}$M.

Calculation of solubility given solubility product:

Task:8.6

Calculate the solubility of silver bromide in $moldm^{-3}$ given that the solubility product is $7.7x10^{-13}mol^2dm^{-9}$ at 291K.

Task:8.7

Aluminium hydroxide is a sparingly soluble base.

a. Write the equation for the solubility of aluminium hydroxide.
b. Write down the solubility product expression for aluminium hydroxide.
c. If the solubility product of aluminium hydroxide at 298K is $5.0x10^{-33}$. Calculate the solubility of aluminium hydroxide at 298K.

Task:8.8

Calcium phosphate is a sparingly soluble salt.

a. Write down the equation for the solubility of calcium phosphate
b. Expression for the solubility product.
c. Calculate the solubility of calcium phosphate at 25^0C, if its solubility product at that temperature is $6.072x10^{-21}mol^5dm^{-15}$

8.1.1: Factors that affect solubility and K_{sp} of sparingly soluble electrolytes:

A. Temperature:

- If dissolution of a sparingly soluble electrolyte is accompanied by evolution of heat. Then, decrease in temperature will increase the solubility and hence the solubility product will increase while increase in temperature decreases solubility (leads to precipitation). Hence solubility product decreases.
- If dissolution of a sparingly soluble electrolyte is accompanied by absorption of heat from the surrounding i.e. endothermic, increase in temperature leads to increase in solubility and hence increase in solubility product. Decrease in temperature decreases solubility (leads to precipitation) and also decreases solubility product value.
- This takes place in accordance to van't Hoff's law of mobile equilibrium.

B. Common ion effect:

- For a saturated solution of a sparingly soluble electrolyte, when a very strong electrolyte solution containing an ion common to one of the ions in the saturated solution is added, then some of the sparingly soluble electrolyte is

precipitated. This decreases solubility meanwhile solubility product remains constant.

- Consider the saturated solution of silver chloride below:
  $AgCl(s) + aq \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
- When sodium chloride solution is added to the system, due to excess chloride ions from the completely dissociated sodium chloride, the ionic product tends to exceed the solubility product of silver chloride.
- More of the chloride ions combine with silver ions in order to restore solubility product. Hence silver chloride is precipitated, leading to decrease in its solubility.

Definition:

Common ion effect is the precipitation of a sparingly soluble electrolyte from its saturated solution by addition of an ion common to one of the ions in the saturated solution at a given temperature.

Calculations involving common ions

- For any calculation involving common ion effect on solubility, the concentration of ions due to sparing solubility of the electrolyte is ignored and the concentration of the introduced common ion is considered to be the only one maintaining solubility product.

Worked example:8.5

Calculate the solubility of barium sulphate in:

a. Water,
b. 0.2M sulphuric acid, if its solubility product is $1.0x10^{-10}mol^2dm^{-6}$.

Solution:

a. Let $[Ba^2]$ be x, hence $[SO_4^{2-}]$=x

From $K_{sp}=[Ba^{2+}][SO_4^{2-}]$

$1.0x10^{-10}=x.x$

$x=\sqrt{1.0x10^{-10}}=1.0x10^{-5}$

RFM of $BaSO_4$ is (137+32+64)=233

Solubility = $233x1.0x10^{-5}$ =0.00233g/1000g of water.

b. $[SO_4^{2-}]$=0.2, let $[Ba^2]$ be x.

$\Rightarrow 1.0x10^{-10}=0.2x$

$x=5.0x10^{-10}$

Since 1mol of barium sulphate on dissolution produces 1mol of barium ions, solubility of barium sulphate is $5.0x10^{-10}$ $=233x5.0x10^{-10}1.15x10^{-8}$g/1litre of the solution.

Worked example:8.6

Lead (II) sulphate is very sparingly soluble in water and its solubility product is $1.6x10^{-8}mol^2dm^{-6}$.

a. Write down an expression for the solubility of lead (II) sulphate.

6g of lead (II) sulphate were dissolved in 1*l* of water.

b. Determine the percentage of the salt that dissolved.
c. If 0.04M sodium sulphate solution was used, what percentage of the salt dissolves?

Solution:

a. $K_{sp}=[Pb^{2+}][SO_4^{2-}]$
b. Let $[Pb^{2+}]=[SO_4^{2-}]$=x

$\Rightarrow 1.6x10^{-8}=x.x$

$x=\sqrt{1.6x10^{-8}}=1.26x10^{-4}M$

Since 1mol of lead (II) sulphate produces 1mol of sulphate ions, solublility of lead (II) sulphate is $1.26x10^{-4}$M.

RFM of $PbSO_4$ =207+32+64=303

Solubility = 0.038g/*l*

%age solubility= $\frac{0.038}{5} x100 = 0.76\%$

c. $[SO_4^{2-}]$=0.04M, Let $[Pb^{2+}]$=x

$\Rightarrow 1.6x10^{-8} = 0.04x$

$x = 4.0x10^{-7}$

Solubility $= 4.0x10^{-7} x303 = 1.212x10^{-4}$

%age solubility= $\frac{1.212}{5} x100 = 2.424x10^{-3}\%$

Task:8.9

The solubility product of calcium carbonate is $5.0x10^{-9}$. Calculate at the same temperature the solubility of calcium carbonate:

a. In water.
b. In 0.05M sodium carbonate solution.

Task:8.10

Aluminium hydroxide is a sparingly soluble electrolyte and its solubility product at 298K is $1.0x10^{-32}$.

a. Write down the equation for the dissolution of aluminum hydroxide.
b. Calculate the solubility of aluminium hydroxide in water.
c. What would be observed when aluminium nitrate solution is added to a saturated solution of aluminium hydroxide?
d. Calculate the solubility of aluminium hydroxide in 0.0125M aluminium nitrate solution.

Task:8.11

Lead (II) sulphate is sparingly soluble in water with a solubility of 0.0045g/100g of water.

a. Calculate the solubility of lead (II) sulphate in 0.004M sulphuric acid.

b. How many times is the solubility of lead (II) sulphate in water greater than that in the sulphuric acid?

Task:8.12

Iron (II) hydroxide is a sparingly soluble base with a solubility of 0.0006g/100g of water at room temperature. Calculate the percentage decrease in solubility when iron (II) hydroxide is dissolved in 0.06M sodium hydroxide solution.

Task:8.13

Silver chloride is a sparingly soluble salt

a. Write down the equation for its solubility.
b. Derive the solubility product expression for silver chloride.
c. The solubility of silver chloride is 0.00148g/1000g of water. Calculate the solubility of silver chloride in 0.005M barium chloride solution.

Applications of common ion effect:

1. **Purification of common salt:**
   - Common salt always appears moist due to presence of deliquescent impurities like magnesium chloride and calcium chloride.
   - To obtain a pure sample of sodium chloride, a saturated solution of the impure salt is made and hydrogen chloride gas bubbled into.
   - Here, the excess chloride ions from hydrogen chloride added combine with sodium ions of the impure salt to precipitate pure sodium chloride (common salt).
2. **Salting out of soap:**
   - In the process of saponification, when vegetable oil is boiled with sodium hydroxide solution, a saturated solution of sodium stearate (soap) is produced.

- Addition of concentrated solution of sodium chloride (brine) leads to precipitation (salting out of soap) of sodium stearate as a result of excess sodium ions which tend to exceed solubility product of sodium stearate.

C. ***Complex ion formation:***

- Some ions of a saturated solution of a sparingly soluble electrolyte are complexed (undergo complexation) by addition of a second solution. The complexed ion is thus removed from contributing to the solubility equilibrium.
- So the sparingly soluble electrolyte ionizes to restore the solubility product and hence its solubility increases.
- Generally complex ion formation increases solubility of a sparingly soluble electrolyte, but the solubility product remains constant.

Example:

Lead (II) iodide is more soluble in potassium iodide solution than in water.

Explanation:

- Lead (II) iodide dissolves in water according to the equation:

  $PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$
- However, when lead (II) iodide is added to potassium iodide, the iodide ions from the sparing solubility of lead (II) iodide complexes with the iodide ions from the complete dissociation of potassium iodide to form triiodide ions according to the equation:

  $2I^-(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$
- This reduces the molar concentration of iodide ions in the solution, and hence the ionic product below the solubility product below the solubility product of lead (II) iodide. reduced
- In order to restore the solubility product of lead (II) iodide, more lead (II) iodide then dissolves, hence its solubility increases.

- Silver chloride is more soluble in aqueous ammonia than in water.
- Lead (II) chloride is more soluble in concentrated hydrochloric acid than in dilute hydrochloric acid.
- Copper (II) carbonate is more soluble in aqueous ammonia than in water.
- Aluminium hydroxide is more soluble ion sodium hydroxide solution than in water.
- Copper (I) chloride is more soluble in ammonia solution than in water.

D. ***Addition of a solution of a strong electrolyte with no common ions (uncommon ion effect):***

- Here, the strong electrolyte is selected such that its addition to the solubility equilibrium of the sparingly soluble electrolyte precipitates one of the ions in the solution.
- This reduces the ionic product of the sparingly soluble electrolyte below its solubility product. Hence more of the electrolyte ionizes (dissolves), leading to increase in its solubility.

Example:

Lead (II) chloride is more soluble in silver nitrate solution than in water.

Explanation:

- Lead (II) chloride dissolves in water according to the equation:

  $PbI_2(s) + aq \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$
- When in silver nitrate, the iodide ions are precipitated according to the equation:

  $Ag^+(aq) + I^-(aq) \rightleftharpoons AgI(s)$

- This reduces the molar concentration of iodide ions in the solubility equilibrium and hence ionic product below the solubility product of lead (II) chloride.
  To restore the solubility product of lead (II) chloride, more of it dissolves. Hence its solubility increases.

Task:8.14
Barium sulphate is more soluble in lead (II) nitrate solution than in water. Explain.

Task:8.15
Silver iodide is sparingly soluble in water, but dissolves readily in lead (II) nitrate solution. Explain.

E. Other factors that affect solubility and hence solubility product include:
- Size of the cation and the anion (ionic radius).
- Ionic charge.

8.1.2: Applications of solubility product:

a. Use of potassium chromate (VI) in Argentometry:
- When silver nitrate solution is titrated against sodium chloride solution containing a little amount of potassium chromate (VI) solution, only silver chloride is precipitated as long as there are any chloride ions in the solution.
- Only when all the chloride ions have been fully reacted does a red precipitate of silver chromate appear.
- This is explained by the solubility product of the two silver salts: $[Ag^+][Cl^-]=1.0\times10^{-10}mol^2dm^{-6}$ and $[Ag^+]^2[CrO_4^{2-}]=2.5\times10^{-12}mol^3dm^{-9}$.
- Suppose the molar concentrations of chloride ions and chromate (VI) ions are each 0.1M;
- $[Ag^+]$ required to precipitate one mole of AgCl is given by;

$$[Ag^+]=\frac{K_{sp}}{[Cl^-]}=\frac{1.0\times10^{-10}}{0.1}=1.0\times10^{-9}moldm^{-3}$$

- $[Ag^+]$ required to precipitate one mole of Ag_2CrO_4 is given by;

$$[Ag^+]=\sqrt{\frac{K_{sp}}{[CrO_4^{2-}]}}=\sqrt{\frac{2.5\times10^{-12}}{0.1}}=5.0\times10^{-6}moldm^{-3}$$

- Thus even if the concentrations of chloride ions and chromate ions in the solution are equal, it is easier by adding Ag^+ to reach the solubility product of AgCl than that of Ag_2CrO_4 in spite of the low solubility product of the latter.
- Hence AgCl precipitated first.

b. Predicting precipitation:
- If the solubility product of lead (II) sulphate at 298K is 1.6×10^{-8} mol^2dm^{-6}. After mixing 0.006M of lead (II) ions with equal volume of 0.006 M of sulphate ions. Will a white precipitate of lead (II) sulphate form?

Solution:
By mixing equal volumes of the two ions, their molar concentrations halve:
New $[Pb^{2+}]$ = 0.003 and new $[SO_4^{2-}]$ = 0.003M
Ionic product = $[Pb^{2+}][SO_4^{2-}] = (0.003)^2 = 9.0\times10^{-6}mol^2dm^{-6}$
Ionic product > solubility product.
Hence lead (II) sulphate will immediately precipitate out.

c. selective precipitation and gravimetric analysis:
- A mixture of soluble salts can be separated basing on the difference in their solubility products. Here, the salts in the solution are selectively (stepwise) precipitated as their insoluble counter parts and the masses of the precipitate after filtering can be determined (gravimetric analysis).

- For example, a mixture of magnesium chloride, barium chloride and calcium chloride can be separated as follows:
  a. Addition of potassium chromate only precipitates out barium chromate as both magnesium and calcium chromates are soluble. The precipitate is then filtered out.
  b. Addition of sodium sulphate to the solution only precipitates calcium (as calcium sulphate), since magnesium sulphate is soluble. The precipitate is then filtered out.
  c. Finally, magnesium ions are removed by addition of sodium carbonate, as precipitated calcium carbonate.
- Both the precipitating reagents and their order of addition matter. When order of addition is altered, two cations or more are precipitated at the same time. This affects determination of the proportions of the different cations.

d. ***Precipitation of sulphides of divalent metals:***
- When hydrogen sulphide gas is bubbled into a solution of divalent cations, the sulphide of a cation is precipitated depending on its solubility product and nature of the reaction medium (neutral, acidic or alkaline).

Sulphide	K_{sp}/mol^2dm^{-6}
CuS	$1.0x10^{-40}$
SnS	$1.0x10^{-28}$
MnS	$1.0x10^{-16}$

i) Sulphides of divalent cations of low solubility product are favourably precipitated in acidic medium i.e. is the presence of dilute acids like hydrochloric acid.

Explanation:
- When hydrogen sulphide is bubbled into the solution, it ionizes according to the equation:
  $H_2S(g) + aq \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$
- In the presence of hydrochloric acid, because of the presence of many hydrogen ions from complete ionization of hydrochloric acid, the ionization of hydrogen sulphide is suppressed. Thus only a few sulphide ions are produced.
- Therefore, only copper (II) sulphide with a very low solubility product would be precipitated.

ii) Sulphides of divalent cations of high solubility product are favourably precipitated in alkaline medium i.e. in the presence of hydroxyl ions.

Explanation:
- When hydrogen sulphide is bubbled into the solution, it ionizes according to the equation:
  $H_2S(g) + aq \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$
- In the presence of hydroxyl ions, the hydroxyl ions combine with some of the hydrogen ions from the partial ionization of hydrogen sulphide to form water. More hydrogen sulphide ionizes producing a high concentration of sulphide ions.
- Therefore, manganese (II) sulphide with a high solubility product would favourably be precipitated.

iii) Sulphides of divalent cations of moderate solubility product are favourably precipitated in neutral medium since the partial ionization of hydrogen sulphide can generate enough sulphide ions to exceed their solubility products.

e. ***Precipitation of hydroxides:***

- In qualitative analysis, when aqueous ammonia is added to a solution of a cation, the cation is precipitated as its hydroxide.
- However, in a mixture of cations, the precipitation of a cation as its hydroxide depends on the solubility product of the hydroxide and the presence or absence of ammonium chloride.

Hydroxides	K_{sp}
$Fe(OH)_3$	1.0×10^{-38}
$Al(OH)_3$	1.0×10^{-33}
$Mg(OH)_2$	4.0×10^{-12}

Addition of aqueous ammonia to the solution of the cations into which ammonium chloride is added:

- When ammonia is added to a mixture of these cations into which ammonium chloride is added, then it's only the hydroxides of the cations of low solubility product which are precipitated out.

Explanation:

- Partial ionization of aqueous ammonia:
  $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
- Ammonium chloride, a strong electrolyte completely ionizes to produce ammonium ions. This suppresses the partial ionization of ammonium hydroxide. Thus only a small amount of hydroxyl ions are produced.
- Therefore only cations with low solubility products will precipitate out. From the table above it is iron (III) hydroxide that precipitates out.

8.1.3: Experimental determination of solubility product:

1. **By volumetric analysis/titrimetric method:**
   - A saturated solution of a sparingly soluble electrolyte is prepared at a certain temperature.
   - The mixture is filtered to obtain only the saturated solution without the undissolved solid.
   - The solution is pipetted and titrated with a suitable standard solution using a suitable indicator until consistent titre values.
   - From the end point volume of the standard titrant, the concentration of one of the ions of the sparingly soluble electrolyte is determined from which the concentration of the other ion and hence solubility product are calculated.

Determination of K_{sp} of sparingly soluble hydroxide ($Mg(OH)_2$, $Ca(OH)_2$):

- Calcium hydroxide is dissolved in water to obtain its saturated solution at a given temperature.
- The solution is then filtered.
- The filtrate is pipetted and titrated with standard hydrochloric acid until consistent titre value using methyl orange indicator.
- From the end point volume of hydrochloric acid, the molar concentration of hydroxyl ions in the saturated solution is calculated.
- From the solubility equation of calcium hydroxide:
  $Ca(OH)_2(s) + aq \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$,
  The molar concentration of calcium ions is calculated.
- From the solubility product expression:
  $K_{sp} = [Ca^{2+}][OH^-]^2$, the solubility product is the calculated.

Assumptions:

a. During filtering, the equilibrium was not disturbed.
b. Titration is done at the that temperature the equilibrium was attained.

- To determine the solubility product for other sparingly soluble electrolytes, apart from hydroxides, the procedures above are generally similar.
- However, the standard titrant and indicator vary depending on the anion of the electrolyte, or some medium as summarized in the table below:

Nature of electrolyte	Titrant	Indicator
Iodate (acidified)	Thiosulphate solution	Starch
Iodide	Thiosulphate solution	Starch
Chloride	Silver nitrate	Chromate (VI)
Oxalate	Manganate (VII)	Nil

- For the case of titration of oxalate with say potassium manganate (VII), the end point is detected by the change in colour of potassium manganate (VII) itself. So, no indicator is necessary.

2. Conductivity measurement:

- Conductivity measurement can work for all sparingly soluble electrolytes.
- What should be clearly noted is that the saturated solution of the electrolyte must be prepared using conductivity water.
- Conductivity measurement as a method for determination of solubility product is discussed under applications of conductivity measurement in chapter 9.

8.2: Acid – base equilibria

8.2.1: Theories of acids and bases:

- The definitions of an acid and a base are inseparable. Three important theories have been coined in attempt to define an acid and hence a base.

a. Arrhenius theory:

- According to Arrhenius;

An acid is a substance that ionizes/dissociates on dissolving in water to produce hydrogen ions. For example:

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
$$HCl(g) + (aq) \longrightarrow H^+(aq) + Cl^-(aq)$$
$$H_2SO_4(l) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$$
$$H_2SO_4(l) + (aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$
$$HNO_3(l) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$
$$HNO_3(l) + (aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

- Therefore to Arrhenius, HCl, H_2SO_4 and HNO_3 are acids.

A base is a substance that combines with an acid to form a salt for example: copper (II) oxide (CuO), lead (II) oxide (PbO), sodium oxide (Na_2O), zinc oxide (ZnO), aluminium oxide (Al_2O_3).

- Alkalis are soluble bases. An alkali is therefore a substance which on dissolving in water dissociates to produce hydroxyl ions. For example:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq) \longrightarrow 2Na^+(aq) + 2OH^-(aq)$$
$$K_2O(s) + H_2O(l) \longrightarrow 2KOH(aq) \longrightarrow 2K^+(aq) + 2OH^-(aq)$$
$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

- Therefore, to Arrhenius, Na_2O, K_2O, MgO are alkalis.

Key objections/weaknesses of the theory:

i. To the theory, an acid is not itself without water
ii. Certain substances show acidic properties yet when dissolved in water, they do not directly produce

A mixture of CH_3CH_2OH of mass 0.9g and ... 0.9g at 90° was allowed to reach equilibrium
(i) Calculate the mass of ether $CH_3CH_2COOCH_2CH_3$ at equilibrium
KC = 0.06

hydrogen ions. For example a solution of an ammonium salt liberates hydrogen gas with metals like magnesium.

$$2NH_4^+(aq) + Mg(s) \longrightarrow 2NH_3(g) + Mg^{2+}(aq) + H_2(g)$$

b. Brϕnsted – Lowry theory:

An acid is a substance which can donate a proton (H^+) to a base. A base is thus a substance which can accept a proton from an acid.

- An acid – base reaction is therefore a proton transfer.

$$HA + B^- \rightleftharpoons HB + A^-$$

- In the forward direction, acid HA transfers a proton to base B^- to form acid HB and base A^-
- In the backward reaction, acid HB transfers a proton to base A^- to form acid HA and base B^-
- Therefore when an acid donates its proton (H^+) to a base, the acid becomes a new base and the base on accepting a proton becomes a new acid.
- The base formed from an acid and the acid only differs by hydrogen and thus are conjugates; also the acid formed from a base and the base are conjugates.
- An acid – base equilibrium is therefore a dynamic equilibrium between the two conjugate acid – base pairs i.e.

$$\text{Acid1} + \text{Base2} \rightleftharpoons \text{Acid2} + \text{Base1}$$

- For Examples

$$\underset{\text{Acid1}}{HCl(aq)} + \underset{\text{Base2}}{H_2O(aq)} \rightleftharpoons \underset{\text{Acid2}}{H_3O^+(aq)} + \underset{\text{Base1}}{Cl^-(aq)}$$

$$\underset{\text{Acid1}}{HCl(aq)} + \underset{\text{Base2}}{NH_3(aq)} \rightleftharpoons \underset{\text{Acid2}}{NH_4^+(aq)} + \underset{\text{Base1}}{Cl^-(aq)}$$

Conjugate acid – base pairs

Acid	Base
HCl	Cl^-
NH_4^+	NH_3
H_3O^+	H_2O
HNO_3	NO_3^-
CH_3COOH	CH_3COO^-

Amphoteric substances:

- From Brϕsted – Lowry definition of an acid and hence a base, certain substances can act as acids by donating protons; then on the other hand can act as bases by accepting protons. These are therefore amphoteric substances.

Case I: Water:

a. Acidic behaviours:

$$\underset{\text{Base}}{NH_3(g)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$\underset{\text{Base}}{H_2O(l)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

b. Basic behaviours:

$$\underset{\text{Acid}}{HCl(g)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

$$\underset{\text{Acid}}{H_2SO_4(l)} + \underset{\text{Base}}{2H_2O(l)} \rightleftharpoons 2H_3O^+(aq) + SO_4^{2-}(aq)$$

Case II: Ammonia:

$$\underset{\text{Base}}{NH_3(aq)} + \underset{\text{Acid}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + NH_2^-(aq)$$

- From Brϕnsted – Lowry theory, a base can only accept a proton by forming a coordinate/dative covalent bond with the proton. Therefore a base must have at least a

lone pair of electrons to be accepted by an acid for the formation of a coordinate/dative covalent bond.

c. Lewis theory:

- A base is a substance which can donate a lone pair of electrons for the formation of coordinate covalent bond.
- An acid is a substance which can accept a lone pair of electrons for the formation of coordinate/dative covalent bond.
- For example;

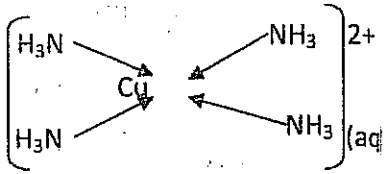
1. $BF_3(g) + :NH_3(g) \longrightarrow F_3B \leftarrow NH_3(g)$

Lewis acid Lewis base

Dative bond

2. $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons$

Lewis acid Lewis base



8.2.2: Ionic product of water:

- Water is self ionized to a very small extent according to the equation.

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

- Applying the law of mass action to the second self ionization equation;

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

Since the degree of ionization is very very small,

$[H_2O]$ at equilibrium $\approx [H_2O]$ initially, and $\approx$ a constant K.

$\Rightarrow K.K_c = [H^+][OH^-]$

But $K.K_c = K_w$, the ionic product of water.

$\Rightarrow K_w = [H^+][OH^-]$ 8.4

- The expression 8.4 is called ionic product of water. At $25^0C/298K$, K_w has a value of $1.0 \times 10^{-14}\ mol^2dm^{-6}$.
- Since 1 mole of water ionizes to give one mole of hydrogen ions (H^+) and 1 mole of hydroxyl ions (OH^-),

$\Rightarrow [H^+] = [OH^-] = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ moldm^{-3}$

- The self ionization of water is endothermic which means more water will ionize with increase in temperature. Hence, the K_w value increases with temperature as illustrated in the table below.

Temperature/K	K_w/mol^2dm^{-6}
273	0.11×10^{-14}
283	0.30×10^{-14}
293	0.68×10^{-14}
323	5.77×10^{-14}
373	57.3×10^{-14}

pH of a solution:

- pH of a solution (potenz hydrogen) in the logarithm to the base ten of the reciprocal of the molar concentration of hydrogen ions in the solution.
- If $[H^+]$ is the molar concentration of hydrogen ions in the solution, then from the definition,

$$pH = \log_{10}\left(\frac{1}{[H^+]}\right) = \log_{10}[H^+]^{-1}$$

$$pH = -\log_{10}[H^+]$$

pH of strong acids:

A strong acid is completely ionized.

Worked example: 8.7

Calculate the pH of a solution containing;

a. 0.005M hydrogen ions.
b. 0.035M hydrochloric acid.
c. Pure water at 298K.
d. 0.0125M sulphuric acid.

Solution:

a. $[H^+] = 0.005$

$pH = -\log 0.005 = 2.30$

b. 1mol of HCl produces 1mol of H^+ according to the equation:

$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

$[H^+]=0.035$

$pH = -\log 0.035 = 1.46$

c. At 298K, $[H^+]=1.0x10^{-7}$

$pH = -\log 1.0x10^{-7} = 7.0$

d. 1mol of H_2SO_4 produces 2mol of H^+ according to the equation:

$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$

$[H^+] = 2x0.0125 = 0.025M$

$pH = -\log 0.025 = 1.60$

Task:8.16

Calculate the molar concentrations of hydrogen ions of the following solutions, whose pHes are:

a. 2.4
b. 1.83
c. 5.23

Task:8.17

The pH of sulphuric acid is 2.20. Calculate the concentration of the sulphuric acid in g/*l*.

pH of strong bases:

A strong base is completely dissociated in solution.

Correspondingly $pOH = -\log_{10}[OH^-]$

$pK_w = -\log_{10}K_w$

Where K_w= ionic product of water.

$K_w = [OH^-][H^+] = 1.0x10^{-14} mol^2dm^{-6}$ at 298K

$-\log_{10}Kw = -\log_{10}(1.0 \times 10^{-14})$at 298K

$pK_w = 14$; at 298K

From$K_w = [H^+]\ [OH^-]$

Taking $-\log_{10}$ of both sides:

$-\log_{10}Kw = -\log_{10}[H^+] + -\log_{10}[OH^-]$

$pK_w = pH + pOH$

Worked example:8.8

Calculate the pH of the following solutions:

a. 0.004M hydroxyl ions.
b. 0.01M NaOH
c. 0.56g/100g of water KOH solution.

Solution:

a. $pOH = -\log 0.004 = 2.40$

$pH = 14 - 2.40 = 11.60$

b. 1mol sodium hydroxide completely dissociates to produce 1mol of hydroxyl ions according to the equation:

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

$[OH^-]=0.01$

$pOH = -\log 0.01 = 2.00$

$pH = 14 - 2.00 = 12.00$

c. RFM of KOH = (39+16+1) = 56.

100cm3 of water dissolved 0.56g

1000g would dissolve $\frac{1000x0.56}{100} = 5.6g$

$$[KOH] = \frac{5.6}{56} = 0.1$$

1mol potassium hydroxide completely dissociates to produce 1mol of hydroxyl ions according to the equation:

$KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$

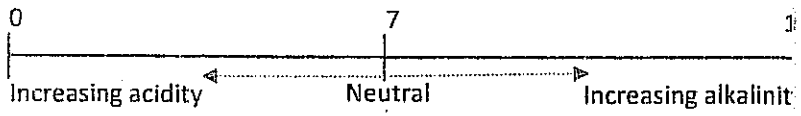
$[OH^-]=0.1$

$pOH = -\log 0.1 = 1.00$

$pH = 14 - 1.00 = 13.00$

The pH scale

- An acidic solution has a pH of less than 7; an alkaline solution has a pH of greater than 7 and a neutral solution has a pH of 7.
- The pH scale shows the range of the pHes of different solutions. This is practically between 0 and 14.



Take note:

i. A strongly acidic solution can have a pH of less than 0 e.g. the pH of 10M hydrochloric acid is –1.

ii. A strongly alkaline solution can have a pH of greater than 14. However the pH values generally lie within the range 0–14.

8.2.3: Ionization of weak acids and bases:

- Weak acids and bases are only partially/incompletely ionized or dissociated.
- The pH of solutions of weak acids/bases depends on:

i. The acid/base ionization/dissociation constant.

ii. The degree of ionization/dissociation.

iii. Concentration/dilution.

iv. Temperature.

Ionization of weak acids:

- Examples of weak acids include: all organic acid, hydrocyanic acid, solution of hydrogen sulphide, sulphurous acid, carbonic acid, etc.
- Consider a weak acid HA, of volume, v and α is the degree of ionization.

Ionization equation: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Initially	1mol	0mol	0mol
Stoichiometrically	1mol	1mol	1mol
At equilibrium	(1–α)mol	αmol	αmol
Equilibrium conc.	$\frac{1-\alpha}{v}$	$\frac{\alpha}{v}$	$\frac{\alpha}{v}$

- Applying the law of mass action;

$$K_c = \frac{[H^+][A^-]}{[HA]}$$

But for weak acids, equilibrium constant is given by K_a, acid ionization constant.

$$\Rightarrow K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_a = \frac{\left(\frac{\alpha}{v}\right)\left(\frac{\alpha}{v}\right)}{\left(\frac{1-\alpha}{v}\right)} = \frac{\alpha^2}{(1-\alpha)v}$$

$$\therefore K_a = \frac{\alpha^2}{(1-\alpha)v} \quad \text{.....8.5}$$

- The equation 8.5 above is known as **Ostwald's law of dilution.**

If the acid HA is very very weak, then α is very very small.

$\Rightarrow (1-\alpha) \approx 1$

Hence, $K_a = \frac{\alpha^2}{v}$

pH expression:

$[H^+] = \frac{\alpha}{v}$

$\Rightarrow pH = -\log\left(\frac{\alpha}{v}\right)$

K_a in terms of concentration:

- Consider a weak acid HA of concentration c and α degree of ionization.

Ionization equation: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Initially	cmol	0mol	0mol
Stoichiometrically	1mol	1mol	1mol
At equilibrium	(1−α)cmol	αcmol	αcmol

- Applying the law of mass action;

$K_c = \frac{[H^+][A^-]}{[HA]}$

$\Rightarrow K_a = \frac{(\alpha c)(\alpha c)}{(1-\alpha)c} = \frac{\alpha^2 c}{(1-\alpha)}$

$\therefore K_a = \frac{\alpha^2 c}{(1-\alpha)}$ 8.6

The equation 8.6 above is the alternative form of Ostwald's dilution law.

If the acid HA is very very weak, then α is very very small.

$\Rightarrow (1-\alpha) \approx 1$

$K_a = \alpha^2 c$

pH expression:

$[H^+] = \alpha c$

$\Rightarrow pH = -\log \alpha c$

alternatively

$[H^+] = [A^-]$

$Ka = \frac{[H^+]^2}{[HA]}$

$[H^+] = ka[HA]$.

Worked example:8.9

Calculate the acid ionization constant of methanoic acid if its 0.01M solution is 13.2% ionized.

Solution:

From $K_a=\alpha^2c$

$K_a=(0.132)^2x0.01$

$K_a=1.7x10^{-4}moldm^{-3}$

Worked example:8.10

The pH of a 0.0022M Solution of ethanoic acid is 3.7. Calculate:

a. The degree of ionization,
b. The ionization constant of the acid.

Solution:

a. $[H^+] = anti\log -3.7 = 2x10^{-4}$

$[H^+] = \alpha c$

$2x10^{-4} = 0.0022\alpha$

$\alpha = 0.09$

$\alpha = 9\%$

b. $K_a = \alpha^2 c$

$K_a = 0.09^2 x0.0022$

$K = 1.8x10^{-5} moldm^{-3}$

Task:8.18

A solution of 0.007M of benzoic acid has a pH of 3.45. Calculate the:

a. Hydrogen ions concentration,
b. The degree of ionization and
c. The ionization constant of the acid.

Task:8:19

Propanoic acid is a weak acid.

a. Write the equation for the ionization of propanoic acid.
b. Write down the expression for its ionization constant.
c. The pK_a and pH of propanoic acid are 4.87 and 4 respectively. Calculate its degree of ionization and concentration.

Task:8.20

The second ionization constant of a dibasic acid is $4.39 \times 10^{-5} moldm^{-3}$ at 298K.

a. Calculate the degree of ionization of 0.01M solution of the acid.
b. Sketch a diagram to show how the degree of ionization of the acid varies with dilution.

Ionization of weak bases:

- Examples of weak bases include: ammonia solution and solutions of amines.
- Consider a weak base B of volume v and α is the degree of ionization.

Ionization equation: $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

Initially	1mol	0mol	0mol
Stoichiometrically	1mol	1mol	1mol
At equilibrium	(1−α)mol	αmol	αmol
Equilibrium conc.	$\frac{1-\alpha}{v}$	$\frac{\alpha}{v}$	$\frac{\alpha}{v}$

- Applying the law of mass action;

$K_c = \frac{[BH^+][OH^-]}{[B]}$, assuming water is in large excess.

- But for weak bases, equilibrium constant is given by K_b, base ionization constant.

$$\Rightarrow K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$K_b = \frac{\left(\frac{\alpha}{v}\right)\left(\frac{\alpha}{v}\right)}{\left(\frac{1-\alpha}{v}\right)} = \frac{\alpha^2}{(1-\alpha)v}$$

$$\therefore K_b = \frac{\alpha^2}{(1-\alpha)v} \quad \text{.....8.7}$$

- The equation 8.7 above is known as Ostwald's law of dilution.

If the base, B is very very weak, then α is very very small.

$\Rightarrow (1-\alpha) \approx 1$

Hence, $K_b = \frac{\alpha^2}{v}$

$$pOH = -\log\frac{\alpha}{v}$$

$$pH = 14 - pOH$$

$$\therefore pH = 14 + \log\frac{\alpha}{v}$$

K_b in terms of concentration:

- Consider a weak base B of concentration c and α degree of ionization.

Ionization equation: $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

Initially	cmol	0mol	0mol
Stoichiometrically	1mol	1mol	1mol
At equilibrium	(1−α)cmol	αcmol	αcmol

- Applying the law of mass action;

$K_b = \frac{[BH^+][OH^-]}{[B]}$, assuming water is in large excess.

$$\Rightarrow K_b = \frac{(\alpha c)(\alpha c)}{(1-\alpha)c} = \frac{\alpha^2 c}{(1-\alpha)}$$

$$\therefore K_b = \frac{\alpha^2 c}{(1-\alpha)} \quad \text{.....8.8}$$

The equation 8.8 above is the alternative form of Ostwald's dilution law.

If the base, B is very very weak, then α is very very small.

$\Rightarrow (1-\alpha) \approx 1$

$K_b = \alpha^2 c$

$pOH = -\log \alpha c$

$pH = 14 - pOH$

$\therefore pH = 14 + \log \alpha c$

Worked example:8.11

The pH of 4.2% ionized aqueous ammonia is 10.5. Calculate:

a. The hydroxyl ions concentration and
b. The base ionization constant of the ammonia.

Solution:

a. $pOH = 14 - pH$

$pOH = 14 - 10.5 = 3.5$

$[OH^-] = anti\log 3.5 = 3.2x10^{-4}$

$[OH^-] = 3.2x10^{-4}\, moldm^{-3}$

b. $[OH^-] = \alpha c$

$c = \frac{3.2x10^{-4}}{0.042} = 0.0075M$

$K_a = \alpha^2 c$

$K_a = 0.042^2 x0.0075$

$K = 1.3x10^{-5}\, moldm^{-3}$

Worked example:8.12

Phenylamine is a weak base of pK_a 4.62 and is 10% ionized. Calculate:

a. Its concentration,
b. Hydroxyl ions concentration and hence
c. Its pH.

Solution:

a. $K_a = anti\log -4.62 = 2.4x10^{-5}$

$K_a = \alpha^2 c$

$2.4x10^{-5} = 0.1^2 c$

$c = 2.4x10^{-3}\, moldm^{-3}$

b. $[OH^-] = \alpha c$

$= 0.1x2.4x10^{-3} = 2.4x10^{-4}$

$[OH^-] = 2.4x10^{-4}\, moldm^{-3}$

c. $pOH = -\log[OH]$

$pOH = -\log 2.4x10^{-4} = 3.62$

$pH = 14 - pOH$

$pH = 14 - 3.62 = 10.38$

Task:8.21

A 0.01M solution of ammonia is 4% ionized.

a. Calculate the pH of the ammonia solution (K_w=1.0x10^{-14}).
b. Determine the base ionization constant, K_b for the ammonia solution.

Factors that determine the strength of acids:

- To discuss the factors that determine the strength of acids, Brønsted – Lowry definition of an acid is adopted. An acid is therefore stronger when it can donate protons easily.
- The following are indicators of the strength of acids:

a. pH: Lower the pH, the stronger the acid.
b. pK_a and K_a: the smaller the pK_a value, the stronger an acid. The bigger the K_a value, the stronger the acid.
c. Degree of ionization: The bigger the degree of ionization, the stronger an acid.

- All acids can be divided into three major groups:

i. Hydrogen halides: hydrochloric acid (HCl), hydrofluoric acid (HF), hydroiodic acid (HI) and hydrobromic acid (HBr).
ii. Oxo/oxy acids: these are oxygen containing acids: sulphuric acid (H_2SO_4), nitric acid (HNO_3), carbonic acid (H_2CO_3), nitrous acid (HNO_2), chloric (VII) acid ($HClO_4$), etc.
iii. Organic carboxylic acids: methanoic acid (HCOOH), ethanoic acid (CH_3COOH), chloroethanoic acid ($ClCH_2COOH$), benzoic acid (C_6H_5COOH), oxalic acid ($C_2O_4H_2$), etc.

Factors:

- *Nature of the solvent:*
  All the above acids are more acidic in ammonia than in water. This is because ammonia is more basic than water.
- *Bond strength:*
  For hydrogen halides, the acidity of the solution depends on bond strength of H–X which in turn depends on electronegativity of the halogen atom. The H–X bond strength of the four members of the hydrogen halides increases in the order HI<HBr<HCl<HF. This is because the electronegativity of the halogen atoms increases in the order I<Br<Cl<F. Hence hydrogen iodide is the most acidic because it releases its protons more readily than all the above. The acidic strength therefore increases in the order HF<HCl<HBr<HI.

- Oxo acids are generally taken to be hydroxides of the form $EO_x(OH)_y$, E is the central non-metal atom i.e: Sulphuric acid $H_2SO_4 \equiv SO_2(OH)_2$, nitric acid $HNO_3 \equiv NO_2(OH)$, chloric (VII) acid $HClO_4 \equiv ClO_3(OH)$ and phosphoric acid $H_3PO_4 \equiv PO(OH)_3$.
- For oxy acids, the more electronegative the central atom, the more are the electrons pulled towards itself and the easier the acid loses protons and hence the stronger acid it is. For example $H_2SO_3>H_2CO_3$ because sulphur is more electronegative than carbon.
- The acidic strength also depends on the number of oxygen atoms attached to the non – metal central atom. The more the number of oxygen atoms attached, the stronger the acid. This is because oxygen atoms pull electrons and hence weaken the O – H bond making protons released readily. for example $HClO_4>HClO_3>HClO_2>HClO$, $H_2SO_4>H_2SO_3$ and $HNO_3>HNO_2$
- The strength of organic acids RCOOH depends on;

a. The length of the $RCOO^-$. The $RCOO^-$ is electron withdrawing (has negative inductive effect) hence weakens the O–H bond) with release of protons. The shorter the $RCOO^-$, the stronger the acid. Hence the order of strength : $HCOOH>CH_3COOH>CH_3C_2COOH>CH_3CH_2CH_2COOH$
b. When R is substituted, say with chlorine, chlorine is highly electronegative and so weakens the O–H bond hence increase in acidity: $CH_3COOH<ClCH_2COOH<Cl_2CHCOOH<Cl_3CCOOH$

8.2.4: Hydrolysis of salts:

- Salt hydrolysis is the reaction between a salt and water in which the equilibrium existing between the hydroxyl and hydrogen ions (K_w) is disturbed, hence the pH of the salt solution is less than or greater than 7.
- In salt hydrolysis, the cation of a weak base interacts with water to produce unionized weak base: or the anion of a weak acid interacts with water to produce unionized weak acid.

Case I: Salt formed from strong bases and weak acids:

- These include:
- Sodium ethonoate (from sodium hydroxide and ethanoic acid)
- Sodium carbonate (from sodium hydroxide and carbonic acid)
- Potassium cyanide (from potassium hydroxide and hydrocyanic acid)
- Taking sodium ethanoate;
- When dissolved in water, the salt being a strong electrolyte is completely dissociated according to the equation;

  $CH_3COONa(s) + aq \longrightarrow CH_3COO^-(aq) + Na^+(aq)$
- The produced ethanoate ions then combine with some of the hydrogen ions from self ionization of water to form unionized ethanoic acid.

  $CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$
- This disturbs the equilibrium existing in the ionic product (K_w) of water since some hydrogen ions have been removed.
- Consequently to restore K_w, more water molecules ionize producing more hydroxyl ions making the molar concentration of hydroxyl ions excess to the molar concentration of hydrogen ions.

- Hence pH becomes greater than 7. Thus an aqueous solution of any salt from weak acid and strong base is alkaline.

Alternatively,

- Sodium ethanoate dissolves in water according to the molecular equation:

  $CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NaOH(aq)$
- The produced ethanoic acid is a weak acid which only partially ionizes in water to produce a few hydrogen ions. But, the produced sodium hydroxide is a strong base which completely dissociates in water to produce many hydroxyl ions.
- The excess hydroxyl ions neutralize all the hydrogen ions in the solution, leaving some hydroxyl ions unneutralized, hence making the solution alkaline.

The expression for hydrolysis constant, K_h:

- The hydrolysis equation is given by:

  $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

  Or,

  $CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NaOH(aq)$
- Applying the law of mass action to the first hydrolysis equation,

  $\Rightarrow K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$, assuming water is in large excess.

The expression for pH:

- Consider an aqueous solution of sodium ethanoate of molar concentration, c.
- Assuming sodium ethanoate (a strong electrolyte) is fully dissociated according to the equation:

  $CH_3COONa(s) + (aq) \rightleftharpoons CH_3COO^-(aq) + Na^+(aq)$

Since 1mole of sodium ethanoate produces 1mole of ethanoate ions on dissociation, $[CH_3COONa]=[CH_3COO^-]=c$.

From the hydrolysis equation, $[CH_3COOH]=[OH^-]$

$$\Rightarrow K_h = \frac{[OH^-]^2}{c}$$

From ionic product of water,

$$[OH^-] = \frac{K_w}{[H^+]}$$

$$\Rightarrow K_h = \frac{\left(\frac{K_w}{[H^+]}\right)^2}{c}$$

$$[H^+] = \frac{K_w}{\sqrt{c.K_h}}$$

Taking $-\log_{10}$ of both sides,

$$pH = pK_w - \frac{1}{2}pK_h + \frac{1}{2}\log c$$

Worked example:8.13

Sodium ethanoate undergoes hydrolysis in water.

a. Write the equation for the hydrolysis of sodium ethanoate.
b. Calculate the pH of 0.05M solution of sodium ethanoate, given that its hydrolysis constant is $5.5x10^{-10}moldm^{-3}$.

Solution:

a. $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
b. Assuming sodium ethanoate is completely dissociated, $[CH_3COONa]=[CH_3COO^-]=0.05M$
   Since 1mol of CH_3COO^- produces 1mol of CH_3COOH and OH^-, $[CH_3COOH]=[OH^-]=x$
   From hydrolysis expression;

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$5.5x10^{-10} = \frac{(x)(x)}{0.05}$$

$$x = \sqrt{0.05x5.5x10^{-10}} = 5.2x10^{-6}M$$

$$pOH = -\log 5.2x10^{-6} = 5.28$$

$$pH = 14 - 5.28 = 8.72$$

Worked example:8.14

a. Write the equation for the hydrolysis of sodium propanoate.
b. When a certain mass of sodium propanoate was dissolved in 1*l* of water, $10cm^3$ of this solution required $7.0cm^3$ of $6.0x10^{-6}M$ hydrochloric acid for complete neutralization. Calculate the mass of sodium propanoate dissolved in 1*l* of water ($K_h=6.0x10^{-10}moldm^{-3}$).

Solution:

a. $CH_3CH_2COO^-(aq)+H_2O(l) \rightleftharpoons CH_3CH_2COOH(aq) + OH^-(aq)$
b. $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$
   Moles of hydrochloric acid reacted
   $$= \frac{6.0x10^{-6}x7.0}{1000} = 4.2x10^{-8}$$
   Since reaction ratio is 1:1
   Moles of OH^- reacted $=1.25x10^{-8}$
   $10cm^3$ of the solution contain $1.25x10^{-5}$
   $1000cm^3$ will contain $\frac{4.2x10^{-8}x1000}{10} = 4.2x10^{-6}$
   Since $[OH^-]=[CH_3CH_2COOH]$, let $[CH_3CH_2COO^-]$ be x
   $$K_h = \frac{[CH_3CH_3COOH][OH^-]}{[CH_3CH_2COO^-]}$$

$$6.0x10^{-10} = \frac{(4.2x10^{-6})(4.2x10^{-6})}{c}$$

$c = 0.03M$

RFM of CH_3CH_2COONa=(12x3)+(1x5)+(16x2)+(23x1)=96

1mol of the salt weighs 96g

0.03mol will weigh $\frac{96x0.03}{1} = 2.88g$

Hence mass of sodium propanoate in 1*l* of water is 2.88g.

Relationship between K_a, K_h and K_w

From the hydrolysis equation of sodium ethanoate:

$CH_3COO^-(aq) + H_2O(aq) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

$$\Rightarrow K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

- Multiplying both the denominator and the numerator by $[H^+]$

$$\Rightarrow K_h = \frac{[CH_3COOH][OH^-][H^+]}{[CH_3COO^-][H^+]}$$

But, $[OH^-][H^+]=K_w$

$$\Rightarrow K_h = K_w \frac{[CH_3COOH]}{[CH_3COO^-][H^+]}$$

$$\frac{[CH_3COOH]}{[CH_3COO^-][H^+]} = \frac{1}{K_a}$$

Where K_a is the acid ionization constant for ethanoic acid.

$$\Rightarrow K_h = \frac{K_w}{K_a}$$

Task:8.22

Sodium benzoate undergoes hydrolysis in water.

a. Write the equation for the hydrolysis of sodium benzoate.

b. The pH of a solution formed by dissolving 7.2g in of sodium benzoate in 1*l* of water is 8.6. Calculate the hydrolysis constant of sodium benzoate.

c. Use your answer in b) above to calculate the acid ionization constant of benzoic acid.

Case II: Salts formed from strong acids and weak bases:

- These include:
- Ammonium chloride (from ammonium hydroxide and hydrochloric acid)
- Phenyl ammonium chloride (phenylamine and hydrochloric acid)
- Phenyl ammonium nitrate (phenylamine and nitric acid)
- Alkyl ammonium sulphate (from any alkyl amine and sulphuric acid)
- Taking ammonium chloride:
- When dissolved in water, the salt being a strong electrolyte is completely dissociated according to the equation;

  $NH_4Cl(s) + (aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$
- The produced ammonium ions then combine with some of the hydroxyl ions from self ionization of water to form unionized ammonium hydroxide.

  $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_4OH(aq)$
- This disturbs the equilibrium existing in the ionic product (K_w) of water since some hydroxyl ions have been removed.
- Consequently to restore K_w, more water molecules ionize producing more hydrogen ions making the molar concentration of hydrogen ions excess to the molar concentration of hydroxyl ions.
- Hence pH becomes less than 7. Thus an aqueous solution of any salt from weak base and strong acid is acidic.

Alternatively,

- Ammonium chloride dissolves in water according to the molecular equation:

  $NH_4Cl(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + HCl(aq)$
- The produced ammonium hydroxide is a weak base, which only partially ionizes in water to produce a few hydroxyl ions. But, the produced hydrochloric acid is a strong acid, which completely ionizes in water to produce many hydrogen ions.
- The excess hydrogen ions neutralize all the hydroxyl ions in the solution, leaving some hydrogen ions unneutralized, hence making the solution acidic.

The expression of hydrolysis constant, K_h:

- The hydrolysis equation is given by:

  $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$

  From the law of mass action,

  $K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$, assuming water is in large excess.

The pH expression:

- Consider an aqueous solution of ammonium chloride of molar concentration, c.
- Since ammonium chloride is a strong electrolyte, $[NH_4Cl]=[NH_4^+]=c$
- Also from hydrolysis equation, 1 mole of ammonium ions produces 1 mole of ammonium hydroxide and 1 mole of hydrogen ions. Hence, $[NH_4OH]=[H^+]$
- From the hydrolysis constant expression,

$$\Rightarrow K_h = \frac{[H^+]^2}{c}$$

$$[H^+] = \sqrt{c.K_h}$$

Taking $-\log_{10}$ of both sides;

$$\Rightarrow pH = \frac{1}{2}(pK_h - \log c)$$

Task:8.23

The pH of 0.02M ammonium nitrate solution is 5.45.

a. Explain this observation.

b. Calculate the hydrolysis constant of ammonium nitrate.

Task:8.24

Methylammonium chloride undergoes hydrolysis according to the equation:

$CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$

a. Write the expression for its hydrolysis constant.

b. When 6.75g of methylammonium chloride was dissolved in $500cm^3$ of water, the pH was 2.33. Calculate the hydrolysis constant of the salt.

c. Calculate the volume of the above solution that would react completely with $10cm^3$ of 0.25M sodium hydroxide solution.

Relationship between K_h, K_b and K_w

- From hydrolysis constant expression;

  $$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$
- Multiplying both the denominator and the numerator by $[OH^-]$

$$\Rightarrow K_h = \frac{[NH_4OH][H^+][OH^-]}{[NH_4^+][OH^-]}$$

But, $[H^+][OH^-]=K_w$

Hence, $K_h = K_w \frac{[NH_4OH]}{[NH_4^+][OH^-]}$

But $\frac{[NH_4OH]}{[NH_4^+][OH^-]} = \frac{1}{K_b}$, for ammonium hydroxide.

$$\Rightarrow K_h = \frac{K_w}{K_b}$$

Task:8.25

Phenylammonium chloride hydrolyses in water.

a. Write the equation for the hydrolysis and the hydrolysis constant expression for phenylammonium chloride.
b. Calculate the pH of a 0.04M phenylammonium chloride if its hydrolysis constant is 4.2×10^{-10}. State your assumptions in the calculation.
c. Calculate the base ionization constant of phenylamine using your answer in b) above.

Case III: Salts of strong acids and strong bases:

- Examples include:
  - Sodium chloride (from sodium hydroxide and hydrochloric acid)
  - Sodium sulphate (from sodium hydroxide and sulphuric acid)
  - Potassium nitrate (from potassium hydroxide and nitric acid)
- Here no hydrolysis takes place i.e. the ionic equilibrium, K_w of water is not disturbed hence the pH of their solutions is 7.

Case iV: Salts of weak acids and weak bases:

- Examples include:
  - Ammonium carbonate (from ammonium hydroxide and carbonic acid)
  - Ammonium cyanide (from ammonium hydroxide and hydrocyanic acid)
  - Ammonium ethanoate (from ammonium hydroxide and ethanoic acid).
- Taking the case of ammonium carbonate:
  - Here both the anion and the cation undergo hydrolysis.
  - The anion hydrolyses to produce a weak acid according to the equation:

$$CO_3^{2-}(aq) + 2H_2O(l) \rightleftharpoons H_2CO_3(aq) + 2OH^-(aq)$$

  - The cation hydrolyses to produce a weak base according to the equation:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

  - The produced hydrogen and hydroxyl ions neutralize themselves.
  - The pH of the resultant solution depends on the relative strength of the weak acid and the weak base, which is indicated by their ionization constants–the bigger the ionization constant the stronger the weak acid/base.
  - If;
    a. $K_b > K_a$, then the solution is alkaline i.e pH>7.
    b. $K_b < K_a$, then the solution is acidic i.e pH<7.
    c. $K_b = K_a$, then the solution is neutral i.e pH=7.

Action of highly charged cations

- Salt solutions of trebly charged cations (Al^{3+}, Fe^{3+}, Cr^{3+}) and some doubly charged cations are acidic.

Explanation:

- They have high charge density and hence are highly hydrated in aqueous solution. The cation strongly attracts the lone pairs of electrons on the oxygen atoms of water. This polarizes and weakens the O–H bonds leading to the loss of proton to the solution hence making it acidic.
- Consider a solution of aluminium sulphate:
- The aluminium ion is heavily hydrated and exists as hexaaquoaluminium ion ($Al(H_2O)_6^{3+}$)

Stepwise hydrolysis equations:

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH^-]^{2+}(aq) + H^+(aq)$$
$$[Al(H_2O)_5OH^-]^{2+}(aq) \rightleftharpoons [Al(H_2O)_4(OH)_2]^+(aq) + H^+(aq)$$
$$[Al(H_2O)_4(OH^-)_2]^+(aq) \rightleftharpoons [Al(H_2O)_3(OH)_3](s) + H^+(aq)$$

Overall hydrolysis equation:

$Al(H_2O)_6^{3+}(aq) + 3H_2O(l) \rightleftharpoons Al(H_2O)_3(OH)_3(s) + 3H_3O^+(aq)$

Or:

$Al(H_2O)_6^{3+}(aq) + (aq) \rightleftharpoons Al(H_2O)_3(OH)_3(s) + 3H^+(aq)$

- Likewise chromium (III) ion in aqueous solution exists as hexaaquochromium (III) ion and iron (III) as hexaaquoiron (III) ion. They undergo similar hydrolysis as aluminium ion.

Worked example:8.15

A piece of clean magnesium ribbon was immersed in a solution of chromium (III) sulphate.

a. State what was observed.
b. Explain your observation.

Solution:

a. Effervescence of a colourless gas; green precipitate.
b. Chromium (III) ion in solution is highly hydrated, and exists as hexaaquochromium (III) ion. Due to the high charge density, the O–H bond in water of the hydrated ion is highly polarized leading to release of protons according to equation:

   $Cr(H_2O)_6^{3+}(aq) + (aq) \rightleftharpoons Cr(H_2O)_3(OH)_3(s) + 3H^+(aq)$

   The green precipitate is due to formation of chromium (III) hydroxide. The produced hydrogen ions then react with the magnesium ribbon to produce hydrogen gas which comes out as effervescence.

   $Mg(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g)$

Worked example:8.16

Sodium carbonate power was added to a solution of iron (III) nitrate.

a. State what was observed.
b. Explain your observation.

Solution:

a. Effervescence of a colourless gas; a brown precipitate.
b. Iron (III) ion in solution is highly hydrated, and exists as hexaaquoiron (III) ion. Due to the high charge density, the O – H bond in water of the hydrate is highly polarized leading to release of protons according to equation:

   $Fe(H_2O)_6^{3+}(aq) + (aq) \rightleftharpoons Fe(H_2O)_3(OH)_3(s) + 3H^+(aq)$

   The brown precipited is due to formation of iron (III) hydroxide. The produced hydrogen ions then react with the carbonate ions of the sodium carbonate to produce carbon dioxide which comes out as effervescence.

   $2H^+(aq) + CO_3^{2-} \longrightarrow CO_2(g) + H_2O(l)$

8.2.5: Buffer solutions:

- These are solutions that are resistant to change in pH on addition of small quantities of an acid, an alkali or water.
- There are 2 types of buffer solutions:

a. Acidic buffers.

These are buffer solutions that maintain a pH<7 i.e. the solution is acidic. An acidic buffer solution is made of a solution of a weak acid and its salt of a strong base for example;

- Ethanoic acid and sodium ethanoate
- Phosphoric acid and sodium phosphate
- Boric acid and sodium tetraborate (borax)
- Carbonic acid and sodium carbonate.

b. Basic buffers:

These are buffer solutions that maintain pH>7. A basic buffer solution is made of a solution of a weak base and its salts of a strong acid for example;

- Ammonia solution and ammonium chloride
- Ammonium hydroxide and ammonium sulphate
- Ammonium hydroxide and ammonium nitrate.
- Generally any amine solution/amine salt of a strong acid.

Mechanism of the action of an acidic buffer: a case of ethanoic acid and sodium ethanoate solution:

- In the solution ethanoic acid is weakly ionized according to the equation:

  $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$
- While sodium ethanoate (a strong electrolyte) is completely dissociated according to the equation:

  $CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$

- When a small quantity of an acid is added, then the excess hydrogen ions is removed by combining with ethanoate ions (from sodium ethanoate) to form unionized ethanoic acid.

  $CH3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq)$
- When a small quantity of an alkali is added, it is eliminated by combining with the unionized ethanoic acid.

  $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_20(l)$
- Addition of water dilutes the salt and the acid equally, and so no effect on pH.

pH expression for the acidic buffer above:

- Partial ionization of ethanoic acid:

  $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$.....8.9
- Complete dissociation of sodium ethanoate:

  $CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$
- Applying the law of mass action to equation 8.9,

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Making $[H^+]$ the subject,

$$\Rightarrow [H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Assuming ethanoic acid is a very weak acid, then it implies that: $[CH_3COOH]_{initially}$ or [acid]=$[CH_3COOH]_{equilibrium}$. Also assuming sodium ethanoate is completely dissociated, then it implies that: $[CH_3COO^-]_{equilibrium}$=$[CH_3COONa]$ or [salt].

$$\Rightarrow [H^+] = K_a \times \frac{[Acid]}{[Salt]}$$

Taking $-\log_{10}$ of both sides

Designing an acidic buffer of a desirable pH:

- From the above equation expressing the pH for an acidic buffer, the value of pH of an acidic buffer at a given temperature depends on:
  i. The ionization constant of the weak acid and
  ii. The proportions of the acid and its salt of a strong base, at a constant temperature.
- Therefore, to design an acidic buffer at a certain temperature:
- A weak acid of known ionization constant, whose pK_a value is close to the desired pH is selected.
- Its suitable salt with a strong base is also selected.
- Known quantities of the acid and the salt are mixed so as to vary the pH of the resultant solution either slightly above or below the pK_a value.
- When the:
  i. [Salt]>[Acid], then the pH of the solution is greater than pK_a
  ii. [Salt]<[Acid], then the pH of the buffer is less than pK_a
  iii. [Salt] = [acid], then the pH of the buffer is equal to pK_a

Worked example:8.17

A buffer solution contains 0.2M ethanoic acid and 0.2M sodium ethanoate. Calculate, if K_a=1.8 x10^{-5} for ethanoic acid:

a. The pH of the buffer solution.
b. The change in pH when 0.01cm^3 of 1M hydrochloric acid is added to the solution.

Solution:

a. Ionization equation of ethanoic acid is given by:

$CH_3COOH(aq) \quad CH_3COO^-(aq) + H^+(l)$

From $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$$\Rightarrow [H^+] = K_a x \frac{[CH_3COO^-]}{[CH_3COOH]}$$

Assuming the acid is very weak, [CH_3COOH]=[Acid]=0.2.
Assuming sodium ethanoate is a strong electrolyte (is completely dissociated), [CH_3COO^-]=[salt]=0.2.

$$\Rightarrow [H^+] = K_a x \frac{[salt]}{[acid]}$$

$$pH = -\log(1.8x10^{-5} + \log\frac{0.2}{0.2}$$

$$pH = 4.74$$

b. 1000cm^3 of HCl contain 1mol.

0.01cm^3 will contain $\frac{0.01x1}{1000} mol = 1.0x10^{-5} mol$

The added HCl reacts with ethanoate ions according to the ionic equation:

$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$

1mol 1mol

1.0x10^{-5}mol 1.0x10^{-5}mol

Hence number of moles of ethanoate reacted = 1.0x10^{-5}mol

Number of moles of ethanoate ions in the mixture

=(0.2 - 1.0x10^{-5}) = 0.19999mol

Number of moles of ethanoic acid formed = 1.0x10^{-5}mol

Total number of moles of ethanoic acid in the mixture

=(0.2+1.0x10^{-5})=0.20005mol.

Total volume = (1000+0.01)=1000.01cm^3

New [CH_3COO^-] = $\frac{1000x0.19999}{1000.001} = 0.199988M$

New [CH_3COOH] = $\frac{1000x0.20005}{1000.01} = 0.200048$

Assuming the acid is very weak, $[CH_3COOH]=[Acid]=0.200048M$.

Assuming sodium ethanoate is a strong electrolyte (is completely dissociated), $[CH_3COO^-] = [salt]=0.199988M$.

$$\Rightarrow [H^+] = K_a x \frac{[salt]}{[acid]}$$

$$pH = -\log 8.6x10^{-5} + \log \frac{0.200048}{0.199988}$$

$$pH = 4.74 + 0.00013$$

$$pH = 4.74013$$

Note that there is no significant change in pH.

Task:8.26

Calculate the pH of a solution made by dissolving 0.53g of benzoic acid in a solution containing 1.28g of sodium benzoate to make 1*l* of the solution. Given that the acid ionization constant of benzoic acid is $6.29x10^{-5}moldm^{-3}$.

Task:8.27

0.61g of benzoic acid was dissolved in 1*l* of 0.02M sodium benzoate. Given that the acid ionization constant of benzoic acid is $6.29x10^{-5}moldm^{-3}$.

a. Calculate the pH of the resultant solution.

b. Explain what happens to the pH if a small amount of :

- Alkali,
- Acid was added to the above solution.

Task:8.28

$20cm^3$ 0.2M sodium hydroxide was added to $80cm^3$ of 0.2M propanoic acid solution. Calculate the pH of the resultant solution. State any assumptions made ($pK_a = 4.87$)

Task:8.29

a. 3.28g of sodium ethanoate was dissolved in $1dm^3$ of 0.01M ethanoic acid.

What is the pH of the resultant solution? ($K_a=1.86x10^{-5}moldm^{-3}$).

b. Calculate the pH of the solution formed when $1cm^3$ of 1M hydrochloric acid is added to:

- $1cm^3$ of water.
- Into the above solution.

Task:8.30

Calculate the volume of 1M methanoic acid that must be added to $1dm^3$ of 0.0M sodium methanoate solution to give a solution whose pH is 3.5, $pK_a=3.75$.

Task:8.31

A solution was made by dissolving 7.2g of ethanoic acid in 12.0g of sodium ethanoate to make 1*l* solution. To the solution was added $0.8cm^3$ of 1M hydrochloric acid. Calculate the pH of the solution, clearly stating your assumptions.($pK_a=4.74$)

Task:8.32

A buffer solution of pH 4.5 was prepared from ethanoic acid ($K_a=1.8x10^{-5}$) and sodium ethanoate. The concentration of sodium ethanoate was 0.2M.

a. Write the equations for the reactions that take place on addition of small amount of the following solutions:

- Dilute hydrochloric acid.
- Dilute sodium hydroxide.

b. Calculate the concentration of ethanoic acid in the solution.

Mechanism of the action of a basic buffer: a case of ammonium hydroxide and ammonium chloride solution:

- In the solution, ammonium hydroxide is partially ionized according to the equation:

  $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
- While ammonium chloride is completely dissociated according to the equation:

  $NH_4Cl(aq) \longrightarrow NH_4^+(aq) + OH^-(aq)$
- When a small quantity of an acid is added, the excess hydrogen ions combines with the unionized ammonium hydroxide according to the equation:

  $NH_4OH(aq) + H^+(aq) \longrightarrow NH_4^+(aq) + H_2O(l)$
- This eliminates the excess hydrogen ions that tend to reduce pH of solution.
- When a small quantity of an alkali is added, the excess hydroxyl ions combine with ammonium ions from the complete dissociation of ammonium chloride to form unionized ammonium hydroxide, according to the equation:

  $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_4OH(aq)$
- The excess hydroxyl ions which tend to increase pH are eliminated.
- Addition of water dilutes the salt and the weak base equally, and so does not affect the pH.

pH expression for the basic buffer above:

- Partial ionization of ammonium hydroxide:

  $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

  Applying the law of mass action to the above equation:

$$\Rightarrow K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

Making $[OH^-]$ the subject,

$$\Rightarrow [OH^-] = K_b \times \frac{[NH_4OH]}{[NH_4^+]}$$

From ionic product of water,

$$[OH^-] = \frac{K_w}{[H^+]}$$

$$\Rightarrow \frac{K_w}{[H^+]} = K_b \times \frac{[NH_4OH]}{[NH_4^+]}$$

Making $[H^+]$ the subject of the above equation,

$$\Rightarrow [H^+] = \frac{K_w}{K_b} \times \frac{[NH_4^+]}{[NH_4OH]}$$

Taking $-\log_{10}$ of both sides:

$$\Rightarrow pH = (pK_w - pK_b) + \log\frac{[NH_4OH]}{[NH_4^+]}$$

Assuming ammonium hydroxide is a very weak base, then: $[NH_4OH]_{equilibrium} = [NH_4OH]_{initially}$, or [Base]. Also assuming ammonium chloride is completely ionized, the $[NH_4^+]_{equilibrium} = [salt]$

$$\Rightarrow pH = (pK_w - pK_b) + \log\frac{[Base]}{[salt]}$$

Designing a basic buffer of desirable pH:

- From the above equation expressing the pH of a basic buffer, the pH of a basic buffer at a constant temperature therefore depends on:

  i. The ionic product of water,

  ii. The base ionization constant of the weak base,

  iii. The proportions of the weak base and its salt of a strong acid in the solution.
- Hence to design a basic buffer of a given pH at a given temperature:

  - The ionic product of water at the temperature should be known.

- A weak base whose difference between its pK_b and pK_w at the temperature is close to the desirable pH, is selected.
- A suitable salt of the base with a strong acid is also selected.
- Known quantities of the base and the salt are mixed so as to vary the pH of the resultant solution above or below the (pK_w–pK_b) value.
- When the:
  a. [Salt]<[Base], then the pH of the solution is greater than ($pK_w - pK_a$)
  b. [Salt]>[Base], then the pH of the buffer is less than ($pK_w - pK_a$)
  c. [Salt] = [Base], then the pH of the buffer is equal to (pK_w–pK_a)

Worked example:8.18

$20cm^3$ of 1M hydrochloric acid solution was added to $80cm^3$ of 1M ammonia solution. Calculate the pH of the resultant solution.(K_b for ammonia solution is $1.8x10^{-5}$).

Hydrochloric acid is a limiting reactant in this case:

Moles of HCl reacted $= \frac{20x1}{1000} = 0.02mol$

$HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(l)$

From reaction ratio, number of moles of NH_4OH reacted and number of moles of NH_4Cl formed = 0.02mol.

Initial number of moles of $NH_4OH = \frac{80x1}{1000} = 0.08mol$

Number of moles of NH_4OH unreacted = (0.08 – 0.02) = 0.06mol

Total volume = (20 + 80) = $100cm^3$.

$$[NH_4Cl] = \frac{0.02x1000}{100} = 0.2M$$

$$[NH_4OH] = \frac{0.06x1000}{100} = 0.6M$$

Ionization equation for aqueous ammonia:

$NH_4OH(aq) + aq \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$[OH^-] = K_b x \frac{[NH_4OH]}{[NH_4^+]}$$

Assuming aqueous ammonia is a very weak base, $[NH_4OH]$=[Base]=0.6M

Assuming ammonium chloride is a strong electrolyte (is completely dissociated), $[NH_4^+]$=[Salt]=0.2M.

$$pOH = -\log 1.8x10^{-5} + \log\frac{0.2}{0.6}$$

$$pOH = 4.26$$

From $pH = 14 - pOH$

$$pH = 14 - 4.26$$

pH=9.74

Task:8.33

What mass of ammonium chloride must be added to $50cm^3$ of 0.05M aqueous ammonia to give a solution of pH = 8.6?(pK_b=4.74)

Task:8.34

Calculate the pH of the resultant solution, if the following are added to $50cm^3$ of 0.5M aqueous ammonia (pK_b=4.74)

a. $20cm^3$ Of 0.5M sulphuric acid.
b. $50cm^3$ of 0.25M nitric acid
c. Would you expect the pH of the solution to be <7,>7 or =7, when $50cm^3$ of 0.5M hydrochloric acid is added? Exlain.

Applications of buffer solutions:

1. In fermentation.
2. Culturing of micro – organisms.
3. Intravenous injections.
4. Cultivation of certain crops which require a particular pH to thrive well.

8.2.6: Acid – base indicators:

- An acid – base indicator is a weak acid or a weak base that changes colours according to hydrogen ions concentration.
- In acidic medium, the colour of the indicator is completely different from the colour of the indicator in alkaline medium; the colour in one medium is due to the unionized molecules of the acid and the other colour is due to the ionized anion of the acid.
- Therefore, because of these colour differences, an acid – base indicator is used to detect the end point in an acid – base titration.
- Consider an indicator, which is a weak acid, given by the general formula, HIn:
- The partial ionization equation of the indicator is given by:

$$HIn(aq) + aq \rightleftharpoons H^+(aq) + In^-(aq)$$

Colour1 colour2

a. In acidic medium, because of the high concentration of hydrogen ions from the acid, partial ionization of the indicator is suppressed. So the unionized molecules dominate. Hence in acidic medium, the indicator shows colour1.
b. In alkaline medium, the excess hydroxyl ions of the alkali combine with the hydrogen ions of the indicator. So the indicator has to ionize the more to restore the equilibrium. Thus more anions of the indicator are produced. So, in alkaline medium, the indicator shows colour2.

c. In neutral medium, the proportions of the ionized and the unionized molecules are the same, and so the indicator shows a blend of colour1 and colour2.

- Examples of acid – base indicators include:

a. Phenolphthalein,
b. Methyl orange,
c. Bromothymol blue,
d. Litmus,
e. Congo red

The working ranges of indicators:

Applying the law of mass action to the partial ionization equation of the indicator below:

$$HIn(aq) + aq \rightleftharpoons H^+(aq) + In^-(aq)$$

$$K_{in} = \frac{[H^+][In^-]}{[HIn]}$$

$$\Rightarrow [H^+] = K_{in} \times \frac{[HIn]}{[In^-]}$$

$$pH = pK_{in} + \log\left(\frac{[In^-]}{[HIn]}\right)$$

- When the $[In^-] = [HIn]$, the $pH = pK_{in}$, and the indicator shows a blend of colours.
- It is only when one form of the indicator [HIn] or $[In^-]$, is approximately ten – fold excess that one colour will be clearly distinguished by the human eye.

When $[In^-] = 10\,[HIn]$,

$$pH = pK_{in} + \log\left(\frac{10[HIn]}{[HIn]}\right)$$

$$pH = pK_{in} + \log 10$$

$$pH = pK_{in} + 1$$

When $10[In^-] = [HIn]$,

$$pH = pK_{In} + \log\left(\frac{[In^-]}{10[HIn]}\right)$$

$$pH = pK_{In} + \log\frac{1}{10}$$

$$pH = pK_{In} - 1$$

- Thus between two points at which human eye can detect the unionized form in excess and the anion form in excess there will be a change in pH of approximately two units. This range of pH is known as the 'theoretical' working range of the indicator.
- The table below gives the practical working ranges of different indicators:

Indicator	pK_{In}	pH range	Acid colour	Base colour
Thymol blue	1.7	1.2-2.8	Red	Yellow
Methyl orange	3.7	3.2-4.2	Red	Yellow
Bromophenol blue	4.0	2.8-4.6	Yellow	Blue
Bromocresol green	4.7	3.8-5.4	Yellow	Blue
Methyl red	5.1	4.2-6.3	Red	Yellow
Bromothymol blue	7.0	6.0-7.6	Yellow	Blue
Phenol red	7.9	6.8-8.4	Yellow	Red
Thymol blue (2nd)	8.9	8.0-9.6	Yellow	Blue
Phenolphthalein	9.3	8.2-10.0	Colouless	Red
Thymolphthalein	9.7	8.3-10.5	Colourless	Blue

- Thymol blue has two working ranges. This is because thymol blue is a weak dibasic acid.

$$H_2In(aq) + aq \rightleftharpoons H^+(aq) + HIn^-(aq)$$

Red yellow

$$HIn^-(aq) + aq \rightleftharpoons H^+(aq) + In^-(aq)$$

Yellow blue

- When choosing an indicator for an acid – alkali titration, the end point pH (the vertical portion) of the titration curve must correspond to the practical working range of the indicator.

8.2.7: Acid – alkali (base) titrations and titration curves:

- Titration is the running of a solution from a burrete (titrant) into another solution in a conical flask (titrand) in order to determine (always) the concentration of the titrand.
- Titration is an important technique in the determination of quantities of a chemical reaction like:

a. Concentration,
b. Reaction/stoichiometric ratio,
c. Purity,
d. Amounts in a mixture.

- In acid – alkali titrations, the titrant and titrand are only acids and alkalis. Any can be the titrant (the buretted solution) or the titrand (the pipetted solution).

a. When an alkali is pipetted into a conical flask and an acid solution is run into by means of burette, the pH of the solution is the flask decreases.
b. When an acid is pippetted into a conical flask and an alkali is run into by means of a burette, the pH of the solution in the flask increases.

- The variation in pH of the solution in the conical flask and the volume of either an acid or an alkali added can be plotted to obtain a graph called a titration curve.

Definition:

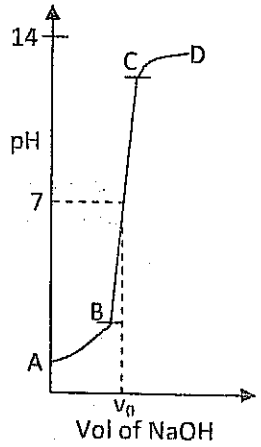
A titration curve is a graph obtained by plotting the variation of pH of a solution when it is being titrated against.

- During acid – alkali titration, when the end point is near, then addition of a small amount of either the alkali or the acid is followed by a sharp increase in the pH of the pipetted solution. When plotted on a graph, this is indicated as the portion of the graph with a very steep gradient. The end point volume of the titrant and the pH for the titration is the mid point of that portion.

A. Addition of a base/alkali to a monoprotic/monobasic acid.

- In this titration, there will be only one end point.

Case I: Titration curve for a strong acid and strong base (Hydrochloric acid and Sodium hydroxide):

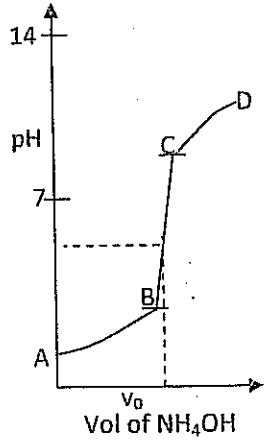


- Low pH at A due to pH of pure hydrochloric acid – a strong acid.
- The pH rises along AB due to removal of H^+ by addition of sodium hydroxide solution according to the equation:

  $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$
- Sharp rise in pH between B and C due to end point. The end point is the mid point of BC with pH= 7. V_0 is the volume of sodium hydroxide at the end point. The end point pH is 7 because sodium chloride being a salt of a strong base and a strong acid does not hydrolyse.
- Rise in pH along CD is due to excess sodium hydroxide solution added.

  Without excess sodium hydroxide, the part of the curve CD does not appear.

Case II: titration curve for a strong acid and weak base (Hydrochloric acid and ammonium hydroxide)



- Low pH at A due to the pH of pure hydrochloric acid – a strong acid.
- pH rises very gradually along AB with volume of ammonia solution added because ammonium hydroxide is a weak base and so does not provide enough hydroxyl ions to neutralize the many hydrogen ions in hydrochloric acid solution.

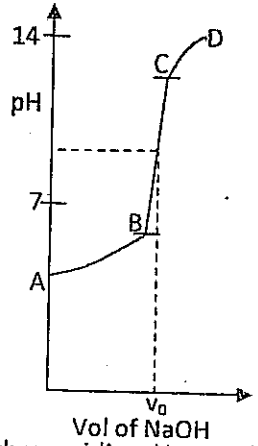
  $HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(l)$
- Also, the produced ammonium chloride hydrolyses producing hydrogen ions.

  $NH_4^+(aq) + H_2O(l) \longrightarrow NH_4OH(aq) + H^+(aq)$
- Sharp rise along BC is due to the end point of the titration. The end point pH is below 7 (acidic) because of the hydrolysis of ammonium chloride according to the equation.

  $NH_4^+(aq) + H_2O(l) \quad NH_4OH(aq) + H^+(aq)$
- V_0 is the volume of ammonium hydroxide (aqueous ammonia) at the end point.
- The gentle rise in pH along CD is due to excess ammonium hyroxide (a weak base) added beyond the end point; and the

combination of the produced ammonium chloride and the excess ammonium hydroxide constitutes a basic buffer which resists rise in pH.

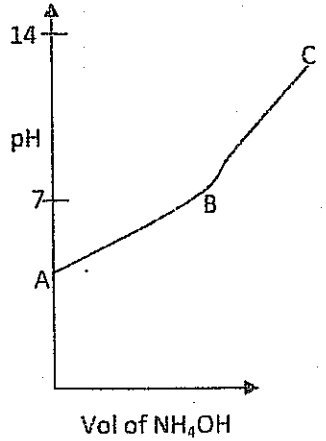
Case III: titration curve for a weak acid and a strong base (ethanoic acid and sodium hydroxide)



- Relatively higher acidic pH at A because ethanoic acid is a weak acid (has a few hydrogen ions).
- pH rises gradually along AB as sodium hydroxide solution is added because the produced sodium ethanoate and the unreacted ethanoic acid constitute an acidic buffer hence resist rise in pH.
- Sharp rise along BC due to the end point; end point pH (mid point of BC) is greater than 7 (alkaline pH) because sodium ethanoate produced hydrolyses in water to produce hydroxyl ions, according to the equation:

  $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
- Sharp rise in pH along CD is due to excess sodium hydroxide solution added.

Case IV: titration curve for a weak acid and a weak base (ethanoic acid and ammonium hydroxide):



- Relatively higher acidic pH at A because ethanoic acid is a weak acid.
- Gradual rise in pH along AB, B the end point (point of inflexion)
- At the end point the following equilibria exist as a result of the formation of ammonium ethanoate.

  $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

  $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$
- The end point pH therefore depends on the relative strength of ethanoic acid and ammonium hydroxide.

a. If $pK_a > pK_b$; pH > 7
b. If $pK_a < pK_b$; pH < 7
c. If $pK_a = pK_b$; pH = 7

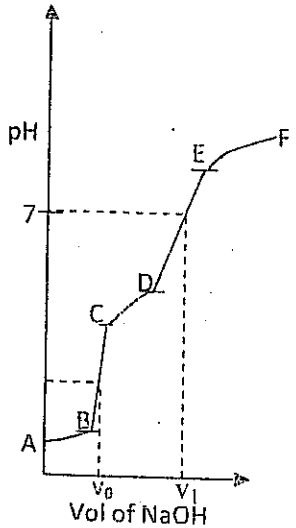
B. Addition of a base/alkali to a polyprotic acid:

- A polyprotic acid is an acid that can produce more than one mole of hydrogen ions on ionization. The one that can

produce only two moles of hydrogen ions is called a diprotic acid.

- When an alkali is added to a solution of a polyprotic acid in a titration, the acid is neutralized stepwise, giving distinct end points until all the hydrogen ions are neutralized.

Case I: addition of sodium hydroxide solution into sulphuric acid:



- Low pH at A because sulphuric acid is a strong acid
- The pH rises along AB because of half neutralization of sulphuric acid to hydrogensulphate ions.

  $NaOH(aq) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + H_2O(l)$
- v_0 is the volume of sodium hydroxide solution for half–way neutralization of sulphuric acid (first end point).
- The rise in pH along CD is due to complete neutralization of sulphuric acid to sodium sulphate.
- The sharp rise in pH along DE is due to the end point, with corresponding volume v_1.
- The second end point pH is at 7 because sodium sulphate does not hydrolyse in water.

$NaOH(aq) + NaHSO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l)$

- Rise in pH along EF is due to excess sodium hydroxide solution added beyond the end point.

Task:8.35

Calculate the pH of a solution after $5cm^3$ of 0.1M sodium hydroxide solution have been added to $25cm^3$ of 0.1M ethanoic acid (pK_a=4.79)

Task:8.36

Show that the pH of $25cm^3$ of 0.1M hydrochloric acid after addition of xcm^3 of 0.1M sodium hydroxide solution is $1+\log\left\{\frac{25+x}{25-x}\right\}$, hence, calculate the pH when $x=10cm^3$.

Task:8.37

The table below shows the values of pH and volumes of a base (v) added to an acid.

pH	1	1.4	2.6	3	3.4	3.6	4	4.4	5.6	8	10.4	10.8
v/cm^3	0	2.4	3	6	9	10.6	12	13	14	15	16	16.6

a. Plot a graph of pHagainst volume of the base added.
b. State whether the acid and the base are strong or not. Give reasons for your answer.
c. Determine the pH and the volume of the base used at the end point.

Task:8.38

Dilute hydrochloric acid was added to $25cm^3$ of 0.1M ammonia solution and the pH of the solution, tabulated against volume of hydrochloric acid added (vol) as shown below:

Vol/cm^3	10	15	16.5	17	20	25
pH	9.08	8.3	6.7	2.97	1.96	1.6

a. Plot a graph of volume of hydrochloric acid added against pH of the mixture.
b. Explain the shape of the graph.
c. Calculate the molarity of the hydrochloric acid.
d. The pH ranges of some indicators are given below.

Indicator	pH range
Thymol blue	1.2 – 2.8
Methyl orange	4.8 – 6.0
Phenolphthalein	6.6 – 8.0

Which one of the above indicators is the most suitable for end point detection during the titration? Give a reason for your answer.

e. Calculate the molarity of ammonium chloride at the end point and hence its hydrolysis constant.

(a) Write the equation of ionisation of phenol in H_2O.
(b) If the pH of a 1.0×10^{-2} dm^3 sln of phenol is 5.95. Calculate the dissociation constant ka of phenol.
(c) 10litres of aqueous sln of trichloro ethanoic acid was completely neutralised by 10cm^3 of 0.01M NaOH. Calculate the pH of the sln of trichloro ethanoic acid.
(d) the sln of trichloroethanoic acid in b, was add to a 0.1M Sodium trichloro ethanoate. calculate the pH of the resultant sln, (ka of trichloro ethanoic acid is 431 0.224 mol/dm^3 at 25°C

CHAPTER NINE: ELECTROCHEMISTRY:

9.0 Introduction

- When electric current is passed through aqueous solutions of some compounds or when they are molten, the electrical energy in the current triggers chemical reactions.
- This is an illustration of conversion of electrical energy into chemical energy, which is then locked up in bonds of the products of the reaction.
- Conversely, when many chemical reactions take place in well designed devices (dry cells, accumulators, generators, etc.) electrical energy is produced (electric current is generated).
- More interesting, the eel (electric fish) as a means for defense, converts its own ATP energy (chemical energy) to electrical energy of a considerable voltage.
- These are illustrations of conversion of chemical energy to electrical energy.
- Therefore, chemical and electrical energy are inter–convertible.

Definitions:

1. **Electrochemistry:**
   Is the branch of chemistry that explains the inter–conversion between chemical energy and electrical energy in a chemical reaction.
2. **Electrolysis:**
   Is the breakdown of a chemical substance by passing direct electric current through it.
3. **Electrolytic cell/voltameter/coloumeter:**
   This is the chemical set up in which electrolysis is done.

- An electrolytic cell is made up of:

a. A substance molten/fused if ionic or dissolved in water if ionic/covalent which can conduct electricity called an electrolyte.

b. Two pieces of conductors called electrodes which are dipped in the electrolyte with a separation between them.

c. Source of power (battery/accumulator/generator) whose terminals are connected to pieces of conductors which in turn are connected to the electrodes.

4. **Electrolyte:**

Is a substance which when molten or dissolved in water conducts electric current.

- An electrolyte can be can:

a. A molten ionic compound.

b. An ionic compound dissolved in water.

c. A covalent compound dissolved in water.

- Electrolytes conduct electricity because when molten/in aqueous solution, they contain free ions which are the conducting particles.
- Those electrolytes which conduct electricity when both molten and in solution are referred to as **true electrolytes.** For example: sodium chloride, sodium hydroxide, potassium nitrate, among others.
- Those electrolytes which conduct electricity in solution only are called **potential electrolytes**. For example: hydrochloric acid, nitric acid sulphuric acid, among others.
- Some aqueous solutions of the electrolytes at least poorly conduct electricity because of partial ionization/dissociation in solution. Such electrolytes are called **weak electrolytes**. For example: ethanoic acid, benzoic acid, ammonia solution, an aqueous solution of an amine among others.
- Then, there are those aqueous solutions that readily conduct electricity because they are fully ionized/dissociated in their solutions and are referred to as **strong electrolytes**. For example: sodium chloride, potassium nitrate, potassium hydroxide, copper (II) sulphate, hydrochloric acid among others.

5. **Electrodes**

These are the points where electrons leave and enter an electrolyte in an electrolytic cell.

- The electrode connected to the positive terminal of the source of power is called the **anode**. At the anode electrons leave the electrolyte.
- The electrode connected to the negative terminal is called the **cathode**. It is where electrons enter the electrolyte.
- Electrodes are made of conductors: metals and carbon (graphite).
- Electrodes which can contribute to the product of electrolysis are called **active electrodes**. For example copper.
- Those electrodes that cannot contribute to the product whatsoever nature of the electrolysis are called **inert electrodes:** For example: graphite and platinum.

6. **Internal circuit:**

This is the part of an electrolytic circuit within the electrolyte.

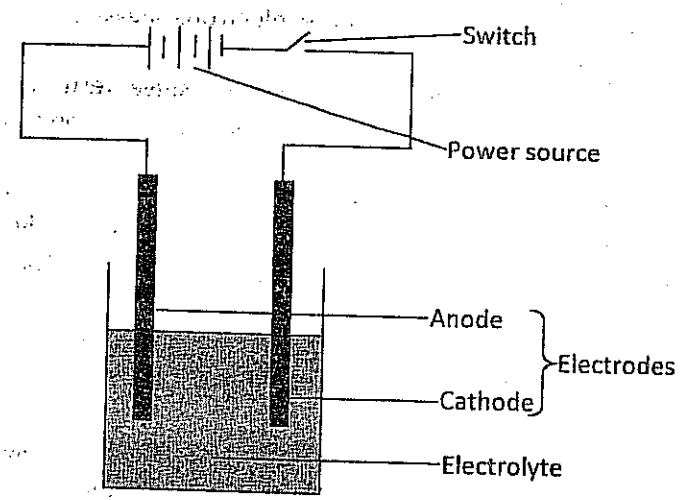
- It is made up of that part of the electrodes dipped in the electrolyte and the electrolyte itself.

7. **External circuit:**

This is the part of the electrolytic circuit outside the electrolyte.

- It is made up of: power source, connecting wires and part of the electrodes outside the electrolyte.

Diagram of the electrolytic cell:



9.1 Events during electrolysis:

- The electrolyte is dissociated/ionized into cations and anions. When an electric field is applied across the electrolyte with the two electrodes dipped into. The cations are attracted to the cathode and the anions are attracted towards the anode.
- At the anode, the anion is discharged by losing electrons to become a neutral atom or molecule:
  Anion ⟶ a neutral atom or molecule + electron(s)
- At the cathode, the cation gains the electrons of the anion to get discharged as a neutral atom or molecule.
  Cation + electron(s) ⟶ a neutral atom or molecule.
- These movements of cations toward cathode and anions toward anode are what is referred to as ionic migration, and constitute electrical conduction in an electrolyte.

To demonstrate ionic migration:

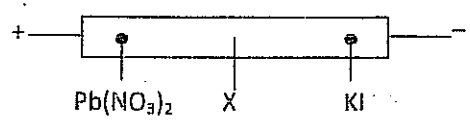
- A piece of filter paper is cut to the size of a microscope slide and placed on top of a microscope slide using crocodile clips.
- The filter paper is moistened with water and a small crystal of potassium manganate (VII) is placed mid way between the two clips.
- The clips are then connected to a direct current power supply and the paper observed for ten minutes.
- Purple colour is seen spreading towards the clip connected to the positive terminal of power source.

Explanation:

- Potassium managanate (VII) dissolves in the moisture in the filter paper and completely dissociates into purple manganate (VII) ions and colourless potassium ions according to the equation:
  $KMnO_4(s) + aq \longrightarrow K^+(aq) + MnO_4^-(aq)$
- When the field is applied, the purple manganate (VII) ions migrate towards the anode (the clip connected to the positive terminal of the power source). Hence the spreading of the purple colour.

Task:9.1

The diagram below shows a moistened piece of filter paper with small crystals of lead (II) nitrate and potassium iodide put at the spots indicated. The filter paper was connected to a direct current supply as shown below:



The spot labeled X was viewed under a microscope after some time.

a. State what was observed.
b. Explain your observation.

If lead (II) nitrate was replaced by silver nitrate and potassium iodide by potassium chromate (VI)

c. State what was observed.
d. Explain your observation.

9.2 Products of electrolysis:

- During electrolysis, the product of the electrochemical reaction can come from the electrolyte or the electrodes themselves.
- In the electrolysis of an aqueous solution of an electrolyte, there are always two anions and two cations for discharge. But only one ion must be discharge at each of the electrode at a time.
- So, what determines which ion to be discharged selectively, and which ion should not be discharged?

Factors that determine selective discharge of ions:

a. Nature of the electrode:

- In the electrolysis of aqueous copper (II) sulphate solution:
- If copper electrodes are used:

Anodic reaction:

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e$

Cathodic reaction:

$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

- If graphite electrodes are used:

Anodic reaction:

$4OH^-(aq) \quad 4H_2O(l) + O_2(g) + 4e$

Cathodic reaction:

$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

b. Concentration:

- This majorly determines the selective discharge of anions. If there is more than one anion at the anode, the one that is of higher concentration is discharged in preference to the other of lower concentration.
- Consider the electrolysis of aqueous sodium chloride solution:
- If the solution is dilute:

Anodic reaction:

$4OH^-(aq) \longrightarrow 4H_2O(l) + O_2(g) + 4e$

- If the solution is concentrated:

Anodic reaction:

$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$

c. Position of an ion in electrochemical series:

- This majorly determines the selective discharge of cations. For two cations at the cathode, the one that can easily be reduced (one with most positive electrode potential) is selectively discharged in preference to the one that can easily be oxidized (one with most negative electrode potential).
- In other words, the less electropositive metal is discharged in preference to the more electropositive metal.
- Consider electrolysis of sodium chloride solution:

Ions at the cathode (Na^+, H^+)

Anodic reaction:

$2H^+(aq) + e \longrightarrow H_2(g)$

- Consider the electrolysis of copper (II) sulphate solution:

Ions at the anode (Cu^{2+}, H^+)

Anodic reaction:

$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

9.3 Laws of electrolysis:

- In an electrolytic process the amount of a substance (discharged) i.e liberated or deposited depends on current and the time duration for which the current is passed through the electrolyte.
- The quantitative connection between these quantities was investigated by Faraday and stated as his laws of electrolysis.

First law:

The amount of a substance liberated at an electrode (anode/cathode) during electrolysis is proportional to the current and the time duration for which it is passed.

- Mathematically if m is the mass of a substance liberated, t is the time taken for current, I to be passed through the electrolyte then;

$m \propto It$

But, It is quantity of electric charge, Q

$m = KQ$

If mass 'm' is in grams, current, I is in amperes and time, t is in seconds

Then unit of K is $gA^{-1}S^{-1} = gC^{-1}$

K is a quantity that depends on the substance. For example for silver, $K = 1.118 \times 10^{-2} gC^{-1}$.

Second law:

The quantity of electricity required to liberate one mole of any element is proportional to the charge number of its ion.

- The quantity, charge number is the number of positive (for cations) and negative (for anions) charges possessed by the ions.

Ions	Charge number, Z
Na^+	1
Al^{3+}	3
SO_4^{2-}	2
PO_4^{3-}	3
Cu^+	1

- The discharge of an ion to liberate an element is either by gain or loss of electron(s). Therefore the quantity of electricity (electric charge) required to liberate one mole of an element is connected to the charge on an electron.
- For an ion with charge number Z, the amount of electricity required to liberate one atom is given by; Ze, where e is the charge on an electron.
- To discharge one mole of an element, one mole of its ions containing Avagado's constant, 6.02×10^{23} is required.
- Amount of electricity to liberate one mole = $Ze \times 6.02 \times 10^{23}$
- For singly charged ions like silver, chloride, sodium, hydrogen and hydroxide, the value of Z= 1.
- Quantity of electricity required to liberate one mole is given by: $= 6.02 \times 10^{23} \times e$, but $e = 1.6 \times 10^{-19}$

  $= 6.02 \times 10^{23} \times 1.6 \times 10^{-19}$

  $= 96320C$

  $\approx 96500 Cmol^{-1}$ (for a singly charged ion)
- This value, $96500 Cmol^{-1}$ is called Faraday's constant, F.
- For one mole of doubly charged ions the discharge requires $2F = 2 \times 96500 = 193000 Cmol^{-1}$.
- For one mole of a trebly charged ions, it requires 3F.

Worked example:9.1

A steady current of 0.45A was passed through copper and silver coulometers arranged in series for 25 minutes.

a. Calculate the moles of copper and silver liberated.
b. Explain the difference between the two moles.

Solution:

a. Quantity of electricity passed, Q =It
= (0.45x25x60) = 675C
Equation for liberation of copper:
$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$
2x96,500C of charge liberate 63.5g of copper.
675C will liberate $\frac{(675x63.5)}{193000} = 0.222g$ of copper.
Moles of copper liberated $= \frac{0.222}{63.5} = 0.0035$
Equation for liberation of silver:
$Ag^{+}(aq) + e \longrightarrow Ag(s)$
96,500C of charge liberate 108g of silver.
675C will liberate $\frac{(675x108)}{96500} = 0.755g$
Moles of silver liberated $= \frac{0.755}{108} = 0.007$

b. Ratio of moles of silver liberated to moles of copper liberated is $\frac{0.007}{0.0035} = 2:1$, which is in accordance to Faraday's second law of electrolysis.
In fact, Faraday's second law of electrolysis states: 'when the same quantity of electricity is passed through solutions of different electrolytes, the relative numbers of moles of elements liberated are inversely proportional to the number of the charges of each of the elements respectively'.

Task:9.2

The table below shows the quantity of electricity and the mass of copper deposited on the cathode when a steady current is passed through a solution of copper (II) sulphate using copper electrodes.

Quantity of electricity/C	Mass of copper /g
189	0.063
378	0.129
576	0.187
756	0.250

a. Plot a graph of mass of copper liberated against quantity of electricity passed.
b. What is the relationship between mass of copper liberated and the quantity of electricity passed?
c. State the law verified by the data.

Task:9.3

0.2 faradays of electricity were passed through solutions of copper (II) sulphate and dilute sulphuric acid. Calculate:

a. The mass of copper liberated.
b. The volume of hydrogen evolved at s.t.p.

Task:9.4

By passing a current of 0.65A for 35 minutes through water, copper and silver coulometers, the following masses of elements were liberated: 0.0143g of hydrogen, 0.113g of oxygen, 0.449g of copper and 1.532g of silver. Show that these results agree with Faraday's second law of electrolysis. [H=1, O=16, Cu=63.5 and Ag=108].

9.4 Applications of electrolysis:

a. Manufacture of chlorine
b. Manufacture of sodium hydroxide.
c. Purification of copper.
d. Electroplating of metals.
e. Extraction of metals.

9.5 Electrolytic conductivity or electrical conduction in electrolytes:

Electronic conductors and electrolytic conductors (Electrolytes):

- Electronic conductors are generally metals and carbon in the form of graphite. The electric current is carried by continuous drifting of electrons, when a voltage is applied across the conductor.
- For the case of metals, as the valency electrons carry the electric current, they continuously collide with the metal ion lattice. More so, the positively charged metal ion lattice continuously attracts the negatively charged electrons.
- The collision of electrons with the lattice and the attraction of the electron tend to hinder electrons from conducting electric current i.e: offer resistance.
- As the temperature is increased, the metallic ions in the lattice vibrate with greater amplitude, hence the resistance increases.
- The resistance offered in directly proportional to the length of the conductor and inversely proportional to the cross sectional area if the temperature remains constant.
- If, l is the length of the conductor and A is its cross sectional area, then mathematically resistance R is given by:

$$R \propto \frac{l}{A}$$

Introducing constant of proportionality:

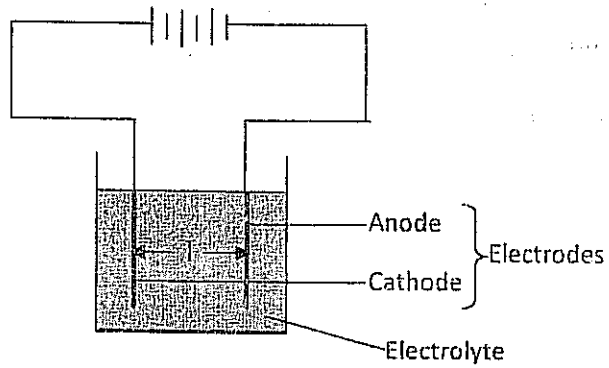
$$R = \rho\frac{l}{A} \quad \text{.....9.1}$$

The constant ρ is known as **resistivity** of the electronic conductor which is characteristic of the material. i.e every conductor has its own unique resistivity.

- Generally any material which conducts electricity does not do so at will. Electrolytes also offer resistance to the flow of

electricity and more so the values depend on two parameters: length and cross sectional area.

- Consider electrodes in the form of plates of cross sectional area A immersed in an electrolyte with separation l as shown below.



- If R is electrolytic resistance, then:

$R = \rho\frac{l}{A}$, where ρ is electrolytic resistivity.

- If l is 1cm and A is 1cm^2, then:

$$R = \rho\left(\frac{1cm}{1cm^2}\right)$$

$$\Rightarrow \rho = Rcm$$

- ρ in this case is known as specific electrolytic resistivity.

Definition:

Specific electrolytic resistivity is the resistance of a volume of an electrolyte between two electrodes of cross sectional area 1cm^2 and placed 1cm apart at a constant temperature.

Causes of resistance in an aqueous electrolyte:

a. Unionized water molecules obstruct conducting ions.
b. Head on collision between the oppositely charged ions as they migrate.

c. Viscosity of water due to hydrogen bonds and van der Waal's forces.
d. Solvation/hydration makes the ions bulkier.
e. Attraction between oppositely charged ions.

- Since for an electrolyte in solution, electrical resistance and hence electrolytic resistivity are caused by so many factors above, whose magnitude of effect caused by each is not easily quantifiable, it is more meaningful to discuss them in terms of the reciprocal, so as to minimize the contribution of each.
- Reciprocating resistance and electrolytic resistivity in equation 9.1,

  $\frac{1}{R} = L =$ Conductance of unit Ω^{-1} or Siemens(S),

  $\frac{1}{\rho} = \kappa =$ Electrolytic conductivity with the unit Ω^{-1}cm or Scm.
- The equation 9.1, therefore becomes:

  $$\kappa = L\left(\frac{l}{A}\right) \quad \text{.....9.2}$$
- The quantity $\frac{l}{A}$ is known as the cell constant.
- When l=1cm and A=1cm^2, then K is the specific conductivity or specific conductance of the solution.

Definitions:

a. Conductance is the reciprocal of the resistance of a solution of an electrolyte.
b. Electrolytic conductivity is the reciprocal of resistivity of an electrolyte.
c. Specific electrolytic conductivity in the conductance of a solution between two electrodes of cross sectional area 1cm^2 placed 1cm apart.

d. The cell constant is the ratio of distance of separation between two electrodes to the cross sectional area.

Or

The cell constant is the ratio of conductance of a solution of an electrolyte to its electrolytic conductivity.

Worked example:9.2

The resistance of 0.1M solution of potassium chloride in a conductivity cell is found to be 29.0Ω. If the conductivity of this solution is 1.29Ω^{-1}m^{-1}. Calculate the cell constant.

Solution:

From $\kappa = L\left(\frac{l}{A}\right)$

$$\Rightarrow 1.29 = \left(\frac{1}{29.0}\right)\frac{l}{A}$$

$$\frac{l}{A} = 37.41m^{-1} \text{ or } 0.374cm^{-1}$$

Task:9.5

Using the same cell in worked example 9.2 above, the resistance of a 0.1M solution of silver nitrate was 34.9Ω.

a. Explain why the resistance of silver nitrate is bigger than that of potassium chloride, yet they are of the same concentration.
b. Calculate the conductivity of this solution.

Take note:

The cell constant is a scalar quantity, whose value is constant. Its value only depends on the design of the cell. Its value for a cell is never variable.

Factors that affect electrolytic conductivity of a solution:

A. Temperature:

- For strong electrolytes, since they are completely ionized in water, increase in temperature increases electrolytic conductivity just because temperature decreases the viscosity of water i.e. weakens the hydrogen bonds and van der Waal's forces of attraction between the water molecules.
- For weak electrolytes, in addition to temperature reducing viscosity of water, overall effect of temperature on electrolytic conductivity depends on the enthalpy change that accompanies the ionization process.
- For weak electrolytes which ionize endothermically, increase in temperature increases the degree of ionization of the electrolyte hence producing many conducting ions therefore electrolytic conductivity increases.
- Decrease in temperature decreases the degree of ionization hence reducing the number of conducting particles and therefore, electrolytic conductivity decreases.

B. Concentration:

- Concentration is expressed as the number of moles of a solute in a given volume of a solution. The reciprocal of concentration is called dilution, symbolized 'V'.

$$V = \frac{1}{c}$$

Definition:

Dilution is the volume of a solution containing a given number of moles of the solute.

Worked example:9.3

Calculate the dilution of the following solutions:

a. 0.1M sulphuric acid.
b. 0.585g of sodium chloride in 1l.
c. Hydrogen ions in 9.8g per litre of sulphuric acid.

Solution:

a. From $V = \frac{1}{c}$

$$V = \frac{1}{0.1} = 10dm^3mol^{-1}$$

b. RFM of NaCl = (23 + 35.5) = 58.5

Molarity of the sodium chloride solution $\frac{0.585}{58.5} = 0.01M$

From $V = \frac{1}{c}$

$$\Rightarrow V = \frac{1}{0.01} = 100dm^3mol^{-1}$$

c. RMM of H_2SO_4 =(2 + 32 + 64) = 98

Molarity of sulphuric acid $\frac{9.8}{98} = 0.1M$

Sulphuric acid completely ionizes according to the equation:

$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$

Since 1 mole of sulphuric acid produces 2 moles of hydrogen ions, molarity of hydrogen ions is 0.2M.

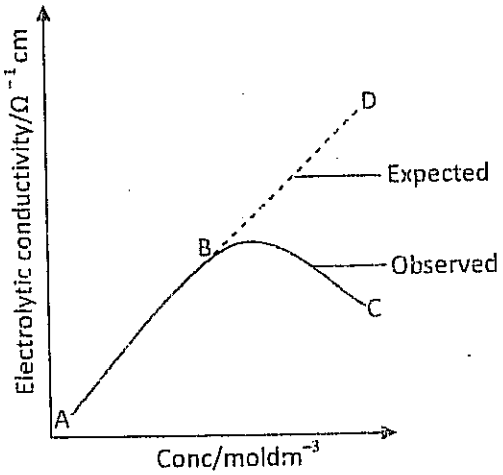
From $V = \frac{1}{c}$

$$\Rightarrow V = \frac{1}{0.2} = 5dm^3mol^{-1}$$

Effect of concentration on electrolytic conductivity:

a. **Strong electrolytes:**

- For strong electrolytes, electrolytic conductivity first increases with concentration then decreases as concentration increases, as shown in the graph below.



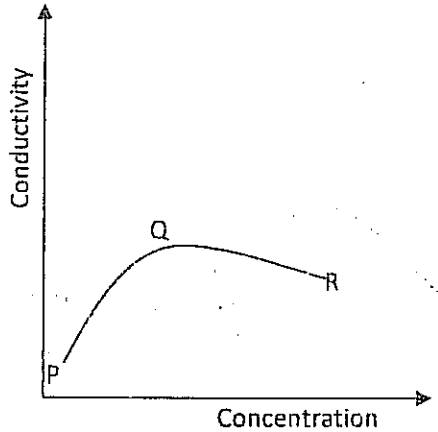
Description of the graph:

- Initially, electrolytic conductivity is proportional to concentration along AB. As concentration increases, electrolytic conductivity decreases along BC i.e. deviates from linearity.

Explanation:

- Increase in conductivity along AB with concentration is due to increase in the number of conducting ions. The cause of deviation from linearity i.e. instead of along BD but to BC is due to interaction of ions of opposite charges at high concentration making not all the ions to participate in the conductivity.

b. Weak electrolytes



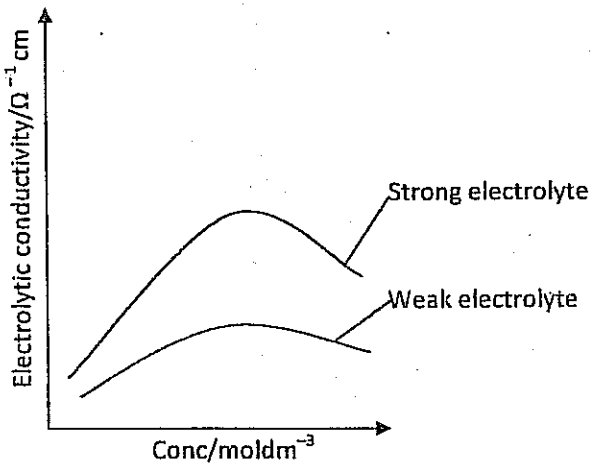
Description:

- Initially electrolytic conductivity increases with concentration though more slowly than for strong electrolytes along PQ then decreases along QR.

Explanation:

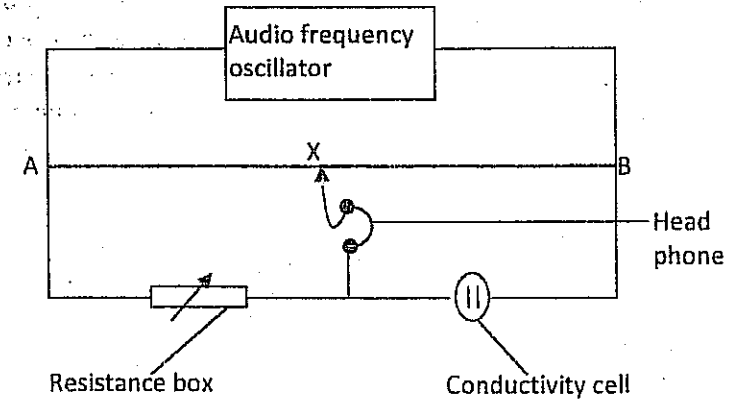
- Increase in conductivity along PQ with increase in concentration is due to the increase in number of conducting ions per unit volume. As concentration increases, the degree of ionization decreases. So the unionized weak electrolytes dominate the solution. This means that only a small number of conducting particles per unit volume hence decrease in conductivity.

Variation of conductivity for both weak and strong electrolyte with concentration on the same axes:



Measurement of electrolytic conductivity of solution/liquid:

- The solution/liquid whose electrolytic conductivity is to be measured is transferred into a conductivity cell and thermostated at 298K.
- The conductivity cell is connected to a bridge circuit as shown below:



- The sliding contact (jockey) is then moved along a meter wire AB until minimum noise is detected in the head phone.
- If R_{cell} is the resistance of liquid/solution and R_{box} in the resistance of resistance box and X is the null point;

$$\Rightarrow \frac{R_{cell}}{R_{box}} = \frac{BX}{AX}$$

$$\therefore R_{cell} = \frac{BX}{AX} \times R_{box}$$

From $\kappa = \frac{1}{R_{cell}} \times \frac{l}{A}$, the electrolytic conductivity is calculated since the cell constant of the conductivity cell is known.

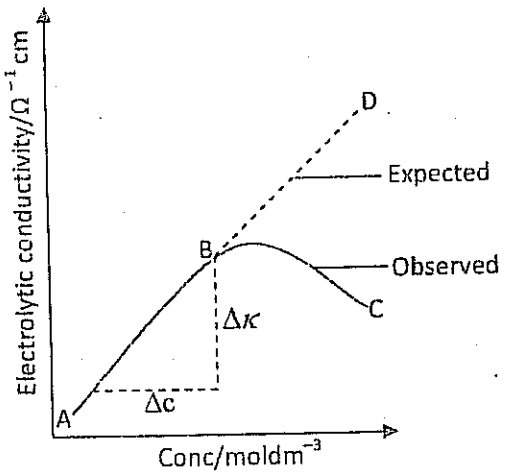
9.6 Molar conductivity (Λ)

Definition:

Is the conductance of a one cubic centimetre solution containing one mole of a solute (electrolyte) between two electrodes placed 1cm apart at a constant temperature.

Mathematically; $\Lambda = \frac{\kappa}{c}$ where, Λ is the molar conductivity, κ is the electrolytic conductivity and c is the concentration of the electrolyte.

- From the graph of variation of electrolytic conductivity with concentration of a strong electrolyte;



- From the linear portion of the graph (along AB),

Slope $= \frac{\Delta\kappa}{\Delta c}$, the molar conductivity.

The unit of molar conductivity:

From $\Lambda = \frac{\kappa}{c}$

Unit $= \frac{\Omega^{-1}cm^{-1}}{moldm^{-3}}$ but $1dm^3 = 1000cm^3$

$1000\Omega^{-1}cm^2mol^{-1}$

Worked example:9.4

Calculate the molar conductivities of the following solutions.

a. 0.1M potassium chloride solution whose electrolytic conductivity is $1.29\Omega^{-1}m^{-1}$

b. 0.01M ethanoic acid whose electrolytic conductivity is $0.163\Omega^{-1}m^{-1}$.

Solution:

a. From $\Lambda = \frac{\kappa}{c}$

$$\Lambda = \frac{0.129}{0.1} = 0.0129\Omega^{-1}dm^2mol^{-1}$$

b. From $\Lambda = \frac{\kappa}{c}$

$$\Rightarrow \Lambda = \frac{0.0163}{0.01} = 1.63x10^{-4}\Omega^{-1}dm^2mol^{-1}$$

Task:9.6

Calculate the molar conductivities of:

a. 0.0005M solution of potassium chloride with conductivity of $0.00739\Omega^{-1}m^{-1}$.

b. 0.05M ethanoic acid of conductivity $3.70\ \Omega^{-1}m^{-1}$

Factors which affect the value of molar conductivity:

i) Ionic radius:

- An ion with a small radius has a high charge density. In the process of salvation (hydration), the ion attracts greater shells of water molecules (becomes bulkier), lowering the mobility and hence reducing the molar conductivity.

Task:9.7

Explain why the molar conductivity increases in the order: $Li^+ < Na^+ < K^+$

ii) The charge on the ion/charge number:

- An ion with greater charge is more attracted towards an electrode with greater mobility hence higher molar conductivity.

Task:9.8

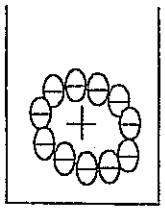
- Explain why the molar conductivity increases in the order $Na < Mg^{2+} < Al^{3+}$

iii) Concentration:

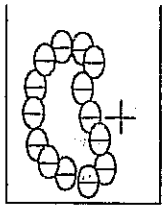
a. Weak electrolytes like ethanoic acid, carbonic acid, benzoic acid, etc., molar conductivity decreases with increase in concentration. At high concentration, more molecules of the weak electrolyte stay unionized, even the few ions produced are obstructed from conducting by unionized molecules hence lower conductivity.

b. Strong electrolytes like mineral acids, strong alkalis like sodium hydroxide and inorganic salts like sodium hydroxide, Molar conductivity decreases with increase in concentration because at high concentration, opposite ions tend to attract one another and pair up. This leads to cancellation of the charges, a phenomenon known as **inert pair effect**. Also at higher concentrations, opposite ions tend to surround one another, a phenomenon known as ionic interference.

- There are two types of ionic interferences: symmetrical and asymmetrical ionic interferences.
- Symmetrical interference occurs when a given ion is surrounded equally in all directions by the opposite ions, as shown below



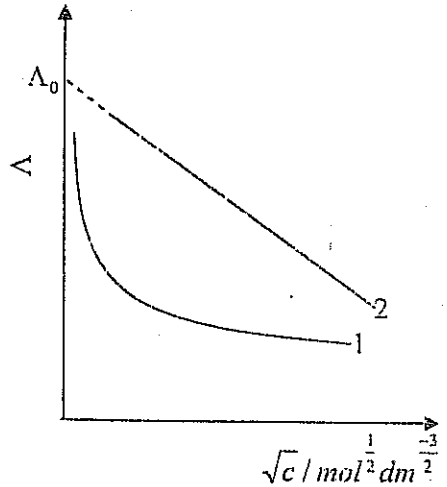
Symmetrical interference



asymmetrical interference

- When the field is applied across the solution, the symmetrical distribution is distorted (cations move towards cathode, anions move towards anode) against the backward drag of oppositely charged shells. This reduces mobility and hence molar conductivity.

Variation of molar conductivity (Λ) with square root of concentration (c).



Graph 1: for weak electrolyte:

- Starting from high concentration, molar conductivity increases with dilution. This is because addition of water (dilution) increases the degree of ionization.

Graph 2: strong electrolyte:

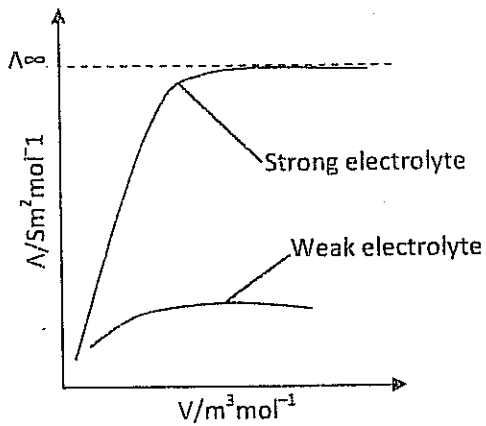
- Molar conductivity increases as the concentration is reduced, this is because of reduced ionic interference.
- From the graph, the equation of the line 2 is given by;

  $\Lambda_c = -m\sqrt{c} + \Lambda_0$

  When c = 0, (at zero concentration/infinite dilution)

  $\Lambda_c = \Lambda_0$
- At infinite dilution/zero concentration, each ion moves freely and is independent of the other. Therefore the molar conductivity is contributed in part by each ion the solution.

Variation of molar conductivity (Λ) with dilution (V):



Kohlrausch's law:

States that "the molar conductivity of an electrolyte at infinite dilution (zero concentration) is the sum of the molar conductivities of the individual ions.

$\Lambda_0^{\pm} = \Lambda_0^{+} + \Lambda_0^{-}$ or $\Lambda_\infty^{\pm} = \Lambda_\infty^{+} + \Lambda_\infty^{-}$

- For solutions of sodium chloride, silver nitrate and hydrochloric acid at infinite dilution, the molar conductivities are given by;

$\Lambda_o^{NaCl} = \Lambda_0^{Na^+} + \Lambda_0^{Cl^-}$

$\Lambda_o^{HCl} = \Lambda_0^{H^+} + \Lambda_0^{Cl^-}$

$\Lambda_o^{AgNO_3} = \Lambda_0^{Ag^+} + \Lambda_0^{NO_3^-}$

Worked example:9.9

Calculate the molar conductivity of ethanoic acid at zero concentration, given the following molar conductivities at infinite dilution:

Substance	Molar conductivity (Λ_0) $\Omega^{-1}m^2mol^{-1}$
Sodium ethanoate	0.0091
Hydrochloric acid	0.04262
Sodium chloride	0.01265

Solution:

$\Lambda_0 CH_3COOH = \Lambda_0 CH_3COONa + \Lambda_0 HCl - \Lambda_0 NaCl$

= 0.0091 + 0.04262 + 0.01265

$= 0.03907\Omega^{-1}m^2mol^{-1}$

Task:9.9

The table below gives the molar conductivities at infinite dilution of some ions:

Cations	$\Lambda_\infty / \Omega^{-1}cm^2mol^{-1}$	Anions	$\Lambda_\infty / \Omega^{-1}cm^2mol^{-1}$
Na^+	50.1	NO_3^-	71.4
Mg^{2+}	106.1	$C_2O_4^{2-}$	148.4
Al^{3+}	189	Cl^-	76.4
Cu^{2+}	107.2	SO_4^{2-}	159.6

a. Explain why molar conductivity increases in the order: $Na^+ << Mg^{2+} << Al^{3+}$

b. Calculate the molar conductivity at infinite dilution for the following substances:

- Magnesium chloride.
- Aluminium nitrate.
- Sodium oxalate.
- Copper (II) sulphate.

Task:9.10

The values of molar conductivity at infinite dilution at 298K of some electrolytes are shown in the table below:

Electrolyte	$\Lambda_\infty / \Omega^{-1} cm^2 mol^{-1}$
Nitric acid	421
Sodium ethanoate	91
Sodium nitrate	122
Potassium nitrate	145

Calculate the molar conductivity at infinite dilution for:

a. Potassium ethanoate.
b. Ethanoic acid.
c. Explain the difference between molar conductivity of sodium ethanoate and molar conductivity of potassium ethanoate.

Task:9.11

a. Define the following:

- Electrolytic conductivity,
- Cell constant and
- Molar conductivity

b. In a conductivity cell, 0.02M potassium chloride solution had a resistance of 74.58Ω. If the molar conductivity of this solution is $138.3\Omega^{-1}cm^2mol^{-1}$, determine the cell constant of the cell.

Task:9.12

The table below gives the molar conductivities at infinite dilution of some substances:

Electrolyte	$\Lambda_\infty / \Omega^{-1} cm^2 mol^{-1}$
Hydrochloric acid	425.0
potassium ethanoate	114.4
Potassium chloride	149.9

a. Explain why the molar conductivity at infinite dilution of potassium chloride is bigger than that of potassium ethanoate.
b. Calculate the molar conductivity at infinite dilution of ethanoic acid.

Task:9.13

The table below shows the values of molar conductivity of potassium chloride, potassium ethanoate and hydrochloric acid at different concentrations, collected at 291K.

Conc/moldm^{-1}	Molar conductivity/$\Omega^{-1}cm^{-1}mol^{-1}$		
	KCl	CH_3COOK	HCl
1.00	130	99.0	374
9.00	127	95.0	368
25.00	123	91.0	363
81.00	117	85.0	352
100.00	115	83.0	350

Plot suitable graphs and use it to determine: Molar conductivity at infinite dilute for: potassium chloride, hydrochloric acid and hence ethanoic acid.

9.7 Applications of conductivity measurements:

1. ***Determination of solubility and hence solubility product of a sparingly soluble electrolyte:***

- The electrolytic conductivity of conductivity water at a given temperature κ_w is determined.
- The electrolytic conductivity of a given saturated solution of a sparingly soluble electrolyte in conductivity water at the same temperature κ_{soln} is determined.

- The electrolytic conductivity of the electrolyte (solute alone), κ_{salt} is given by; $\kappa_{salt} = \kappa_{soln} - \kappa_{w}$
- Since the electrolyte is very sparingly soluble, $\Lambda_{\infty}^{salt} \approx \Lambda_{\infty}^{soln}$

$$From \Lambda_{c}^{salt} = \frac{\kappa_{soln}}{c}$$

$$\Rightarrow c = \frac{\kappa_{soln}}{\Lambda_{c}^{soln}}$$

- From the concentration, solubility and hence solubility product of the salt are determined.

Task:9.14

The electrolytic conductivity of a saturated solution of silver chloride at 298K is $1.887 \times 10^{-4} \Omega^{-1} m^{-1}$, and that of water is $5.5 \times 10^{-6} \Omega^{-1} m^{-1}$. Calculate the solubility and hence solubility product of silver chloride at 298K. Given that the mola conductivity at infinite dilution of silver chloride is $140 \Omega^{-1} cm^{2} mol^{-1}$.

Task:9.15

The electrolytic conductivity of a saturated solution of silver chloride at 298K is $3.41 \times 10^{-6} ohm^{-1} cm^{-1}$, and the electrolytic conductivity of water alone is $1.60 \times 10^{-6} ohm^{-1} cm^{-1}$. The salt listed below have the following molar conductivities at infinite dilution:

- Silver nitrate: 133.4 $ohm^{-1} cm^{2} mol^{-1}$.
- Potassium nitrate: 145.0 $ohm^{-1} cm^{2} mol^{-1}$.
- Potassium chloride: 149.9 $ohm^{-1} cm^{2} mol^{-1}$.

a. Calculate the molar conductivity of silver chloride at zero concentration.

b. Calculate the solubility and hence the solubility product of silver chloride at 298K.

2. Determination of degree of ionization of a weak electrolytes:

- The electrolytic conductivity of the weak electrolyte κ is determined
- If the concentration of the weak electrolyte is 'c' then its molar conductivity at concentration 'c' is given by $\Lambda_{c} = \frac{\kappa}{c}$.
- The molar conductivity of the same electrolytes at infinite dilution can be determined using standard values of conductivities of other electrolytes.
- According to Arrhenius, degree of ionization of a weak electrolyte is given by: $\alpha = \frac{\Lambda_{c}}{\Lambda_{\infty}}$.

Task:9.16

a. Write an expression for:

- Acid ionization constant, K_a for ethanoic acid.
- The relationship between acid ionization constant, K_a and the degree of ionization of the acid, α.

b. The electrolytic conductivity of a 0.016M ethanoic acid at 293K is $0.192 Scm^{2} mol^{-1}$. Calculate:

- The molar conductivity of ethanoic acid at 293K.
- The degree of ionization at 293K if its molar conductivity at infinite dilution is $364 \Omega^{-1} cm^{2} mol^{-1}$.
- The pH of the acid.

c. State the factors that affect the pH value of a weak acid.

3. Determination of ionization constant of a weak electrolyte:

- If the concentration of a weak electrolyte is 'c', then from the ionization equation;

	$HA(aq) \rightleftharpoons$	$H^+(aq)$	$+ A^-(aq)$ (aq)
Initially:	c moles	0mol	0mol
Stoichiometrically:	1 mol	1 mol	1 mol
At equilibrium:	(1–α)c	αc	αc

From $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(\alpha c)(\alpha c)}{(1-\alpha)c} = \frac{\alpha^2 c}{(1-\alpha)c}$

But, $\alpha = \frac{\Lambda_c}{\Lambda_\infty}$.

- $K_a = \frac{\left(\frac{\Lambda_c}{\Lambda\infty}\right)^2 c}{1 - \frac{\Lambda_c}{\Lambda_\infty}}$

4. *Determination of ionization constant of water:*

- The conductivity of extremely pure water at 298K is determined using a sensitive bridge circuit.
- The molar conductivity of water is then determined since one mole of water has a volume of $18cm^3$.
- The molar conductivity of water at zero concentration is obtained from the values for some standard alkalis.
- From which the degree of self ionization of water, the concentrations of hydrogen and hydroxyl ions are determined, hence ionic product of water.

Illustration:

- The electrolytic conductivity of water at 298K is $5.5x\ 10^{-6}\Omega^{-1}m^{-1}$
- One mole of water has a volume of $18cm^3$.

Concentration of water is given by $\frac{1}{18} molcm^{-3}$

$= 5.6x10^4\ molm^{-3}$

$\Lambda_c = \frac{\kappa}{c} = \frac{5.5x10^{-6}}{5.6x10^4} = 1.0x10^{-10}\ m^2 mol^{-1}$

$\Lambda_0^{H_2O} = \Lambda_0^{NaOH} + \Lambda_0^{HCl} - \Lambda_0^{NaCl}$

$= 0.02484 + 0.04262 - 0.01265 = 0.0548 m^2 mol^{-1}$

- The degree of ionization of water is given by:

$\alpha = \frac{\Lambda_c}{\Lambda_0}$

$\Rightarrow \alpha = \frac{1.0x10^{-10}}{0.0548} = 1.8x10^{-9}$

Converting the concentration of water into mol/dm^3

$\Rightarrow c = 5.6x10^4 x10^{-3} = 56 moldm^{-3}$

$[H^+] = [OH^-] = \alpha c = 1.8x56x10^{-9} = 1.0x10^{-7}$

$K_w = [H^+][OH^-] = (1.0x10^{-7})^2$

$K_w = 1.0x10^{-14}$

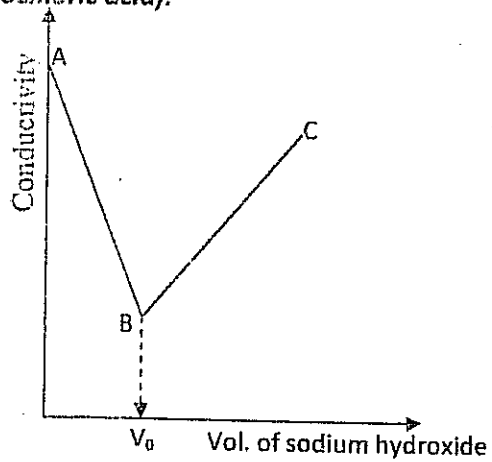
5. *Determination of equilibrium constant.*
6. *Measurement of pH.*

7. *Potentiometric/Electrometric/Conductimetric titrations:*

- This is the application of conductance measurement to determine the end point of a titration.
- In practice a standard titrand is put into a conductivity cell and using a wheat stone bridge, its resistance is determined.
- Aliquots of the titrant are added from the burette; the mixture magnetically stirred and its resistance determined.

- A plot of conductivity/conductance against volume of titrant added gives a conductimetric titration curve from which the end point is determined.
-

Case1: Strong acid/strong base pair (sodium hydroxide and hydrochloric acid):



Description:

- High conductivity at A; as sodium hydroxide solution is added, the electrolytic conductivity decreases along AB to a minimum at B (end point). With addition of more sodium hydroxide solution, conductivity increases along BC.

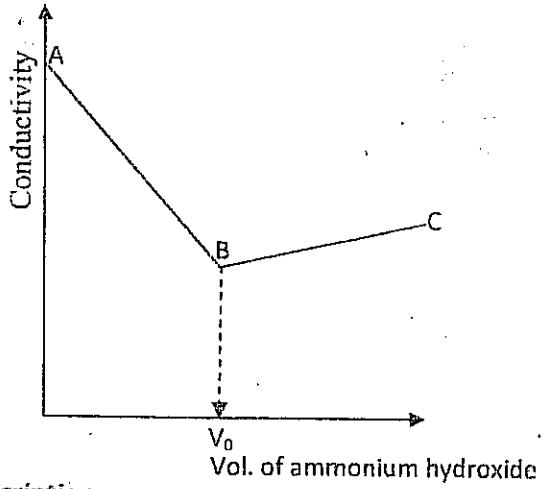
Explanation

- High conductivity A because of the presence of highly conducting hydrogen ions in pure hydrochloric acid. Conductivity decreases along AB as sodium hydroxide solution is added because the rapid conducting hydrogen ions have been replaced by the less conducting sodium ions according to the reaction:

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

- Conductivity increases along BC because of fast conducting hydroxyl ions from sodium hydroxide.
- V_0 is the volume of sodium hydroxide solution required to completely neutralize the hydrochloric acid.

Case 2: Strong acid/weak base pair (hydrochloric acid and ammonium hydroxide)



Description:

- High conductivity at A; as ammonium hydroxide solution is added, the electrolytic conductivity gradually decreases along AB to a minimum at B (end point). With addition of more ammonium hydroxide solution, conductivity gradually increases along BC.

Explanation

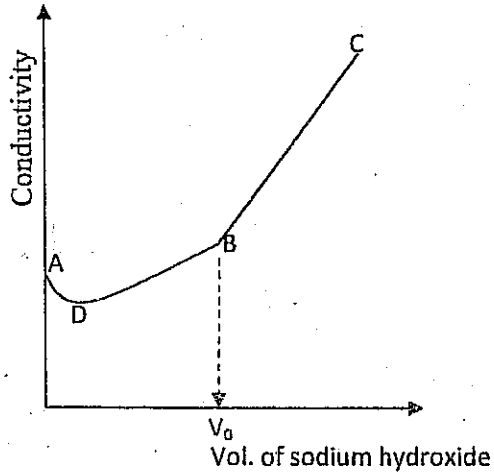
- High conductivity at A because of the fast conducting hydrogen ions of completely ionized hydrochloric acid.
- Conductivity gradually decreases along AB because ammonium hydroxide solution being a weak base produces just a few hydroxyl ions which remove the fast

conducting hydrogen ions and replace by the less conducting ammonium ions by the reaction;

$HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(l)$

- B is the end point with the corresponding volume, V_0
- The only slight increase in conductivity/conductance along BC is due to excess ammonium hydroxide added beyond the end point. However, the ionization of ammonium hydroxide is suppressed by the presence of highly dissociated ammonium chloride. Hence gradual rise in conductivity along BC.

Case 3: Weak acid/strong base pair (ethanoic acid and sodium hydroxide):



Description:

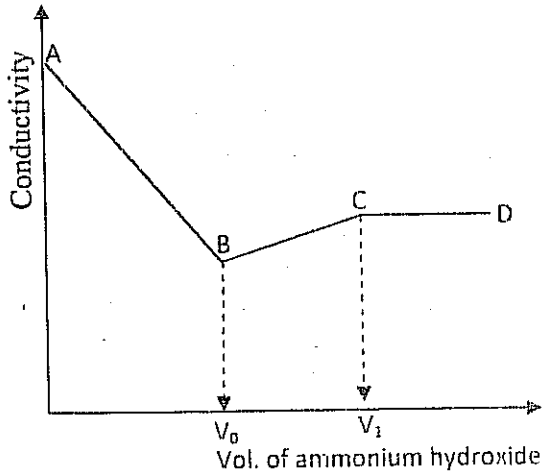
- Low conductivity at A; as sodium hydroxide solution is added, the conductivity rapidly decreases along AD. It then gently rises along DB, (B is the end point). With addition of more sodium hydroxide solution, conductivity sharply increases along BC.

Explanation:

- Low conductivity at A because ethanoic acid is a weak acid so only slightly ionizes producing few conducting ions.
- Rapid decrease in conductivity along AD is because the rapidly conducting few hydrogen ions of ethanoic acid are rapidly removed by addition of completely dissociated sodium hydroxide solution.
- The conductivity rises gradually along DB because of formation of sodium ethanoate which is completely dissociated.
- The sharp rise in conductivity along DC is due to the fast mobile hydroxyl ions from excess sodium hydroxide solution.

Case 4: A mixture of a weak acid and a strong acid/a weak base pair (ethanoic acid mixed with hydrochloric acid and ammonium hydroxide)

In this case, the strong acid first reacts with the base giving a distinct end point. The weak acid then reacts giving a second end point.



Description:

- High conductivity at A; Conductivity decreases along AB; slightly rises along BC, and remains more or less constant along CD as more and more ammonium hydroxide solution is added. V_0 is the volume of ammonium hydroxide required to neutralize hydrochloric acid and v_1-v_0 is the volume of ammonium hydroxide required to neutralize ethanoic acid.

Explanation:

- High conductivity at A because of the presence of high conducting hydrogen ions from hydrochloric acid which is completely ionized.
- Decrease in conductivity along AB as ammonium hydroxide is added due to removal of fast conducting hydrogen of the hydrochloric acid according to the equation:

  $NH_4OH(aq) + HCl\ (aq) \longrightarrow NH_4Cl(aq) + H_2O(l)$
- B is the end point for neutralization of hydrochloric acid.
- Conductivity increases along BC because of he production of ammonium ions which are fairly fast conducting by the reaction;

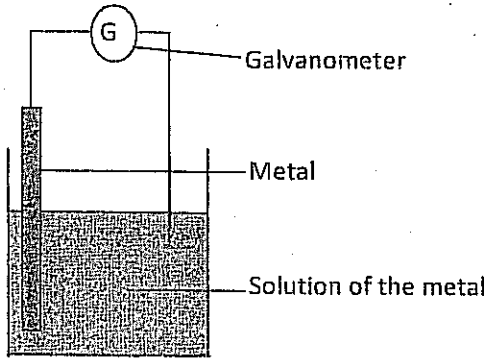
$CH_3COOH(aq) + NH_4OH(aq) \longrightarrow CH_3COONH_4(aq) + H_2O(l)$

- C is the second end point
- The conductivity level off along CD because the mixture of ammonium ethanoate and ammonium hydroxide constitutes a buffer which suppresses ionization of excess ammonium hydroxide.

9.8 Electromotive force (emf)/galvanic/voltaic cells:

9.8.0 Introduction

- An emf/galvanic/voltaic cell is an electrochemical cell that employs redox reactions to produce electrical energy. Or a device which converts chemical energy to electrical energy.
- An emf/galvanic/voltaic cell is made up of two electrodes also called half cells, each always made up of a piece of metal dipped into a solution of its ions. For example: zinc foil dipped in a solution of zinc sulphate, copper wire dipped into a solution of copper (II) chloride, etc.
- When in such arrangement, the piece of metal is then connected by a conductor through a galvanometer, to the solution, the galvanometer shows deflection.



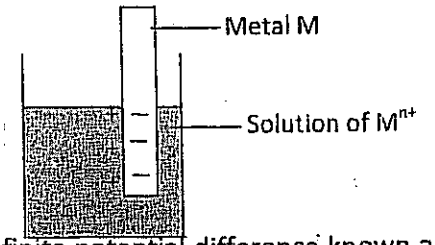
- This deflection indicates flow of current and hence potential difference/voltage across the metal and its solution.
- That voltage/potential difference generated between a metal and a solution of its ions when they are in contact is called **electrode potential.**

9.8.1 The origin of electrode potential

- When a metal is dipped into a solution of its ions, the metal atoms at its surface tend to ionize (lose electron); while the metal ions is the solution tend to gain the lost electrons to become atoms i.e.

$M(s) \rightleftharpoons M^{n+}(aq) + ne$ and $M^{n+}(aq) + ne \rightleftharpoons M(s)$

- The two processes take place at different rates at the start, and if the metal is highly electropositive, then, the tendency to ionize dominates the tendency to gain electrons.
- Hence electrons accumulate on the surface of the metal i.e. the metal surface becomes more negative with respect to the solution as shown below:



- Hence a definite potential difference known as electrode potential is generated between the solution and the metal surface.
- An electrode potential is a standard electrode potential (E^{θ}) if the metal is dipped into 1M solution of its ions at 298K.

Definition:

Standard electrode potential is the potential difference generated when an electrode is dipped into 1M solution of its ions at 298K.

9.8.2 Types of electrodes:

a. Metal/metal ions electrodes:

- This electrode is made up of a piece of metal dipped into a solution of its ions. Examples include:
  - Zinc electrode :$Zn(s)/Zn^{2+}(aq)$
  - Copper electrode $(Cu(s)/Cu^{2+}(aq)$.
  - Aluminium electrode: $Al(s)/Al^{3+}(aq)$
  - Magnesium electrode: $Mg(s)/Mg^{2+}(aq)$
  - Silver electrode: $Ag(s)/Ag^{+}(aq)$
  - Sodium electrode: $Na(s)/Na^{+}(aq)$
  - The electrode (half cell) reaction, taking the case of zinc electrode is given by:

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e$ or $Zn^{n+}(aq) + 2e \rightleftharpoons Zn(s)$

b. Gas electrodes:

- Made up of a gas under pressure and on the surface of a catalyst bubbled into a solution of its ions. Examples include:
  - Hydrogen electrode:$Pt, {}^{1}/_{2}H_2(g)/H^{+}(aq)$
  - Chlorine electrode:$Pt, {}^{1}/_{2}Cl_2(g)/Cl^{-}(aq)$
  - Fluorine electrode:$Pt, {}^{1}/_{2}F_2(g)/F^{-}(aq)$
  - The electrode (half cell) reaction taking the case of chlorine gas electrode is given by:

${}^{1}/_{2}Cl_2(g) + e \rightleftharpoons Cl^{-}(aq)$ or $Cl^{-}(aq) \rightleftharpoons {}^{1}/_{2}Cl_2(g) + e$

c. Metal/metal sparingly soluble salt electrode:

- Made up of a piece of metal coated with desirable sparingly soluble salt, then the set up immersed into a solution with anion common to that of the sparingly soluble salt of the metal. Examples include:
  - Silver metal coated with silver chloride immersed in chloride solution: $Ag(s)/AgCl(s),Cl^{-}(aq)$
  - Lead metal coated with lead (II) sulphate immersed into sulphate solution: $Pb(s)/PbSO_4(s),SO_4^{2-}(aq)$

- Magnesium metal coated with magnesium carbonate immersed into carbonate solution: $Mg(s)/MgCO_3(s),CO_3^{2-}(aq)$
- Here the chloride, sulphate and carbonate ions can be from any soluble salt containing the anion or any strong acid containing the anion.
- The electrode (half cell reaction) taking the case of lead metal coated with lead (II) sulphate electrode is given by:

1st $PbSO_4(s) + aq \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

2nd the excess sulphate ions of the strong electrolyte then supply electrons to the formed lead (II) ions.

$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$

Over all electrode reaction is given by addition of the two reactions:

$PbSO_4(s) + 2e \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$ or

$Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e$

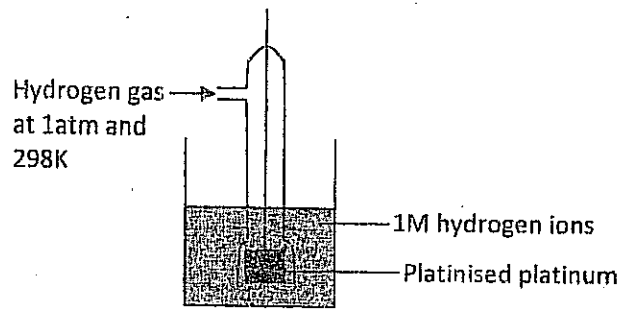
d. Ion – ion half cell:

- This type of electrode is made up of an inert electrode such as platinum metal dipping into a solution containing ions of the same metal in two different oxidation states.
- Example: iron (II)–iron (III) electrode: $(Pt(s), Fe^{2+}(aq)/Fe^{3+}(aq)$.
- The electrode (half cell) reactions are given by;

$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e$ or $Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$

9.8.3 Standard hydrogen electrode (S.H.E)

- A standard hydrogen electrode is made of hydrogen gas at a pressure of one atmosphere and a temperature of 298K adsorded on the surface of platinum catalyst, and bubbled into a solution of 1M aqueous hydrogen ions.
- Diagram of the standard hydrogen electrode is shown below:



- The electrode potential of a standard hydrogen electrode is conventionally taken as zero (0.0V).
- Under this theoretical/non practicable condition, when a moving coil galvanometer is connected across, the platinum wire and the 1M hydrogen ions of the electrode, it shows completely "no deflection".
- Standard hydrogen electrode on this theoretical account is taken as a reference electrode from which the electrode potential of others can be estimated.

Measurement of standard electrode potentials:

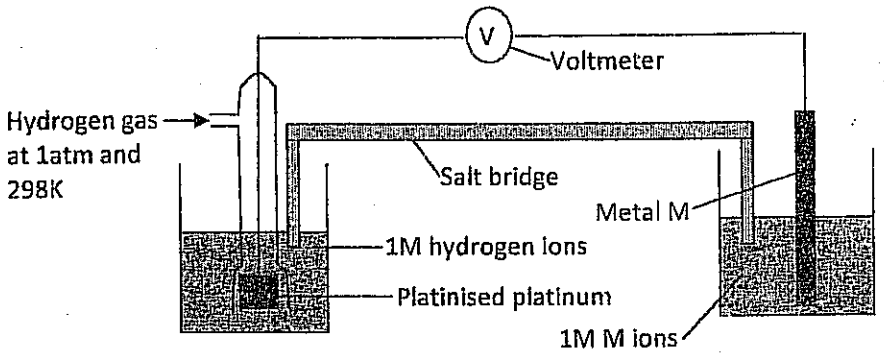
- The absolute value of electrode potential of a cell cannot be measured, instead a value, just close to can be estimated using a standard hydrogen electrode.

Explain why it is impossible to measure the absolute value of an electrode potential.

- To measure the value of electrode potential of an electrode using an electronic voltmeter (a high resistance voltmeter). It should be connected across the electrode, one terminal to the piece of the metal and the other to the solution.
- The conductor dipped into the solution then constitutes another electrode of definite potential.
- Hence the registered value by the voltmeter is for the half cell of interest and the half cell constituted by the wire.
- Hence it is impracticable to measure the absolute value of electrode potential of a cell.

Describe how to measure the standard electrode potential of a cell using a standard hydrogen electrode.

- The electrode whose potential is to be determined is connected to the right of standard hydrogen electrode by means of a suitable salt bridge and a conductor connected through a high resistance voltmeter (an electronic voltmeter) as shown below.



- Then the reading of the voltmeter, negative or positive gives the value of the standard electrode potential of the electrode, with respect to standard hydrogen electrode.

Take note:

- Conventionally, electrons should flow from left to right; correspondingly the conventional direction of current should be from right to left.
- When metal M is above hydrogen in the activity series, the M electrode becomes negative with respect to the hydrogen electrode and hence electrons flow from right to left, and the conventional current flows from left to right
- Hence the voltage of the set up (electrode) is a negative potential. Here metal M can be: zinc, iron, aluminum. Magnesium, sodium, etc.
- When metal M is below hydrogen in the activity series say copper, gold, silver, etc. the hydrogen electrode becomes

negative with respect to the metal electrode. Hence electrons flow from left to right (normal direction) the electrode potential registered is positive.

Standard electrode potential (E^{θ}) values:

- All electrode potentials are quoted as reduction potentials and the associated equation is a reduction reaction.
- The arrangement of elements according to their electrode potentials gives rise to the electrochemical series, in which the most reactive metal, with the most negative reduction potential is on top.
- The more negative a reduction potential, the easier it is for oxidation process to take place and the more difficult is for reduction to take place.
- These elements with greatest negative electrode potentials have greater tendency to donate electrons, and therefore exist as the anode (with a negative polarity as electrons accumulate on their surfaces). The metals are strongest reducing agents.

Electrodes	Electrode potentials(E^{θ})/V
$Li^{+}(aq)/Li(s)$	−3.04
$K^{+}(aq)/K(s)$	−2.92
$Ca^{2+}(aq)/Ca(s)$	−2.82
$Na^{+}(aq)/Na(s)$	−2.71
$Mg^{2+}(aq)/Mg(s)$	−2.37
$Al^{3+}(aq)/Al(s)$	−1.66
$Zn^{2+}(aq)/Zn(s)$	−0.76
$Fe^{2+}(aq)/Fe(s)$	−0.44
$Pb^{2+}(aq)/Pb(s)$	−0.13
$H^{+}(aq)/H_2(g)$	0.00
$Cu^{2+}(aq)/Cu(s)$	+0.34
$Ag^{+}(aq)/Ag(s)$	+0.80

9.8.4 Cell connection, notation and equation:

- Electrode potentials are always quoted for reduction processes, (when an electrode is reduced) hence referred to s reduction potentials.
- The standard electrode potentials of half cells can have a negative value or a positive value.

a. **Negative electrode potential** means the half cell can easily loose electron(s); if a metal electrode, then the metal is highly electropositive. Such an electrode is a **reductant electrode.**

b. **Positive electrode potential** means the half cell can easily gain electron(s); if a metal electrode, then the metal is less electropositive. Such an electrode is an **oxidant electrode.**

- The electrode where reduction takes place is called the **cathode**, while the electrode where oxidation takes place is called the **anode.**
- When connecting two half cells and hence drawing cell notation, the anode is put to the right and the cathode to the left so that conventionally, electrons flow from right to left and current from left to right.
- The following rules are used when connecting two half cells to constitute a full cell:

a. If the E^{θ} values are both negative, then the half cell with more negative value of E^{θ} constitutes left electrode.

b. If only one E^{θ} value is negative, then the cell constitutes the left electrode.

c. If both E^{θ} values are positive, the half cell with the smaller E^{θ} value constitutes left electrode.

d. The salt bridge is indicated by '//', while porous partition by broken double slashes (⁞⁞).

Worked example:9.10

Given the electrodes below:

- $Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$; $E^{\theta} = -0.126V$
- $Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$; $E^{\theta} = -0.737V$
- $Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$; $E^{\theta} = +0.337V$
- $Ag^{+}(aq) + e \rightleftharpoons Ag(s)$; $E^{\theta} = +0.779V$

Write the cell convention, over all cell equation and calculate the over all emf of the cells made by the following combinations.

a. Lead and zinc electrodes.
b. Zinc and copper electrodes.
c. Copper and silver electrodes.
d. Lead and silver electrodes.

Solution:

a. Cell convention:
$Zn(s)/Zn^{2+}(aq)//Pb^{2+}(aq)/Pb(s)$
Cell equation:
$Zn(s) + Pb^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Pb(s)$
Over all emf:
$0.737 + -0.126 = +0.611V$

b. Cell convention:
$Zn(s)/Zn^{2+}(aq)//Cu^{2+}(aq)/Cu(s)$
Cell equation:
$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$
Over all emf:
$0.737 + 0.337 = +1.074V$

c. cell convention:
$Cu(s)/Cu^{2+}(aq)//Ag^{+}(aq)/Ag(s)$
Cell equation:
$Cu(s) + 2Ag^{+}(aq) \quad Cu^{2+}(aq) + Ag(s)$
Over all emf:
$-0.337 + 0.779 = +0.442V$

d. Cell convention:
$Pb(s)/Pb^{2+}(aq)//Ag^{+}(aq)/Ag(s)$
Cell equation:
$Pb(s) + 2Ag^{+}(aq) \rightleftharpoons Pb^{2+}(aq) + 2Ag(s)$
Over all emf:
+0.126 + 0.779 = +0.905V

Take note:

a. All the electrodes taken to the left become anodes. Hence, their electrode potentials become oxidation electrodes. The sign changes.
b. Multiplying/dividing an electrode equation by an integer does not multiply/divide the electrode potential.
c. Over all efm can also be obtained from the formula:
Reduction potential of reduced electrode – reduction potential of the oxidized electrode.

Worked example:9.11

The equations for some half cell reactions are given below:
$SO_4^{2-}(aq) + H_2O(l) + 2e \rightleftharpoons SO_3^{2-}(aq) + 2OH^{-}(aq)$:–0.90V

$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$;+0.337V

a. Write the convention for the combined two half cells.
b. Write the over all cell equation.
c. Calculate the efm of the cell.

Solution:

a. $Pt(s)/SO_3^{2-}(aq),OH^{-}(aq)//SO_4^{2-}(aq),H_2O(l)/Pt(s)$
b. $SO_3^{2-}(aq) + 2OH^{-}(aq) + Cu^{2+}(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l) + Cu(s)$
c. 0.90 + 0.337 = +1.237V

Take note:

a. For the half cells of ions to be connected, an inert electrode (platinum) must be inserted into the mixtures of the ions.
b. Ions and liquids are separated by commas.

Spontaneity of cell reactions:

- For a cell reaction to be spontaneous /feasible, the overall emf of the cell should be positive and the change in free energy should be negative.

$\Delta G^{\theta} = -nFE^{\theta}$

Where;

ΔG^{θ} = **Gibb's** Free energy change.
n = Number of moles of electrons participating in the over all reaction.
F = Faraday's constant = $96500Cmol^{-1}$
E^{θ} = Overall emf of the cell.

Worked example:9.12

Using the worked examples 9.10 and 9.12, calculate the maximum work done by each cell.

Solution:

Taking example 9.10 part b):
n = 2, F = $96,500Cmol^{-1}$ and E^{θ}= +1.237V

From $\Delta G^{\theta} = -nFE^{\theta}$
$\Rightarrow \Delta G^{\theta} = -(2x96500x1.074) = -207,282J$
Taking worked example:9.11
n = 2, F = $96,500Cmol^{-1}$ and E^{θ}= +1.237V
From $\Delta G^{\theta} = -nFE^{\theta}$
$\Rightarrow \Delta G^{\theta} = -(2x96500x1.237) = -238,741J$

Worked example:9.13

A cell was set up as shown below:

$Mg(s)/Mg^{2+}(aq)//Ca^{2+}(aq)/Ca(s)$.

a. If the reduction potentials of magnesium and calcium electrodes are respectively –2.37V and –2.87V. Calculate the over all emf of the cell.
b. What conclusion can you draw from the value of over all emf.

Solution:

a. +2.37+ –2.87 = –0.50V.
b. Over all emf means the cell reaction is not feasible.

Task:9.17

The standard electrode potentials of some half cells are shown below:

$Zn^{2+}(aq)+2e \rightleftharpoons Zn(s); E^{\theta} = -0.737V$

$Cu^{2+}(aq)+ 2e \rightleftharpoons Cu(s); E^{\theta} = +0.337V$

a. Write the cell convention for the cell formed by combining the two half cells.
b. Write the equations for the reactions taking place at the anode and the cathode.
c. Calculate the maximum obtainable energy from the cell for the displacement of one mole of copper.
d. Draw a well labeled diagram of the cell.

Task:9.18

For the cell convention:

$Hg(l),HgCl_2(s),Cl^-(aq)//Cr_2O_7^{2-}(aq),H^+(aq),Cr^{3+}(aq)/Pt(s)$, the over all efm is +0.996V.

a. Write the equation for the reactions at each electrode.
b. Write the over all cell reaction equation.
c. Calculate the maximum work done by the cell.

Task:9.19

The standard electrode potentials for some half cells are given below:

$Fe^{3+}(aq)/Fe^{2+}(aq)$; +0.76V

$^1/_2I_2(aq)/I^-(aq)$; +0.54V

a. Write the convection for the combined cell.
b. Calculate the over all emf and hence the maximum work done by the cell.
c. Draw a labeled diagram of the cell.

Task:9.20

The convention of a cell is given below:

$Pt(s)/Fe^{2+}(aq),Fe^{3+}(aq)//MnO_4^-(aq),Mn^{2+}(aq),H^+(aq)/Pt(s)$

a. write the eqiuations for the half reactions at the anode and the cathode.
b. Write the over all equation for the cell reaction.
c. The electrode potentials for the systems: $Fe^{2}(aq)/Fe^{3+}(aq)$ and $Mn^{2+}(aq)/MnO_4^-(aq)$ are +0.76V and =+1.51V respectively. Deduce whether the cell reaction is feasible or not. Give a reason for your answer.

Task:9.21

Given the half cell reactions:

$Zn^{2+}(aq)+2e \rightleftharpoons Zn(s); E^{\theta} = -0.76V$.....i

$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq); E^{\theta} = +0.77V$.....ii

$MnO_4^-(aq) + 8H^+(aq) + 5e \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l); E^{\theta} = +1.51V$.....iii

$MnO_4^-(aq) + e \rightleftharpoons MnO_4^{2-}(aq); E^{\theta} = +0.56V$.....iv

a. Write the convention for the cell made by half reactions i) and ii).
b. Draw the diagram of the above cell.
c. Write the cell convention for the cell made up by combining the half cell reactions iii) and iv).
d. Draw the diagram of the above cell.

Task:9.22

a. Describe the standard hydrogen electrode.
b. The absolute value of an electrode potential can not be determined. Explain.
c. Give the differences between an electrolytic cell and an emf cell.
d. Describe with the aid of a well labeled diagram, how the standard hydrogen electrode can be used to measure the electrode potential of copper. Would you expect the value of the potential to be negative or positive? Explain your answer.

Task:9.23

The electrode potential values for some half cell reactions are given below:

Given the half cell reactions:

$Zn^{2+}(aq)+2e \rightleftharpoons Zn(s); E^{\theta}=-0.76V$.....i

$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq); E^{\theta}= +0.77V$.....ii

$MnO_4^-(aq) + 8H^+(aq) + 5e \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l); E^{\theta}= +1.51V$....iii

$MnO_4^-(aq) + e \rightleftharpoons MnO_4^{2-}(aq); E^{\theta}= +0.56V$.....iv

$Cu^{2+}(aq)+ 2e \rightleftharpoons Cu(s); E^{\theta} = +0.34V$.....v

$MnO_4^{2-}(aq) + 4H^+(aq) + 2e \rightleftharpoons MnO_2(aq) + 2H_2O(l); E^{\theta}= +2.26V$.vi

a. State the species that is the best reducing and the best oxidizing agents.
b. Write the cell convention for the cell made by combining the electrodes of the half cells i) and ii). Write the over all cell reaction and hence calculate the over all emf of the cell.

9.8.5 Factors that affect the magnitude of standard electrode potential of a metal and hence over all emf:

- Hypothetically, for a metal to ionize when dipped into a solution of its ions, and hence generate an electrode potential, the following processes must occur;

a. Sublimation of the solid metal atoms to gaseous atoms requiring input of atomization energy.
- Sublimation of a metal involves melting and boiling of the metal. The higher the melting and boiling point of a metal, the more positive the electrode potential.

b. Ionization of the gaseous atoms requiring input of ionization of energy of the metal.
- The bigger the ionization energy, the more positive the electrode potential of the metal.

c. Hydration of the produced ions which is an exothermic process.
- The more negative the hydration energy of a metal ion, the more negative is the electrode potential of a metal.
- Hence the electrode potential of a metal is negative or positive depending on the values of the three enthalpy terms:
  i) If $(\Delta H_{atm} + I.E) > \Delta H_{hyd}$, then E^{θ} is positive.
  ii) If $(\Delta H_{atm} + I.E) < \Delta H_{hyd}$, then E^{θ} is negative.
  iii) If $(\Delta H_{atm} + I.E) = \Delta H_{hyd}$, then E^{θ} is 0.0V. This is only for the conventional standard hydrogen electrode!

d. Temperature.
e. Concentration.
- The electrode potential of the efm cell is related to temperature and concentration according to Nernst equation:

$$E = E^{\theta} + \frac{RT}{nF} In \frac{[oxidised]}{[reduced]}$$

Where:

E is the electrode potential/emf at the concentration and temperature.
E^{θ} is the standard electrode potential/emf.
R is the universal gas constant.
T is the thermodynamic temperature.
n is the number of moles of electrons participating in the cell reaction.
F is the Faraday's constant ($9500 Cmol^{-1}$)
[oxidized] and [reduced] are the respective molar concentrations of the oxidized and reduced species in the cell reaction.

- For the electrode:
  $Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s); E^{\theta} = -0.126V$

$$E = -0.126 + In\frac{8.31T}{19000}\frac{[Pb]}{[Pb^{2+}]}$$

But [Pb], molar concentration of a solid is its density (a constant)

$$\Rightarrow E = -0.126 - In\frac{8.31}{19000}T[Pb^{2+}]$$

- For the full cell:
  $Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq); E^{\theta} = +0.77V$

$$E = +0.77 + In\frac{8.31T}{9500}\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

9.8.6 Types of full emf cells/galvanic/voltaic cells:

- There are two main types of full cells: primary cells and secondary cells.

a. Primary cells:

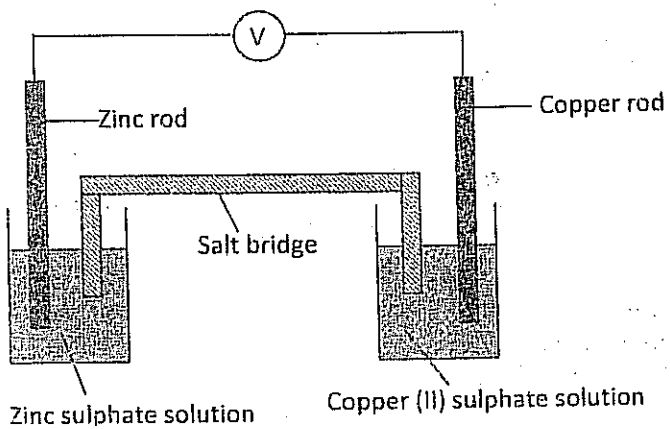
- A primary cell is an emf cell in which as the cell generates electrical energy, the chemicals it is composed of is used up. It can not therefore be recharged.

- A simple emf cell made up of two metal – metal ions electrodes (Galvanic couple) is known as Galvanic cell of Voltaic cell. A typical example of Voltaic cell is Daniel's cell.

Types of primary cells:

i) Daniel's cell:

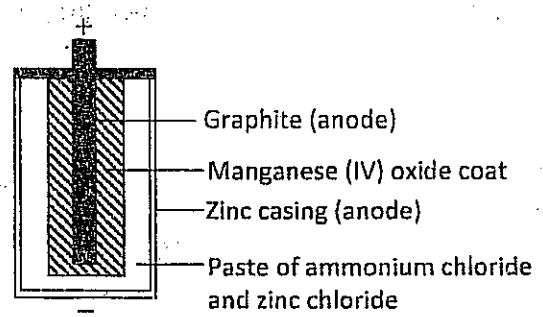
- It consists of a zinc rod dipping into a solution of zinc sulphate connected by a salt bridge of pasted potassium chloride to a copper electrode consisting of a copper rod dipping into a solution of copper (II) sulphate as shown below:



- Anodic reaction:
  $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e; E^{\theta} = +0.76V$
- Cathodic reaction:
  $Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s); E^{\theta} = +0.34V$
- Over all reaction:
  $Cu^{2+}(aq) + Zn(s) \rightleftharpoons Cu(s) + Zn^{2+}; E^{\theta} = +1.10V$
- Cell convention:
  $Zn(s)/Zn^{2+}(aq)//Cu^{2+}(aq)/Cu(s)$
  At times porous partition is used instead of salt bridge.

ii) Leclanche' cell (dry cell):

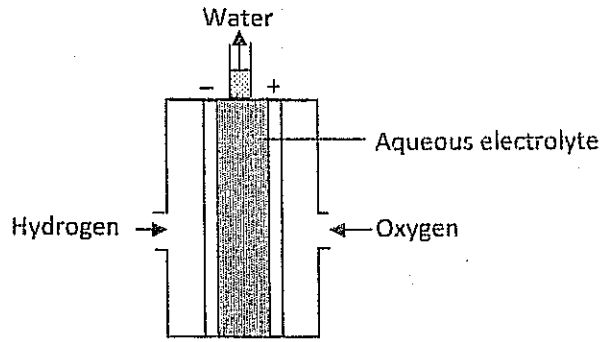
- It is a house – hold item in torches, radios, toys, etc. It is a convenient portable source of electricity since its components are solids or pastes, which are tightly sealed from the environment.
- A dry cell is made up of; zinc container encasing the cell (anode); graphite rod surrounded by a layer of manganese (IV) oxide (cathode); mixture of pasted zinc chloride and ammonium chloride in water (electrolyte).



- Anodic reaction:
  $2NH_4^+(aq) + 2e \rightleftharpoons 2NH_3(g) + H_2(g)$
- Cathodic reaction:
  $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e;$
- Over all reaction:
  $2NH_4^+(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2NH_3(g) + H_2(g)$ $E^\theta = +1.50V$

iii) Fuel cell:

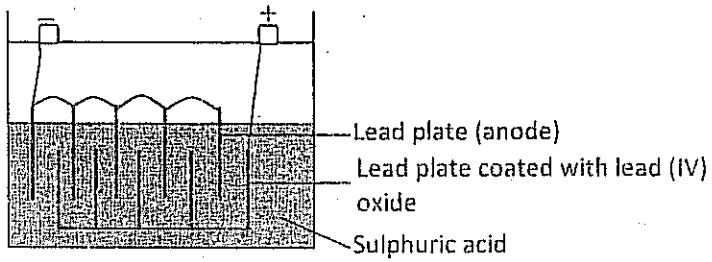
- Is a primary cell in which the reactants are continuously replaced as the products are continuously removed.
- A simple fuel cell can be made up of; a porous carbon containing platinum catalyst in a concentrated solution of an alkali into which hydrogen and oxygen (reactants) are continuously bubbled and water (product) removed.



- Anodic reaction:
  $2H_2(g) + 4OH^-(aq) \rightleftharpoons 4H_2O(l) + 4e$
- Cathodic reaction:
  $O_2(g) + 2H_2O(l) + 4e \rightleftharpoons 4OH^-(aq)$
- Over all reaction:
  $O_2(g) + 2H_2(g) \rightleftharpoons 2H_2O(l)$
- A fuel cell is used in spacecrafts, where it can generate up to 12 kilowatts of power.

b. Secondary cells:

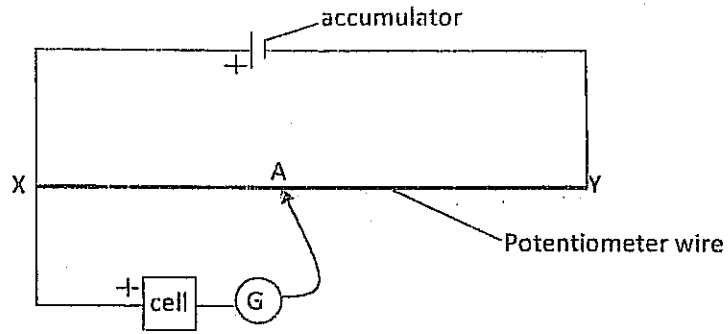
- These are cells that can be recharged by passing electricity through it from an external source. As the cell produces electric current, its voltage keeps reducing (discharging).
- A typical secondary cell is lead storage cell or lead accumulator. It is made up of; a lead anode; a grid of lead packed with lead (IV) oxide (cathode) and desirably diluted sulphuric acid (electrolyte).



- Anodic reaction:
  $Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e$
- Cathodic reaction:
  $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightleftharpoons PbSO_4(s) + 2H_2O(l)$
- Over all reaction:
  $PbO_2(s) + Pb(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2H_2O(l)$
- From the over all equation for the cell reaction, as the cell continuously produces current, the sulphuric aid gradually gets dilute as its sulphate and hydrogen ios are used up.
- This leads to a decrease in relative density of the sulphuric acid, with a subsequent decease in the voltage of the cell (discharge).
- To recharge the cell, it is connected to an external source of electricity, which triggers the reactions:
- Anodic reaction:
  $PbSO_4(s) + 2e \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$
- Cathodic reaction:
  $PbSO_4(s) + 2H_2O(l) \rightleftharpoons PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e$
- The produce sulphate and hydrogen ions combine to form sulphuric acid. This increases the concentration and hence relative density of sulphuric acid–the essence of recharge!
- Lead acid accumulators are used in car engines as battery.

Experimental determination of emf of a full cell:

- The cell whose emf is to be determined is connected to a potentiometer circuit with an accumulator of known emf (E), through a moving coil galvanometer (G) and jockey as shown below:



- The jockey is slid along the potentiometer wire until a null point at which the galvanometer shows no deflection.
- This point A along the potentiometer wire is then noted.

Calculation:

If E_{cell} is the efm of the cell,

At balance, $\frac{XY}{XA} = \frac{E}{E_{cell}}$

$\Rightarrow E_{cell} = \frac{XA}{XY} \times E$

9.8.7 Types of electrochemical cells:

- There are two types of electrochemical cells:

a. Electrolytic cells or voltameter or coulometer.
b. Electromotive force (emf) cells.

Differences between an electrolytic cells and an emf cell:

a. An electrolytic cell is the apparatus in which electrolysis is carried out; an emf cell is a device that employs redox reaction to produce electricity.
b. An electrolytic cell converts electrical energy to chemical energy; an emf cell converts chemical energy to electrical energy.
c. In an electrolytic cell, oxidation occurs at the positive electrode, is an emf cell, oxidation occurs at the negative electrode.

Take note:

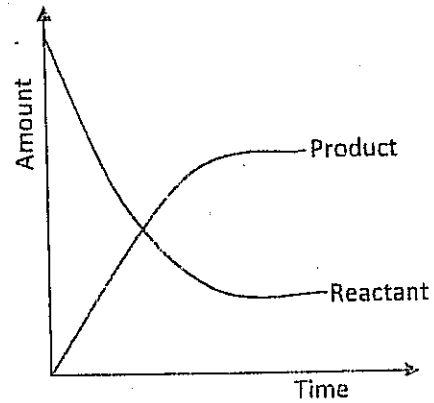
- Whereas the oxidation takes place in the negative electrode of the emf cell, it is still the anode. So in emf cell, the polarity of the anode in negative and that of the cathode is positive.

CHAPTER TEN: CHEMICAL KINETICS:

10.0: Introduction:

- When a chemical reaction proceeds the amount of reactant decreases, the amounts of products increases until equilibrium is attained (incase of reversible reactions) or until one of the reactant is used up, then, the amount of the other reactant remains constant.

Graphical illustration:



- The decrease in the amount of the reactant or the increase in amount of product can be expressed per unit time to give a quantity called the **rate of the reaction**. Rate of a reaction is the subject matter of chemical kinetics.
- Chemical kinetics is therefore the study of rates of chemical reactions and factors affecting them.
- These factors are:

a. Temperature
b. Concentration of the reactants
c. Pressure
d. Catalysts
e. State of sub division of solids (surface area)

10.1: Ways of expressing the amounts of reactants/products:

- Volume of reactants/products.
- Mass of reactants/products.
- Concentrations of reactants/products.
- Pressure/partial pressure of reactants/products.
- Conductivity value of reactants/products.
- pH of reactants/products.

10.2: Rate of reaction

- Consider the reaction below:

  $P + Q \longrightarrow S + R$
- The rate of the reaction can be expressed in terms of;

a. Rate of decrease in concentration of P or Q.

$$Rate = -\frac{d[P]}{dt} = -\frac{d[Q]}{dt}$$

b. Rate of increase in concentration of S or R.

$$Rate = \frac{d[S]}{dt} = \frac{d[R]}{dt}$$

Therefore $Rate = -\frac{d[P]}{dt} = -\frac{[Q]}{dt} = \frac{d[R]}{dt} = \frac{d[S]}{dt}$

10.3: Key terms

a. **Elementary reaction:**

Is a reaction that proceeds in one step, from the reactant direct to the product.

b. **Rate determining step (r.d.s):**

Is the slowest step in a chemical reaction.

c. **Rate law:**

- Even if the rate of a chemical reaction can be expressed in terms of either the amounts of the reactant or product, the rate law summarizes the relationship between the rate of a chemical reaction and the concentration of the reactant.

The rate law states that "the rate of any chemical reaction at a constant temperature is directly proportional to the molar concentration of the reactant raised to certain power, whose value is only experimentally determined.

- Consider the reaction;

  $A \longrightarrow Product$
- From the rate law;

  Rate $\propto [A]^x$
- Introducing a constant of proportionality;

  Rate $= -K[A]^x$ 10.1

d. **Rate constant/rate coefficient:**

- From equation 10.1, K is the rate constant/rate coefficient. Rate constant is therefore that constant of proportionality linking the rate of a chemical reaction to the molar concentration of the reactant as expressed in the rate equation, at a given temperature.
- From equation 10.1, when [A] = 1 (unity),

  Then Rate $= -K(1)^x$

  Rate = Rate constant.

  Therefore, rate constant is rate of reaction at a given temperature when the molar concentration of the reactant is unity.

e. **Order of a reaction:**

- From the equation 10.1, x is the order of the reaction with respect to reactant A.

  Order of a reaction with respect to a reactant is that power to which the concentration of reactant is raised as expressed in the rate equation.
- Over all order of the reaction is the sum of powers to which the molar concentrations of reactants are raised in the rate equation.
- Consider the chemical reaction below;

$$A+B+C+D \longrightarrow P+Q$$

- The rate equation is given by:
  Rate = $-K[A]^a[B]^b[C]^c[D]^d$
  'a' is the order of reaction with respect to reactant A
  'b' is the order of reaction with respect to reactant B
  'c' is the order of reaction with respect to reactant C and
  'd' is the order of the reaction with respect to reactant D
  Over all order = (a + b+ c+ d)

f. Half life:

This is the time taken for the amount of a reactant to reduce by half the initial value.

Or:

Time taken for half the amount of a product in a given reaction to form.

g. Molecularity:

This is the number of chemical species (atoms, molecules or ions) that take part in the rate determining step.

Differences between molecularity and order:

Molecularity	Order of a reaction
Takes on only whole numbers; is never zero	Can be fractional, zero or whole numbers.
Theoretically deduced	Empirically deduced
Number of chemical species that take part in the rate determining step	That empirical power to which the concentration of the reactant is raised as expressed in the rate equation

h. Reaction mechanisms:

Is the step by step description of the pathways followed by reactant in forming product.

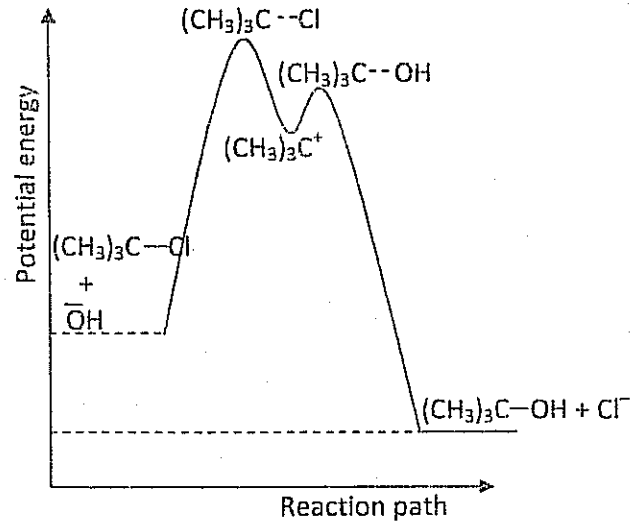
a. Hydrolysis of tertiary alkylhalide (2 –chloro – methylpropane) using sodium hydroxide solution:

Step 1 $(CH_3)_3C{-}Cl \underset{r.d.s}{\overset{slow}{\rightleftharpoons}} (CH_3)_3C^+ + Cl^-$

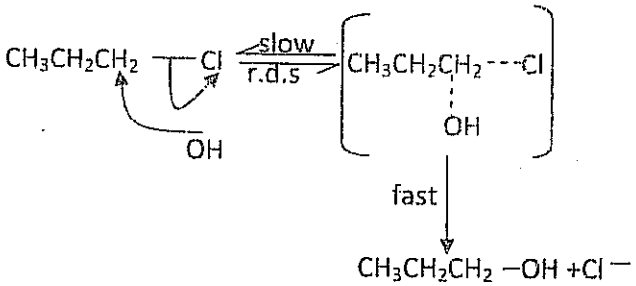
Step 2: $(CH_3)_3C^+ + \overset{-}{O}H \xrightarrow{fast} (CH_3)_3C{-}OH$

In the above reaction, the molecularity of the reaction is one since only one molecule is involved in the rate determining step (r.d.s). The mechanism for the reaction is therefore known as Substitution Nucleophilic Unimolecular (S^N1).

Energy profile for S^N1

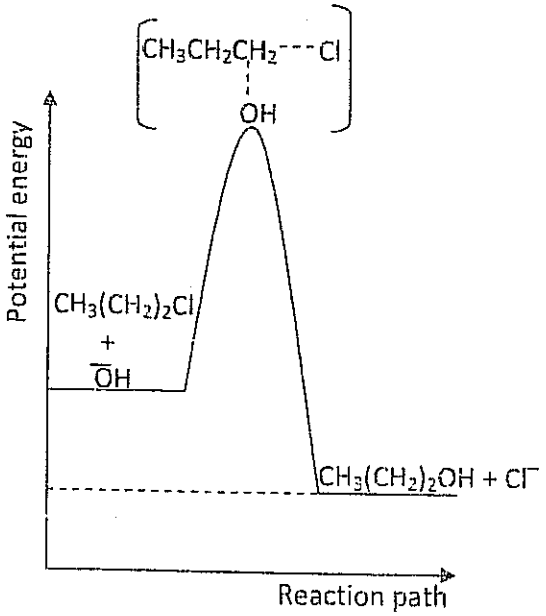


b. *Hydrolysis of primary alkylhalide (1 – chloro – propane) using sodium hydroxide solution:*



- In the above reaction, the molecularity of the reaction is two since two molecules are involved in the rate determining step (r.d.s). The mechanism for the reaction is therefore known as Substitution Nucleophilic Bimolecular (S^N2).

Energy profile for S^N2:



10.4: Classification of chemical reactions according to over all order:

a. **Zero order:**

- Consider a zero order elementary reaction of the general equation:

A ⟶ Product.

Rate = $-K[A]^0$

$$\frac{d[A]}{dt} = -K[A]^0$$

$$\frac{d[A]}{dt} = -K$$

Separating variables and integrating:

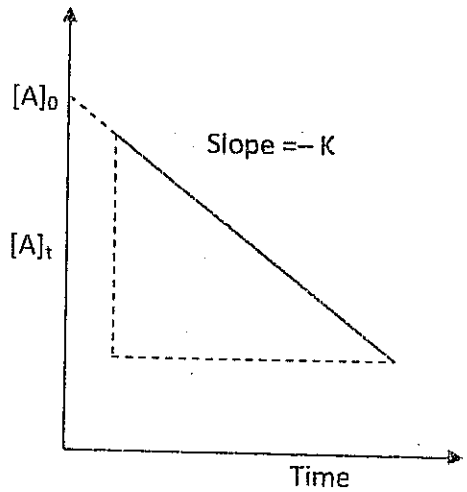
$$\int_{[A]_0}^{[A]_t} d[A] = \int_{t=0}^{t=t} -Kdt$$

$$[A]\Big|_{[A]_0}^{[A]_t} = -K\Big|_{t=0}^{t=t}$$

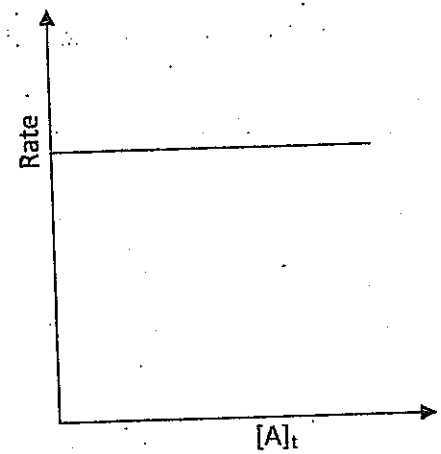
$$\therefore [A]_t - [A]_0 = -Kt$$

$$\Rightarrow [A]_t = -Kt + [A]_0 \quad \text{.....10.2}$$

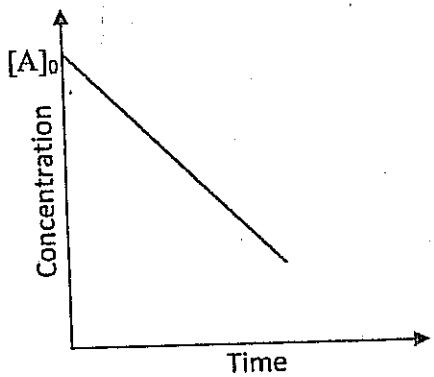
Graph of molar concentration of reactant ($[A]_t$) against time (t):



Graph of molar concentration of the reactant $[A]_t$ against rate:



Graph of concentration against time:



Half life of zero order reactions:

When $t=t_{1/2}$, $[A]t=\frac{[A]_0}{2}$

From, $[A]_t = -Kt + [A]_0$

$$\Rightarrow \frac{[A]_0}{2} = -Kt_{\frac{1}{2}} + [A]_0$$

$$\therefore t_{\frac{1}{2}} = \frac{[A]_0}{2K} \quad \text{.....10.3}$$

Hence for zero order reaction, $t_{\frac{1}{2}} \propto [A]_0$

First order reactions:

- Consider a first order elementary reaction of the general equation:

A $\longrightarrow$ Product.

Rate = $-K[A]^1$

$$\Rightarrow \frac{d[A]}{dt} = -K[A]$$

Separating variables and integrating:

$$\int_{[A]0}^{[A]t} \frac{1}{[A]} d[A] = \int_{=0}^{=t} -Kdt$$

$$\Rightarrow In[A]\Big|_{[A]0}^{[A]t} = -K\Big|_0^t$$

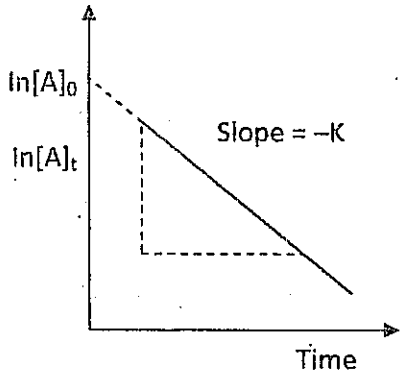
$\ln[A]_t - \ln[A]_0 = -Kt$

$$\therefore In[A]_t = -Kt + In[A]_0 \quad \text{.....10.4}$$

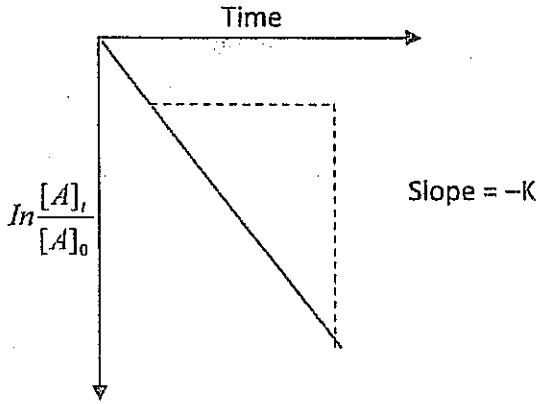
Also,

$$In\frac{[A]_t}{[A]_0} = -Kt \quad \text{.....10.5}$$

Graph of $In[A]_t$ against time:



Graph of $In\frac{[A]_t}{[A]_0}$ against time:



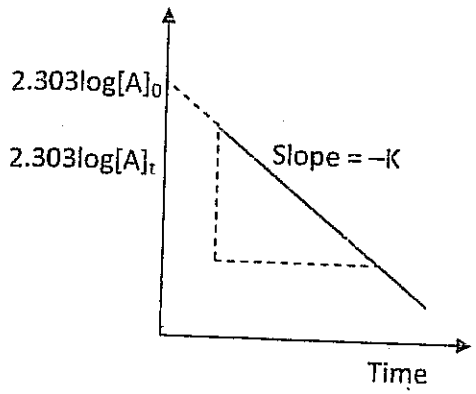
Converting natural log in equation 10.4 to $\log_{10}$:

$$2.303\log[A]_t = -Kt + 2.303\log[A]_0 \quad \text{.....10.6}$$

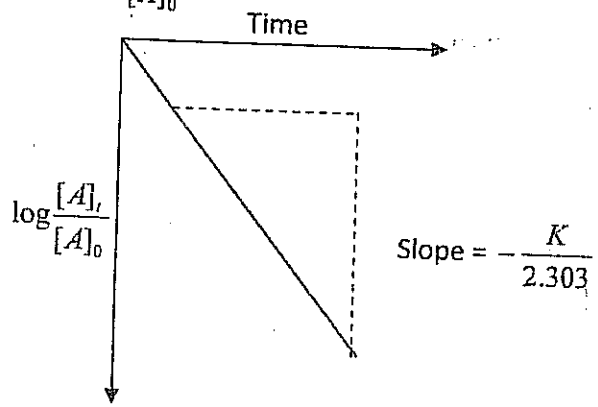
Also,

$$\log\frac{[A]_t}{[A]_0} = -\frac{K}{2.303}t \quad \text{.....10.7}$$

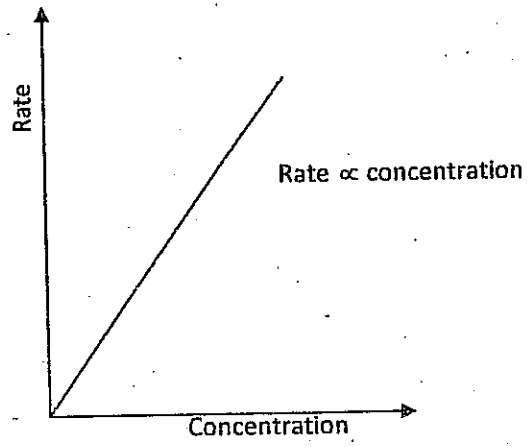
Graph of $\log[A]_t$ against time:



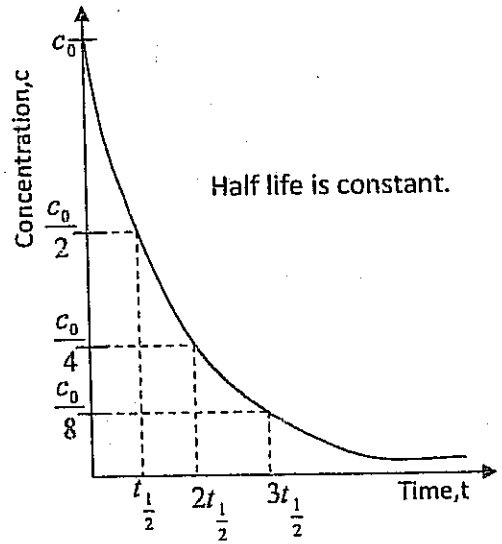
Graph of $\log\frac{[A]_t}{[A]_0}$ against time:



Graph of rate against molar concentration:



Graph of concentration against time:



Show that half life of a first order reaction is constant (independent of initial concentration).

From the integrated first order rate equation:

$$In[A]_t = -Kt + In[A]_0$$

When $t = t_{\frac{1}{2}}, [A]_t = \frac{[A]_0}{2}$

$$\Rightarrow In\frac{[A]_0}{2} = -Kt_{\frac{1}{2}} + In[A]_0$$

$$Kt_{\frac{1}{2}} = In2$$

$$t_{\frac{1}{2}} = \frac{In2}{K} \text{ or } t_{\frac{1}{2}} = \frac{0.693}{K} \quad \text{.....10.8}$$

A typical example of first order process is radioactive decay.

Second order reactions:

Consider a second order elementary reaction of the general form;

	A ⟶	Product
Initially	a_0	0
After time,t	(a_0-x)	x

Rate = $K[A]^2$

$$\frac{dx}{dt} = K(a_0 - x)^2$$

Separating variables and integrating,

$$\frac{dx}{(a_0 - x)^2} = Kdt$$

$$\int \frac{1}{(a_0 - x)^2} dx = \int Kdt \text{ (Integrate in parts)}$$

$$\Rightarrow \frac{1}{(a_0 - x)} + c = Kt$$,c = constant of integration.

When t = 0, x = 0

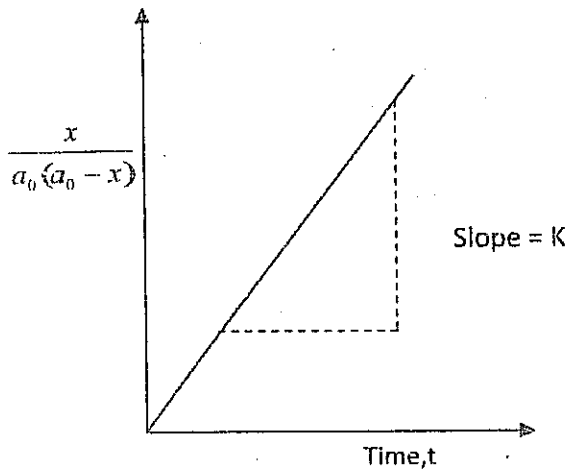
$$\Rightarrow \frac{1}{(a_0 - 0)} + c = K(0); \Rightarrow c = \frac{1}{a_0}$$

$$\therefore \frac{1}{(a_0 - x)} - \frac{1}{a_0} = Kt \quad \text{.....10.9}$$

Or

$$\frac{x}{a_0(a_0 - x)} = Kt \quad \text{.....10.10}$$

Graph of $\frac{x}{a_0(a_0 - x)}$ against time:



The half life of second order reactions:

From the integrated equation for second order reactions;

$$\frac{1}{(a_0 - x)} - \frac{1}{a_0} = Kt,$$

When $t = t_{\frac{1}{2}}$, $x = \frac{a_0}{2}$

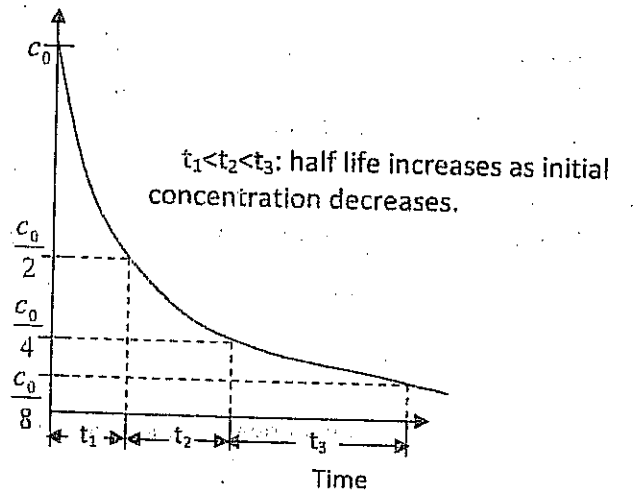
$$\Rightarrow \frac{1}{\left(a_0 - \frac{a_0}{2}\right)} - \frac{1}{a_0} = Kt_{\frac{1}{2}}$$

So that

$$t_{\frac{1}{2}} = \frac{1}{Ka_0} \quad \text{.....10.11}$$

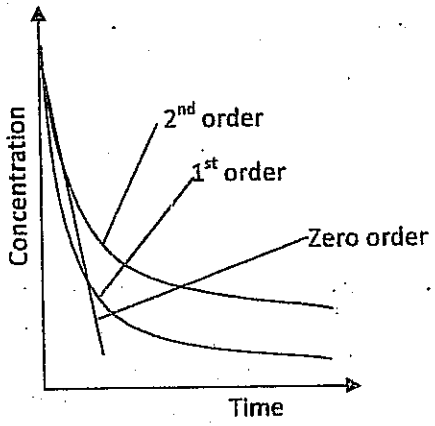
Hence for second order reactions, half life is inversely proportional to initial concentration of the reactant.

Graph of concentration of reactant against time:



Summary of indicators or order of a reaction:

a. **Graphically:**



b. **In terms of half life:**

1st order	Half life is constant
zero order	Successive half lives decrease
2nd order	Successive half lives increase

Worked example:10.1

The integrated equation for a first order reaction is given by:

$2.303\log\left(\frac{a}{a-x}\right) = Kt$, where a is the initial concentration of the reactant in the elementary reaction.

a. Derive the expression for its half life.
b. If the half life for the above reaction is 120 seconds. Calculate the decay constant.
c. Calculate the percentage of the reactant that remains after 300 seconds.

Solution:

a. From $2.303\log\left(\frac{a}{a-x}\right) = Kt$, when $t=t_{1/2}$, $x={}^{a}/_{2}$

$$\Rightarrow 2.303\log\left(\frac{a}{a-\frac{a}{2}}\right) = Kt_{\frac{1}{2}}$$

$$2.303\log\left(\frac{a}{\frac{a}{2}}\right) = Kt_{\frac{1}{2}}$$

$$2.303\log 2 = Kt_{\frac{1}{2}}$$

$$0.693 = Kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{0.693}{K}$$

b. From $t_{\frac{1}{2}} = \frac{0.693}{K}$, but $t_{1/2}=120$

$$\Rightarrow 120 = \frac{0.693}{K}$$

$$K = \frac{0.693}{120} = 0.0058s^{-1}$$

Hence the decay constant is $0.0058s^{-1}$

c. From $2.303\log\left(\frac{a}{a-x}\right) = Kt$, t = 300s.

$$\Rightarrow 2.303\log\left(\frac{a}{a-x}\right) = 0.0058x300$$

$$\log\left(\frac{a}{a-x}\right) = \frac{1.73}{2.303}$$

$$\left(\frac{a}{a-x}\right) = anti\log 0.7523$$

$$\left(\frac{a}{a-x}\right) = 5.65$$

Reciprocating,

$$\left(\frac{a-x}{a}\right) = 0.177$$

Percentage of the reactant that remains after 300s is 17.7%

Worked example:10.2

Benzene diazonium chloride decomposes according to the following equation:

$C_6H_5N_2Cl(aq) \longrightarrow C_6H_5Cl(aq) + N_2(g)$

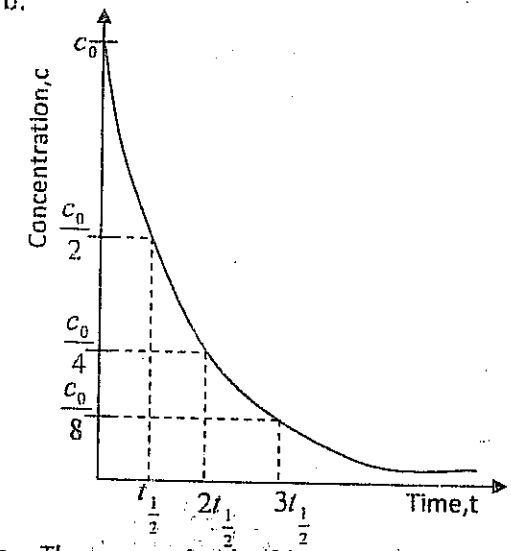
The reaction is first order with respect to benzene diazonium chloride.

a. Write the expression for the rate equation.
b. Sketch a graph to show variation is the concentration of benzene diazonium chloride with time.
c. Use the graph to show how order of the reaction can be proved to be first order with respect to benzene diazonium chloride.

Solution:

a. Rate = $[C_6H_5N_2Cl]^1$ or rate = $[C_6H_5N_2Cl]$

b.



c. The successive half lives are obtained from the graph as shown above. Should the successive half lives remain constant, then it is first order reaction.

Worked example:10.3

The table below shows the half lives for decomposition of ammonia:

Initial pressure/atmospheres	35.3	17.3	7.73
Half life/seconds	456	222	100

a. Deduce the order of the reaction.
b. Calculate the rate constant for the reaction.

Solution:

a. Since the half lives decrease as the initial concentration (now pressure) decreases, the reaction is zero order.

b. From $t_{\frac{1}{2}} = \frac{[A]_0}{2K}$

Taking the first set of values in the table;

$$\Rightarrow 456 = \frac{35.3}{2K}$$

$$K = \frac{17.65}{456} = 0.0387$$

Hence decay constant is 0.0387atms^{-1}

Task:10.1

a. Define the following terms:

- Order,
- Rate constant and
- Half life of a reaction.

The data below were obtained for the reaction:

$2A \longrightarrow$ products

Time/hours	0	1.3	2.0	4.0	5.3
$Log_{10}A$	–0.07	–0.24	–0.33	–0.57	–0.74

b. Plot a suitable graph and use it to determine the order of the reaction.

c. Calculate the rate constant and hence the half life of the reaction.

Task:10.2

a. Define the terms: rate of reaction and molecularity of a reaction.

The table below shows the volumes, V of decomposing hydrogen peroxide remaining after some times.

Time/minutes	0	5	10	15	20
Volume/cm^3	12.3	9.2	6.9	5.2	3.9

b. Plot a suitable graph and use it to determine the order of decomposition of hydrogen peroxide.

c. Calculate the rate constant for the decomposition of hydrogen peroxide.

Task:10.4

A solution of an ester and sodium hydroxide at 298K initially contained 0.01M of each of them. When samples of the mixture were titrated with standard hydrochloric acid, the following results were obtained.

Time/s	0	180	300	420	600	900	1260
$[OH^-]$	10.0	7.40	6.34	5.50	4.64	3.63	2.88

a. Plot a graph of molar concentration of the alkali against time.

b. From the graph, deduce two half lives of the reaction.

c. Deduce the order of the reaction.

d. Calculate the rate constant of the reaction and state its unit.

Task:10.4

At 30^{0}C, benzene diazonium chloride decomposes according to the equation:

$C_6H_5N_2Cl(aq) \longrightarrow C_6H_5Cl(aq) + N_2(g)$

A certain solution of the salt that can produce 160cm^3 of nitrogen on complete decomposition had produced 40cm^3 of nitrogen after 40 minutes. This decomposition is known to be of first order.

a. Determine the half life for the decomposition of benzene diazonium chloride.

b. Calculate the time that will be taken for the salt to produce 115cm^3 of nitrogen.

Task:10.5

For the reaction of A in aqueous phase;

A(aq) ⟶ products

The table below shows the kinetics data for the reaction.

Vol of A/cm^3	3.0	4.0	5.0	6.0	8.0	10.0
Time/seconds	69.0	45.0	35.0	31.0	24.0	18.5

a. plot a graph of $^1/_t$ against volume of A.
b. what is the order of reaction with respect to A?
c. determine the rate constant for the reaction.
d. Write the rate equation for the reaction in terms of molar concentration of A as the only unknown.

Task:10.6

a. Write the equation for the hydrolysis of methyl ethanoate.

In an experiment to determine the rate of hydrolysis of methyl ethanoate, dilute hydrochloric acid was added to the mixture at a constant temperature, and the following results were obtained.

Time/minutes	Fraction of the ester remaining
0	1.00
60	0.65
120	0.43
180	0.28
240	0.19

b. Explain why:

- Dilute hydrochloric acid was added.
- Temperature was kept constant

c. Plot a graph of fraction of ester remaining against time.
d. Measure the gradients of the curve for the following fractions of the ester remaining: 1.0, 0.8, 0.6, 0.4 and 0.2.
e. Plot a graph of the gradients against fractions of the ester remaining.
f. What is the order of the reaction with respect to the ester?

Task:10.7

Below are rate data for the reaction between magnesium ribbon and dilute hydrochloric acid:

Rate/$moldm^{-3}s^{-1}$	[HCl]/M
0.004	0.50
0.011	0.80
0.022	1.10
0.034	1.40

a. Plot a graph of:
- rate against [HCl]
- rate against $[HCl]^2$

b. What is the order of the reaction with respect to hydrochloric acid?

10.5: Experimental determination of order and rate constant of a reaction:

- There are two main methods for determining the order of a reaction with respect to a reactant and hence over all order of the reaction.
- Each method involves setting the reaction in a thermostat or at room temperature; then monitoring the change in concentration of either the reactant or a product.

Continuous experiment method:

- Here, as the reaction proceeds, the variation in concentration of one of the reactants is continuously followed using some method depending on the nature of the reaction:

a. Volumetric analysis; here the reaction mixture after some times is then rapidly cooled by transferring into a large volume of ice–cold water; then titrated with a suitable standard solution.

b. Monitoring pressure changes; suitable for gaseous reactions in which pressure changes. The pressure changes are recorded at some time intervals.
c. Monitoring conductivity changes; for reactions where conductivity changes.

Experimental determination of order of catalysed decomposition of hydrogen peroxide:

- First, $10cm^3$ of the original hydrogen peroxide is titrated with a standard solution of potassium peroxide and its titre volume, V_0 noted.
- $10cm^3$ of hydrogen peroxide is transferred into a conical flask, $1cm^3$ of 1M sodium hydroxide solution is added then as $1cm^3$ of iron (III) chloride (catalyst) solution is added, a stop clock is started.
- The mixture is shaken for five minutes and $10cm^3$ of 1M sulphuric acid added to stop the reaction.
- The mixture is then titrated with a standard potassium manganate solution until end point. The titre volume then noted.
- The above procedure is then repeated five more times, allowing the decomposition to proceed for 10, 15, 20, 25 and 30 minutes respectively.
- Then titre volumes of potassium manganate (VII) are plotted against time.
- To show that the decomposition of hydrogen peroxide is first order, the successive half lives are obtained from the curve, which will be constant.

Task:10.8

Describe an experiment to show that catalytic decomposition of hydrogen peroxide is a first order reaction.

Initial rate method:

- Initial rate is the rate of a reaction when an infinitesimal amount of a reactant is used up.
- This method is suitable for determining of order of a reaction which has many reactants.
- The molar concentrations of all the other reactants are held constant (they are made in large excess) and only concentration of one reactant varied. In this way, the reaction is made to have a **pseudo over all order** with respect to that reactant.
- The initial rate of the reaction is determined with respect to that reactant when the concentrations of the other reactants are constant.
- The order of the reaction with respect to the reactant is deduced from the variation of rate of reaction and the concentration of the reactant.
- The procedure is then repeated for all the other reactants, from which the over all order of the reaction is determined.

Worked example:10.4

Substances A and B react in acidic medium to produce products according to the equation:

$A(aq) + B(aq) + H^+(aq) \longrightarrow$ products

The table below shows some results about the reaction:

[A] $moldm^{-3}$	[B] $moldm^{-3}$	$[H^+]$ $moldm^{-3}$	Initial rate/ $moldm^{-3}s^{-1}$
0.10	0.10	0.10	$8.0x10^{-4}$
0.10	0.20	0.10	$1.6 x10^{-3}$
0.20	0.20	0.10	$3.2 x10^{-3}$
0.10	0.10	0.20	$3.2 x10^{-3}$

a. Deduce the order of the reaction with respect to A, B and hydrogen ions.
b. Determine the rate constant and state its units.

Solution:

a. ***Method 1:***

From the first and second sets of values;

When [A] and [H^+] are constant, but [B] is doubled, the reaction rate is doubled. Hence 1st order with respect to B.

From the 2nd and the 3rd sets of values;

When [A] is doubled, but [B] and [H^+] are kept constant, the rate is doubled. Hence 1st order with respect to A.

From the 1st and 4th sets of values;

When [H^+] is doubled, but that of A and B are kept constant, the rate is multiplied four times. Hence 2nd order with respect to H^+

a. **Method 2**

Let the rate expression be Rate = K $[A]^a[B]^b[H^+]^c$

From the first and second sets of values;

$8.0x10^{-4} = K(0.10)^a(0.10)^b(0.10)^c$ i

$1.6x10^{-3} = K(0.10)^a(0.20)^b(0.10)^c$ ii

Dividing i) by ii):

$$\Rightarrow \frac{1.6x10^{-3}}{8.0x10^{-4}} = \frac{K(0.10)^a(0.20)^b(0.10)^c}{K(0.10)^a(0.10)^b(0.10)^c}$$

$2^1 = 2^b$,hence b = 1.

From the 2nd and the 3rd sets of values;

$1.6x10^{-3} = K(0.10)^a(0.20)^b(0.10)^c$ .....iii)

$3.2x10^{-3} = K(0.20)^a(0.20)^b(0.10)^c$ .....iv)

Dividing iv) by iii):

$$\Rightarrow \frac{3.2x10^{-3}}{1.6x10^{-3}} = \frac{K(0.20)^a(0.20)^b(0.10)^c}{K(0.10)^a(0.20)^b(0.10)^c}$$

$2^1 = 2^a$,hence a = 1.

From the 1st and 4th sets of values;

$8.0x10^{-4} = K(0.10)^a(0.10)^b(0.10)^c$ .....v)

$3.2x10^{-3} = K(0.10)^a(0.10)^b(0.20)^c$ .....vi)

Dividing vi) by v):

$$\Rightarrow \frac{3.2x10^{-3}}{8.0x10^{-4}} = \frac{K(0.10)^a(0.10)^b(0.20)^c}{K(0.10)^a(0.10)^b(0.10)^c}$$

$4 = 2^c$, hence c = 2.

b. The rate equation is Rate = K $[A][B][H^+]^2$

Taking the first set of values;

$\Rightarrow 8.0x10^{-4} = K(0.10)(0.10)(0.10)^2$

$K = 8dm^9mol^{-2}s^{-1}$

Worked example:10.5

In the table below are the results for the hydrolysis of 2–bromo – 2 – methylpropane at 298K using sodium hydroxide solution.

$[(CH_3)_3CBr]$/ $moldm^{-3}$	[NaOH]/ $moldm^{-3}$	Rate/ $moldm^{-3}s^{-1}$
0.400	2.00	0.0080
0.400	1.00	0.0080
0.200	1.00	0.0040
0.100	1.00	0.0020

a. Deduce the order of the reaction with respect to 2 – bromo – 2 – methylpropane and sodium hydroxide solution.

b. Write the rate expression for the reaction.

c. Determine the rate constant and indicate its units.

Solution:

a. ***Method 1:***

From 1st and 2nd sets of values:

When $[(CH_3)_3CBr]$ is constant, [NaOH] is doubled, rate is constant. Hence the rate of reaction is independent of [NaOH]. Zero order w.r.t NaOH.

From the 3rd and the 4th sets of values:

When $[(CH_3)_3CBr]$ is doubled, and that of [NaOH] is kept constant, the rate is halved. Hence rate of the reaction is directly proportional to $[(CH_3)_3CBr]$. Hence 1st order with respect to $(CH_3)_3CBr$.

Method 2:

Let the rate equation be rate $=K[NaOH]^b[(CH_3)_3CBr]^a$

From 1st and 2nd sets of values:

$0.0080 = K(2.00)^a(0.400)^b$ .....i)

$0.0080 = K(1.00)^a(0.400)^b$ .....ii)

Dividing i) by ii):

$$\Rightarrow \frac{0.0080}{0.0080} = \frac{K(2.00)^a(0.400)^b}{K(1.00)^a(0.400)^b}$$

$1 = 2^a$. Hence a = 0.

From the 3rd and the 4th sets of values:

$0.0080 = K(1.00)^a(0.400)^b$ .....iii)

$0.0040 = K(1.00)^a(0.200)^b$ .....iv)

Dividing iii) by iv):

$$\Rightarrow \frac{0.0080}{0.0040} = \frac{K(1.00)^a(0.400)^b}{K(1.00)^a(0.400)^b}$$

$2 = 2^a$. Hence, a = 1.

b. Rate expression is given by: Rate = $[(CH_3)_3CBr]$

c. Taking the first set of values:

$0.0080 = K(0.400)$

$K = 0.02s^{-1}$

Worked example:10.9

In an experiment on the combination of two atoms of A to give A_2 molecule in the gas phase and in the presence of substance Y in the reaction:

$A + A + Y \longrightarrow A_2 + Y$

When concentration of Y is fixed at $1.0x10^{-3}$, the results below were obtained:

[A]/ moldm^{-3}	Rate/ moldm^{-3}s^{-1}
$1.0x10^{-5}$	$8.70x10^{-4}$
$2.0x10^{-5}$	$3.48x10^{-3}$
$4.0x10^{-5}$	$1.39x10^{-2}$

When concentration of A is fixed at $1.0x10^{-5}$, the results below were obtained:

[Y]/ moldm^{-3}	Rate/ moldm^{-3}s^{-1}
$1.0x10^{-2}$	$8.70x10^{-4}$
$5.0x10^{-3}$	$4.35x10^{-3}$
$1.0x10^{-2}$	$8.69x10^{-3}$

a. Determine the order of the reaction with respect to A and Y.

b. Determine the over all order of the reaction.

c. Calculate the rate constant for the formation of A_2.

Task:10.10

The following information was obtained for the reaction between X and Y.

Initial rate/ moldm^{-3}s^{-1}	[X]/ moldm^{-3}	[Y]/ moldm^{-3}
$1.0x10^{-4}$	$1.2x10^{-1}$	$1.2x10^{-1}$
$4.0x10^{-4}$	$2.1x10^{-1}$	$1.2x10^{-1}$
$8.0x10^{-4}$	$2.0x10^{-1}$	$2.4x10^{-1}$

a. What is the order of the reaction with respect to X and Y?

b. Calculate the rate constant for the reaction.

Task:10.11

The table below shows the data obtained for the reaction between A ana B.

Initial rate/ $moldm^{-3}s^{-1}$	[B]/ $moldm^{-3}$	[A]/ $moldm^{-3}$
1.0	0.15	0.15
4.0	0.15	0.30
2.0	0.30	0.15

a. Calculate the order of the reaction with respect to each of the reactants.
b. Write the rate equation for the reaction.
c. Calculate the rate constant for the reaction.

Task:10.12

P and Q react to produce R.

a. Write the rate equation in terms of concentrations of P and Q.
b. What are the reaction orders with respect to P and Q?
c. What is the over all reaction order?

The following experimental data was obtained for the above reaction carried out at a constant temperature.

Initial rate/ $moldm^{-3}s^{-1}$	[P]/ $moldm^{-3}$	[Q]/ $moldm^{-3}$
12.5	1.00	1.00
25.0	2.00	1.00
50.0	1.00	2.00

d. Determine the rate equation for the reaction.
e. Calculate the rate constant for the reaction.

Task:10.13

Mercury (II) chloride reacts with aqueous oxalate ions according to the equation:

$HgCl_2(aq) + C_2O_4^{2-}(aq) \quad 2Cl^-(aq) + 2CO_2(g) + Hg_2Cl_2(s)$

The following kinetics data was obtained for the above reaction:

Initial rate/ $moldm^{-3}s^{-1}$	$[HgCl_2]$/ $moldm^{-3}$	$[C_2O_4^{2-}]$/ $moldm^{-3}$
0.52	0.0836	0.202
2.08	0.0836	0.404
1.06	0.0418	0.404

a. Write down the rate expression for the above reaction.
b. Deduce the order of the reaction with respect to each of the reactants.
c. Calculate the value of the rate constant and state its units.

Task:10.14

The following data was obtained for the reaction between P and Q.

Initial rate/ $moldm^{-3}s^{-1}$	[P]/ $moldm^{-3}$	[Q]/ $moldm^{-3}$
$2.7x10^{-5}$	$3.0 x10^{-2}$	$3.0 x10^{-2}$
$5.4x10^{-5}$	$3.0 x10^{-2}$	$6.0 x10^{-2}$
$10.8x10^{-5}$	$6.0 x10^{-2}$	$3.0 x10^{-2}$
$21.0x10^{-5}$	$6.0 x10^{-2}$	$6.0 x10^{-2}$

a. Write the rate expression for the reaction.
b. Determine the order of the reaction with respect to both P and Q.
c. Calculate the rate constant for the reaction.
d. What happens to the rate of the reaction when [P] is trebled but [Q] is doubled?

10.6: Factors that affect rates of chemical reactions:

1. **Concentration for solutions and pressure for gases:**

- The effect of concentration of a reactant on rate of chemical reaction is stated as the rate law.
- Increase in concentration of the reactant increases the rate of a chemical reaction; while decrease in concentration decreases the rate of a chemical reaction.

- But, why does increase in concentration of reactant increase rate of reaction and decrease in concentration decrease the rate of reaction?

The collision theory of chemical reaction:

- According to this theory, a chemical reaction is looked at as mere collisions between the particles of reactants. As they collide, they then form the product.
- Any factor that increases the frequency of collision of the particles increases the rate of chemical reaction and any factor that decreases the frequency of collision decreases the rate of chemical reaction.
- Increase in concentration means many particles per unit volume. This increases the frequency of collision of the randomly moving particles hence faster reaction. Decrease in concentration means fewer particles per unit volume. This reduces the frequency of collision of the randomly moving particles and hence slower rate of reaction.
- However, experiments on reaction between hydrogen and iodine to produce hydrogen iodide have shown that frequency of collision is often far too high to account for the observed rate.

a. Not all collisions result into a reaction. More often, some molecules collide and rebound like two tennis balls. So only a small fraction of collisions actually result into a chemical reaction.

b. The reaction involves breaking of bonds between hydrogen atoms on one hand and the iodine atoms on the other. So only if two molecules collide with enough energy are the bonds broken and new ones formed. Hence the molecules need to have activation energy – ref the transition state theory, in chapter six.

2. **Temperature:**

- Increase in temperature increases the frequency of collisions of the particles and the proportion of the particles with the required activation energy and hence the rate of the reaction increases. On average, the rate of reaction doubles per 10K rise in temperature.
- Increase in temperature also increases the value of rate constant. According to Arrhenius, the rate constant, K and Kelvin temperature, T are related by the equation:

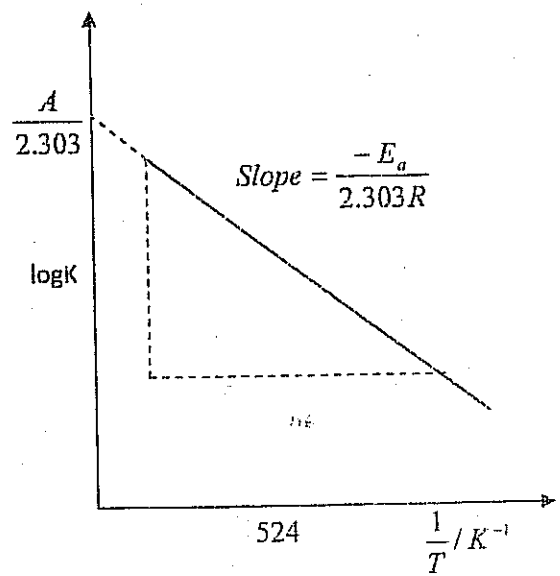
$InK = \frac{-E_a}{RT} + A$ A is Arrhenius constant and R is gas constant and E_a is the activation energy for the reaction.

Converting natural log to $\log_{10}$;

$$\Rightarrow 2.303 \log K = \frac{-E_a}{RT} + A$$

$$\log K = \frac{-E_a}{2.303RT} + \frac{A}{2.303} \quad \text{.....10.12}$$

Graph of logK against $\frac{1}{T}$:



- The activation energy E_a can be calculated if the rate constants K_1 and K_2 at two temperatures T_1 and T_2 are known.

At T_1

$$\log K_1 = \frac{-E_a}{2.303RT_1} + \frac{A}{2.303} \quad \text{.....10.13}$$

At T_2,

$$\log K_2 = \frac{-E_a}{2.303RT_2} + \frac{A}{2.303} \quad \text{.....10.14}$$

Subtracting equation 10.14 from equation 10.13;

$$\log K_1 - \log K_2 = \left(\frac{-E_a}{2.303RT_1} + \frac{A}{2.303}\right) - \left(\frac{-E_a}{2.303RT_2} + \frac{A}{2.303}\right)$$

$$\log \frac{K_1}{K_2} = \frac{E_a}{2.303RT_2} - \frac{E_a}{2.303RT_1}$$

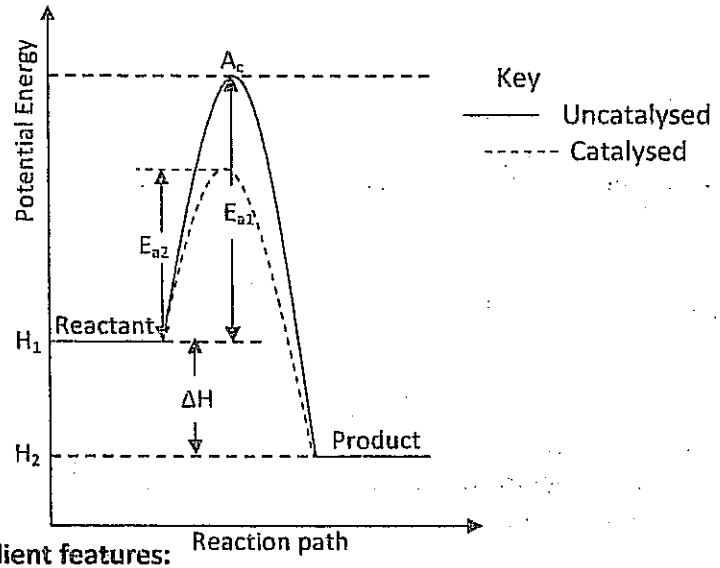
$$\therefore \log \frac{K_1}{K_2} = \frac{E_a}{2.303R}\left\{\frac{1}{T_2} - \frac{1}{T_1}\right\} \quad \text{.....10.15}$$

3. **catalyst:**

- Catalysis is change of rate of chemical reactions brought by a substance called a catalyst, which remains qualitatively and quantitatively unchanged.
- A catalyst is therefore a substance that alters the rate of a chemical reaction and remains qualitatively and quantitatively unchanged.
- In catalysis, a catalyst provides an alternative pathway of different activation energy from that without a catalyst.
- Those catalysts that alter reaction mechanisms by providing pathways of lower activation energies speed up reaction rates and are called **positive catalysts.**

- Those catalysts that alter reaction mechanisms by providing pathways of higher activation energies slow down reaction rates and are called **negative catalysts.**

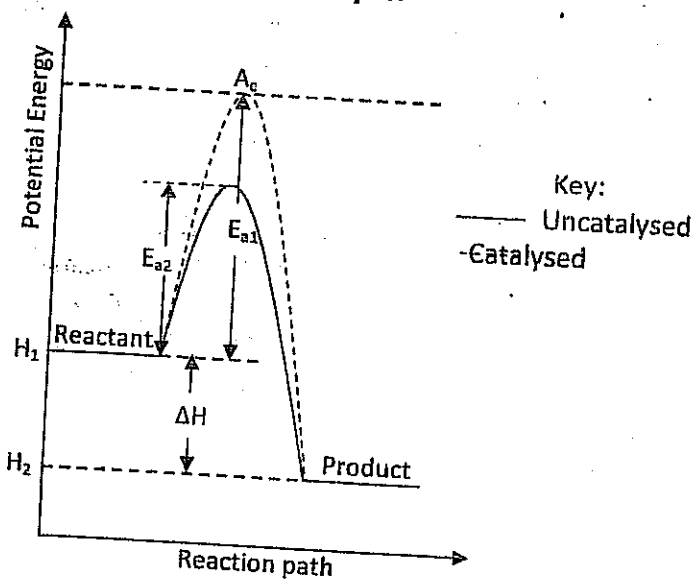
Energy profile for positive catalysis:



Salient features:

- Activation energy for the uncatalysed path is higher than the activation energy for the catalysed path.
- Energy contents of the reactant and the product have remained the same.
- The enthalpy change for the reaction not changed.
- The position of the equilibrium incase of a reversible reaction not disturbed.
- Also for reversible reactions, K_p or K_c is not affected.

Energy profile for negative catalysis:



Salient features:

- Activation energy for the uncatalysed path is lower than the activation energy for the catalysed path.
- Energy contents of the reactant and the product have remained the same.
- The enthalpy change for the reaction not changed.
- The position of the equilibrium incase of a reversible reaction not disturbed.
- Also for reversible reactions, K_p or K_c is not affected.

4. Surface area:

- Surface area only affects rates of reactions in the solid state. Increase in surface area exposes many particles to collide. This increases the frequency of collision, hence faster reaction.

- Decrease in surface area decreases the frequency of collisions as only a few particles are exposed, hence slows down the rate of reaction.
- Surface area is always increased by grinding the lump of solid into fine powder.

Worked example:10.6

For the reaction; A + B ⟶ product

a. Write the rate expression for the above reaction.

If the over all order for the reaction is two; 1st with respect to both A and B; explain what happens to the rate of the reaction when:

b. [A] is doubled, while that of [B] is kept constant.

c. [B] is trebled, while that of [A] is kept constant.

Solution:

a. Rate = $[A]^a[B]^b$

b. New rate = 2x[A][B].
New rate = 2x old rate.
Hence the rate doubles.

c. New rate = 3x[A][B].
New rate = 3x old rate.
Hence the rate trebles.

Worked example:10.7

The rate expression for the reaction between X and Y is given by:

Rate = $K[X][Y]^2$

Explain what happens to the rate of the reaction when:

a. [X] is kept constant, but that Y is doubled.

b. Both [X] and [Y] are doubled.

c. The temperature of the reaction mixture is reduced.

Solution:

a. New rate = $K[X](2[Y])^2$
New rate = $4K[X][Y]^2$
New rate = 4 x old rate.
Hence the rate is multiplied four times.

b. New rate = $K(2[X])(2[Y])^2$
New rate = $8K[X][Y]^2$
New rate = 8 x old rate
Hence the rate is multiplied eight times.

c. The rate of the reaction would reduce since only a small proportion of the reactants particles would have just the activation energy.

Worked example:10.8

The rate constant for a certain reaction determined at 298K was found to have increased by a factor of eight at 310K and a further factor of eight at 321K. Determine the activation energy of the reaction.

Solution:

Let the rate constant at 298K be K
T_1=310K
K_1=8K
T_2=321K
K_2=64K

From $\log\frac{K_1}{K_2} = \frac{E_a}{2.303R}\left\{\frac{1}{T_2} - \frac{1}{T_1}\right\}$

$$\Rightarrow \log\frac{8K}{64K} = \frac{E_a}{2.303 \times 8.414}\left\{\frac{1}{321} - \frac{1}{310}\right\}$$

$$E_a = \frac{-17.29}{-0.0032} = 5360$$

Hence the activation energy is 5,360Jmol^{-1}

Task:10.15

The rate equation for a reaction is given by:
Rate = $K[A]^2[B]$
Explain what happens to the rate of the reaction when:

a. The temperature is increased.
b. The temperature is reduced.
c. A negative catalyst is added.
d. A positive catalyst is added.
e. A catalyst is added.
f. The molar concentration of A is halved and that of B is kept constant.
g. The molar concentration of A is doubled and that of B is kept constant.
h. The molar concentrations of both A and B are doubled.
i. The molar concentration of B is doubled, but that of A is kept constant.

Task:10.16

The following data was obtained at 1400K for the reaction below:

$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

Initial pressure of ammonia/atm	35.3	17.3	7.73
Half life of the reaction/seconds	456	222	100

a. Deduce the order of the reaction and hence write the rate expression for the reaction.
b. Calculate the rate constant for decomposition of ammonia, and state its units.

What happens to the following when the above reaction is repeated at 2000K? Give a brief explanation.

c. Equilibrium constant.
d. Rate constant.

e. Total pressure of the system.

Task:10.17

The rate equation for a reaction is given by:
Rate = K [A] $[B]^2$

What happens to the rate of the reaction if:

a. [A] is multiplied four times, [B] is kept constant.
b. [B] is trebled, [A] is kept constant.
c. Calculate the first and second half lives of B if its initial concentration is 0.001M and the rate constant is $1mol^2dm^{-6}$.

Task:10.18

The table below shows the different values of the rate constant, K for the decomposition of hydrogen iodide at different temperatures, θ:

θ/^{0}C	405	454	488	543	582
K x10^{-5}/$dm^3mol^{-1}s^{-1}$	4.23	43.07	177.80	1432.00	5012.00

a. Plot a suitable graph and use it to determine the activation energy for the decomposition of hydrogen iodide (R=8.3$Jmol^{-1}K^{-1}$)
b. What happens to the activation energy if a positive catalyst is added to the reaction mixture?

Task:10.19

The following data are for the decomposition of dinitrogen pentoxide:

Rate constant/ $dm^3mol^{-1}s^{-1}$	0.00049	0.002	0.03	0.3
Temperature/^{0}C	17	27	47	67

a. Plot a graph of $\log_{10}K$ against $\frac{1}{T}$.
b. Use the graph to determine the activation energy. R=8.3$Jmol^{-1}K^{-1}$

Appendix 1: Answers to numerical tasks:

Chapter one

Task:1.1 228.8m^3
Task:1.2a)i. 22.18dm^3 ii. 24.04dm^3 b) i. 25.43dm^3 ii. 19.79dm^3 iii. 17.73dm^3
Task:1.3 i. 8.39 ii. 0.082
Task:1.4 0.023
Task:1.5 0.22
Task:1.6N_2=0.78,O_2=0.21, CO_2=0.03, noble gases =0.97
Task:1.7CO_2=304mmHg, N_2=76mmHg,CO=152mmHg, C_3H_8=228mmHg
Task:1.8,Cl_2=141mmHg, N_2=707mmHg, O_2=7mmHg
Task:1.9 1334cm^3
Task:1.10a)N_2=7.6x10^4Nm^{-2}, H_2=4.0x110^4Nm^{-2} b) 1.16x10^5Nm^{-2}
Task:1.11CO_2=4.2x104Nm^{-2}, N_2=4.0x104Nm^{-2}, O_2=1.05x104Nm^{-2}, C_3H_8=3.15x104Nm^{-2} b) the same.
Task:1.12 92
Task:1.13 Nitrogen dioxide
Task:1.14 50cm
Task:1.15 44
Task:1.16 a) 2 b) C_2H_7N
Task:1.17 6.9minutes
Task:1.18 a) Chlorine–35, Chlorine–37 b) Chlorine–37
Task:1.19 35.49
Task:1.20 63.3
Task:1.21 A for M^{3+} B for M^{2+} and C for M^+
Task:1.22 a) A for Gallium – 69, B for Gallium – 70 b) 69.4
Task:1.24 a) X–10=20% and X–11=80% b) X–10=0.2, X–11=0.8
Task:1.25 a) 80
158 due to two Br–79 in a molecule (Br_2)
160 due to one Br–79 and one Br–81 in a molecule (Br_2)
162 due to two Br–81 in a molecule (Br_2)
Task:1.26 i. C_3H_8 ii) Propane
Task:1.27i. C_4H_{10}
ii. $CH_3CH_2CH_2CH_3$–butane, $CH_3CH(CH_3)CH_3$–2–methylpropane,iii.2--methyl propane.
Task:1.28 C_3H_8
Task:1.29 C_4H_{10}
Task:1.30i.C_4H_8iii.Methyl–cyclopropane and cyclobutane.

Chapter two

Task:2.1 i)9.1x10^{-8}m ii) 3.6x10^{-7}m iii) 8.2x10^{-7}m iv) 9.3x10^{-7}m v) 3.9x10^{-7}m vi) 9.5x10^{-7}m
Task:2.2 i)82$kJmol^{-1}$ ii) 53$kJmol^{-1}$ iii)13$kJmol^{-1}$ iv)6.8$kJmol^{-1}$ v)131 $Jmol^{-1}$ vi)13$Jmol^{-1}$
Task:2.3 i)5x10^{38}Hz ii)8. 5x10^{39}Hz iii)8.6x10^{39}Hz iv)8.9x10^{39}Hz v) 9.4x10^{39}Hz

Task:2.8 a)$3.2x10^{-2}min^{-1}$ b)21.5min c) $3.2x10^{-2}min^{-1}$, 21.5min

Chapter four

Task:4.1 72,
Task:4.2 1.44g
Task:4.3 72,
Task:4.4 i. 3170 iii. 72
Task:4.5 1.04g,
Task:4.6 14
Task:4.7b)i.0.5^{0}Cii.0.2atm iii. 1.03g
Task:4.8 800,
Task:4.9 c) i. 365,
Task:4.10 0.08g,
Task:4.11 39.9^{0}C/mole/1000g of camphor,
Task:4.12a)3.33Kg b) 1.72Kg, 2.47Kg, 5Kg c) 19.4^{0}C, 13.4^{0}C 6.66^{0}C,
Task:4.13 d) 0.117^{0}C,
Task:4.14 b) 4.5^{0}C, 0.5^{0}C c) 5^{0}C/mole/1000g of benzene
Task:4.16 0.06g
Task:4.17 600,
Task:4.18 75g
Task:4.19 a) ≈252 b) 420
Task:4.20b)≈890
Task:4.22 i. ≈76,000 ii. 1000 monomers long.
Task:4.23 a) i.–0.186^{0}C, ii.–0.186^{0}C b) –7.44^{0}C,
Task:4.24 122, 242
Task:4.25≈252,
Task:4.26 ≈128Nm^{-2}

Chapter five

Task:5.2 +88.2 $kJmol^{-1}$
Task:5.3 – 86.8$kJmol^{-1}$,–121.7 $kJmol^{-1}$
Task:5.4 a) –3909.8$kJmol^{-1}$ b)–3872.1 $kJmol^{-1}$
Task:5.5 +54.6 $kJmol^{-1}$, +232.5 $kJmol^{-1}$
Task:5.6 +836.2 $kJmol^{-1}$, – 836.2 $kJmol^{-1}$ (reaction a) is not feasible)
Task:5.7 b)–55 $kJmol^{-1}$
Task:5.8 –1714.5 $kJmol^{-1}$
Task:5.9 rhombic
Task:5.10–787 $kJmol^{-1}$
Task:5.11 a)–3916 $kJmol^{-1}$, b) –4587.6 $kJmol^{-1}$, c)–2621.1 $kJmol^{-1}$, d)–5964.6 $kJmol^{-1}$, e)–1202.7 $kJmol^{-1}$
Task:5.14 b)–120 $kJmol^{-1}$, –206 $kJmol^{-1}$
Task:5.15 d) –90.72$kJmol^{-1}$
Task:5.16 b) 23, c)–84 $kJmol^{-1}$
Task:5.17b) 0.2mol, 5M c)0.2mol, 5M
Task:5.18–50.76 $kJmol^{-1}$
Task:5.20 c)–948 $kJmol^{-1}$
Task:5.21 b)–105 $kJmol^{-1}$
Task:5.25 $Mg(OH)_2$=+914 $kJmol^{-1}$, $Ca(OH)_2$=+868 $kJmol^{-1}$
Task:5.26 b)–58.8 $kJmol^{-1}$
Task:5.30 a) –616$kJmol^{-1}$
Task:5.31–374 $kJmol^{-1}$

Chapter six

Task:6.1 c) At 350^{0}C=2g, at 225^{0}C=18.5g
Task:6.3 a) $P_W^0 = 161.8Nm^{-2}$, $P_M^0 = 6.493Nm^{-2}$ b) $Y_W = 0.09$ $Y_M = 0.89$
c) $X_M = 0.11, X_W = 0.89$
Task:6.6
a) $P_B^0 = 308mmHg$, $P_A^0 = 358mmHg$
b) $P_A = 107.4mmHg$, $P_B = 215.6mmHg$
c) $P_A = 107.4mmHg$, $P_B = 215.6mmHg$
Task:6.7iii.≈3distillations iv. ≈103cm^3
Task:6.11 ≈500
Task:6.12 $P_W^0 = 98.8kPa$ $P_{CB}^0 = 2.2kPa$
Task:6.13 c) i. 79^{0}C ii. 94^{0}C d) i. 74.48^{0}C ii. 70.34g
Task:6.14 a) i. 0.001M ii. 0.052M b) i. 0.019 ii. 52
Task:6.15 a) i. 0.56 ii. 1.78
Task:6.16 i. 8.9 ii. 2
Task:6.17a)19.96587g b) 19.99997g
Task;6.18 i). 0.11 ii. 9.47g
Task:6.19 a) 9.8g b) 8.88g
Task:6.20 a) 4 b) ≈25
Task:6.21 a) 0.0026M b) 0.065M c) 0.068M d) 0.003M e) 133
Task:6.22 i. 0.105 ii. $1.8x10^{-1}$M iii. $4.4x10^{-3}$M iv. 82$mol^{-1}dm^3$
Task:6.23 1.987g
Task:6.24 12.5 or 0.08
Task:6.25 a) 0.1M b) 4
Task:6.26 iii. 636.7 $mol^{-1}dm^3$

Chapter seven

Task:7.1 a) $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$ unit $moldm^{-3}$
b) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$, unit $mol^{-1}dm^3$
c) $K = \frac{[NO]^2}{[N_2]^2[O_2]}$, no unit.
Task:7.3 a) $p_{H_2} = 1atm$, $p_{I_2} = 1atm$, $p_{HI} = 8atm$
b) K_p=64
Task:7.4 $H_2 = 1.9mol$, $I_2 = 2mol$, $HI = 0.2mol$
Task:7.5 b)0.08mol, c) 0.42mol, d) 0.58mol, e) 3.8
Task:7.6 a)4, b)99.4g
Task:7.7 a)0.90mol, b)0.85mol, c)0.14mol
Task:7.8 a)50, b)I_2=0.11mol, H_2=0.11mol, HI=0.78mol
Task:7.9 0.67

Task:7.10 0.84mol
7.11 60
Task:7.12 a)72.34, b)3.0cm^3
Task:3.13 $K_p=K_cRT$, $Kp=K_c(RT)^{-1}$
Task:7.14: a)$K_p=K_c(RT)^{-2}$, b)CO=0.85mol, H_2=1.85mol, CH_3OH=0.15mol, c) $K = 1.6x10^{-8} N^{-2}m^4$ $K_c = 9.5x10^{-2} mol^{-2}$, d)2.1kNm^{-2}
7.16 2.89x10^{-17}

Chapter eight

Task:8.1 c) $2.56x10^{-6} mol^3dm^{-9}$
Task:8.2 c) $1.42x10^{-6} mol^3dm^{-9}$
Task:8.3 c) $3.0x10^{-12} mol^3dm^{-9}$
Task:8.4 c) $4.1x10^{-11} mol^3dm^{-9}$
Task:8.5 b) $2.1x10^{-15} mol^3dm^{-9}$
Task:8.6 $8.8x10^{-7} moldm^{-3}$
Task:8.7 $1.3x10^{-10}$/100g of water
Task:8.8 c)0.0029g/100g of water
Task:8.9 a) $7.1x10^{-5} moldm^{-3}$ b) $1.0x10^{-7} moldm^{-3}$
Task:8.10 b) $1.0x10^{-8} moldm^{-3}$ d) $9.3x10^{-11} moldm^{-11}$
Task:8.11 a) $5.5x10^{-6} moldm^{-3}$ b) 27 times
Task:8.12 10.90%
Task:8.13 $3.0x10^{-6} g$ /1000g of water
Task:8.16 a) $4.0x10^{-3} moldm^{-3}$ b) $1.5x10^{-2} moldm^{-3}$ c) $6.0x10^{-6} moldm^{-3}$
Task:8.17 $3.2x10^{-3} moldm^{-3}$
Task:8.18 a) $3.5x10^{-4} moldm^{-3}$ b)5.0% c) $1.75x10^{-5} moldm^{-3}$
Task:8.19 c)13.5%
Task:8.20 a)6.6%
Task:8.21 a)10. b)$1.6x10^{-5} moldm^{-3}$
Task:8.22 b $3.17x10^{-10} moldm^{-3}$ c) $3.15x10^{-5} moldm^{-3}$
Task:8.23 b) $6.3x10^{-10} moldm^{-3}$
Task:8.24 b) $2.2x10^{-4}$ c)18.7cm^3
Task:8.25 b) 5.4 c) $2.4x10^{-5}$
Task:8.26 3.89
Task:8.27 a)4.80
Task:8.28 3.18
Task:8.29 a)5.33 b)0.3 c) 5.33
Task:8.30 22.5cm^3
Task:8.31 4.66
Task:8.32 b)0.35M
Task:8.33 0.034g
Task:8.34 a)8.96 b)9.26
Task:8.35 4.12
Task:8.36 1.54
Task:8.37 pH=8, v=15cm^3
Task:8.38 c)0.16M d)methyl orange e)0.06M, $8.35x10^{-11} moldm^{-3}$

Chapter nine

Task:9.3 a) 6.4g b) 4480cm^3
Task:9.5 b)1.07Ω^{-1}m^{-1}
Task:9.6 a) 147.8Scm^{2}mol^{-1}

b)740 Scm^{2}mol^{-1}
Task:9.9 b)
$\Lambda_\infty^{MgCl_2} = 258.9 Scm^2mol^{-1}$
$\Lambda_\infty^{Al(NO_3)_3} = 403.2 Scm^2mol^{-1}$
$\Lambda_\infty^{Na_2C_2O_4} = 248.6 Scm^2mol^{-1}$
$\Lambda_\infty^{CuSO_4} = 266.8 Scm^2mol^{-1}$
Task:9.10
a) $114 Scm^2mol^{-1}$
b) $390 Scm^2mol^{-1}$
Task:9.11 b) 20.7m^{-1}
Task:9.12 b) $389.5 Scm^2mol^{-1}$
Task:9.13
$\Lambda_\infty^{KCl} = 132 Scm^2mol^{-1}$
$\Lambda_\infty^{CH_3COOK} = 101 Scm^2mol^{-1}$
$\Lambda_\infty^{HCl} = 377 Scm^2mol^{-1}$
$\Lambda_\infty^{CH_3COOH} = 346 Scm^2mol^{-1}$
Task:9.14 0.0188g/100g of water, $1.71x10^{-6} mol^2dm^{-6}$
Task:9.15
a) $138.3 Scm^2mol^{-1}$
b) 0.019g/100g of water, $1.75x10^{-6} mol^2dm^{-6}$
Task:9.16 b) $\Lambda_c = 12 Scm^2mol^{-1}$

A=3%, pH=3.3
Task:9.17 c)–207,282J
Task:9.18 c) –576,684J
Task:9.19 b) –21230J
Task:9.23
Best oxidizing–Zn
Best reducing–MnO_4^-

Chapter ten

Task:10.1 b) 1st order c)0.304hr^{-1}, 2.3hr
Task:10.2 b) 1st order c)0.06min^{-1}
Task:10.3 b) generally increases as initial concentration decreases c) 2nd order, d) $1.9x10^{-4} mol^{-2}dm^6s^{-1}$
Task:10.4 a)20min, b)241mins
Task:10.5 b)1st c) $5.0x10^{-3} s^{-1}$ d) $Rate = 5.0x10^{-3}[A]$
Task:10.6 b) $2.7x10^{-1} atms^{-1}$ c) $2.3x10^{-4} atms^{-1}$
Task:10.7 b)2nd

Task:10.9 a)A 2nd ,Y 1st b)3 c) $8.7x10^{10} mol^{-3}dm^9$
Task:10.10 a) Y 1st X 2nd b) $8.3x10^{-2} mol^{-3}dm^9s^{-1}$
Task:10.11 a) A 2nd B 1st b) $Rate = K[A]^2[B]$ c) $2.96x10^2 mol^{-3}dm^9s^{-1}$
Task:10.12 e) $1.25x10 mol^{-3}dm^9s^{-1}$
Task:10.13 b)$HgCL_2$=1, oxalate ion=2, c) $1.55x10 mol^{-3}dm^9s^{-1}$
Task:10.14 b) P 2nd, Q 1st, c) $1 mol^{-3}dm^9s^{-1}$ d) multiplies 18 times.

Task:10.16 a: zero, Rate=K$[NH_3]^0$
or Rate=K b) $3.9x10^{-2}s^{-1}$
Task:10.17a) multiplies 4 times
b) multiplies 4 times
c)1000s, 2000s
Task:10.18 a)+150kJmol^{-1}
b) reduces
Task:10.19 a)+60kJmol^{-1}

Appendix 2: My graphs:

- A graph is made of two variables on a pair of axes: the y – axis or vertical axis and the x – axis or the horizontal axis.
- On the horizontal axis, the values of independent variable – the variable that causes effect on the values of vertical axis variables are plotted.
- On the vertical axis, the values of dependent variable – the variable whose values are obtained as a result of variation in the values of independent variable are plotted.

a. *Plotting a graph:*

- A good graph should:
- Have a precise title describing what have been plotted.
- Axes well labeled with the correct variables and their units indicated.
- Occupy at least three quarters of the page.
- Have points correctly plotted and clearly marked.
- Have proper joining of the points – a straight line or a curve, hence the correct shape.

b. *Describing and explaining a plotted or sketched graph:*

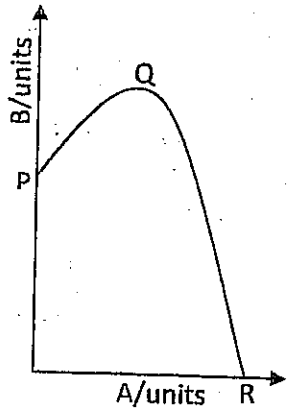
- To describe a graph is answer the question "how is the dependent variable affected by the independent variable?" Just mention the naked facts without accounting for the observation.
- When describing a graph;

i. Define the starting point i.e what does it represent?
ii. Mention what has happened to the independent variable i.e increased or decreased. Then state its effect on the dependent variable i.e increased, decreased or remained constant
iii. Define the last point i.e what does it represent?

- To explain a graph is to answer the question "why the dependent variable affected by the independent variable.

- This therefore calls for accounting for the changes caused on the vertical axis variable by horizontal axis variable. It entails theoretical knowledge about the variables plotted.
- Describing a graph majorly deals with the portion of a graph, although in some cases, a point has to be explained with respect to other similar ones.
- The following are the areas in a graph where important pieces of information are obtained, and when describing and/or explaining a graph, they need to be touched.
- The intercepts of the axes.
- The slope/gradient of the graph.
- Unique points on the graph – maximum, minimum or inflexion.
- Area swept by the graph, though not common in chemistry.

Model example – describe and explain the graph below.



- Steps:

1. Identify the variables of the graph.
2. Study the shape of the graph and identify and label by letters, the unique points of the graph.
3. Then describe and/or explain the shape of the graph.

- Description:

- "B" has a value of "P" when "A" is zero; as "A" increases, "B" also increases from "P" to "Q": at "Q", "B" has a maximum value. Beyond "Q", as "A" increases, "B" decreases up to point "R" where "B" has a value of zero.

❖ If this was a plotted graph, then the values of "B" at "P" and "Q" must be read from the graph and stated in the description. As well, the values of "A" at "Q" and "R".

- Explaining the shape: here, you answer the following questions;
- Why does "B" have a value of "P" when "A" is zero?
- Why does value of "B" increase with increase in value of "A" along PQ
- Why does "B" have a maximum value at "Q"?
- Why does the value of "B" decrease with increase in values of "A" along PQ
- Why does "B" have a value of zero at "R"?

Appendix 3: Systems:

- A system is that part of material world under investigation. The material world can be:
- A test tube containing a chemical
- An egg
- A fume cup board
- A class room
- Atmosphere
- The whole world
- A system is always made of components or part which are inter – connected or involved in a simple or an intricate interplay.
- A case of a test tube containing iron filings displacing copper (II) ions in solution is made up of;
- The test tube demarcating the system
- Unreacted iron filings
- Undisplaced copper (II) ions
- Iron (II) ions.
- Displaced copper (copper metal)
- Water, the solvent

Types of systems:

a. Open system – a system that allows matter and energy to enter and leave freely. Examples include;
- An open bottle of sodium hydroxide solution
- A lake

b. Closed system – a system that does not allow matter to enter or leave, but does allow free interchange of energy. Examples include;
- A closed beaker of water
- A closed bottle of sulphuric acid

c. Isolated system – a system that does not allow matter and energy to enter or leave. This system is ideal – no such exist!

Appendix 4: The origin of science and technology – a perspective:

- Right from the earliest ancient era, the two terms – science and technology have existed. However, the two terms have been and are still being used interchangeably by the illiterates and the literates, both at homes and schools.
- Worst of all, even the students offering science subjects do not clearly know what they are studying – the science. Most of them seem to know the bundled science into subjects like; Physics, Chemistry and Biology. A few is concerned about what the science is and what this "thing" called science originates from.
- Not in prejudice of the ambiguity of the two terms, science and technology can be defined as follows:

❖ Science is the study of systematized information obtained through particular methods and is reproducible.

❖ Technology is the application of systematized information in order to improve on the life of man kind.

- Systematization of information begins from observation. To observe is to detect by the five senses of a perfect person – the sense of sight, hearing, taste, smell and touch.
- After an observation, a spontaneous curiosity of what is the general feature or behavior of the observation. The observer then tries to summarise the observation into a law. A law can be quantitative or qualitative.
- A quantitative law is made of two parts – two quantities/variables which are related and the conditions under which the law is valid (conditions of validity). A qualitative law summarizes the general attributes of a given fact or object.
- Closely to that, a second lust to know more is invoked. Here, one tries to come out with an explanation of what is behind

the observation. As one tries to coin an explanation for an observation, s/he first comes out with an attempt which is tentative known as hypothesis.

- The hypothesis is then tested for validity under certain conditions. If it fails to always account for the observation, then it is rejected, and curiosity continued. Should it account for such an observation consistently, then it turns into a theory.
- A collection of laws and theories on given related observations gives facts.
- A collection of observations, laws, hypotheses, theories and facts is what is called science; and when this collection is assembled into a physical gadget usable by man, it is then called technology.

The dissociation constant of benzene carboxylic acid is 6.7×10^{-5} mol dm^{-3} what is the conc of solution in mol dm^{-3} in which benzene carboxylic acid is (a). 20%

(b) 25% ionised.