

Table of Contents

AN INTRODUCTION TO PHYSICAL CHEMISTRY	3
TOPIC ONE: MATTER.....	4
RELATIVE MOLECULAR OF GASES	22
TOPIC TWO; THE ATOMIC STRUCTURE	30
Discovery of some particles of an atom.....	31
Isotopes.....	35
RADIOACTIVITY	38
Electronic structure of an atom	50
TOPIC THREE: Bonding and structure	55
3.0 interatomic bonds.....	55
3.2 Types of bonds.....	55
POLARISATION AND ITS EFFECTS ON IONIC AND COVALENT BONDS.....	58
INTERMOLECULAR FORCES OF ATTRACTION.....	62
The shapes of molecules and ions	67
TOPIC 4 : THERMOCHEMISTRY	72
Laws of thermo chemistry	81
STANDARD ENTHALPY OF NEUTRALIZATION.....	87
Lattice energy.....	94
Enthalpy changes when ionic compounds dissolve in water.....	102
BOND ENTHALPY or BOND ENERGY.....	105
Topic 5: Physical equilibrium	112
System, phase and component	112
One component system.....	113
TWO COMPONENT SYSTEM	120
Mixtures of two liquids	120
COMPLETELY MISCIBLE LIQUIDS	120
IMMISCIBLE LIQUIDS.....	139
Steam distillation	141
THREE COMPONENT SYSTEMS.	148

a)THE SOLVENT EXTRACTION	154
SOLID-LIQUID EQUILIBRIUM	166
SUB-TOPIC3 :COLLIGATIVE PROPERTIES OF SOLUTION	180
TOPIC6: CHEMICAL EQUILIBRIUM:	201
CHAPTER SEVEN; IONIC EQUILIBRIA	219
Terms used in ionic equilibria	219
Acid-Base theory	219
IONIZATION OF WATER	229
THE HYDROGEN ION INDEX pH	230
BUFFER SOLUTIONS	234
SALT HYDROLYSIS	244
ACID- BASE INDICATORS	249
SOLUBILITY AND SOLUBILITY PRODUCTS	260
TOPIC 8:CHEMICAL KINETICS.....	271
Measuring reaction rate	274
RATE EQUATION OR RATE LAW	275
TYPES OF ORDER OF REACTION	277
REACTION MECHANISMS.....	288
THEORIES RESPONSIBLE FOR OCCURANCE OF CHEMICAL REACTIONS.....	289
Factors which influence rates of reaction.....	291
EXPERIMENTAL DETERMINATION OF ORDER OF REACTION	297
TOPIC 9: ELECTRO CHEMISTRY.....	301
SUB-TOPIC1 :ELECTROLYSIS	301
SUB-TOPIC 2: ELECTROLYTIC CONDUCTION	308
SUB-TOPIC 3 ELECTROLCHEMICAL CELLS.....	322

AN INTRODUCTION TO PHYSICAL CHEMISTRY

Chemistry is the study of the elements and the compound formed when they bond with each other.

There are three main objectives in studying chemistry, these are:

- To discover as much as we can about the behaviour of different kinds of matter.
- To find out the reasons for this behaviour and so obtain a deeper understanding of nature
- To put the knowledge gained to practical use

The subject is subdivided into three main branches: physical chemistry, inorganic chemistry and organic chemistry.

Inorganic chemistry is concerned with describing the properties and reactions of all elements and compound other than those of carbon

Organic chemistry is concerned with chemistry of carbon compounds

Physical chemistry is concerned with how the chemical structure of a substance affects its properties

It attempts to discover general patterns in the behaviour of matter, summarizes these patterns in the form of laws, and then tries to explain them by means of theories.

Laws. A law is a statement which summarizes some general features of substances or their behaviour.

Theories. A scientific theory is a well-substantiated explanation of some aspect of the natural world based on a body of facts that have been repeatedly confirmed through observations and experiments.

TOPIC ONE: MATTER

1.0 Particulate nature of matter

The entire universe is made up of two things **matter** and **energy**.

Matter can be simply described as anything which has mass and occupies space.

Space is that which is occupied by matter

All matter is particulate in nature this basically means that between separate bits of matter there are spaces which contains no matter. This suggests that matter is not continuous and indivisible in space.

Matter is made up of tiny particles held together by bonds that can be seen and felt around us.

Common substances such as clothing buildings, pieces of furniture, food our bodies, metals and non-metals plants animals, air, water are all made up of tinny particles

Matter can be classified into elements, compounds and mixtures each class exists in three states namely solid, liquid and gas .in all these classes and states matter is made up of three basic particles atoms, molecules and ions which are the building blocks or units of matter.

1.1 Atoms, molecules and ions

The three basic particles which make matter are atoms, molecules and ions these are the building block or units of matter.

An atom is the smallest invisible electrically neutral particle of an element that can take part in a chemical reaction.

A molecule is a group of two or more atoms chemically combined. Its the smallest, stable particle of an element or compound that exists by its self.

A n ion is an electrically charged particle formed from an atom or group of chemically combined atoms, by loss or gain of one or more electrons.

1.2 evidence of particle in matter

1.21 Brownian motion

Brownian motion provides a strong evidence for presence of moving particles. The motion of liquid molecules was studied by Robert Brown who examined a suspension of pollen grain in water under a microscope. The grains were observed to move in a random pattern over small distances. this random movement called Brownian motion was found to occur in many other liquids besides water and is evidence that molecules of pollen grains were constantly bombarded by the mobile liquid molecules.

Brownian motion in gases can be demonstrated by viewing a suspension of smoke particles in small glass cell through a microscope while the cell is illuminated by a beam of light. The smoke particles of a gas are constantly in motion in all directions with different speed. This is because they are constantly bombarded by air molecules which are mobile

1.22 Diffusion

is the random movement of particles to fill the available space and spread evenly.

Is the movement of fluid molecules from a region where they are highly concentrated to a region where their concentration is low.

For gaseous molecules diffusion is spreading of gases from a region of high pressure to a region of low pressure.

For gasses, diffusion takes place in all directions. The lighter the gas the faster the rate of diffusion eg ammonia diffuses faster than hydrogen chloride because ammonia is lighter.

The diffusion of gasses is demonstrated by graham's law of diffusion

1.80 The kinetic theory of matter

The theory explains the behavior of matter and their physical properties in terms of movement of its constituent particles.

The main points of the theory are:

- All matter is made up of tiny moving particles invisible to the naked eye.
- Different substances have different types of particles (atoms, molecules or ions) which have different sizes.
- The particles move all the time, the higher the temperature the faster they move on average.
- Heavier particles move slowly than lighter ones at a given temperature.

Physical state of matter

State of matter: solid, liquid and gas

The conditions of temperature and pressure determine the state of matter. Matter can be thought of as made of particles which are affected by heat and pressure.

Properties of the states of matter

solid

- At a given temperature solids has a definite volume and shape which may be affected by changes temperature
- Consist of particles that are found to be stationary but vibrating about a fixed position
- Have very high density and are practically incompressible
- In a solid the particles attract one another there are bonds between the particles which hold them close together.
- the particles have little freedom of movement and are only able to vibrate about a fixed position they are arranged in regular manner, which explains why many solids form crystals.

liquid

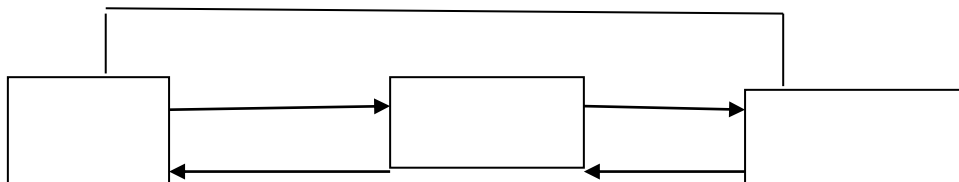
- At a given temperature liquids has a fixed volume and will take up the shape of any container into which it is poured its volume is slightly affected by changes in temperature
- The particles of a liquid are far apart and free to move throughout the entire system the movement in a liquid is ordered
- Liquids are slightly compressible
- The forces of attraction between the particles in a liquid are very weak

Gas

- At a given temperature has neither a definite shape nor volume it will take up the shape of any container into which it is placed
- Particles of the gas are free to move randomly as they have negligible force of attraction; Particles in a gas are far apart from each other
- Gases are easily compressible

Changes of state

- Interconversion of the physical states



The kinetic theory can be used to explain how a substance changes from one state to another

On heating solid the particles gain kinetic energy and this increases their vibration about a fixed position

on application of sufficient heat, the particle breakdown and melt to form a liquid and the process is termed as melting.

Melting is the process by which a solid changes to a liquid at constant temperature.

Melting point is a fixed temperature at which a solid changes to a liquid

On heating the liquid particles gain kinetic energy and they move with greater velocity on applying sufficient heat energy particles break and form a gas and the process is called evaporation.

Evaporation is a process by which liquid changes to a gas .eventually a temperature is reached at which the particles escape from the liquid so quickly to form a gas.

The constant temperature at which a liquid changes to vapour on boiling is called boiling point

Boiling point is a constant temperature at which a vapour pressure of a liquid is equal to atmospheric pressure

Boiling point is affected by

i) Atmospheric pressure the higher the atmospheric pressure, the higher the boiling point

ii) **Altitude** the higher the altitude, the lower the boiling point because atmospheric pressure decrease with altitude.

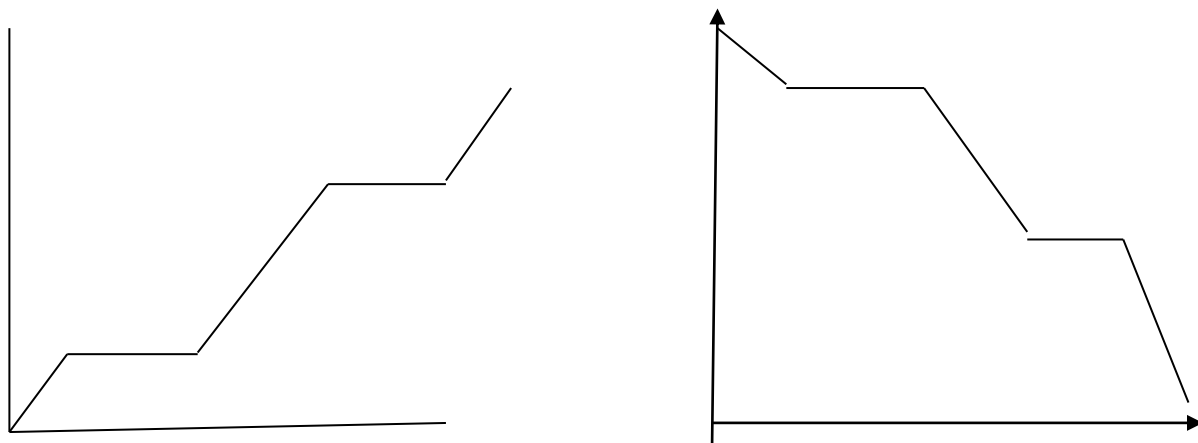
iii) **presence of impurities.** Impurities decrease the escaping tendency of liquid molecules to escape into vapour form. Since liquid boils when its vapour pressure is equal to atmospheric pressure more heat is required and thus increase the boiling point.

During this process of melting and boiling the temperature remains constant because the energy is used to break the bonds between the particles.

When a gas is cooled the average energy of the particles decreases, and the particles move closer together. The forces of attraction between the particles now become significant and cause the gas to condense into a liquid. When a liquid is cooled its particles will move closer and slower until the forces of attraction are stronger enough to hold them tight together forming a solid ie it freezes to form a solid. In each of these changes energy is given out

During this process of condensing and freezing the temperature remains constant because the energy is given out when bond form between the particles

The graphs of temperature against time for the changes from solid to a gas and gas to solid



- Comparison of physical properties between solids, liquids and gases

Molecular structure	solid	liquid	gas
Particle arrangement	Very closely packed	Closely packed	Very far apart
Intermolecular forces	Extremely strong	weak	Very weak
Movement of particles	Vibrating in fixed position	Slowly slide over each other	Moving randomly
compressibility	Cannot be compressed	Can be hardly compressed	Very compressible
diffusion	Cannot diffuse	Diffuse slowly	Diffuse quickly

1.93 Gaseous state of matter

1.94 kinetic theory of gasses

Kinetic theory makes many assumptions in order to explain the reasons gases act the way they do.

According to kinetic theory:

- Gasses consists of small particles called molecules
- Molecules are in the state of rapid random motion colliding with one another and with the walls of the container hence constituting pressure
- The average kinetic energy of the molecules is directly proportional to the average Kelvin temperature.

- iv) The collisions of the molecules are perfectly elastic there is no loss in kinetic energy.
- v) Particles are point masses with no volume. The particles are so small compared to the space between them, that we do not consider their sizes in ideal gases.
- vi) No molecular forces at work. This means that there is attraction or repulsion between the particles.
- vii) All gases at a given temperature have the same kinetic energy.
- viii) lighter gas molecules move faster than heavy molecules.

1.94 Basic gas laws

After experimental observations of the behavior of gases the following laws were formulated

Boyles law:

States that the volume of a given mass of a gas is inversely proportional to its pressure provided that the temperature remains constant.

This law can be stated in mathematical terms as

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = K \quad \text{or} \quad P = \frac{K}{V} \quad \text{or} \quad V = \frac{K}{P}$$

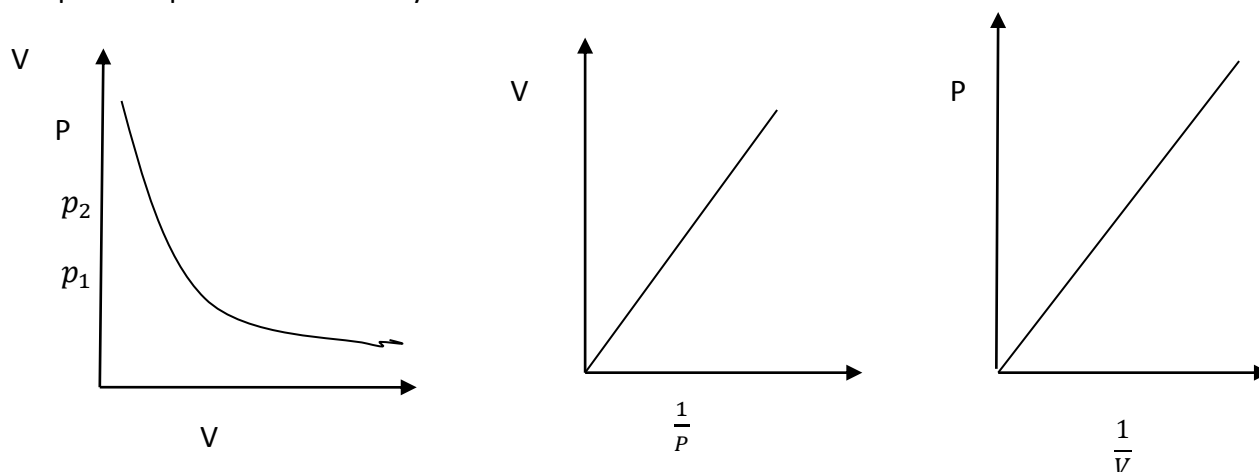
Where V is the volume at pressure P and K is a mathematical constant

If the pressure of the gas is increased from P_1 to P_2 then the volume decreases from V_1 to V_2

$$P_1 V_1 = K \quad \text{and} \quad P_2 V_2 = K$$

$$P_1 V_1 = P_2 V_2$$

Graphical representation of Boyles law



Kinetic theory and Boyles law

Decreasing the volume of a fixed mass of gas at constant temperature increases the number of collisions per unit time between the molecules and the walls of the container which results in an increase of pressure of the gas since pressure is caused by gas colliding with the walls of the vessel. On the other hand increase in volume of the gas decreases the rate of collision per unit time this results in reduction of the pressure of the gas. So the volume is inversely proportional to the pressure at a constant temperature.

Worked example

375cm³ of a gas M has a pressure of 87000Pa. what will be its volume if pressure is reduced to 85000Pa?

Solution

From Boyles law: $P_1V_1 = P_2V_2$

From data: $P_1 = 87000\text{Pa}$

$$P_2 = 85000\text{Pa}$$

$$V_1 = 375\text{cm}^3$$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{87000 \times 375}{85000} = 384\text{cm}^3$$

Charles law

Its states that the volume of a fixed mass of a gas at constant pressure is directly proportional to its absolute temperature

This law can be stated in mathematical terms as

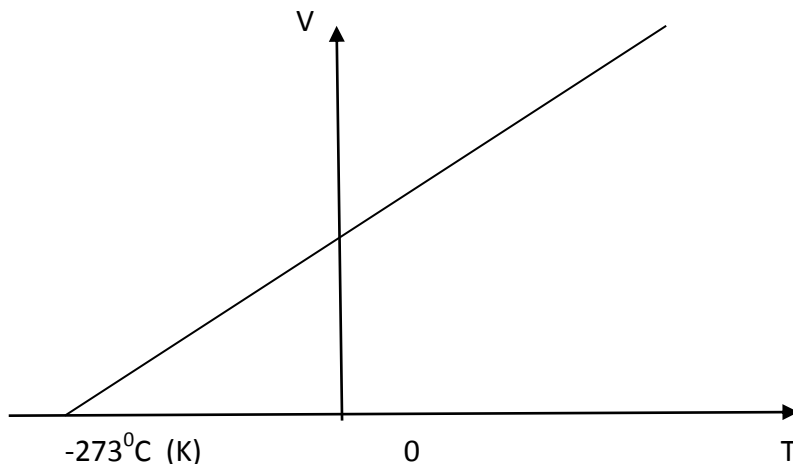
$$V \propto T \text{ or } \frac{V}{T} = K$$

Where V is the volume at temperature T and K is a mathematical constant.

If a gas has a volume V_1 at a temperature T_1 and the temperature is changed to T_2 the new volume V_2 at constant pressure is given by the equation.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad V_2 = \frac{V_1T_2}{T_1}$$

Graphical representation of Charles law



NOTE

The temperature at which all gases would have zero volume is called the absolute zero and is -273°C or 0K . At this temperature the molecules would come to rest and have no kinetic energy and the gas would have zero pressure.

-273°C or 0K is theoretically the lowest temperature possible.

In practice however, the temperature of a gas can't be reduced to absolute zero because all gases liquefy above this temperature.

Kinetic theory of gases and Charles law

When a fixed mass of a gas is heated, the molecules acquire more kinetic energy and so they move faster. Hence the number of collisions they make increases. For a constant pressure to be maintained, more space must be provided for the molecules so that they are further apart than before. The volume is therefore directly proportional to the temperature at constant pressure.

Worked example

At 34°C a sample of a given gas occupies 250cm^3 . Find the new volume at 100°C if the pressure remains constant.

Solution

According to Charles law
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

From data $V_1 = 250\text{cm}^3$

$$T_1 = (34 + 273) \text{ K} = 307\text{K}$$

$$T_2 = (100 + 273) = 373\text{K}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{250 \times 373}{307} = 304 \text{ cm}^3$$

The general gas laws

This is sometimes called the combined gas equation or gas equation. It is an equation representing both the equation that express Boyles and Charles laws. This combined equation allows the volume of a gas to be calculated at a given temperature and pressure provided the volume of the gas is known at another temperature and pressure.

Boyle's law: $V \propto \frac{1}{P}$

Charles law: $V \propto T$

This implies that $V \propto \frac{T}{P}$ or $PV \propto T$ and $PV = KT$ or $\frac{PV}{T} = K$ where K is a constant.

The general gas equation is stated as:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ or } \frac{PV}{T} = \text{Constant}$$

Where V_1 is the initial volume at initial pressure and temperature of P_1 and T_1 , respectively; V_2 is the final volume at final pressure of P_2 and T_2 respectively. The value of the constant depends on the mass of the gas.

Worked example

A fixed mass of a certain gas has a volume of 76cm^3 at 37°C and 85kPa . Find the volume the gas would occupy at stp.

Solution

According to the general gas law: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

From the data $V_1 = 76 \text{ cm}^3$, $P_1 = 85000\text{Pa}$, $T_1 = (37 + 273) = 310\text{K}$

$$P_2 = 100000\text{Pa} , \quad T_2 = 273 \text{ K}$$

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{85000 \times 76 \times 310}{100000 \times 273} = 73.4 \text{ cm}^3$$

Avogadro's law

states that equal volumes of all gases at the same temperature and pressure contains the same number of molecules.

Also the volume of a gas at constant temperature and pressure is directly proportional to the amount of gas or the number of molecules of the gas ie $V \propto n$ and $V = cn$

(where c is a constant and n is amount of a gas in moles)

The volume occupied by one mole of a gaseous molecules at standard temperature and pressure is always close to 22400 cm^3 or 22.4 dm^3 . this quantity is often referred to as the molar volume of the gas.

The ideal gas equation

This an equation that relates the pressure, temperature and volume of a perfect or ideal gas.

An ideal gas or a perfect gas is hypothetical gas that obeys the gas laws at all conditions with its molecules occupying negligible space and forces of attraction between its molecules are nonexistent.

Real gases such as helium, hydrogen and nitrogen (very low molecular masses) obey the equation closely only at high temperatures and low pressures ie when their particles are very far apart.

The equation may be considered as a combination of Boyles law, Charles law and Avogadro's law.

Boyles law: $V \propto \frac{1}{P}$ (n, T constant)

Charles law: $V \propto T$ (n, P constant)

Avogadro's law: $V \propto n$ (P, T constant)

So that the ideal gas equation is:

$$V \propto \frac{nT}{P} \text{ and } V = \frac{nRT}{P} \text{ or } PV = nRT$$

$PV = nRT$ is the ideal gas equation because it holds only when gases are behaving ideal or perfect.

R is molar gas constant its value depends on the units adopted for quantities in the equation.

For one mole of a gas at standard temperature and pressure (stp)

$$P = 101325 \text{ Nm}^{-2} = 101325 \text{ Pa} = 1.0 \text{ atm} = 760 \text{ mmHg}$$

$$V = 22.4 \text{ dm}^3 = 2.24 \times 10^{-2} \text{ m}^3$$

$$T = 273 \text{ K}$$

$$\text{From } R = \frac{PV}{nT} = \frac{101325 \times 2.24 \times 10^{-2}}{1 \times 273} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{From } R = \frac{PV}{nT} = \frac{1.0 \times 22.4}{1 \times 273} = 0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

Conditions under which gases behave as ideal gases

Low pressure

High temperature

GRAHAMS LAW OF DIFFUSION

It states that at constant temperature and pressure the rate of diffusion of gases is inversely proportional to the square root of its density

$$\text{Rate of diffusion of a gas} \propto \frac{1}{\sqrt{\text{density of a gas}}}$$

For two gases A and B

$$R_A \propto \frac{1}{\sqrt{\rho_A}} \quad \text{And } R_B \propto \frac{1}{\sqrt{\rho_B}}$$

$$R_A = \frac{K}{\sqrt{\rho_A}} \quad R_B = \frac{K}{\sqrt{\rho_B}}$$

Dividing i by ii

$$\frac{R_A}{R_B} = \frac{\sqrt{\rho_B}}{\sqrt{\rho_A}} \quad \text{but density} = \frac{\text{mass}}{\text{volume}} \text{ if volume is constant then density is direct proportional to mass}$$

$$\frac{R_A}{R_B} = \frac{\sqrt{m_B}}{\sqrt{m_A}} \quad M_B \text{ and } M_A \text{ are relative mass of gas A and gas B respectively}$$

$$\text{Also rate} = \frac{1}{\text{time}}, \text{ for gas A rate} = \frac{1}{t_A} \text{ and gas B rate} = \frac{1}{t_B}$$

$$\frac{t_A}{t_B} = \frac{\sqrt{\rho_A}}{\sqrt{\rho_B}} \quad \text{and} \quad \frac{t_A}{t_B} = \frac{\sqrt{m_A}}{\sqrt{m_B}}$$

Worked example one

A certain volume of oxygen diffused through a porous membrane in 120 seconds under the same conditions the same volume of a gas X diffuses in 112 seconds determine the relative molecular mass of X (O = 16)

Solution

$$\frac{R_X}{R_{O_2}} = \frac{\sqrt{m_{O_2}}}{\sqrt{m_X}}$$

$$\frac{112}{120} = \sqrt{\frac{16 \times 2}{M_X}}$$

$$M_X = 28$$

Worked example two

A given volume of a gas Z diffuses through a hole in 14.1 seconds while the same volume of carbon dioxide diffuses through the same hole in 10 seconds. Calculate the relative molecular mass of a gas Z.

$$\frac{t_Z}{t_{CO_2}} = \frac{\sqrt{m_Z}}{\sqrt{m_{CO_2}}}$$

R.M.M of carbon dioxide = 12 + 2 × 16 = 32

$$\frac{14.1}{10} = \sqrt{\frac{m_Z}{32}}$$

$$M_Z = 87.5$$

Worked example three

EXAMPLE FOUR

EXERCISES

1.95 Application of diffusion

a) separation of isotopes

diffusion is applied in separation of isotopes eg isotopes of uranium 235 from uranium 238

b) extraction of Helium from natural gas

c) determination of molar mass of gasses

d) determining the density of a gas

e) absorption of nutrients by cells in living organism

1.96 Effusion

Effusion is similar process. Effusion is the process where gas molecules escape from an evacuated container through a small hole. It is assumed that while a molecule is exiting, there are no collisions on that molecule.

1.97 Daltons law of partial pressure

It states that for gases that do not chemically react, the total pressure of the mixture of gases is the sum of their partial pressures .

$P_{\text{total}} = P_A + P_B + P_C + \dots + P_Z$ Where P_A, P_B, P_C, \dots and P_Z are partial pressures of individual gases

Partial pressure of a gas

Is the pressure the gas alone would exert if it occupied the volume that was initially occupied by the mixture of the gases of which it was part.

Consider gases A and B in a given vessel

Using Daltons law, $P_{\text{TOTAL}} = P_A + P_B$

Applying the ideal gas equation $PV = n RT$, $P_A V = n_A RT$

For gases A and B

$$P_A V = n_A RT, \dots\dots\dots (I)$$

$$P_B V = n_B RT \dots\dots\dots (II)$$

Dividing equation I and ii

$$\frac{P_A V}{P_T V} = \frac{n_A RT}{n_T RT} \quad \frac{P_A}{P_T} = \frac{n_A}{n_T} \quad \text{this implies } P_A = \frac{n_A}{n_T} P_T \quad \text{Similarly } P_B = \frac{n_B}{n_T} P_T$$

Where $\frac{n_A}{n_T}$ and $\frac{n_B}{n_T}$ are the mole fraction of the gases A and B

Mole fraction is the ratio of the number of moles of a component of a gas to the total number of moles of the component of the gases in the mixture.

Partial pressure of a gas depends on the number of moles of that gas present and is related to the total pressure by the equation.

Partial pressure = mole fraction x total pressure of the system

Worked example

12g of nitrogen 0.4g of hydrogen and 9.0g of oxygen are put in a one litre vessel at pressure of 22.4 atmosphere calculate the partial pressure of the respective gases.(N=14,H=1.0,O=16)

SOLUTION

Relative molecular mass of nitrogen = $2 \times 14 = 28$, moles of nitrogen = $\frac{12}{28} = 0.43$

Relative molecular mass of oxygen = $2 \times 16 = 32$, moles of oxygen = $\frac{9}{32} = 0.38$

Relative molecular mass of hydrogen = $2 \times 1 = 2$, moles of hydrogen = $\frac{0.4}{2} = 0.2$

Total number of moles $0.43 + 0.38 + 0.2 = 0.91$

Partial pressure of nitrogen $\frac{0.43}{0.91} \times 22.4 = 10.58$ atmosphere

Partial pressure of hydrogen $\frac{0.20}{0.91} \times 22.4 = 4.92$ atmosphere

Partial pressure of oxygen $\frac{0.28}{0.91} \times 22.4 = 6.89$ atmosphere

1.98 Real gases or non-ideal gases

Kinetic theory assumes that all gases behave ideally, however we know that this is not the case. Obviously real gas particles do occupy space and attract each other. These properties become apparent at low temperature or at high pressure.

There are two factors that are responsible for the non- ideal gases

- i) intermolecular forces of attraction

An ideal gas is assumed to have negligible intermolecular forces of attraction. However at low temperature the vander-waals forces of attraction become more pronounced because

the molecules have insufficient energy to overcome the forces of attraction. The molecules become closer together hence resulting into deviation from ideal gas behavior.

ii) Molecular volume

An ideal gas is assumed to occupy negligible volume. However at high pressure the molecules of a gas become so tightly packed that their volume is significant compared to the overall volume.

1.98 modification of the ideal gas equation vander- Waal equation

Vander- waal proposed that we correct for the fact that the volume of areal gas is too large at high pressure by subtracting a term from the volume of a real gas before we substitute it into the ideal gas equation.

If the total volume is V , and the volume occupied by gas molecules is nb the compressible part of the total volume will be $(V-nb)$ then $P(V-nb) = a \text{ constant}$.

If molecules of a gas attract each other, then a molecule in the interior is attracted equally in all sides by other molecules but this isn't true for a molecule outside. And also the velocity of a molecule just about to make an impact with the walls of the container will be reduced by the attraction of the molecules towards the interior of the gas, hence pressure will be reduced.

Note pressure of a gas is due to molecular impacts on the walls of the container.

To correct for the fact that pressure of a gas is smaller than expected from ideal gas equation vander-waal added a term to the pressure in this equation.

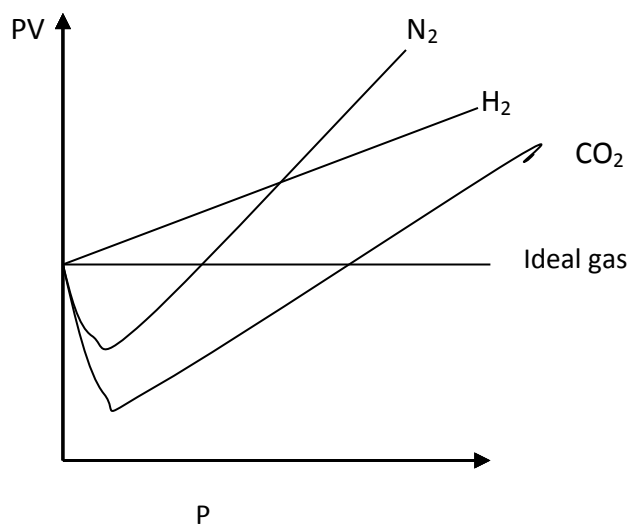
$$\left(P + \frac{an^2}{V^2}\right)(V-nb) = nRT \text{ where } a \text{ and } b \text{ are constants } n \text{ number of molecules.}$$

The ideal gas equation predicts that a plot of PV versus P for gas would be a horizontal line because PV should be a constant.

NOTE

- i) The effect of molecular attraction increases pressure and consequently the volume is less than expected and the value of PV will be less than that of ideal gas.
The gas will be more compressible than the ideal case.
- ii) At low pressure the volume occupied by gas molecules is not significant but at high pressure the molecules are compacted to a degree such that they tend to behave like liquids, which are almost incompressible as a result, at higher pressure the volume of a gas remains larger than the ideal case and consequently the value of PV increases

Experimental data for PV versus V for H_2 , N_2 and CO_2 are given in the figure below.



For nitrogen and carbon dioxide, the values of PV decrease at first as pressure increases because the effect of molecular attraction outweighs the deviation due to molecular volume at low pressure.

Molecular attractions arise from vander-waal forces.

But at high pressure PV increases because the deviation due to molecular volume is greater than that of molecular attraction.

The decrease in PV with increase in pressure shows that initially nitrogen and carbon dioxide are at first more compressible than expected.

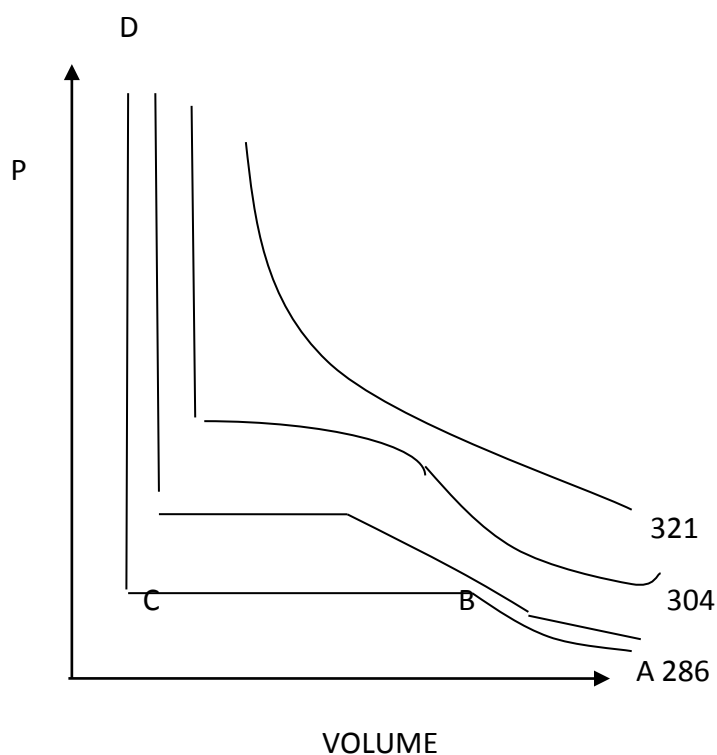
For hydrogen, PV increases from the beginning because deviation due to molecular volume is greater than deviation due to molecular attraction at all pressure.

The increase in PV from the start for hydrogen shows that it's less compressible than expected.

liquefaction of gases

By sufficiently cooling the gas at atmospheric pressure it can be condensed and turned into a liquid. Many gases not all can be liquefied by increasing the pressure at ordinary temperature (compression) or decreasing the temperature. These conditions of temperature and pressure under which gases liquefy were investigated by Andrew.

Andrew plotted graphs of P against V for a fixed mass of carbon dioxide



Isothermals of carbon dioxide

Each isothermal refers to the same mass of carbon dioxide and shows the variation of volume of carbon dioxide with pressure for a particular temperature.

Isothermal 321K almost represents the behavior of an ideal gas.

The isothermal of 286K, ABCD is markedly different. Its course is interpreted in the following way.

The portion AB represents the usual contraction of the volume of a gas as pressure increases and approximates to a hyperbola

The portion BC represents a large contraction in volume for almost no pressure change at B the pressure has become large enough to start the liquefaction of carbon dioxide at 286 K, and from B to C this liquefaction continues and completes itself with only slight increase of pressure at C liquefaction is completed and liquids being almost incompressible, further increase of pressure produces no appreciable volume change.

Portion CD represents almost no volume changes for a very large pressure change.

At higher temperatures such as 295K a similar path EFGH is followed however above 304K its impossible to liquefy a gas however much pressure exerted. This temperature is called critical temperature for carbon dioxide. The pressure required to liquefy the gas at critical temperature is called the critical pressure and the volume of one mole of a gas at the critical temperature and pressure is the critical volume.

Critical temperature: is the temperature above which a gas cannot be liquefied by increasing pressure.

Every gas has its critical temperature above which it cannot be liquefied by increasing pressure for example

$\text{H}_2 = -230^\circ\text{C}$, $\text{N}_2 = -147^\circ\text{C}$, $\text{O}_2 = -119^\circ\text{C}$, $\text{SO}_2 = +157^\circ\text{C}$, $\text{NH}_3 = +131^\circ\text{C}$, $\text{Cl}_2 = +141^\circ\text{C}$

Above the critical temperature a gas may be regarded as a permanent gas since it cannot be liquefied by increasing pressure

Note

Two factors are involved in liquefaction of a gas these are intermolecular attraction which tend to bring the molecules together and thermal energy of molecules which tend to keep them apart

Liquefaction of gases occurs when the intermolecular attraction are greater than thermal energy this is achieved below critical temperature.

Any gas which has critical temperature above room temperature can be liquefied by pressure alone for example NH_3 , Cl_2 , SO_2 CO_2 .

RELATIVE MOLECULAR OF GASES

Relative molecular mass: this is a mass of one molecule of an element or compound divided by the mass of one-twelfth of the mass of an atom of carbon -12 isotopes.

Relative molecular mass of a gas can be obtained by measuring the relative density or vapour density of the gas

Relative density of a gas is defined as the ratio of the weight of equal volume of the gas and hydrogen measured at the same conditions of temperature and pressure.

$$\text{Relative density} = \frac{\text{weight of one mole of a gas}}{\text{weight of one mole of hydrogen}}$$

Relative density of a gas can be obtained by direct weighing or by measuring the rate of diffusion of a gas and comparing it to that of another gas of known relative density.

Relative density is equal to the mass of 11.2dm³ of vapour.

Relative molecular mass = 2 x relative density of a gas or = 2 x vapour density of a gas

This method can be applied to vapours of substances which are liquids or solids at ordinary temperature provided they can be vapourised.

Experimental determination of relative molecular mass of gases

a) Direct weighing

A large container of volume V is weighed when full of a gas at a pressure P and temperature T. the same container is then weighed after evacuation in order to obtain the mass of the gas .

Sample results

Mass of container full of gas = a g

Mass of empty container = b g

Mass of gas = a-b g

From the ideal gas equation $PV = nRT$

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{VP} = \frac{\rho RT}{P}$$

The following precautions should be taken

- i) the gas must be pure
- ii) the container should be completely evacuated
- iii) all weighing should be done at the same temperature and pressure

note

Pressure must be converted to Nm^{-2} , volume must be converted to m^3 , temperature to Kelvin.

Worked example

0.228g of ethoxyethane vapour occupies 94.08 cm^3 at 100°C and 100.8 kNm^{-2} pressure.

Calculate the relative molecular mass of ethoxyethane.

Solution

Using $PV = \frac{m}{M}RT$ and $M = \frac{mRT}{VP}$

$$M = \frac{0.228 \times 8.31 \times 273}{101.3 \times 94.08} = 74.158$$

OR using $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{100.8 \times 94.08 \times 273}{373 \times 101.3} = 68.52 \text{ cm}^3$$

One mole of a gas at stp occupies 22400 cm^3

68.52 cm^3 of the gas weighs 0.228g

22400 cm^3 of the gas will weigh $\frac{0.228 \times 22400}{68.52} = 74.558 \text{ g}$

b)Using a graduated syringe(for volatile liquids and gases)

apparatus

A known quantity of a liquid is injected into a gas syringe, where it vaporizes and the volume occupied by the vapour is measured. The temperature around the syringe and atmospheric pressure are recorded.

The relative molecular mass is then calculated.

Worked example

0.160g of a volatile liquid X was injected into a gas syringe at 12⁰ C and 745mmHg pressure.55.5cm³ of the liquid vapour was produced. Calculate the formula mass of liquid X.

Solution

Using $PV = \frac{m}{M} RT$

$$M = \frac{0.160 \times 8.314 \times 373}{101325 \times 55.5 \times 10^{-6}} =$$

$$\text{OR using } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{745 \times 55.5 \times 273}{373 \times 760} = \text{ cm}^3$$

One mole of a gas at s.t.p occupies 22400cm³

68.52cm³ of the gas weighs 0.228g

$$22400\text{cm}^3 \text{ of the gas will weigh } \frac{0.16 \times 22400}{68.52} = \text{ g}$$

Empirical and molecular formula

The empirical formula of a compound is the simplest formula which expresses the ratio of the number of atoms of the element present in the compound.

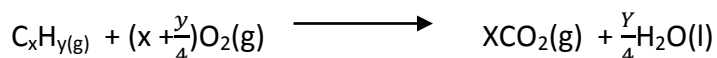
The molecular formula is one which shows the actual number of atoms of the elements present in a molecule or compound.

Knowing the molecular mass of the compound then the molecular formula can also be obtained.

The empirical formula can be obtained by using data from combustion analysis.

Formular of hydrocarbon on explosion

A gaseous hydrocarbon C_xH_y explodes in excess oxygen according to the equation



The initial volume of the hydrocarbon and oxygen are noted

After the explosion the water formed occupies negligible volume at room temperature and pressure.

And the residual gases are carbon dioxide and oxygen.

Carbon dioxide is absorbed in concentrated potassium hydroxide solution.

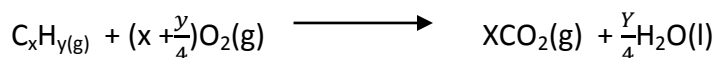
The remaining residual gas will be the unused oxygen gas.

Worked example

15cm³ of gaseous hydrocarbon Z was exploded with 105cm³ of excess oxygen. The residual gas occupied 75cm³, on addition of concentrated potassium hydroxide solution there was a reduction in volume of 45cm³.determine the molecular formula of Z.

Solution:

Let the molecular formula of Z be C_xH_y



Volume of C_xH_y = 15cm³

Volume of CO_2 = 45cm³

Volume of O₂ that reacted = (105-30)cm³ = 75cm³

1cm³ of C_xH_y react with $(x + \frac{y}{4})$ cm³ of O₂ to form Xcm³ of CO₂

15cm³ of C_xH_y react with $15(x + \frac{y}{4})$ cm³ of O₂ to form 15Xcm³ of CO₂

$$15X = 45$$

$$X=3$$

$$15(x + \frac{y}{4}) = 75$$

$$(3 + \frac{y}{4}) = 5$$

$$Y = 8$$

the molecular formula of Z be C₃H₈

Formula of hydrocarbon by oxidation

The hydrocarbon is oxidized by oxygen, hydrogen is oxidised to water and weighed after absorption in concentrated sulphuric acid. Carbon is oxidised to carbon dioxide and weighed after absorption in concentrated potassium hydroxide.

Relative molecular mass of carbon dioxide = 12 +2x16 = 44

Relative molecular mass of water = 1 x2 + 16 = 18

If ag of compound produce Cg of CO₂ and W g of H₂O then

Mass of carbon in carbon dioxide = $\frac{12}{44} \times C$

Percentage of carbon in the compound = $\frac{12}{44} \times \frac{C}{a} \times 100$

Mass of hydrogen in water = $\frac{2}{18} \times w$

Percentage of hydrogen in the compound = $\frac{2}{18} \times \frac{w}{a} \times 100$

Worked example

On complete combustion of 120g of a hydrocarbon Z of molecular mass 70g, 377.1g of carbon dioxide and 154.4g of water was evolved.

- a) Calculate the empirical formula Z.
- b) Determine the molecular formula of Z.

solution

a) Percentage of carbon in the compound $= \frac{12}{44} \times \frac{377.1}{120} \times 100 = 85.7\%$

Percentage of hydrogen in the compound $= \frac{2}{18} \times \frac{154.4}{120} \times 100 = 14.3\%$

Elements	C	H
% composition	85.7	14.3
Number of moles	$\frac{85.7}{12}$	$\frac{14.3}{1.0}$
	7.14	14.3
Mole ratio	$\frac{7.14}{7.14}$	$\frac{14.3}{7.14}$
	1	2

The simplest formula of Z CH_2

b) Molecular formula of Z $(\text{CH}_2)_n = 70$

$$((12 \times 1) + (1 \times 2))_n = 70$$

$$14n = 70$$

$$n = \frac{70}{14} = 5$$

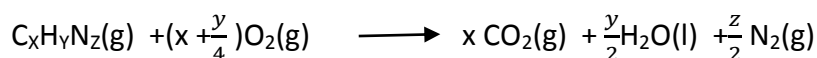
molecular formula = C_5H_{10}

Worked example

0.5g of organic compound Y containing carbon, hydrogen and oxygen gave on combustion 0.6875g of carbon dioxide and 0.5625g of water if the vapour density of the compound is 16. Suggest the structural formula of the compound.

organic compound containing nitrogen

a) compound is burnt so that nitrogen is evolved and measured as a gas.



If a g of the compound produce n cm³ of nitrogen at stp

22400cm³ of nitrogen weigh 28g

n cm³ of nitrogen weighs $(\frac{28x n}{22400})$ g

percentage of nitrogen in the sample $(\frac{28x n}{22400xa} \times 100)$

worked example

0.72g of a compound gave on combustion 1.615g of carbon dioxide and 0.99g of water. 0.42g of the same compound gave 84cm³ of nitrogen at 150C and 760mmHg. Vapour density of a compound is 29.5 find the formula of the compound.

solution

b) Nitrogen can be converted to ammonia sulphate by heating the compound with concentrated sulphuric acid and potassium hydrogen sulphate. The ammonia sulphate is then diluted and heated with excess alkali to expel ammonia gas. The ammonia gas is estimated by absorption in a standard acid.

Worked example

0.708g of compound R gave on combustion 1.056g carbon dioxide 0.54g of water. 1.23g of the same compound yielded ammonia which required 20.4cm³ of 2.0M hydrochloric acid for neutralization. Vapour density of compound is 29.5 calculate the formula of the compound

Chlorine, Bromine or iodine

The halogens are converted to corresponding silver compound by heating with silver nitrate and fuming nitric acid. The silver halide is weighed after purification.

If a g of the compound produce b g of Ag Cl

$$\text{Mass of chlorine in compound} = \left(\frac{35.5 \times b}{143.5} \right) \text{g}$$

$$\text{Percentage of chlorine in the compound} = \left(\frac{35.5 \times b}{143.5 \times a} \times 100 \right)$$

sulphur

sulphur is converted to sulphuric acid by heating with fuming nitric acid and then precipitated as barium sulphate,

if a g of a compound produce w g of barium sulphate

$$\text{mass of sulphur} = \frac{32 \times w}{233}$$

$$\% \text{ of sulphur} = \frac{32 \times w \times 100}{233 \times a}$$

Oxygen

This element is estimated as the difference from 100% after accounting for all other elements.

Note:

The calculation may not give actual integers at this stage it may give ratios such as 1.5:1, 1.33:1, 1.67:1 these are written in the lowest integral equivalents as

1.5:1 becomes 3:2 after multiplying by 2

1.33:1 becomes 4:3 after multiplying by 3

1.67:1 becomes 5:3 after multiplying by 3

TOPIC TWO; THE ATOMIC STRUCTURE

The Dalton's atomic theory

The first modern atomic theory was proposed by John Dalton, who proposed that;

- Matter is made up of atoms (small invisible particles)
- Atoms cannot be created or destroyed
- Atoms of the same element are exactly alike even in mass but differ from atoms of other elements.
- A chemical reaction involves rearrangement of atoms or combination of atoms. During reactions, the individual atoms remain intact.
- When atoms combine, they do so in small whole numbers to form compounds or molecules.

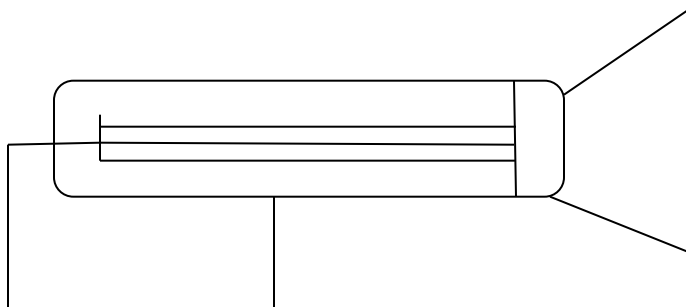
However, in the last hundred years or so it has been proved by great scientists, such as Bohr, Eisten, Moseley, Thomson, Rutherford and Chadwick, that ;

- Atoms can be split into simpler particles i.e neutrons, protons and electrons.
- New atoms can be created and destroyed i.e during radioactivity
- Atoms of the same element can differ in masses e.g in the case of isotopes.
- Not all reactions involve combination of atoms to form molecules or compounds; some actually involve formation and combination of ions.

Discovery of some particles of an atom

a)Discovery of electrons

Electrons were discovered as streams of cathode rays by J.J. Thompson. In his experiment, he applied a high voltage to a gas at low pressure in a discharge tube. A beam of rays that caused a green glow on the screen were observed to be moving from the cathode in a straight line



These rays had the following properties:

- They were deflected by magnetic and electric fields in directions which indicated that they were negatively charged.
- When an object was placed between the cathode and the screen, a shadow was formed on the screen indicating that the rays travel in a straight line.
- The rays had the same properties regardless of the nature of cathode and gas used in the tube.

From the above, the particles were negatively charged and present in all matter and were therefore named **electrons**.

Only further analysis, it was found out that each of these particles had a mass of $\frac{1}{1840}$ times the mass of hydrogen atom.

c)Discovery of protons

When Thompson's experiment was repeated by putting a cathode in the center of the discharge tube, a red glow was observed in the opposite side of the green glow.

When a high voltage is applied to the discharge tube containing a gas at low pressure, the gas molecules are converted to atoms and atoms are ionised by bombardment with fast moving electrons from the cathode.

For example , when hydrogen gas is used;

The electron ejected from the atom is attracted towards the anode and detected by the screen causing a green glow. The positively charged ions are repelled by the anode and attracted towards the cathode and detected on a screen in the opposite direction as a red glow.

- The particles that caused the red glow had the following properties:
- They were deflected by magnetic and electric fields in directions that showed they were positively charged.
- They required much stronger magnetic or electric fields to be deflected unlike cathode rays indicating that they are heavier particles compared to cathode rays.
- Their mass depends on the mass of the gas in the discharge tube .i.e. when hydrogen gas is used , the mass of the particle is equal to the mass of hydrogen atom.
- Masses of the particles from other gases are heavier than those from hydrogen gas.

These were positive rays that were later named protons. symbol 1_1H

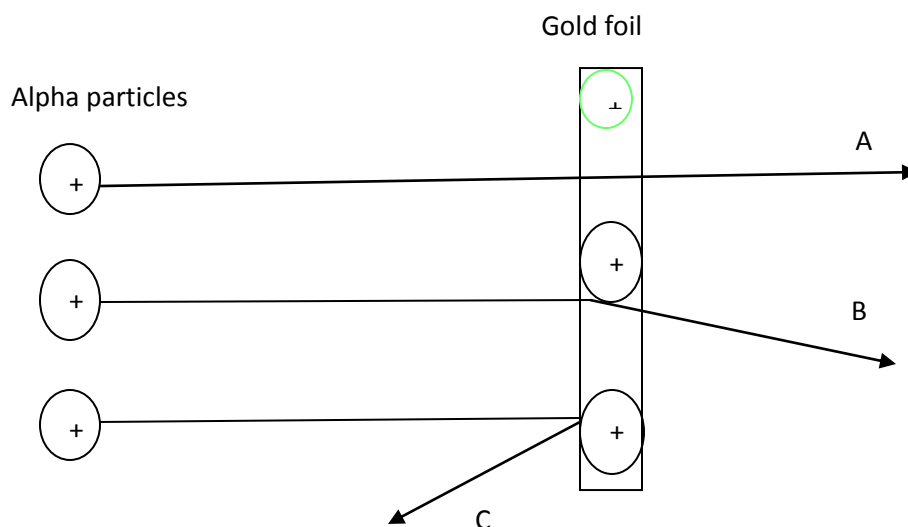
C)Neutrons

An atom consists of positive and negative particles (protons and electrons), and since an atom is neutral, the number of protons must be equal to the number of electrons. The atomic mass of an atom is found to be greater than the mass of protons in it. This therefore implied that there must be other particles that makeup for the extra mass. These particles were called neutrons and had almost the same mass as protons but were neutral (had no charge).

2.1.3 NUCLEAR MODEL OF THE ATOM

Rutherford's experiment

Rutherford directed beam of alpha particles towards a very thin gold foil as shown below



The following observations were made:

- i) Most of the alpha particles went through undeflected
- ii) A few alpha particles suffered a slight deflection of less than 90°
- iii) very few of the alpha particles bounced

conclusion

the atoms consists of a very small positively charged nucleus surrounded by a large space.

The large space contains light negatively charged electrons

When the alpha particles pass through the large space no deflection occurs because its electrons are negatively charged and the alpha particles are positively charged the rebounded particles had collided with the core of the atom the nucleus which is positively charged.

2.2.3 structure of an atom

The atom is made up of three subatomic particles Electrons ,protons and neutrons

The three sub-atomic particles are found in distinct and separate regions. The protons and neutrons are found in the Centre of the atom, which is called the nucleus.

The neutrons have no charge and protons are positively charged.

The nucleus occupies only a very small volume of the atom but is very dense.

The rest of the atom surrounding the nucleus is where electrons are most likely to be found.

The electrons are negatively charged and move around very quickly in electron energy levels.

The electrons are held within the atom by an electro-static force of attraction between themselves and the positive charge of the protons in the nucleus

Characteristic of a proton, a neutron and an electron

particle	symbol	Relative mass(amu)	Relative charge
proton	P	1	+ 1
neutron	n	1	0
electron	e	$\frac{1}{1837}$	-1

Although atoms contain electrically charged particles, the atoms themselves are electrically neutral.

This is because atoms contain equal numbers of electrons and protons.

2.1.4 Atomic number and mass number

Elements are made up of atoms. Atoms are in turn made up of subatomic particles- electrons, protons and neutrons. The symbols of the elements are used in showing the number of different subatomic particles each atom has.

2.1.5 Atomic number Z

The atomic number is the number of protons in the nucleus of an atom.

In the neutral atom it is equal to the number of electrons around the nucleus.

The atomic number is also referred to as proton number.

All atoms of the same element have the same atomic number it has the symbol Z.

2.1.6 The neutrons number

The nucleus contains protons and neutrons. The protons and neutrons are called nucleons. The number of neutrons in each atom differs. The number of neutrons in an atom is given the symbol N

2.1.7 The mass number

The mass number is the sum of the number of protons and neutrons in an atom it can also be called nucleon number.

It is possible for atoms of the same element to have different mass numbers.

This due to different numbers of neutrons. The mass number has the symbol A.

2.1.8 representation of the atom

To indicate the mass number and atomic number of an atom of symbol X:

- i) The mass number, A is placed as a left superscript
 - ii) The atomic number, Z is placed as a left subscript
- A_ZX

The element lithium (Li) has a mass number of 7 and atomic number of 3 it is shown as ${}^7_3\text{Li}$

Isotopes

Isotopes are atoms of the same element which have the same atomic number but different mass numbers. It is the difference in the number of neutrons which brings about the different mass numbers.

Each isotope has a different number of neutrons in the nucleus.

The three naturally occurring isotopes of carbon are represented as $^{12}_6\text{C}$, $^{13}_6\text{C}$ and $^{14}_6\text{C}$ or carbon-12, carbon-13 and carbon-14 respectively.

Note the isotopes of an element react in the same way. This is because chemical reactions involve electrons, neutrons make no difference.

2.1.9 Nuclides

The word nuclide is used to describe any atomic species of which the proton number and nucleon number are specified. Nuclides are written as $\overset{\text{nucleon number}}{\underset{\text{proton number}}{\text{symbol}}}$. The species $^{12}_6\text{C}$ is a nuclide.

2.1.9.1 Isotopic abundance

Most elements consists of mixtures of isotopes the fraction or percentage of each isotope in the mixture is called the isotopic abundance

Example silicon occurs naturally in naturally occurring compounds as silicon

isotope	$^{28}_{14}\text{Si}$	$^{29}_{14}\text{Si}$	$^{30}_{14}\text{Si}$
Percentage abundance	92.28	4.67	3.05

Note percentage abundance add up to 100 whereas fractional abundance add up to 1.00

2.1.9.2 Atomic mass

The mass of an atom is too small to be measured on even the most sensitive balance.

Chemists use relative masses to compare the atomic masses of different elements

An atom of the carbon-12 isotope is chosen as the international standard for the measurement of atomic mass.

Relative isotopic mass is the mass of an atom of an isotope compared with one-twelfth the mass of an atom of carbon-12.

If a natural sample of any isotopic element is collected, each isotope would occur in different amounts.

The different amount of each isotope in the naturally occurring element is called its abundance

When the proportion of the isotope in a sample of the naturally occurring element is expressed as percentage, it is called percentage abundance. It is called fractional abundance when expressed as a fraction.

2.1.9.3 calculating the relative atomic mass of an element having more than one isotope

Relative atomic mass A_r is the average mass of an atom of the element compared with one-twelfth of the mass of an atom of carbon-12

$$A_r = \frac{\text{average mass of isotopes of the element}}{\frac{1}{12} \times \text{mass of a carbon-12 atom}}$$

Worked example

Calculate the relative atomic mass of chlorine given that chlorine has two naturally occurring isotopes

Consists of 75% ^{35}Cl and 25% ^{37}Cl

$$\begin{aligned}\text{Relative atomic mass} &= \frac{\sum \text{isotopic mass} \times \text{percentage abundance}}{100} \\ &= \frac{35 \times 75 + 37 \times 25}{100} = 35.5\end{aligned}$$

Worked example

Copper has two isotopes ^{63}Cu and ^{65}Cu of relative isotopic mass of 62.9 and 64.9 respectively the relative atomic mass of the naturally occurring copper is 63.55. calculate the percentage abundance of each isotope.

Solution

Let the percentage abundance of isotope ^{63}Cu be y and that of ^{65}Cu be $100-y$

$$\begin{aligned}\text{Relative atomic mass} &= \frac{\sum \text{isotopic mass} \times \text{percentage abundance}}{100} \\ &= \frac{63xy + 65x(100-y)}{100} = 63.55\end{aligned}$$

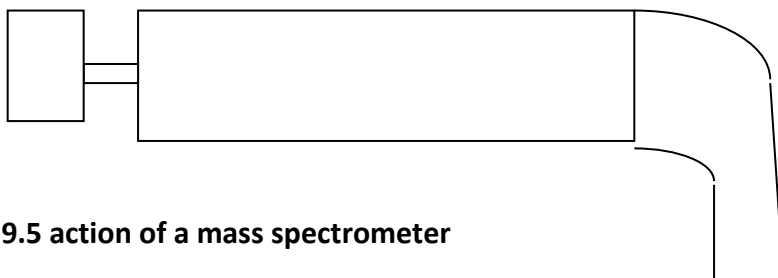
$$y = 67.5$$

$$\%^{63}\text{Cu} = 67.5 \text{ and } \%^{65}\text{Cu} = 32.5$$

2.1.9.3 Measuring relative atomic mass

Relative atomic mass is measured using a mass spectrometer. The mass spectrometer separates species of different masses and measures their masses by electrical methods

2.1.9.4 structure of the mass spectrometer



2.1.9.5 action of a mass spectrometer

- The apparatus is first evacuated to avoid collision between air and ions of element.
- The sample of the substance is vapourised by heating.
- A stream of vapourised sample of the element is passed through a pin sized hole into the ionization chamber where they are subjected to an electron gun emitted by a heated element
- High energy electrons from the cathode are attracted to the opposite anode
- In the process they collide with vapourised sample and knock off electrons from atoms or molecules to form positive ions.
- The positive ions are attracted and accelerated by a stronger electric field so that ions which enter the magnetic field are of the same velocity.
- In the magnetic field the ions are deflected and focused onto the detector According to their mass to charge ratio .
- Changing magnetic field brings species of different mass onto the detector, heavier species are deflected less and need a stronger magnetic field to focus them onto the detector lighter species need weaker magnetic fields.
 - The detector collects the species of different masses separately and the collected charges constitute an electric current.
 - The separate amounts of electric currents are proportional to the percentage abundance of each species of different mass.

The instrument amplifies the percentage abundance and mass and records it as a mass spectrum.

2.1.9.5 relative atomic mass from a mass spectrum.

A mass spectrum shows percentage abundance versus the mass of each species in mass spectrometer.

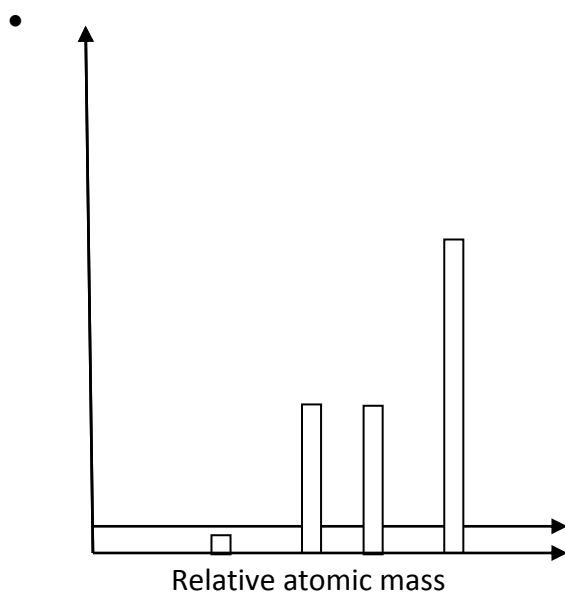
The mass spectrum is calibrated(based) on the carbon-12 scale and therefore the relative atomic or molecular mass of all species can be read directly

Isotopes present in the sample are shown as peaks.

The area under each trace at any mass point is proportional to the abundance of that mass.

Each peak indicates one isotope with its percentage abundance and relative atomic mass or mass number.

- The number of peaks is equal to the number of isotopes.



RADIOACTIVITY

Radioactivity is the spontaneous disintegration of the nuclei of certain isotopes with emission of beta particles, alpha particles or gamma rays.

Certain elements have an unstable isotope. The nuclei of these atoms break up spontaneously with the emission of certain type of radiation. The atoms of these isotopes with unstable nuclei are radioactive and they are called radioisotopes.

Radioisotopes : are atoms with unstable nucleus which disintegrate spontaneously to give off one or more type of radiation.

Examples of radioactive isotopes are $^{14}_6\text{C}$, $^{235}_{92}\text{U}$ $^{60}_{27}\text{Co}$

There are two types of radioisotopes naturally occurring isotopes and artificially radioisotopes. Elements such as Uranium which spontaneously emit energy without absorption of energy are said to be naturally radioactive.

Artificially radioactive isotopes may be produced by adding energy to stable nuclei.

When these unstable atoms spontaneously break up they are said to disintegrate or decay.

The result of this process is that energy is released in the form of heat and radiation is emitted from the nucleus.

Radioactive elements can emit one or more of the three types of radiation the types of radiation are alpha, beta and gamma

Properties of radioactive elements

They are very unstable and disintegrate to stable nuclides.

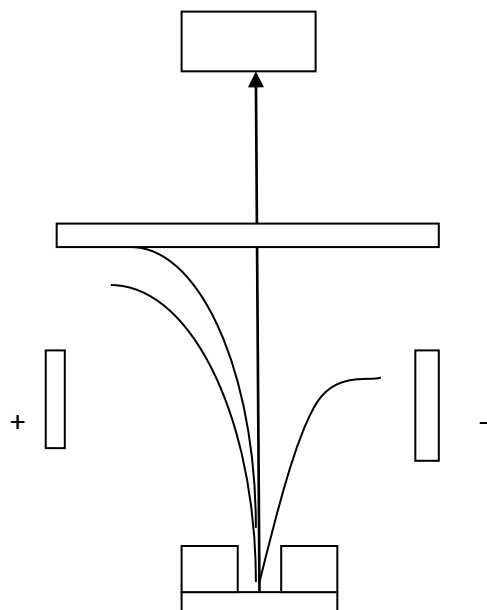
They emit particles alpha and beta or rays gamma upon disintegration.

They affect photographic materials due to emission of particles and rays.

When they disintegrate they release a lot of energy.

They also ionize gases and produce phosphorescence.

Nature and properties of radiations



Type of radiation	Nature	Electrical charge	Effect of electric field	Effect of magnetic field	Relative penetrating power	Relative ionizing power
Alpha(α)	2 protons and 2 neutrons written as $({}^4_2\text{He})$ <i>helium nucleus</i>	+2	Deflected to the negatively charged plate	Deflected by magnetic field	Very low penetrating power. Particles do not pass through paper and have a range of only a few cm in air	Very high, particles produce large numbers of ions as they penetrate gases
Beta(β)	B- particle in the form of electrons (${}^{-1}_0e$)	-1	Deflected to the positively charged plate deflection is greater than that of α -particle due to	Deflected by a magnetic field in the opposite direction to α -particle. They can be	Very good penetrating power, particles can pass through a few cm thickness of	Low ionizing power, particles produce weak ionization in gases

			much smaller mass of the beta particle	deflected by a much weaker magnetic field due to their much smaller mass	aluminium foil.	
gamma	Electromagnetic wave contains no particle thus atomic number and atomic mass is unchanged when an atom emits gamma rays nucleus only loses energy	No charge 0	Unaffected by electric field hence no deflection	Unaffected hence no deflection	Very high penetrating power	Very low ionizing power

Detection of radiations

Use of photographic film the radiations destroy the film if exposed for some time

They cause surface of some substances to glow

They cause ionization of air molecules

Results of radioactive decay

Radioactive changes involve the nucleus and are called nuclear reactions

During nuclear reactions one element may be converted to another either by radioactive decay or by atomic fission or atomic fusion.

Alpha particle emission.

Many of the heavy elements (atomic number 83 and above) undergo α -decay, eg radon-220, polonium-218 and plutonium-238.

An alpha particle is a helium nucleus so that its loss causes a decrease of 2 in the atomic number and 4 in the mass number.



Beta particle emission

β -decay occurs in both heavy elements and light elements (atomic number less than 83) in β -decay, a neutron changes into a proton plus an electron the electron is lost while the proton remains in the nucleus:

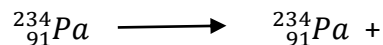


The daughter nucleus therefore contains one less neutron and one more proton than the parent nucleus. The mass number is unchanged, but the atomic number is increased by one. For example,



Gamma radiations

When gamma radiation is emitted, there is no change in the atomic number or mass number of the isotope. For example,



Notice Ω

That the totals of mass number and proton number are the same on both sides of the equation

Gamma radiation is emitted during α -decay and β -decay, and is due to change within the nucleus.

Differences between nuclear and chemical reactions

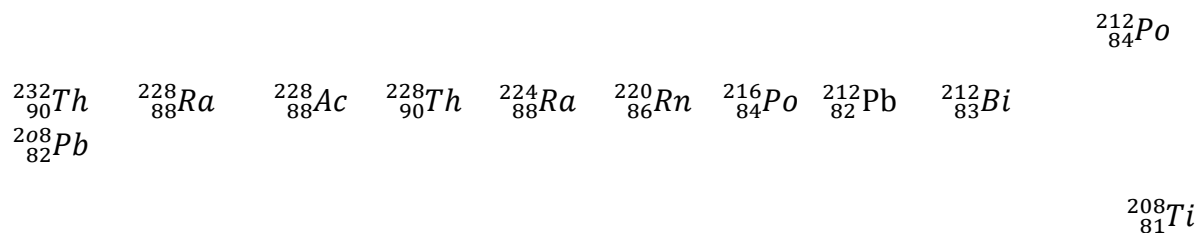
	Nuclear reactions	Chemical reactions
occurrence	Takes place inside the nucleus	Takes place in the outer

	or with the nucleus. Protons, neutrons and electrons involved	electronic shell. Valence electrons involved
Energy involved	Large amount of energy released.	Much less energy released
products	New nuclide is formed	New compound but not nuclide is formed.
conditions	Not governed by environmental factors	Governed by environmental factors such as temperature.

Decay series

When the product of a radioactive disintegration is itself unstable, then a further radioactive disintegration will occur. This goes on until eventually a stable isotope is formed each step involving the loss of either an alpha or beta or occasionally both.

Consider the thorium decay series



Half-life

Half-life $t_{1/2}$ of a radioactive nuclide is the time taken for the radioactivity of that nuclide to decay to half of its original value.

Its independent of the amount of substance taken.

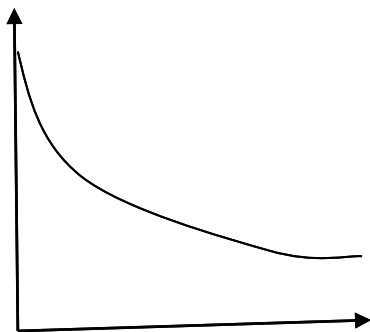
It's the same whatever the initial amount of substance.

It's possible to characterize radioactive isotopes by quoting their half-lives

The half-life period for polonium-214 is 1.6×10^{-4} seconds. This means that after 1.6×10^{-4} seconds the activity of a sample of this isotope of polonium will have been reduced by half.

After another 1.6×10^{-4} seconds the activity will only be $\frac{1}{4}$ of the original level.

The half-life of a pure radioactive nuclide can be conveniently found using a graphical method.



Half-life is used as a measure of the relative stability of an isotope

The shorter the half-life, the faster is the decay of the nuclide.

The longer the half-life, the slower the decay of the nuclide.

Half-lives of different isotopes of the same element are not the same.

The rate at which atoms of a radioactive nuclide decay, is directly proportional to the number of atoms of the nuclide in the sample.

$$\text{Rate} = KN$$

$$\frac{dN}{dt} = -KN$$

Where N is the number of atoms and

K is the constant of proportionality, called the decay constant

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

$$\ln N = -Kt + c$$

$$N = N_0 e^{-Kt}$$

$$\ln \frac{N}{N_0} = -Kt \quad \text{or} \quad \ln \frac{N_0}{N} = Kt \quad \text{converting to base ten} \quad 2.303 \log \frac{N_0}{N} = Kt$$

at half-life period, $t = t_{\frac{1}{2}}$, $N = \frac{N_0}{2}$, therefore

$$2.303 \log \left(\frac{N_0}{\frac{N_0}{2}} \right) = K t_{\frac{1}{2}}$$

$$2.303 \log 2 = K t_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{0.693}{K}$$

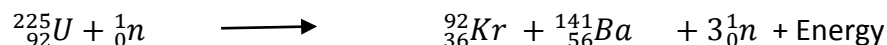
Worked example

Nuclear fission or atomic fission

Nuclear fission is the splitting of atomic nucleus into two approximately equal fragments, about half the size of the original nucleus, together with a number of smaller particles (neutrons, protons and α -particles).

A large amount of heat energy is released.

Spontaneous fission is the natural fission whereas induced fission is the fission of a nucleus brought about by bombarding a nucleus with neutrons.



During fission there is loss in mass and this mass is converted into energy according to Einstein's equation $E = MC^2$ Where E is energy, M is mass and C is speed of light.

Each of the fission neutrons (two or three) that are released can initiate the fission of another nucleus. This results in a nuclear chain reaction such as a nuclear chain reaction when unchecked produces a huge explosion. This is the basis of an atomic bomb.

Nuclear fusion

Is the process whereby two light nuclei join to form a heavier one. A large amount of energy is released during this reaction. It occurs at extremely high temperatures this is because large energies have to be given to the positively charged nuclei to overcome strong repulsive forces between them and unite them.

This is the basis of the hydrogen bomb. Thermo nuclear reaction take place on the stars and the sun producing a very high temperature of approximately 15×10^6 °C

Uses of radioactive isotopes

1. In carbon dating- carbon-14 can be used to calculate the age of plant and animal remains. Living plants and animals take in carbon which includes the radioactive isotope carbon-14. When a plant or animal dies it takes in no more carbon-14 and that which is already present decays. The rate of decay decreases over years and the activity that remains can be used to calculate the age of plant or animal.
2. Radioactivity is used to destroy cancer cells cobalt-60 is used to provide gamma rays to destroy cancer cells without harming patients' health tissues.
3. Used in surgery. Surgical instruments are more effectively sterilized by radioactivity than boiling.
4. Used for detection of leakage in underground water and fuel pipes. By introducing a short lived radioisotope into the pipe the level of radioactivity on the surface can be monitored. A sudden increase of surface radioactivity shows where water or fuel is leaking.
5. Tracer studies, tracer techniques use radioactive isotopes to track the path of an element through the body. Radioactive iodine is administered to patients with defective thyroids to enable doctors to follow the path of iodine through the body in the treatment of goitre.
6. In industry as tracers in detection of wear in machinery eg bearings, pistons.

7. Nuclear power stations harness the tremendous amounts of energy released when uranium-235 undergoes nuclear fission. The energy released, by this controlled chain reaction is then used to produce electricity.
8. Food preservation, the preservation of food using gamma rays is quite widespread worldwide. Treating food with gamma rays can: slow down the ripening of some fruits and sprouting of potatoes, kill highly dangerous micro-organisms such as salmonella, kill micro-organisms that spoil food.

Effects of radioisotopes

A radioactive material, despite its importance and numerous uses can be dangerous. Large dosages of ionizing radiations can kill living cells and whole organisms or can cause illness.

Low dosages over long periods can cause foetal deformities, leukemia, and bone cancer and other forms of cancer.

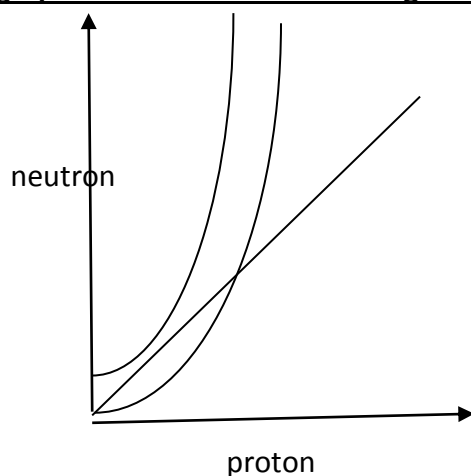
Stability of the nucleus and binding energy

A stable nucleus is one which does not undergo radioactive disintegration. A relatively stable nucleus possesses a very long half life. Light nuclei atomic numbers less than 20 are stable if their neutron to proton ratio is one, nuclides with even number of protons or neutrons or both are more stable than those with odd number of protons or neutrons.

Unstable nuclides are atoms having number of neutrons much greater than the number of protons and therefore undergo radioactive disintegration or decay emitting alpha or beta particles

Nuclides with atomic number greater than 83 are heavy and unstable hence undergo radioactive decay.

A graph of number of neutrons against number of protons



The graph shows a stable belt shaded area running diagonally starts to curve upwards at atomic number 20 and stops abruptly at atomic number 83.

All the known stable nuclei lie within the shaded area. Along the dotted line the nuclides have equal number of neutrons and protons.

Factors that determine stability of a nucleus

Atomic number/ atomic mass

Stability reduces as atomic mass increases. Atoms with atomic number greater than 83 are too heavy to be stable.

Half- life

The longer the half-life, the more stable the nucleus.

Binding energy

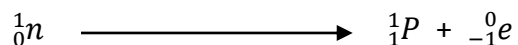
The greater the binding energy, the more stable the nucleus.

Binding energy is the energy given out when a nucleus is formed from the individual neutrons and protons or it is the energy required to separate the nucleus into the individual nucleons.

Neutron to proton ratio

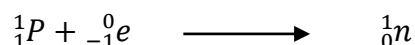
Very light nuclei atomic number less than 20 are stable if their neutron to proton ratio is 1. Relative light nuclei atomic number between 19 and 83 are stable if their neutron to proton ratio is slightly greater than 1

Nuclei with high neutron to proton ratio lying above the belt of stability gain stability by beta decay during beta ,a neutron splits up forming a proton and an electron



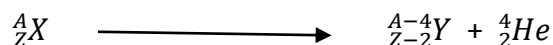
The proton remains in the nucleus but the electron is ejected. This results in the decrease in the number of neutrons in the isotope by one and the protons increases by one

Nuclei with low neutron to proton ratio lying below the belt of stability gain stability by positron decay or electron capture. The unstable nucleus captures an electron from its inner-most shell and the electron combines with a proton in the nucleus to form a neutron



The isotopes which undergo electron capture have fewer neutrons than stable isotopes.

Nuclei with atomic number greater or equal to 84 are heavy and lie beyond the upper right edge of the stable belt. These gain stability by emission of alpha particles which decreases both the number of neutrons and protons by two.



Very heavy nuclei cannot achieve stability with single emission such unstable nuclei undergo a series of emission.

Electronic structure of an atom

ATOMIC SPECTRUM

When an element or compound is heated in a flame, or by means electric discharge, they emit energy in form light. Analysis of this light with a spectroscope shows that a discontinuous spectrum appears in form of light, and this is known as atomic/line spectrum. And is a typical characteristic of an atom.

An atomic spectrum consists of patterns of lines which are found at various wave lengths and the actual pattern is different for each element.

The lines might be so closely grouped that they appear in bands. This is called band spectrum and is characteristic of a molecule.

NB: When energy is supplied to an atom, the outermost electrons are the first most likely to absorb energy .The energy gained by the electron causes it to move an added distance from the nucleus.

An electron which has been removed from a given level, but still within the influence of the nucleus may still fall back to the initial energy level with the emission of light energy .The energy given out is of definite amount for each unit is known as Quantum.

Quantum theory therefore states that matter cannot absorb or emit energy in continuous amounts but in small continuous units called quanta.

If energy supplied is enough to move an electron from an energy level, it will emit light of only one kind of wavelength on returning.

When the energy is enough to move an electron many energy levels away from the ground state, it returns in series of moves emitting different wavelengths of light for each transition level .

If energy is not enough to move an electron, no spectrum is emitted, and the energy absorbed by an atom just increases its potential energy.

$$\text{Emitted energy} = K.E = hf - hf_0$$

$$\text{But } f = \frac{c}{\lambda}$$

$$\text{Energy} = h\frac{c}{\lambda} - h\frac{c}{\lambda_0}$$

$$E = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

where

h is plank's constant

f is new frequency

f_0 is thresh hold frequency

c is velocity of light

energy at a given energy level $= \frac{hc}{\lambda}$

HYDROGEN SPECTRUM

When electric discharge is passed through hydrogen gas at low pressure in a test tube, it glows reddish pink .Many molecules break into single molecules.

If the light emitted is passed through a prism, the atomic spectrum of hydrogen which consists of series of sharp lines are recorded on a photographic plate .The atom emits both visible and invisible radiation.

FORMATION OF HYDROGEN SPECTRUM

When electricity is passed through a discharge tube containing hydrogen gas at low pressure the molecules break up into single hydrogen atoms.

The single electron of the hydrogen atom absorbs energy and is promoted from ground state (energy level $n= 1$) to higher energy levels where it becomes unstable.

When the electron falls back to the ground state, energy is given out in the form of radiations of particular wavelength.

On passing this light through a prism a discontinues line spectrum consisting of several sharp lines is obtained

This gives rise to the emission spectrum of hydrogen recorded on a photographic plate.

Four strong coloured lines were observed in the visible region of this spectrum by balmer, in the ultraviolet region by layman, in the infrared region by Paschen, bracket and pfund these series of lines were named after these scientists who discovered them. NB:In a hydrogen spectrum , there are four most prominent lines labeled h_α , h_β and h_γ and they are called balmer series. They are caused by electrons moving from higher energy to second level. They appear in Red, Green, Blue, and Violet.

The electron may fall back directly to ground state or it may fall in steps through different energy level

($n=2, n=3$, etc). to each energy level the electron falls, a different series of lines is found for example the balmer series are formed when the electron falls back to energy level $n=2$.

The wavelength of the lines and series to which they belong are related by the equation.

$$\frac{1}{\nu} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

Where ν = wave length of a particular line

R_H = Rydbergs constant (109678 cm^{-1})

n = energy level to which the electron has fallen

m = energy level from which the electron has fallen.

Emission line series and their regions

series	n	m	Region of the series
Layman	1	2,3,4,5	Ultraviolet
Balmer	2	3,4,5,	Visible
Paschen	3	4,5,6	Infrared
Bracket	4	5,6,7	Infrared
pfund	5	6,7,8	infrared

OR:

When light is passed through hydrogen atom electrons jump from ground state to excited state after absorbing energy of definite amount, thus forming absorption spectrum which is needed on a photographic plate.

THE EMISSION SPECTRUM OF HYDROGEN

The hydrogen spectrum is a series of lines, some in the visible region and others in the invisible region. In each series, the spacing between the adjacent lines decreases as frequency of the waves giving the lines increases or as wavelength decreases. The decrease in the spacing is

caused by decreased nuclear attraction on the electrons resulting into continuum in each series,

Evidence of existence of energy levels in atom

The hydrogen spectrum provides an evidence for existence of energy levels within an atom .

This is because;

Hydrogen has one electron yet it produces a spectrum containing many lines separated from each other.

There are several series of lines e.g. balmer series, layman series etc. each series representing a particular energy level to which an electron returns.

The spacing between adjacent lines in each series differs

There is a continuum in each series of lines

The light giving each line is of definite energy or frequency.

Give out light of different colours.

Each of the big line comprises of two small lines.

Bohr's explanation of the hydrogen spectrum

An atom consists of a small, heavily positively charged nucleus around which electrons revolve in definite circular paths called orbits.

These orbits are associated with definite energies called energy levels.

They are designated as K, L, M, N,.....etc shells or numbered as 1,2,3,4etc from the nucleus.

No energy is radiated by the electron while it is rotating in a permissible orbit.

The one electron of hydrogen being closet to the nucleus is in its lowest energy shell ($n=1$) or normal ground state it can absorb a definite amount of energy and jump to a higher energy state. This excited state being unstable, the electron comes back to a lower level.

The sample of hydrogen gas contains a large number of atoms and when energy is supplied, the electrons in the different hydrogen atoms absorbs different amounts of energies these are raised to different energy states for example, the electrons in some atoms may jump to second energy level while in others it may be to the third M fourth N and so on. These electrons come

back from higher energy levels to the ground state in one or more jumps emitting different amount of energies. Different line depends upon the difference in energies of the levels

The difference in energy levels become smaller with increasing distances of the energy levels from the nucleus

The convergence limit is reached when $n=\infty$ when an electron jumps from $n=1$ to $n=\infty$, the electron is said to be completely removed from the atom. The atom is said to be ionized and the energy required for this change is called ionization energy.

Electron distribution in atoms

TOPIC THREE: Bonding and structure

3.0 interatomic bonds

A chemical bond is inter-atomic or intermolecular or inter-ionic attraction which holds the constituents together.

A chemical bond can be formed when electrons are transfer from one atom to another or shared between two atoms.

During the transfer of electrons, one atom loses electron(s) which is or are simultaneously gained by another atom.

Electrons that are available and therefore can be involved in the bonding are the outermost electrons.

Atoms lose, gain or share outermost electrons in order to complete their octet and obtain a stable configuration.

3.2 Types of bonds

The chemical bond may be ionic, covalent, metallic or molecular (hydrogen bonding)

3.2.1 The ionic or electrovalent bond

When an atom loses one or more electrons it becomes a cation, which is positively charged ion. Atoms of metals form ions by loss of electrons. When an atom gains one or more electrons it becomes an anion, which is a negatively charged ion. Cations and anions attract each other to form electrovalent bond. in a reaction involving a metal and a non-metal, metal atoms lose electrons to attain the electron configuration of the nearest noble gas while non-metal atoms gain electrons also to attain the electron configuration of the nearest noble gas.

Therefore the ionic bond is an electrostatic attraction between the positively charged ions and the negatively charged ion.

Metals form positively charged ions because they have low ionization energies; non-metals form negatively charged ions because they have high values of electro negativities and electron affinities.

The following are some of the characteristics of electrovalent compounds

- They are usually solids at room temperature, with high melting points. This is due to the strong electrostatic forces holding the crystal lattice together. A lot of energy is therefore needed to separate the ions and melt the substance.
- They are usually hard substances

- They usually cannot conduct electricity when solid, because the ions are not free to move.
- They mainly dissolve in water. This is because water molecules are able to bond with both the positive and negative ions, which breaks up the lattice and keeps ions apart.
- They usually conduct electricity when in the molten state or in aqueous solution. The forces of attraction between the ions are broken and the ions are free to move.
- Ionic compounds are generally non-volatile and crystalline.

3.2.2 The covalent bond

This is a bond formed by sharing of electrons between two atoms in which each atom contributes an electron(s) in the formation of the bond e.g X-Y

The covalent bond is formed when the two atoms achieve the noble gas stability by sharing a pair of electrons, where each of the bonding atoms contributes one electron to the pair.

It is generally the tendency of non-metals to form covalent bonds.

If two atoms have both high electro negativities and the difference between their electro negativities is small or none, they are most likely to form a covalent bond.

There are three types of covalent bonds

a) simple covalent bond

This is a covalent bond formed between two similar atoms or two different atoms with the same electro negativity for example carbon to carbon, carbon to hydrogen. Compounds with such a covalent bonds are purely non-polar and are insoluble in water soluble in organic solvents and are made up of discrete molecules.

b) polar covalent bond

this is a bond formed between two atoms in which one atom is more electro negative than the other

the more electro negative atom attracts the shared electrons towards itself gaining partial negative charge and inducing partial positive charge on the less electronegative atom e g in HCl chloride atom is more electro negative than hydrogen

$\text{H}^+ \text{ --- } \text{Cl}^-$ the result brings about a dipole.

A dipole is a separation of 2 positive charges by a small distance

such compounds are soluble in non-polar solvents but also readily soluble in water.

c) the co-ordinate covalent or dative bond

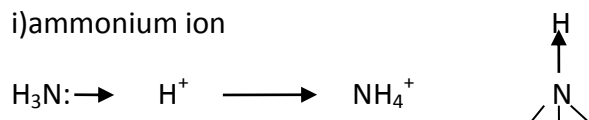
This is a bond formed between two atoms in which the shared electron pair is contributed by one atom.

The atom contributing the electron pair must be having a lone pair of electrons and the atom which is accepting the lone pair must be having an empty orbital

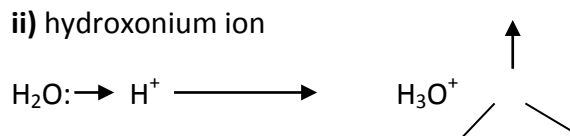
A coordinate bond once formed becomes similar in properties to a normal covalent bond. However it is weaker than normal covalent bond

When the difference between coordinate and normal covalent bond need not be shown, both bonds may be represented by a single line. When it is necessary to show the difference, the coordinate bond is shown by an arrow pointing to the acceptor atom. The following are typical molecules involving dative bonding.

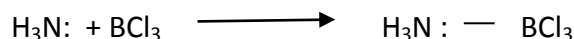
i) ammonium ion



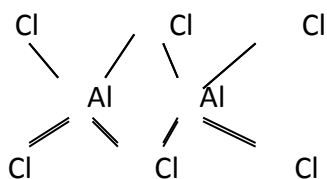
ii) hydroxonium ion



iii) dative bonds can be formed between molecules eg ammonia combines with boron chloride through a dative bond



some chloride dimerise in vapour form through dative bond e.g. AlCl_3 or FeCl_3



The covalent bond may be shown by dots, crosses or a line (-) or dash to represent the bonding electrons.

For example



In these examples each hydrogen atom acquires the helium structure (doublet) each carbon atom achieves the neon configuration, and each chlorine atom acquires the argon configuration.

It is possible to form multiple bonds between two non-metal atoms. When two electrons are shared between two atoms one from each atom we represent them by single line eg Cl-Cl.

When four electrons are shared such that each atom contributes two electrons we may represent the double bond formed by two lines e.g. $\text{O}=\text{O}$ likewise when six electrons are shared such that each atom contributes three electrons we may represent the triple bond by three lines $\text{N}\equiv\text{N}$.

The following are some characteristics of covalent compounds

- Low molecular weight covalent compounds are volatile gases; others are liquids at room temperature. They exist as solids when their molecular weights are high.
- Their melting and boiling points are relatively low compared to ionic compounds
- They are generally insoluble in water but soluble in organic solvents
- They do not conduct electricity both in the molten state and in solution
- Generally they do not form ions in solution.

POLARISATION AND ITS EFFECTS ON IONIC AND COVALENT BONDS

The bonding in most compounds is intermediate between purely ionic and purely covalent.

Purely ionic bonds cannot exist, as the proximity of the ions involved in the bond allows some degree of sharing electron density between them.

The electrons tend to be more or less shared hence purely ionic bond gains some degree of covalency.

If the positive ion is small and/or highly charged, it will attract the electrons in the anion and repel its nucleus bringing about distortion

This distortion of the electron cloud of the negative ion is called **polarization**.

Therefore, all ionic bonds have some covalent character. Thus, an ionic bond is considered a bond where the ionic character is greater than the covalent character. The larger the difference in electro negativity between the two atoms involved in the bond, the more ionic (polar) the bond is

Electro negativity is the tendency of an atom to attract bonding electrons towards its self so as to become negatively charged in a covalent bond.

The ability of a cation to polarize an anion is called its polarizing power and it depends on the strength of the electric field used to pull electrons away from the anion. The stronger the electric field the greater the polarization of the anion and the more covalent character introduced.

The electric field strength is based on the charge density of the cation. The charge density is proportional to the charge to radius ratio of the cation. It means the greater the charge to radius ratio value, the greater the polarizing power of the cation for an ion which is polarizable.

The ability of an anion to get polarized is called its polarisability it depends on the product of anionic radius and magnitude of charge. The higher the product the greater the covalent character or polarisability.

Polarization in ionic bonds is increased by the following factors which introduces covalent character into ionic bonds

- i) small cation radius with high charge.
- ii) large anion radius with high charge.

Some of the covalent properties polarization can induce are low melting or low boiling point and solubility in organic solvents

$$\text{Polarizing power of a cation} = \frac{\text{charge on the ion}}{\text{ionic radius}}$$

For a cation to have high polarizing power, it must be having high charge and small ionic radius for example Lithium, beryllium, boron and aluminium ions. The charges on the above ions are higher compared to their radius therefore most of their compounds have higher degree of covalence

Larger negative ions are more easily polarized, but the effect is usually important when positive ions with charges of 3+ (e.g. Al^{3+}) are involved. However, 2+ ions (e.g. Be^{2+}) or even 1+ (e.g. Li^+) show some polarizing power because their ionic radii are so small.

Decrease in ionic character in period 3

chlorides	charge	Radius(nm)	Charge density	Melting point($^{\circ}$ C)	Solubility in non polar solvents
NaCl	+1	0.102	9.8	801	Insoluble
MgCl ₂	+2	0.072	27.8	714	Soluble
AlCl ₃	+3	0.053	56.6	190	soluble

Effects of polarisability of anions

compound	Anionic radius	Anionic charge	Radius x charge	character	Melting point
MgF ₂	0.136	-1	0.136	ionic	1361
MgI ₂	0.216	-1	0.216	Covalent	637

COMPOUND	melting point(k)
Al ₂ O ₃	2290
AlCl ₃	451
CaO	2850
CaCl ₂	1051

We note that the melting point of aluminium chloride is lower than that of aluminium oxide. This is explained by the fact that the chloride ion has a bigger ionic radius than the oxide ion. Aluminium chloride is thus more covalent than aluminium oxide. It can also be argued that aluminium chloride is more covalent than calcium chloride due to very high charge density of the aluminium ion compared to that of the calcium ion.

POLAR COVALENT COMPOUNDS

when a covalent bond is formed between two atoms of different electro negativity, the bonding electrons are not equally shared. This brings about electrical dipoles within the bond .The molecule is said to be polar

e.g H-F

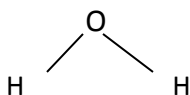
Other examples of polar molecules include water, hydrogen chloride, sulphur dioxide, phosphorous trichloride and ammonia among others.

When the resultant dipole moment is not equal to zero then the molecule is polar and the bond is polar

Because of the dipoles, polar molecules possess some ionic character

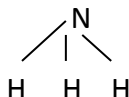
Example

Water



Since the dipole moment is not zero water molecules are polar

Ammonia



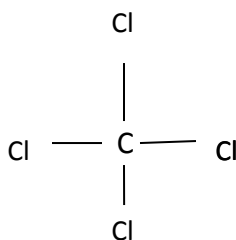
Nitrogen-hydrogen bond is polar, since the dipole moment is not zero ammonia molecule is polar

However, some molecules have polar bonds but they are not polar themselves.

An example of such molecules are

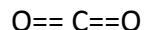
carbon tetrachloride (CCl_4).

.



chlorine is more electro negative than carbon therefore attracts bonding pair of shared electrons towards its self . gaining partial negative charge inducing partial positive charge on carbon the carbon-chloride bond therefore is polar but due to symmetrical arrangement of chloride atoms about carbon the dipole moment in all direction are equal and opposite and therefore cancel out the dipole moment and the resultant dipole moment is equal to zero such that the **CCl_4** molecule is non -polar .

carbon dioxide



Oxygen is more electro negative than carbon therefore attracts bonding pair of shared electrons towards its self gaining partial negative charge inducing partial positive charge on carbon the carbon-oxygen double bond therefore is polar but due to symmetrical arrangement of oxygen atoms about carbon the dipole moment in all direction are equal and opposite and therefore cancel out the dipole moment and the resultant dipole moment is equal to zero such that the CO_2 molecule is non polar .

The metallic bond

In metallic bonding, each metal loses its valency electrons forming metal cations. The metal cations are attracted together by the cloud of lost electrons resulting into strong metallic bonds.

Thus a metallic bond can be defined as an electrostatic force of attraction between positively charged metal ions and a cloud of negatively charged electrons lost by metal atoms. The lost electrons are delocalized and free to move throughout the entire metal lattice thus metals conduct electricity and heat.

The strength of the metallic bonds depends on the atomic radius and the number of valence electrons delocalized. Generally the smaller the atomic radius and the greater the number of valence electrons the stronger the metallic bond.

The alkali metals, which form large cations, have only one electron per atom which is available to enter the delocalized system. The strength of the metallic bond is therefore low, and these metals have low melting points and are soft, malleable and ductile.

Transition metals form small cations and can release quite a number of electrons into the metallic bond. These metals are hard with high tensile strength and have high melting points, corresponding to a strong metallic bonding system.

INTERMOLECULAR FORCES OF ATTRACTION

In any liquid or solid there are forces between molecules these are called inter molecular forces

A dipole is a molecule (or part of a molecule) with a positive end and a negative end for example



When a molecule has a dipole we say it is polarized.

Molecules with permanent dipole are polar.

1) Dipole-dipole forces of attraction

These occur between polar molecules, the dipole is formed by an unequal sharing of electrons.

The dipole-dipole forces are caused by attraction of a partially positive end of a dipole to an oppositely charged end of another nearby dipole.



The intermolecular dipole-dipole forces are weak and in their solid state these substances form softer solids with melting points generally much lower than those of ionic and metallic solids.

Many of those dipole molecules are soluble in water using hydrogen bonding and dipole-dipole attraction. Release of energy makes their dissolution favorable.

2. Vander waal's forces of attraction

Inert gases and other non-polar and polar molecules are bonded by van der Waals forces.

Van der Waals forces are weak electrostatic forces binding all polar and non-polar molecules together.

They are much weaker than covalent, ionic or metallic. They are forces responsible for non-metallic behavior of gases and for the lattice energy for molecular crystals. The dipoles involved can be either permanent or temporary. These intermolecular forces are weaker than the interatomic forces. Less energy is needed to overcome intermolecular forces.

The more polar the molecule, the stronger the van der Waals forces.

There are three factors that cause such forces;

Dipole-dipole interaction

i.e. the electrostatic attraction between two molecules with permanent dipole moment

Induced dipole- induced dipole

These are dipoles of one molecule polarize the neighboring molecule

The electron distribution in a non-polar molecule or atom of an inert gas is not always symmetrical at a given time such that one side has more electrons than the other, it becomes a dipole. This dipole will induce another dipole on a neighboring atom. There will exist a weak

force of attraction between the two existing molecules or atoms. It depends on the number of electrons and therefore size of the molecules.

Dispersion forces caused by small instantaneous dipole in atoms

3.The hydrogen bonds

Hydrogen bonding it is the electrostatic attraction between a strongly partially positive hydrogen atom attached covalently to the highly electro negative elements fluorine, nitrogen or oxygen and a strongly partially negative fluorine, nitrogen or oxygen atom on another molecule.

Hydrogen bonding can form between molecules or within molecule.

Hydrogen bonding are usually shown as broken lines and are longer than covalent bonds.

Hydrogen bonding has considerable effects on the properties of substances which have it.

Effects of hydrogen bonding

The boiling point of hydrogen fluoride is abnormally higher than that of other hydrides of group (vii)

i.e HCl,HBr and HI.

HCl,HBr and HI molecules are held by weak Vander-waals. Boiling point increases with increase in magnitude of the vander waal forces.

The magnitude of vander-waals forces increase with increasing formula mass.

Molecular mass of the hydrides increase in the order $\text{HCl} < \text{HBr} < \text{HI}$. Hydrogen fluoride has an abnormally high boiling point because its molecules associate through hydrogen bonds due to the high electro negativity of fluorine.

-Ammonia has a higher melting point and boiling point than other hydrides of group (v)i.e PH_3 and ASH

-Water is a liquid and has higher boiling point than hydrides of group(VI), which are gases

i.e. H_2S and H_2Se .

-Ice floats on water due to having a lower density than water.

In ice, the water molecules are held by hydrogen bonds. Each oxygen atom is covalently bonded to two hydrogen atoms and then also to two other hydrogen atoms through hydrogen bonds. This gives ice an extremely open tetrahedral structure with low density.

In liquid water, the hydrogen bonds are constantly broken and reformed due to thermal movement of water molecules. This leads to close packing of water molecules thus a higher density than ice.

-The formula mass of ethanoic acid as determined by freezing point depression method in benzene is twice the theoretical formula mass. This is because ethanoic acid associates in benzene through hydrogen bonding to form dimers.

-Alcohol molecules are held by strong hydrogen bonds while Alkane molecules are held by weaker van der Waals forces. Intermolecular forces in alcohols are therefore stronger than those in Alkanes thus alcohols require more energy for these forces to be broken.

EVIDENCE FOR EXISTENCE OF HYDROGEN BONDS

We are surrounded by substances that exhibit presences of hydrogen bonds.

Notable among these includes the following facts;

-Ice has a lower density than water.

-Boiling points of carboxylic acids and alcohols are higher than those of other hydrocarbons of comparable formula mass.

-Amines have higher boiling points than Alkanes of approximately the same molecular mass. Also since primary amines form more hydrogen bonds than secondary amines, primary amines have higher boiling points than secondary amines.

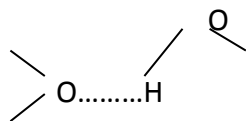
-Molecular masses of carboxylic acids determined by cryoscopic method in organic solvents are observed to be twice the theoretical ones. This is because carboxylic acids dimerise in organic solvents through hydrogen bonding.

-Ammonia, water and hydrogen fluoride have higher boiling points than hydrides of group v,vi,vii respectively.

Types of hydrogen bonding

1.intermolecular hydrogen bonds

This is the type of hydrogen bonds that exist between the same or different molecules.



2.intra hydrogen bonding

this is the type of hydrogen bonding formed between atoms of the same molecule e.g 2-nitrophenol

intra hydrogen bonding reduces the molecular attraction between molecules and consequently reduces the melting and boiling points of a compound

- 2-hydroxybenzoic acid has a lower boiling point than 4-hydroxybenzoic acid. This can be explained by first considering their structures below;

In 2-hydroxybenzoic acid, the functional groups are very close to each other hence molecules form more intra-molecular hydrogen bonds than inter-molecular hydrogen bonds. Therefore very few intermolecular hydrogen bonds need to be broken thus low boiling point.

In 4-hydroxybenzoic acid, the functional groups are very far apart thus 4-hydroxybenzoic acid forms more inter-molecular hydrogen bonds than intra-molecular hydrogen bonds. Therefore very many inter-molecular hydrogen bonds have to be broken for 4-hydroxybenzoic acid to boil. This requires a lot of energy hence a high boiling point.

Representation of covalent bonds

A pair of electrons shared between two atoms is represented in electron dot/cross diagrams or by a dash (-). One, two or three dashes indicate single, double or triple bonds respectively. The bonds are formed starting from the single atoms to achieve the stable configuration. Only outer electrons involved in the bonding are shown. Valence electrons which are actually donated and shared to form covalent bonds are called bonding electrons. Those which are not shared but help in giving the atoms their octet of configuration are called non-bonding electrons.

A pair of electrons on an atom which is not shared is called a lone pair. Lone pairs of electrons can be used for bonding

The shapes of molecules and ions

Shapes of molecules and ions can be predicted using the valency shell electron pair repulsion theory (VSEPR)

The VSEPR theory is based on the following principles:

1. All electrons have electrostatic repulsions for one another
2. Electron pairs around a central atom are distributed so as to minimize repulsion between them
3. The shape of any molecule is determined by the number of electron pairs around a central atom
4. Repulsion decreases in the sequence :lone pair-lone pair>lone pair- bonding pair>bond pair-bond pair
5. Repulsion between orbital's is increased by increased electro negativity of the central atoms the more electronegative the central atom is the greater the electron displacement.

The most stable structure is one where there is maximum distance between electron pairs (i.e least repulsion)

The total number of electron pairs in a molecule is given by VSEPR formula: AX_mE_n

Where;

A=central atom,

X=bond pairs

E=Lone pairs of electrons

M&n= integers

Note:Total electron pairs=bond pairs+lone pairs

Geometry adopted by molecules

Case 1: AX_2 (2 bond pairs and 0 lone pairs)

- Such molecules will adopt a linear structure

X-E-X minimum repulsion when $\angle XAX=180^\circ$)e.g $BeCl_2, CO_2, C_2H_2, HCN$ e.t.c

Case 2: AX_3 (3 bond pairs and 0 lone pairs)

- Such molecules will adopt a trigonal planar structure with a bond angle of 120°
e.g. SO_3, BF_3

Case 3: AX_4 (4bonding pairs and 0 lone pairs)

- Such molecules will adopt a tetrahedral structure with a bond angle of 109.5°
e.g. $CH_4, CCl_4, SO_4^{2-}, PO_4^{3-}$

Case 4: AX_5 (5 bonding pairs and 0 lone pairs)

- Such molecules will adopt a trigonal bi-pyramidal structure. e.g. PCl_5

Case 5: AX_6

- Such molecules will adopt a structure bi-pyramidal or octahedral structure. e.g. SCL_6

Case 6: AX_7

- Such molecules will adopt a pentagonal bi-pyramidal structure. e.g. IF_7

EFFECT OF LONE PAIR ON THE GEOMETRY ADOPTED

NOTE: the lone pair is not considered in naming the geometry adopted

Consider a molecule with 4 electron pairs:

- ❖ AX_4E_0 (e.g. BF_4^- , CH_4 , CCl_4 , NH_4^+)
Geometry adopted = tetrahedral structure
- ❖ AX_3E_1 (e.g. NH_3 , PH_3 , PCl_3 , H_3O^+)
Geometry is trigonal pyramidal
- ❖ AX_2E_2 (e.g. H_2O , H_2S , H_2Te , NH_2^-)
Such molecules will adopt a V-shaped structure

Consider a molecule with 5 electron pairs:

- ❖ AX_5E_0
Such molecules will adopt a trigonal bi-pyramidal structure e.g. PCl_5
- ❖ AX_4E_1
Such molecules normally adopt a distorted tetrahedral structure or square planar e.g. SF_4
- ❖ AX_3E_2
Such molecules will adopt a T-shaped structure e.g. ClF_3
- ❖ AX_2E_3
Such molecules will adopt a linear structure e.g. XeF_2 , ICl_2^-

HOW TO DETERMINE THE NUMBER OF LONE PAIRS AND BOND PAIRS IN A MOLECULE .

NOTE: lone pairs considered are those on the central atom: all valence electrons of central atom considered & only electron(s) contributed to bonding is/are considered for a non-central atom

a) Working out the shapes of molecules with single bonding pairs

The number of electron pairs in molecules containing only single bonds is found by the following steps

1. Identify which atom is at the Centre of the molecule.
(usually the atom of which there is only one).

2. Determine the number of the outer electrons or valence electrons it has, this is equal to its group number within the periodic table.

3. Add one electron for each atom joined to the central atom to the number of the outer electrons




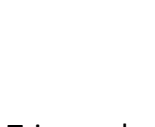


4. Divide the sum by two to get the number of electron pairs.

5. Determine the number of lone pairs (non-bonding pair)

(Number of lone pairs=number of electron pairs – number of bonding atoms)

6. For the structure and name of the shape refer to the last table

Examples of working out of shapes of molecules

molecule	BeCl ₂	BF ₃	CH ₄	PCl ₅	NH ₃	H ₂ O
Bonding atoms	2	3	4	5	3	2
1	Be	B	C	P	N	O
2	2	3	4	5	5	6
3	2+2=4	3+3=6	4+4=8	5+5=10	5 +3=8	6+2=8
4	$\frac{4}{2}=2$	$\frac{6}{2}=3$	$\frac{8}{2}=4$	$\frac{10}{2}=5$	$\frac{8}{2}=4$	$\frac{8}{2}=4$
5	2-2=0	3-3=0	4-4=0	5-5=0	4-3=1	4-2=2
6	 linear	 Triagonal planar	 tetrahedral	 Triagonal bipyramidal	 Triagonal pyramidal	 bent

Working out the shapes of charged molecules with single bonding pairs

The number of electron pairs in molecules containing only single bonds is found by the following steps

1. Identify which atom is at the Centre of the molecule.
(usually the atom of which there is only one).

2. Determine the number of the outer electrons or valence electrons it has, this is equal to its group number within the periodic table.

3. Add one electron for each atom joined to the central atom to the number of the outer electrons, then .Add an electron if the particle is negatively charged; subtract an electron if the particle is positively charged

4. Divide the sum by two to get the number of electron pairs.

5. Determine the number of lone pairs (non-bonding pair)

(Number of lone pairs=number of electron pairs – number of bonding atoms)

6. For the structure and name of the shape refer to the last table

molecule	NH_4^+	H_3O^+	NH_2^-	PCl_4^+	ICl_2	
Bonding atoms	4	3	2	4	2	
1	N	O	N	P	I	
2	5	6	5	5	7	
3	$5+4-1=8$	$6+3-1=8$	$5+2+1=8$	$5+4-1=8$	$7+2+1$	
4	$\frac{8}{2}=4$	$\frac{8}{2}=4$	$\frac{8}{2}=4$	$\frac{8}{2}=4$	$\frac{10}{2}=5$	$\frac{8}{2}=4$
5	$4-4=0$	$4-3=1$	$4-2=2$	$4-4=0$	$5-2=3$	
6						

VSEPR SHAPES OF COMPOUNDS WITH MULTIPLE BONDS

Many molecules and ions contain oxygen. This oxygen is; sometimes double bonded and sometimes single bonded, in which case the oxygen atom carries a minus charge.

The shape of these particles can be worked out by the following these steps:

1. Identify which atom is at the Centre of the molecule.
(usually the atom of which there is only one).

2. Determine the number of the outer electrons or valence electrons it is using in bonds to the oxygens , this is equal to its group number within the periodic table.

3. Determine the number of single bonded oxygen atoms

(For each minus charge on the particle there is one single bonded oxygen atom with a minus charge)

4. Determine the number of double bonded oxygen atoms.

5. Draw the two types of oxygen around the central atom and

6. Check if there are any unused pair of electrons, these will be the lone pairs put them in

6. Choose the shape of the number of electron charge clouds around the central atom.

molecule	CO_3^{2-}	SO_3^{2-}	SO_4^{2-}	SO_3	NO_3^-	ClO_3^-
1	C	S	S	S	N	Cl
2	4	6	6	6	5	7
3	2	2	2	0	1	1
4	1	1	2	3	2	2
5						
6	4-4=0	6-4=2(1p)	6-6=0	6-6=0	5-5=0	7-5=2(1p)
7						

Effect of electro negativity of atoms on the bond angles

Consider the bond angles group(v) hydrides

compound	NH_3	PH_3	AsH_3	SbH_3	
Bond angle	107	94	92	91	

Bond angles within a molecule decreases with decreases in electro negativity of the central atom. This is because the highly electro negative central atom with draws electrons towards its

self this increases repulsion between the bonds as the attraction of the central atom for electrons falls the bonding pairs are less closely held consequently, bond angles of group(v) hydrides reduce in that order

However, bond angles within a molecule reduces with increase in electro negativity of the ligands ie

Compound	PF ₃	PCl ₃	PBr ₃
Bond angle	96.3	100	101

TOPIC 4 : THERMOCHEMISTRY

Thermochemistry is the study of energy changes that accompany chemical reactions.

It deals with the measurements or calculations of heat absorbed or heat given out in a chemical reaction.

In the course of chemical reactions, bonds between atoms are broken and new bonds are made as atoms regroup to form new substances.

Energy is needed to break bonds in reactants and energy is released when new bonds are made in products. It's very, very unlikely that these two processes will be exactly in balance, and so some energy will either be released to the surroundings or absorbed from the surroundings.

Thermochemical terminology

The System is the part under study for example hot water in the beaker

The surroundings the outside of the system

Energy is a measure of systems capacity to do work.

Work an energy transfer that is the result of a force moving a body through a distance.

Heat an energy transfer that is the result of temperature difference between a system and its surroundings.

Temperature is the property of a system that determines the direction of heat flow between the system and its surroundings. Heat flows from a hotter region to the colder.

Enthalpy(symbol H) is a term that describes the heat content of the system. its actual value cannot be measured.

Enthalpy change (symbol ΔH read delta H) is the difference between heat content of the products and reactants measured at constant temperature and pressure during a chemical reaction.

ΔH is measured in kilo joules per mole and at constant pressure.

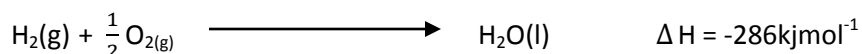
ΔH is written at the end of a chemical equation.

Enthalpy change is called heat of reaction and is denoted as ΔH_{rxn}

Where $\Delta H = \sum H_{\text{product}} - \sum H_{\text{reactant}}$

HEAT OF REACTION

Is the amount of heat evolved or absorbed when the reaction occurs between molar quantities of the substance as represented by the equation



This means that when one mole of hydrogen in gaseous state reacts with half mole of oxygen in gaseous state to form one mole of water with evolution of 286 kJ mol^{-1} of energy.

Per mole relates to the whole equation expressed in mole quantities

TYPES OF HEAT OF REACTION

Exothermic reactions; this is a chemical reaction accompanied by evolution of heat to the surroundings

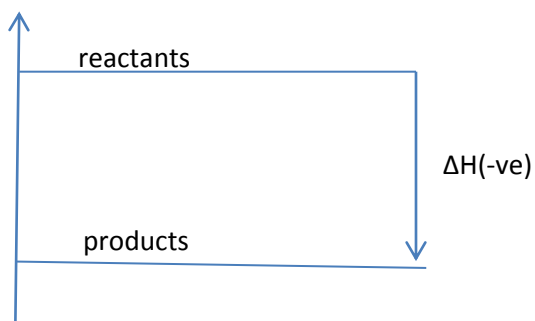
It's characterized by rise in temperature

In such reactions the heat content of products is less than that of the reactants

The enthalpy of reaction is therefore negative.

The negative sign of the enthalpy changes shows that the reacting system has lost heat energy to the surroundings.

These changes can be represented on an energy level diagram.



Examples of exothermic reactions include;

All combustion reactions

Most neutralization reactions

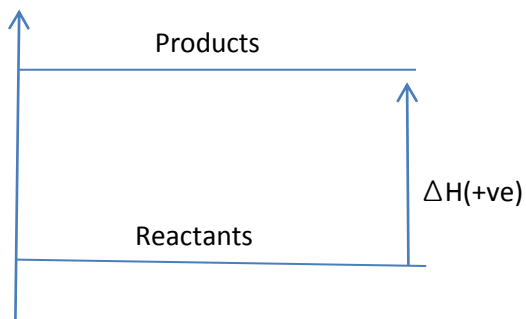
Endothermic reactions; this is a chemical reaction accompanied by absorption of heat from the surroundings

It's characterized by a fall in temperature

In such reactions the heat content of products is more than that of the reactants enthalpy of reaction is positive.

The positive sign of the enthalpy changes shows that the reacting system has gained heat energy from the surroundings.

These changes can be represented on an energy level diagram.



Examples of endothermic reactions include

Dissolution of ammonium nitrate

Formation of carbon disulphur from sulphur and carbon

THE QUANTITY OF HEAT DEPENDS ON

- i) amount of substances involved
- ii) physical state of reactants and products
- iii) temperature at which the experiment is carried out
- iv) pressure at which the experiment is carried
- v) Allotropic form of the element

STANDARD CONDITIONS OF HEAT CHANGES

In order to make comparisons, the energy changes of reactions are determined under standard conditions. Any heat change measured under standard conditions is described as a standard heat of reaction or standard enthalpy change denoted by ΔH^\ominus (which refers to an enthalpy(H)change(Δ) under standard conditions($^\ominus$))

Standard conditions are

- The gases at a pressure of one atmosphere
- Temperature of 25 $^\circ$ C (298K)
- Solutions of unit concentrations
- Substances in their standard states (s, l, g).

The standard state of a substance is the physical state of substance under standard conditions. (s, l, and g) at 1 atmosphere pressure and at 298 K.

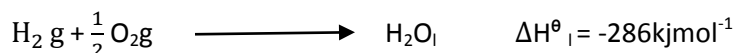
STANDARD ENTHALPY CHANGE

Is the amount of heat given out or taken in when molar quantities of reactants as stated in the equation react together under standard conditions.

TYPES OF STANDARD ENTHALPY CHANGES

STANDARD ENTHALPY OF FORMATION

is the enthalpy change when one mole of the compound is formed from its constituent elements in their standard states at 298K and 1 atmosphere. e.g.



Note

- In all cases the equation must be written so that one mole of a compound is formed
- Start from element the only compound is the equation is the one being formed
- Everything must be present in its standard state
- The enthalpy of formation an element like oxygen in its standard state is zero

The formation of $\text{H}_2(\text{g})$ from $\text{H}_2(\text{g})$ does not involve a chemical change so there is no enthalpy change.

Importance of enthalpy of formation

1. It gives a guide to the stability and reactivity of a compound formed. Compounds with negative values of heat of formation are more stable with respect to their elements and less reactive. Whereas compounds with positive values of enthalpy of formation are more reactive and unstable with respect to their elements.
2. It is used for comparing electro negativity values of elements ie the greater the electro negativity in a binary compound the more exothermic is the heat of formation and the more stable is the compound.

Enthalpies of formation are not measured experimentally but determined indirectly.

Problem

Write equations representing the enthalpy change of formation of

a) sodium iodide, NaI_{s}

.....

b) ethanol, $\text{CH}_3\text{CH}_2\text{OH}_{(\text{l})}$

.....

c) aluminium oxide, $\text{Al}_2\text{O}_{3(\text{s})}$

.....

d) sodium chlorate, $\text{NaClO}_{3(\text{s})}$

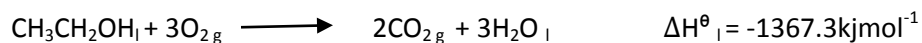
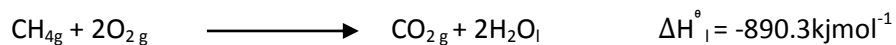
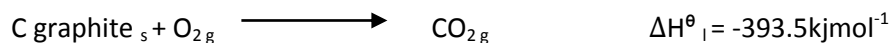
.....

e) ethane, $\text{C}_2\text{H}_{6(\text{g})}$

.....

STANDARD ENTHALPY OF COMBUSTION (ΔH_{c})

This is the heat evolved when one mole of a substance in its standard state is completely burnt in excess oxygen under standard conditions.eg



Note

You must be burning only one mole of the substance

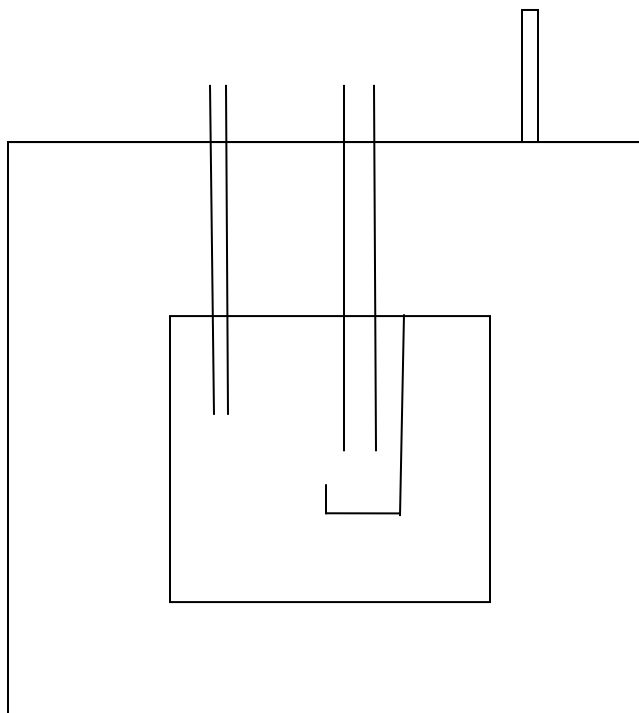
Importance of enthalpy of combustion

1. Since the values can be determined experimentally, the method is used on large scale to determine the heating values of fuel.
2. It helps in nutrition so that suitable food stuff is recommended to an individual depending on its energy requirement.
3. They are used to calculate the enthalpy of formation of substance.
4. The values can be used to estimate the difference in the energy content of allotropies (allotropies are different forms of the same element)
5. It is used to establish structure of organic compounds since compounds with the same number of atoms and similar bonds have almost the same value of enthalpy of combustion.

Experimental determination of enthalpy of combustion of a substance,

(i) Using a bomb calorimeter.

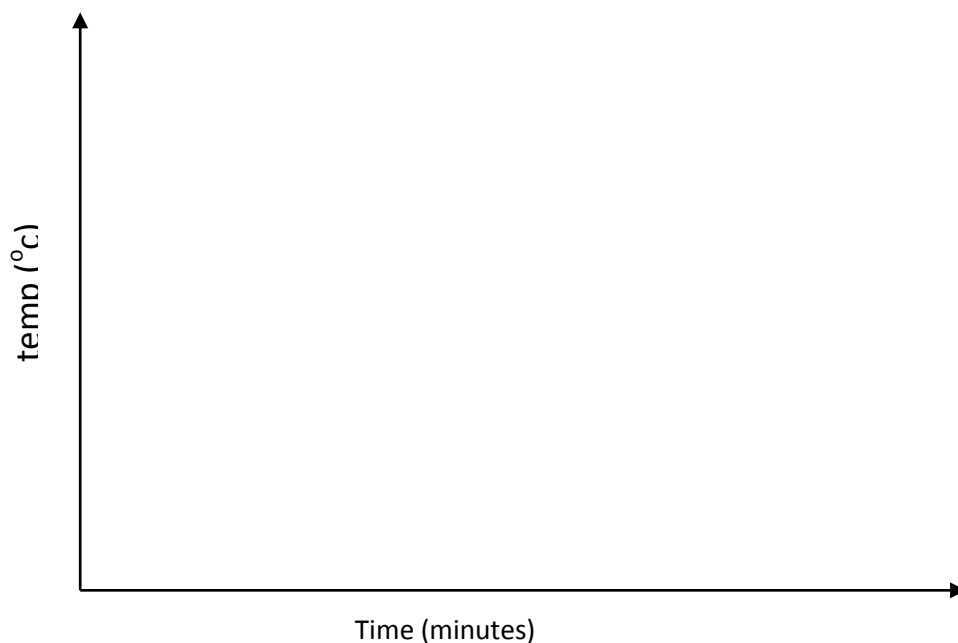
Apparatus setup



Procedure

- ✓ A known mass of a substance (say $a\text{ g}$) to be ignited is placed in a crucible suspended in a bomb calorimeter.
- ✓ The bomb is filled with oxygen and immersed in a calorimeter containing a known volume of water (say $V\text{ cm}^3$)
- ✓ The temperature of water is recorded every minute for five consecutive minutes.
- ✓ The substance is then ignited by passing electric current through the fuse wire.
- ✓ The substance burns and the heat generated raise the temperature of water.
- ✓ The temperature of water is recorded for a period of time after a certain known interval until the temperature has shown a fall for five consecutive minutes.
- ✓ A graph of temperature against time is plotted and the maximum rise in temperature is determined

Graph



Neglecting heat gained by a thermometer and calorimeter.

Heat evolved by burning the compound is equal to the heat gained by water.

$$\begin{aligned}
 \text{Heat gained by water} &= (\text{mass of water}) \times (\text{s.h.c}) \times (\text{temp change}) \\
 &= (\text{density of water} \times \text{volume of water}) \times (\text{s.h.c}) \times (\text{temp change}) \\
 &= (v \times \rho \times C \times \Delta T) \text{ joules}
 \end{aligned}$$

$$\text{Heat evolved by burning ag of substance} = (v \times \rho \times C \times \Delta T) \text{ joules}$$

$$\begin{aligned}
 \text{Heat evolved by burning one mole of substance} &= \frac{V \times \rho \times C \times \Delta T \times m}{1000 \times a} \text{ kJmol}^{-1} \\
 &= \left(\frac{V \times \rho \times C \times \Delta T \times M}{a \times 1000} \right) \text{ kJmol}^{-1}
 \end{aligned}$$

Where ρ is the density of water

C is the heat capacity of water;

M is the molar mass of a substance

Problems

1-Write equations representing the enthalpy change of combustion of

a)hydrogen

b)carbon

c)methane,CH₄ (g)

d)ethanol,C₂H₅OH(l)

e)ethane,C₂H₄ (g).....

2-describe laboratory experiment to determine the enthalpy of combustion of ethanol by spirit lamp

Laws of thermo chemistry

There two laws of thermo chemistry and are based on the principle of conservation of energy

This states that;

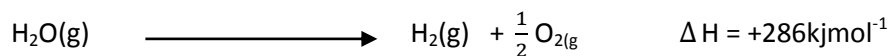
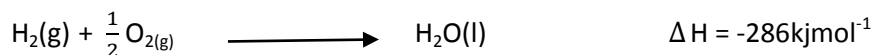
Energy cannot be created nor destroyed but may be converted from one form into another.

The first law was given by **Lavoisier** and **Laplace's** in 1780

It states that

The heat change in a reaction is equal to and opposite to heat change in a reverse reaction

Which means that if the reverse of a chemical reaction is written, the sign of enthalpy change is changed, but its magnitude remain same

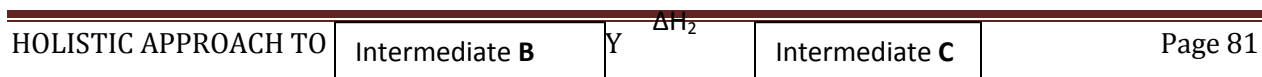


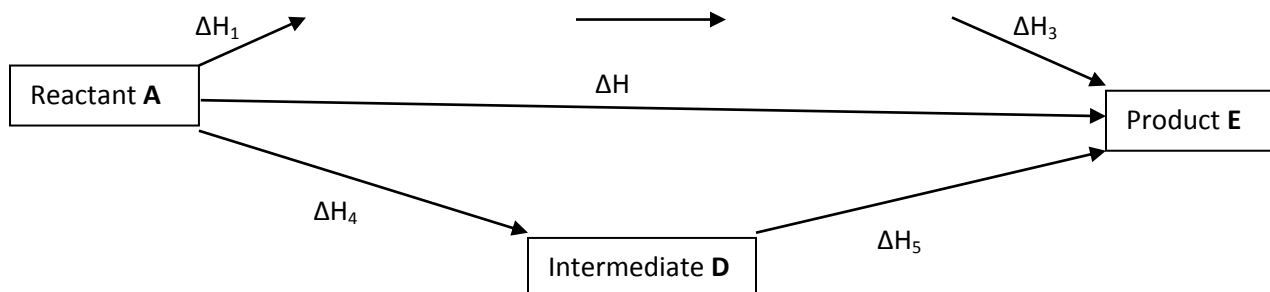
Hess's law of constant heat summation

It states that enthalpy change for a given reaction is independent of the route by which the reaction is achieved, provided that the, pressure and physical states of the reactants and products are the same in each case.

This means that if you convert reactant A into product E in one step or in many steps, the overall enthalpy change is always the same.

For example





$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= \Delta H_4 + \Delta H_5\end{aligned}$$

Significance of Hess's law

It can be used in the determination of enthalpies of reactions which cannot be experimentally determined e.g. enthalpies of formation.

Using Hess's law to calculate enthalpy changes

Step 1

Write down a balanced equation for the enthalpy you are asked to find.

Step 2

Use the information you are given to complete a cycle that you can apply Hess's law to. The direction of arrows depends entirely on the information given.

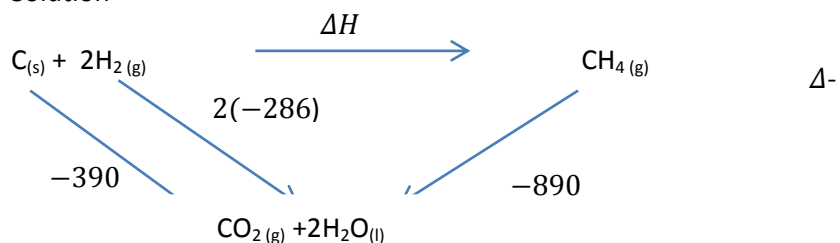
Step 3

Find two routes within the diagram which do not go against the flow of any arrow

Example 1

Calculate the standard enthalpy of formation of methane given that the standard enthalpies of combustion of carbon, hydrogen and methane are -394 , -286 and -890 kJ mol^{-1}

Solution



$$\Delta H - 890 = -390 + 2(-286)$$

$$\Delta H = +890 - 390 + 2(-286)$$

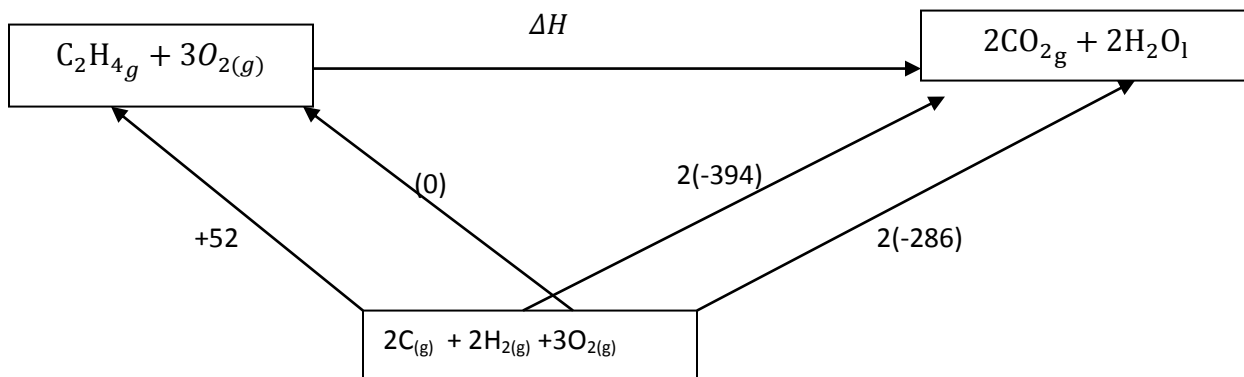
$$\Delta H = -76 \text{ kJ mol}^{-1}$$

Note for enthalpy of combustion data only

$$\Delta H_f = \sum \Delta H(\text{reactant}) - \sum \Delta H(\text{products})$$

Example 2

Calculate the enthalpy change of combustion of ethene, C_2H_4 , given that the standard enthalpies change of formation of ethene, water and carbon dioxide are $+52$, -286 and -394 kJ mol^{-1} respectively



$$\Delta H = 2(-394) + 2(-286) - (+52) - (0) = -1412 \text{ kJ mol}^{-1}$$

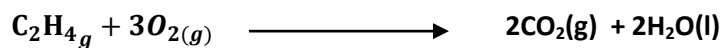
If enthalpy of formation data is provided

$$\Delta H_c = \sum \Delta H(\text{products}) - \sum \Delta H(\text{reactants}).$$

OR by rearranging the equations

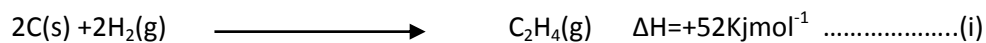
Step 1

write the equation whose enthalpy is required



Step 2

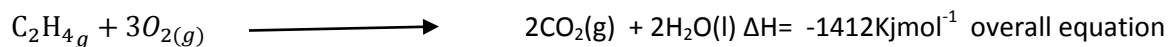
Write equations of reactions from the given data



Step 3

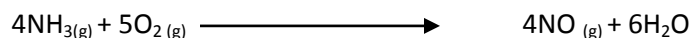
Re arrange the equation above to obtain the required equation

Equation (ii)x2 + equation (iii)x2 + equation (i) reversed

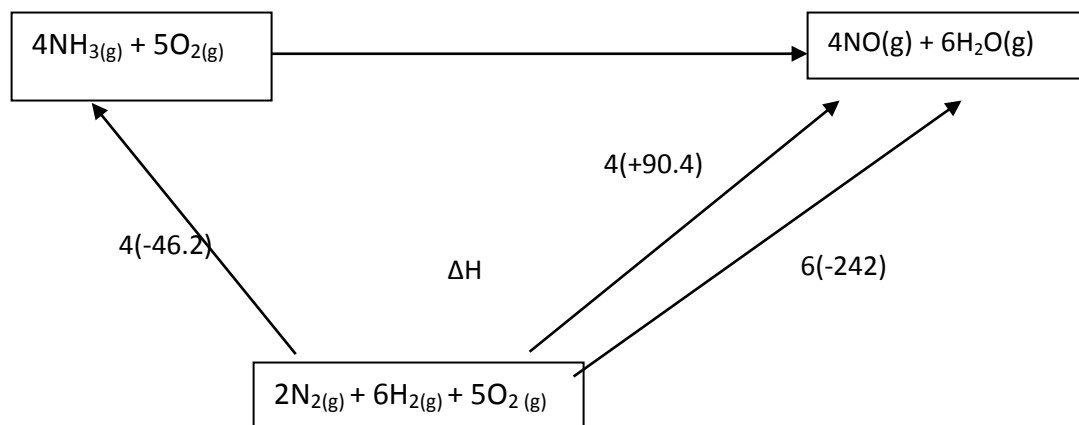


Example three

Calculate the enthalpy change for the reaction

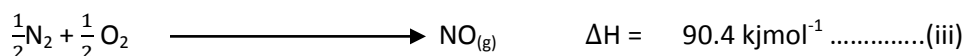
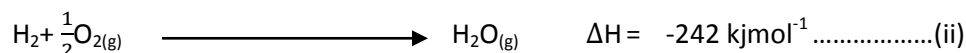
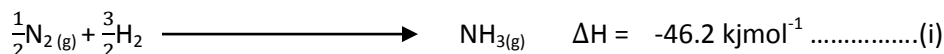


Given that the standard enthalpies of formation of ammonia, nitrogen monoxide and water are -46.2, +90.4 and -242 kJmol⁻¹ respectively

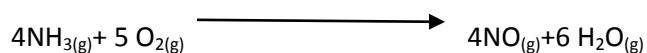


$$\Delta H = (4 \times 90.4 + 6 \times -242) - (4 \times -46.2 + 5 \times 0) = -906 \text{ kJmol}^{-1}$$

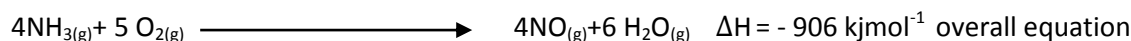
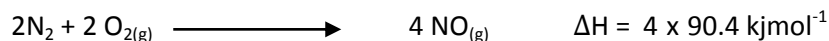
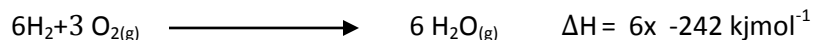
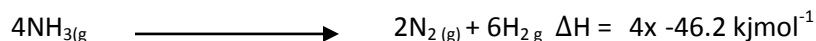
Or rearranging Equations



Equation of interest

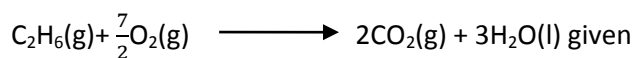


Multiply equation (i) by 4 and reverse it + equation (ii) Multiply by 6 + equation(iii) Multiply by 4



Exercise

1) Calculate the enthalpy change for the reaction

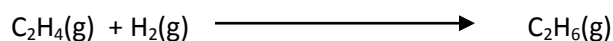


substance	$\text{C}_2\text{H}_6(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
ΔH_f (kJmol ⁻¹)	-85	-394	-286

2. Calculate the heat of formation of propane C_3H_8 given that heat of combustion in the table below.

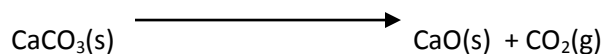
substance	$\text{C}(\text{s})$	$\text{H}_2(\text{g})$	$\text{C}_3\text{H}_8 \text{ g}$
Heat of combustion(kJmol ⁻¹)	-394	-286	-2220

3. Calculate the standard enthalpy change for the reaction



Given that the standard enthalpies of combustion of ethene, hydrogen and ethane are -1411, -286 and -1560 kJmol⁻¹

4. Calculate the enthalpy change for the reaction



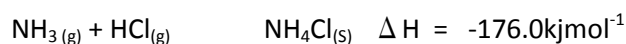
given that the standard enthalpies change of formation of calcium carbonate, (CaCO_3) calcium oxide (CaO) and carbon dioxide are -1207, -635 and -394 kJmol⁻¹ respectively

5. Calculate the standard enthalpy of formation of propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) given that the standard enthalpies of combustion of carbon, hydrogen and propan-1-ol are -394, -286 and -2010 kJmol⁻¹

6 Calculate the standard enthalpy change of formation of solid ammonium chloride, NH_4Cl , using the following data:

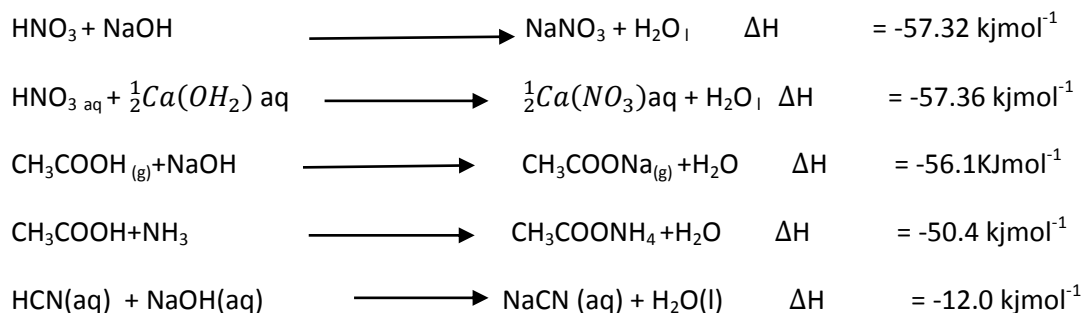
$$\Delta H_f(\text{NH}_3(\text{g})) = -46.1 \text{ kJmol}^{-1}$$

$$\Delta H_f(\text{HCl}(\text{g})) = -92.3 \text{ kJmol}^{-1}$$



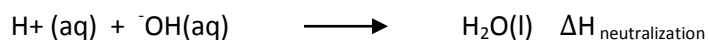
STANDARD ENTHALPY OF NEUTRALIZATION

This is the heat given out when an acid and alkali react together under standard conditions to give one mole of water



Notice

- i) From each equation that one mole of H^+ ions from an acid, reacts with one mole OH^- ions from an alkali to produce one mole of water.



- ii) For strong acids and strong bases the heat of neutralization is almost constant at -57.3 kJmol^{-1} . this because they are fully ionized in their aqueous solutions when the solutions are mixed there is no bond breaking
- iii) For weak bases and acids the enthalpy of neutralization is below -57.3 KJmol^{-1}

The low values are due to the fact that the weak acids and bases are not fully ionized in aqueous solutions. So some energy is used to break the bonds within their molecules before they are fully ionized.

- iv) Enthalpy of neutralization Varies with the degree of weakness of acids or the bases.

IMPORTANCE OF ENTHALPY OF NEUTRALIZATION

- ✓ Provides the relative molecular mass of an acid is known, its basicity can be determined from measurements of the enthalpy of neutralization of the acids.
- ✓ The enthalpy of dissociation or ionization of weak acid or weak base can be determined provided the neutralization data is given.

Experiments to determine enthalpy of neutralization

- a) Experimental determination of the enthalpy of neutralization of sodium hydroxide and sulphuric acid by simple calorimetry

Procedure

- ✓ A known volume of sodium hydroxide (V_b) of known concentration (M_b) is placed in a plastic cup and its temperature (T_1 °C) accurately measured and recorded.
- ✓ A known volume of sulphuric (V_a) of known concentration (M_a) required to neutralize sodium hydroxide is placed in a plastic cup and its temperature (T_2 °C) accurately measured and recorded.
- ✓ The sodium hydroxide is transferred into the acid and the mixture stirred gently with the thermometer.
- ✓ The maximum temperature (T_3 °C) reached is measured and recorded.

NOTE; the thermometer should be thoroughly washed between the two readings as a precaution.

TREATMENT OF RESULTS

Temperature change $\Delta T = \left(\frac{T_2 + T_1}{2} - T_3 \right) ^\circ\text{C}$

Total volume is $V = (V_a + V_b) \text{ cm}^3$

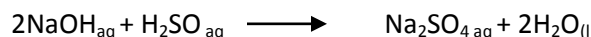
Density of solution (ρ) = 1.0 g cm^3

Mass of the mixture $M = (V \times \rho) \text{ g}$

Specific heat capacity of solution $C = 4.2 \text{ J g}^{-1} \text{ K}^{-1}$

Heat absorbed by solution = (mass of solution x specific heat capacity of solution x *temperature change*) J

Equation of reaction



1 mole of $\text{H}_2\text{SO}_{4\text{aq}}$ produces 2 moles of water

$\frac{M_a \times V_a}{1000}$ mole $\text{H}_2\text{SO}_{4\text{aq}}$ produces $2 \times \frac{M_a \times V_a}{1000}$ moles of water

$2 \times \frac{M_a \times V_a}{1000}$ of water is produced by ($m \times 4.2 \times \Delta T$) J

1 mole of water is produced by $\left(\frac{m \times 4.2 \times \Delta T}{2 \times M_a \times V_b} \right) \text{ kJmol}^{-1}$

The enthalpy of neutralization is $-\left(\frac{M \times 4.2 \times \Delta T}{2 \times M_a \times V_b} \right) \text{ kJmol}^{-1}$

EXAMPLE

When 50cm^3 of 1.0M sulphuric acid was added to 50cm^3 of 2.0M sodium hydroxide solution the temperature rose by 13.6°C . Calculate the enthalpy of neutralization.(specific heat capacity of solution $4.2\text{Jg}^{-1}\text{K}^{-1}$ and density of solution 1.0gcm^{-3})

Temperature change $\Delta T = 13.6^\circ\text{C}$

Total volume is $V = (50 + 50) \text{ cm}^3$

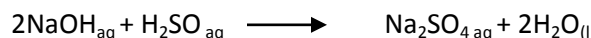
Density of solution $= 1.0\text{gcm}^{-3}$

Mass of the mixture $= (100 \times 1)\text{g}$

Specific heat capacity of solution $= 4.2\text{Jg}^{-1}\text{K}^{-1}$

Heat absorbed by solution $= (\text{mass of solution} \times \text{specific heat capacity of solution} \times \text{temperature change}) \text{ J}$

Equation of reaction



1 mole of $\text{H}_2\text{SO}_{4\text{aq}}$ produces 2 moles of water

$\frac{50 \times 1}{1000}$ mole $\text{H}_2\text{SO}_{4\text{aq}}$ produces $2 \times \frac{50 \times 1}{1000}$ moles of water

$2 \times \frac{50 \times 1}{1000}$ of water is produced by $(100 \times 4.2 \times 13.6) \text{ J}$

1 mole of water is produced by $\left(\frac{100 \times 4.2 \times 13.6}{2 \times 50 \times 1} \right) \text{ kJmol}^{-1}$

Alternative method for determining the enthalpy of neutralization

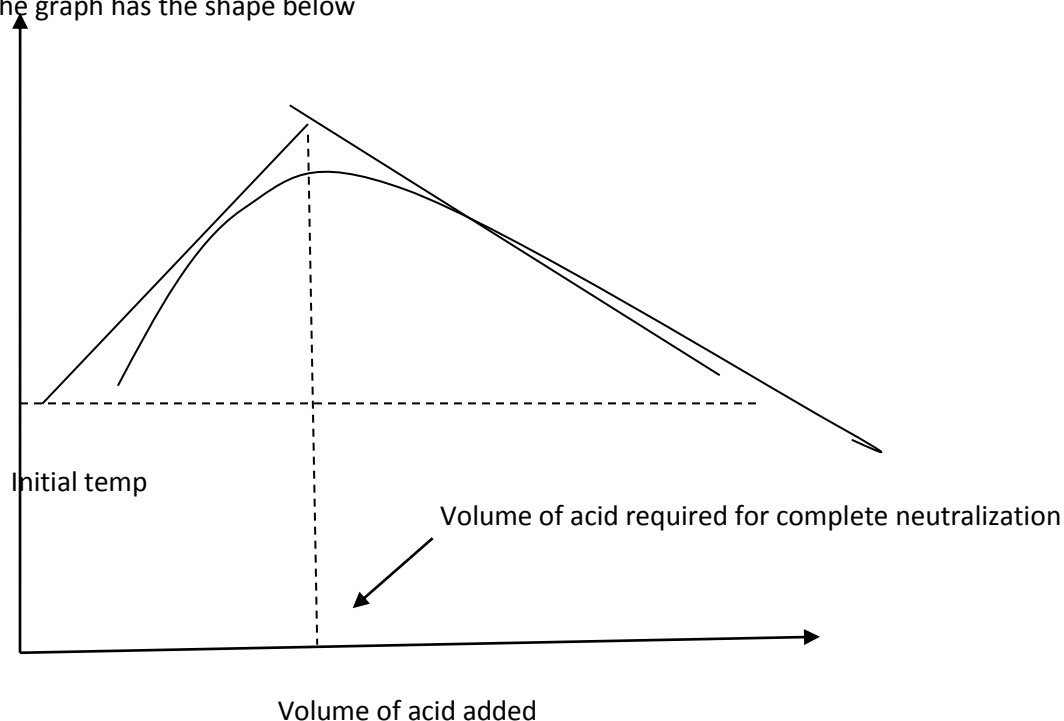
Procedure:

A known volume of alkali V_b is pipette into a plastic cup and its initial temperature $T_1^{\circ}\text{C}$ measured and recorded.

A known volume of acid is then added to the alkali at intervals of 5cm^3 using a burette while taking note of the temperature rise at each interval.

A graph of temperature against volume of acid added is then plotted

The graph has the shape below



From the graph, the maximum temperature and volume of acid for complete neutralization are determined hence the enthalpy of neutralization can be calculated.

Exercise

In an experiment to determine enthalpy of neutralization of the reaction between sodium hydroxide and sulphuric acid, 2.0M sulphuric acid was added at intervals to 40cm^3 of 2.0M sodium hydroxide and the following results were obtained.

Volume of sulphuric acid added (cm^3)	4	8	12	16	20	24	28	32	36
Temperature ($^{\circ}\text{C}$)	29.0	32.0	35.0	36.0	37.0	37.0	36.0	34.0	32.0

- Plot a graph of temperature against volume of sulphuric acid added
- Use the graph to determine the volume of sulphuric acid required to neutralize sodium hydroxide
- Determine the molar enthalpy of neutralization

Enthalpy of precipitation

On mixing some two or more aqueous solution a precipitate is formed for example when sodium chloride solution is added to solution of silver nitrate a white precipitate is formed and the enthalpy accompanying this reaction is called enthalpy of precipitation.

Enthalpy of precipitation is the enthalpy change when one mole of an ionic compound is precipitated from solution.

Example

25.0cm³ of 0.3 M silver nitrate was added to 25cm³ of sodium chloride solution. The temperature of mixture rose by 3.0°C .calculate the enthalpy of precipitation of silver chloride.

Assuming heat capacity of solution is 4.2Jg⁻¹K⁻¹ and density of solution is 1.0gcm⁻³.

Total volume of solution = 25 + 25 = 50cm³

Mass of solution = 100 x 1.0 = 100g

Heat produced = 50 x 4.2 x 3 = 0.63KJ

Moles Ag⁺ in 25 cm³ = $\frac{25 \times 0.3}{1000}$

From the equation Ag⁺(aq) + Cl⁻(aq) \longrightarrow AgCl(s)

Moles of Ag Cl precipitated = 0.0125

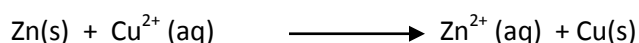
When 0.0125 moles of AgCl is formed it gives out 0.63 KJ

When 1 mole of AgCl is formed it gives out $\frac{0.63}{0.0125} = 50.4 \text{ kJ mol}^{-1}$

Enthalpy of displacement

This is the enthalpy change when one mole of an element is displaced from its solution by another element higher in the reactivity series

Metals higher in reactivity series displace those from solution containing their ions for example



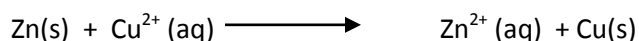
Also more electronegative elements will displace less electronegative elements from solution containing its ions.



Exercise

Excess zinc powder was added to 25cm³ of 1.0M copper(ii) sulphate solution in a plastic beaker and the temperature of solution recorded at some time intervals the data obtained is shown in the table below

Copper (ii) ions react with zinc powder according to the equation



Time (min)	0	2.5	3.0	3.5	5.0	6.0	7.0
Temperature(°C)	27.2	66.0	69.5	68.5	65.0	62.0	59.5

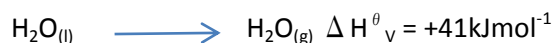
- Plot a graph of temperature against time
- use the graph to determine the molar enthalpy of solution.

Defining some more terms

Standard enthalpy change of vaporization ΔH^θ_v

This is the heat needed to convert one mole of a substance at its boiling point from a liquid state to gaseous state at one atmosphere.

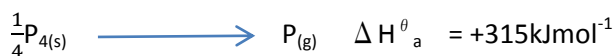
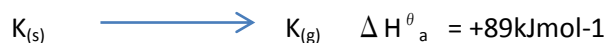
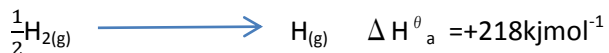
For example to convert one mole of water at 100°C to steam requires 41Kj



Standard enthalpy change of atomization, (ΔH^θ_a)

This is the heat required to produce one mole of gaseous atoms from the element in its standard state.

The following changes represent enthalpy changes of atomization



When the element is in the solid state the enthalpy of atomization is known as enthalpy of sublimation.

Ionization energy

Refers to the minimum energy required to remove completely one mole of electron from a gaseous atom or gaseous ion against the attractive forces of the nucleus to form a positively charged ion

First ionization energy

Is the minimum amount of energy required to remove completely one mole of electron from one mole of gaseous atoms to produce one mole of uni-positively charged gaseous ions.

Example, $\text{Al}_{(\text{g})} \longrightarrow \text{Al}_{(\text{g})}^{+} \Delta H = 1^{\text{st}}$ ionization energy of aluminium

Second ionization energy

Is the minimum amount of energy required to remove completely one mole of electron from one mole of gaseous ion to produce one mole of di-positively charged gaseous ions.

Example, $\text{Al}_{(\text{g})}^{+} \longrightarrow \text{Al}_{(\text{g})}^{2+} \Delta H = 2^{\text{nd}}$ ionization energy of aluminium.

You can then have as many successive ionization energies as there are electrons in the original atom.

The process of removing an electron from an atom requires energy since the electron is being removed against the attractive forces of the nucleus. Therefore the process is endothermic.

Electron affinity

Is the energy change that occurs when one mole of electron is being added to one mole of gaseous atom or ion

First electron affinity

This is the energy given out when one mole of an electron is being added to one mole of gaseous atoms to form one mole of uni-negatively charged gaseous ion.

The more exothermic the value of electron affinity the more stable the ion formed

Example, $\text{O}_{(\text{g})} + \text{e} \longrightarrow \text{O}_{(\text{g})}^{-} \Delta H = -142 \text{KJ mol}^{-1}$ 1st electron affinity of oxygen.

First electron affinity is always an exothermic process because the electron being added is attracted by the nucleus thus heat is given out.

Second electron affinity

This refer to the energy absorbed when one mole of electron is being added to one mole of uni-negatively charged gaseous ions to form one mole of a di-negatively charged gaseous ion

Example, $\text{O}_{(\text{g})}^{-} + \text{e} \longrightarrow \text{O}_{(\text{g})}^{2-} \Delta H = +844 \text{KJ mol}^{-1}$ 2nd electron affinity of oxygen.

Second electron affinities are always positive because energy is needed to force an electron into an already negative ion.

Lattice energy

This term is applied to crystals which are essentially ionic in character

The lattice energy of a crystal is defined as the amount of energy given out when one mole of an ionic crystal lattice is formed from its constituent gaseous ions.



Or is the minimum amount of energy required to break one mole of ionic crystal lattice into its constituent gaseous ions.

Other examples



When ionic crystal is formed from its gaseous ions

Lattice energy values are will be negative because lattice energy involves attraction of oppositely charged particles into a fixed crystal lattice.

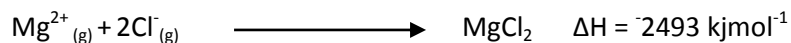
The more negative the lattice energy the more stable the crystal structure.

Lattice energy also indicates how strongly the cat ion and anion are held together in the crystal structure.

Factors affecting the magnitude of lattice energy.

a) The charge on each ion (ionic charge)

Lattice energy is proportional to the product of charges of ions. The larger the product of ionic charge, the bigger the lattice energy. This is because of the strong electrostatic forces of attraction between oppositely charged ions.



e.g. MgCl_2 has bigger lattice energy than NaCl because magnesium has a high charge of positive whereas sodium has a charge of positive one.

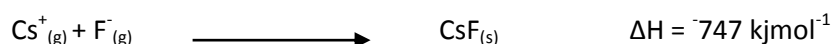
b) Ionic radius

Lattice energy is inversely proportional to the sum of the radii.

The smaller the sum of ionic radii, the bigger the lattice energy.

This is because the higher the charge density $= \frac{Q}{r}$ the higher the electrostatic forces of attraction between oppositely charged ions.

This explains why NaF has bigger lattice energy than CsF because the ionic radius of Na^+ is smaller than that of Cs^+ , Na^+ has higher charge density.



Importance of lattice energy

- Substances with high lattice energy will have high melting points
- The solubility of ionic compounds, will depend upon the relative values of lattice energy and hydration energy the smaller the lattice energy and the greater the hydration energy the larger is the solubility in water.
- Lattice energy can be used to explain the existence of some compound
 - Example why magnesium chloride is MgCl_2 but not MgCl
 - The main factor which favours the formation of MgCl_2 is the very high lattice energy. This more than compensates for the additional energy that has to be supplied for the second ionization of magnesium to form Mg^{2+} from Mg^+ .
- Comparison of the calculated and experimental values for lattice energy gives indication of the degree of covalent bonding in a compound if the theoretical value is less than the calculated value then the solid is not purely ionic there is appreciable covalent character

Born – Haber cycles

The Born – Haber cycle is a technique for applying Hess's law to the standard enthalpy changes which occurs when ionic compound is formed.

It relates the enthalpy of formation of ionic compounds and to the enthalpy of atomization of elements concerned, the ionization energies for the formation of gaseous cat ions, the electron affinity for the formation of gaseous anions and the lattice energy of ionic substances.

This can either be drawn as a Hess's law cycle or as an enthalpy level diagram.

In enthalpy level diagram

Each horizontal line represents the energy level the species existing on this level are written on the line together with their states.

The gaps represent the enthalpy changes accompanying the changes in the species shown.

For convenience we will look at the changes affecting cation first and the anion after wards

Positive enthalpy changes and shown going up the diagram, while negative values are shown going down the diagram

Consider the Born- Haber cycle for formation of sodium chloride

Some thermo-chemical data of sodium and chlorine are given below

Heat of formation of sodium chloride = -602 KJmol^{-1}

Heat of atomization of sodium = $+109 \text{ KJmol}^{-1}$

First ionization energy of sodium = $+494 \text{ KJmol}^{-1}$

Atomization energy of chlorine = $+121 \text{ KJmol}^{-1}$

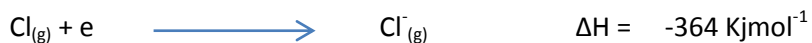
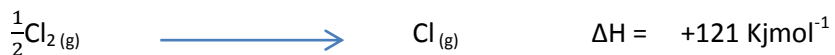
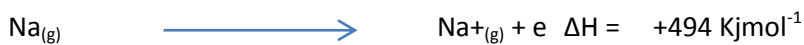
First electron affinity of chlorine = -364 KJmol^{-1}

i) draw an energy level diagram for the formation of sodium chloride

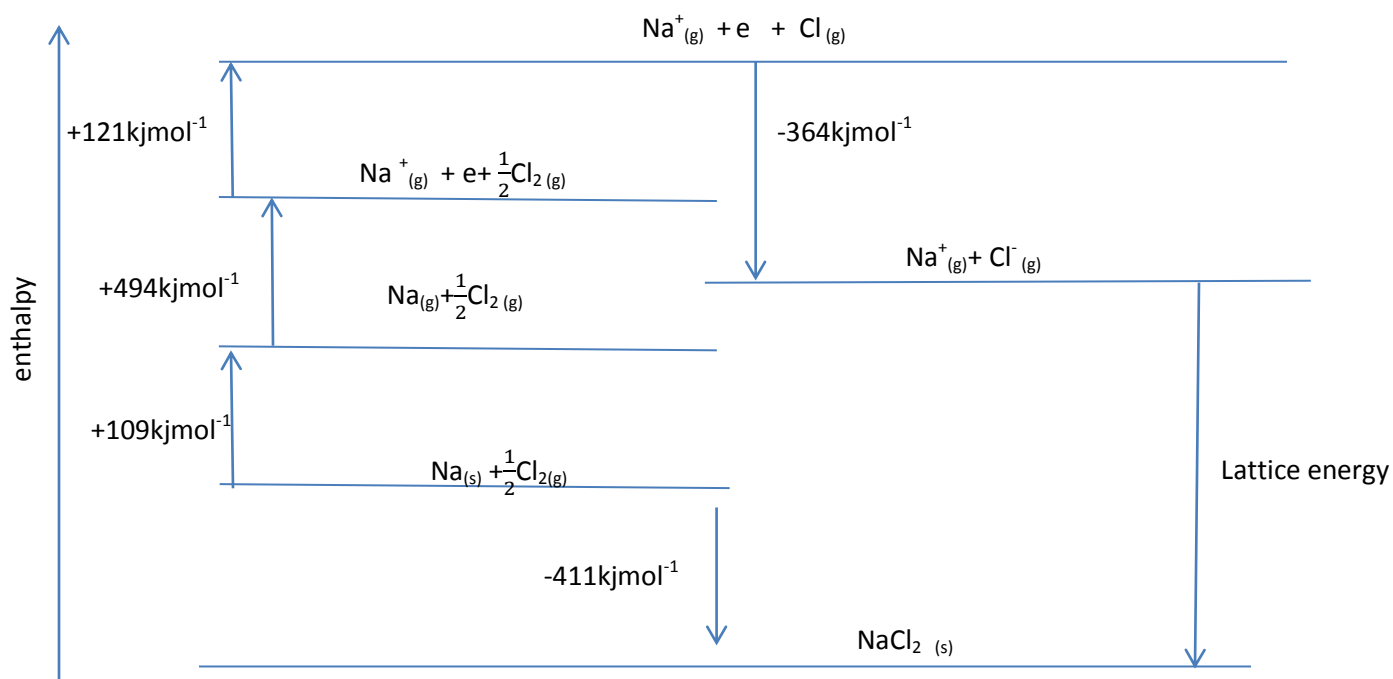
ii) calculate the lattice energy of sodium chloride

solution

From the thermo-chemical data given the following equations can be written



Enthalpy level diagram



Enthalpy diagram showing Born-Haber cycle for formation of sodium chloride

From Hess's law $-411 + (+109) + (+494) + (+121) + (-364) + \text{lattice energy} = -411$

Lattice energy = -771 kJmol⁻¹

Example two

Consider the Born- Haber cycle for formation of magnesium oxide

Some thermo-chemical data of magnesium and oxygen are given below

Heat of formation of magnesium oxide = -602 KJmol^{-1}

Heat of atomization of magnesium = $+150 \text{ KJmol}^{-1}$

First ionization energy of magnesium = $+736 \text{ KJmol}^{-1}$

Second ionization energy of magnesium = $+1450 \text{ KJmol}^{-1}$

Atomization energy of oxygen = $+248 \text{ KJmol}^{-1}$

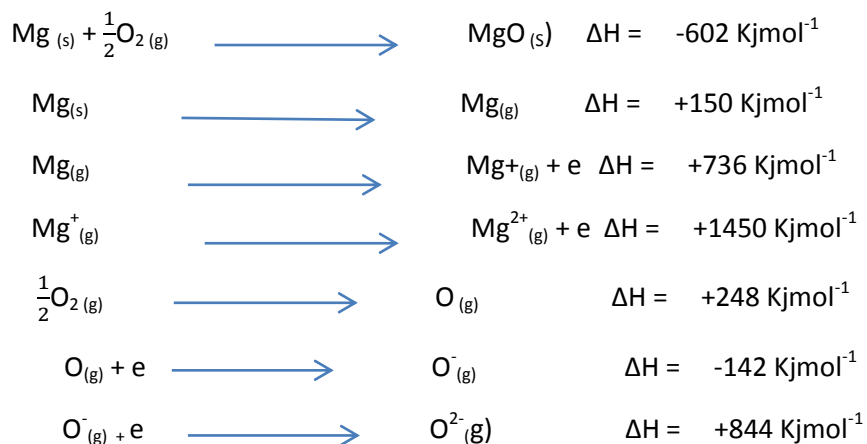
First electron affinity of oxygen = -142 KJmol^{-1}

Second electron affinity of oxygen = $+844 \text{ KJmol}^{-1}$

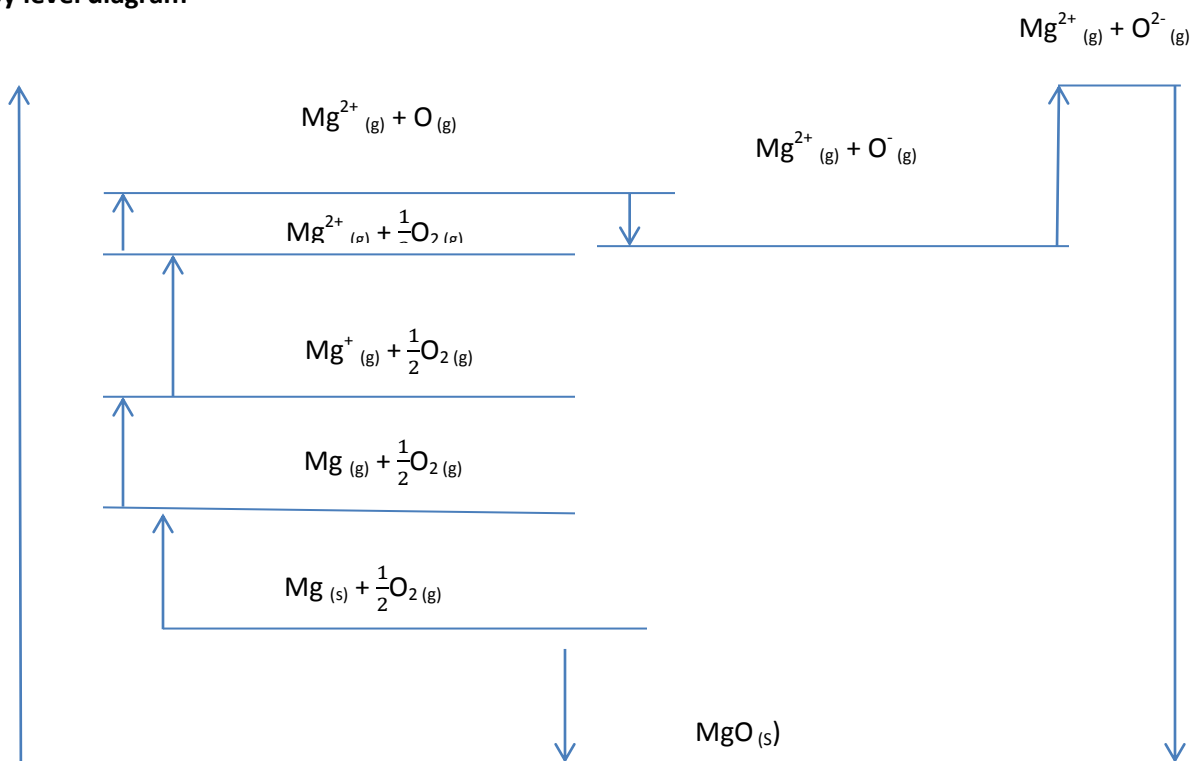
i) draw an energy level diagram for the formation of magnesium oxide

ii) calculate the lattice energy of magnesium oxide

From the thermo-chemical data given the following equations can be written



Enthalpy level diagram

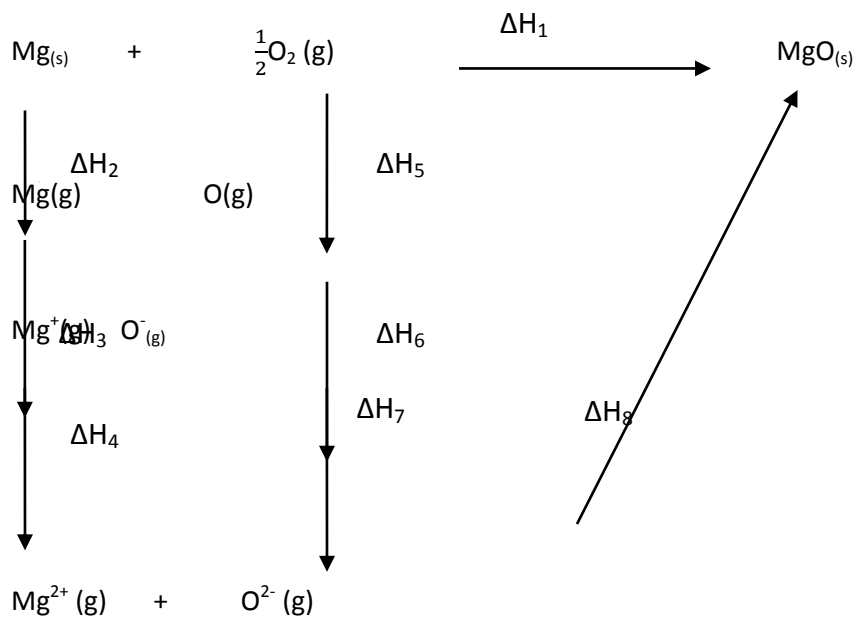


By Hess's law

$$+150 + 736 + 1450 + 248 - 142 + 844 + \text{LE} = -602$$

$$\text{LE} = -3888 \text{ kJ/mol}$$

Born-Haber cycle



Consider the Born- Haber cycle for formation of aluminium oxide

Some thermo-chemical data of aluminium and oxygen are given below

Heat of formation of aluminium oxide = $-1675.7 \text{ KJmol}^{-1}$

Heat of atomization of aluminium = $+324.3 \text{ KJmol}^{-1}$

First ionization energy of aluminium = $+578.0 \text{ KJmol}^{-1}$

Second ionization energy of aluminium = $+1817.0 \text{ KJmol}^{-1}$

Third ionization energy of aluminium = $+2745.0 \text{ KJmol}^{-1}$

Atomization energy of oxygen = $+248 \text{ KJmol}^{-1}$

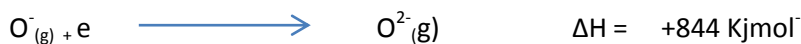
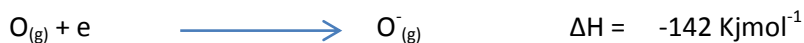
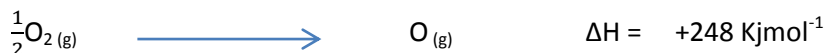
First electron affinity of oxygen = -142 KJmol^{-1}

Second electron affinity of oxygen = $+844 \text{ KJmol}^{-1}$

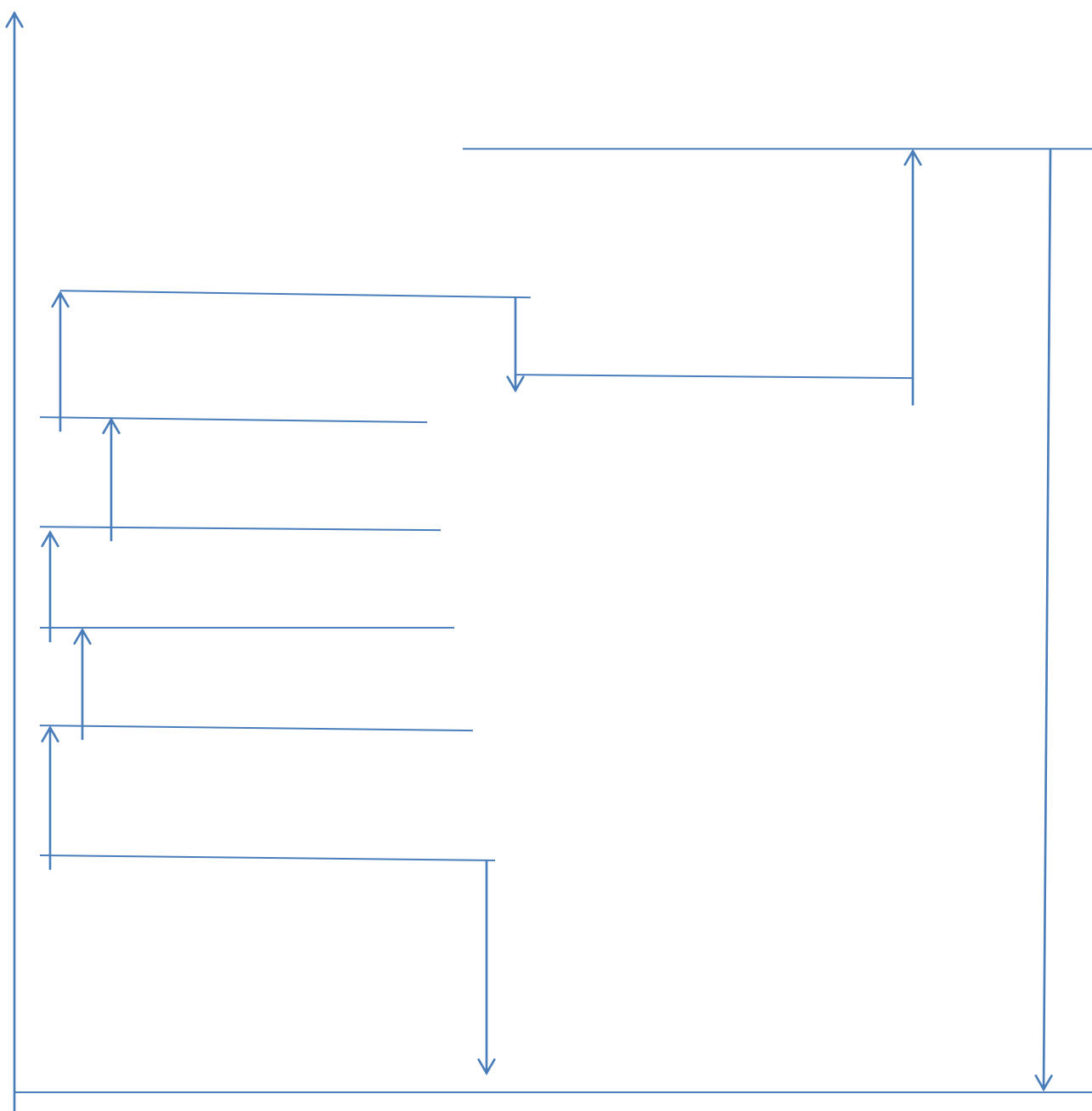
i) draw an energy level diagram for the formation of aluminium oxide

ii) calculate the lattice energy of aluminium oxide

From the thermo-chemical data given the following equations can be written



Energy level diagram



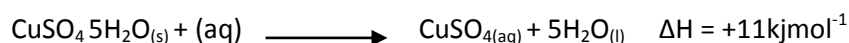
Enthalpy changes when ionic compounds dissolve in water

Enthalpy change of solution

This is the enthalpy change when one mole of ionic compound completely dissolves in a specific amount of water to form infinitely dilute solution.

“Infinitely dilute” means that you have used enough water so that adding some more doesn’t result in any more heat change.

The equation for such reactions would be written as, for example:



The process of dissolving ionic compound in water involves two energy stages.

Stage one

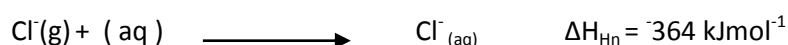
Separating of ionic compounds into oppositely charged gaseous ions and the energy involved is called lattice energy. The process is endothermic.

Stage two

Wrapping them in water molecules and the energy involved is called hydration energy. The process is exothermic

Enthalpy change of hydration

This is the energy given out when one mole of gaseous ions is surrounded by water molecules to form an infinitely dilute solution. It applies equally to positive and negative ions.



Hydration enthalpies are always exothermic because of the formation of attractive forces between the ions and water molecules.

For a cat ion it is the results of the force of attraction between the ion and the

δ^{-} oxygen in water.

For the anion it is the result of the force attraction between the ion and the

δ^{+} hydrogen in water.

The value of the enthalpy of hydration will depend upon the value of the charge on the ion and its ionic radius.

The larger the charge, the more exothermic the enthalpy of hydration



Magnesium ion has a charge of +2 whereas sodium ion has a charge of +1

The larger the ionic radius the less exothermic the enthalpy of hydration

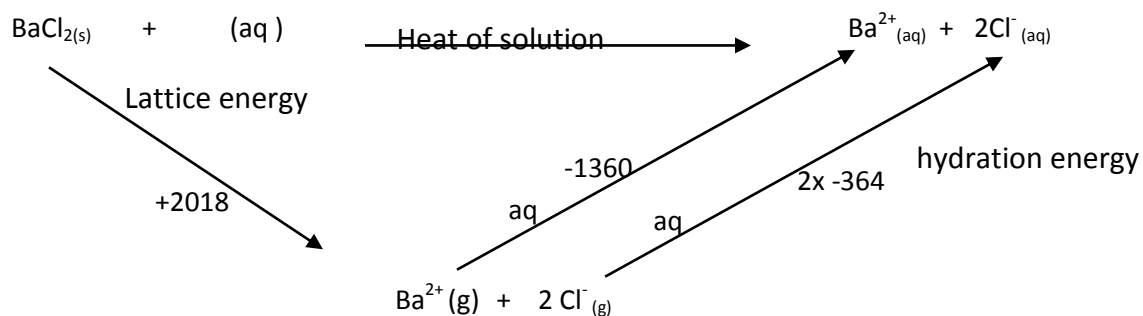


The ionic radius of magnesium ion is less than that of barium ion

Calculating enthalpy change of solution

Consider the dissolution of barium chloride in water.

Using Hess's law cycle



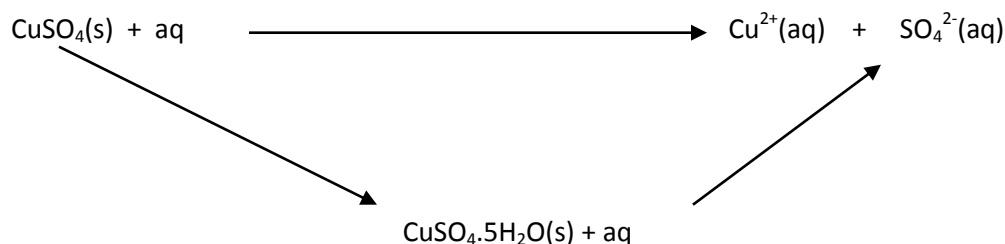
by applying Hess's law

Heat of solution = lattice energy + hydration energy

NOTICE

- When the lattice energy is greater than the hydration energy the enthalpy change of solution will be positive (endothermic)
- Whereas when the hydration energy is greater than the lattice energy the enthalpy change of solution will be negative (exothermic)
- For an ionic compound to dissolve in water easily, the lattice energy should be overcome by the hydration energy such that overall enthalpy change of solution is negative.

- Compounds which dissolve exothermically are more stable than those which dissolve endothermically.
- the dissolution of sodium chloride is endothermic yet sodium chloride readily dissolves in water . the reaction occurs spontaneously because of the increase in the entropy of the system
- Hydrated copper (ii) sulphate crystals dissolves endothermically whereas anhydrous copper(ii) sulphate dissolves exothermically.



For hydrated copper (ii) sulphate, the ions are partly hydrated thus hydration energy is partly lost. When the crystals are dissolved in water, further hydration occurs and this energy is not enough to outweigh lattice energy therefore heat of solution is endothermic. For anhydrous copper (ii) sulphate, the hydration energy is readily available and is able to outweigh lattice energy therefore heat of solution is exothermic.

Experiment to determine the enthalpy of solution of an ionic salt eg sodium chloride

Procedure

- -a known volume of water(v cm^3) is put in a plastic beaker(or insulated calorimeter)
- -the initial temperature of water($t_1^{\circ}\text{C}$) is measured and recorded
- -a known mass of the sodium chloride(ag) is added to the water and stirred
- -the final temperature of solution($t_2^{\circ}\text{C}$) is measured and recorded

Treatment of results

Temperature change Δt $= (t_1 - t_2)$

Mass of solution $= (a + V \times 1)\text{g}$

Heat change $= \text{mass of solution} \times C \times \Delta t = (a + V) \times 4.2 \times \Delta t$

ag of the salt evolves $= ((a + V) \times 4.2 \times \Delta t) \text{ joules}$

One mole of the salt will evolve $= \frac{(a + V) \times 4.2 \times \Delta t \times W}{1000 \times a} \text{ kJmol}^{-1}$

Where W is the molar mass of the salt.

BOND ENTHALPY or BOND ENERGY

During chemical reactions between covalent compounds, a number of bonds in reactants are broken and new bonds are formed in products.

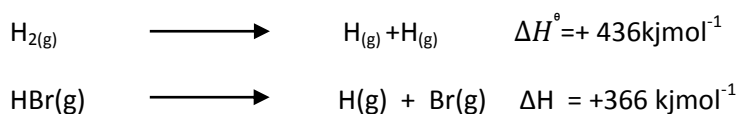
Forming bonds liberates energy and breaking bonds requires energy

Bond energy is the energy required to break one mole of covalent bond into its constituent gaseous atoms.

or This is the energy released when one mole of a particular covalent bond is formed from its constituent gaseous atoms.

Bond dissociation energy (or enthalpy) and average bond energy

For simple diatomic molecules (one containing only two atoms) like hydrogen, H_2 or hydrogen bromide, HBr , the energy needed to break one mole of the bond is referred to as bond dissociation energy (or bond dissociation enthalpy):



For poly atom molecule (one containing more than two atoms) like methane, the energy required to break a given bond will depend upon the nature of the other atoms or groups joined to it and will vary from compound to compound for instance the energy required to break the O-H bond in an alcohol is not the same as the energy needed to break the same bond in an organic acid.

Therefore this energy required to break a particular bond in poly atomic molecule is called average bond energy or just bond energy

Average bond enthalpy may be taken as

the average calculated from the sum of the bond dissociation enthalpies of all similar bonds in a molecule

$$\text{The average of the four C-H bond enthalpy for methane} = \frac{425+470+416+335}{4} = \frac{1646}{4} \approx 412 \text{ kJ mol}^{-1}$$

Or Average bond enthalpy may be taken as

As the average of the average bond energy of all compounds containing that particular bond

Where the average bond energy of all compounds containing C-H bond is 413 kJ mol^{-1}

In a poly atomic molecules, the energy required to break a given bond will depend to some extent on the nature of the remainder of the molecule and will vary from compound to compound

Below are some of the bond enthalpies at 25°

BOND	$\Delta H/\text{kJmol}^{-1}$
H-H	436
C-C	348
C=C	612
C \equiv C	838
C-H	413
C-O	358
C=O	805
N-N	158
N=N	410
N \equiv N	945.4
C-F	484
C-Cl	338
C-Br	275
C-I	238
Br-Br	192
Cl-Cl	243.3
F-F	158
I-I	151

Factors affecting bond energies

Number of bonding electrons

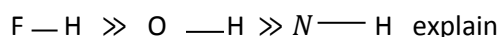
The more electrons that are contributed in the formation of the bond, the greater the strength of that bond eg triple bonds between carbon atoms are stronger than the double bonds which are in turn stronger than the single bonds

Single bonds < double bond < triple bonds

Bond polarity

As the difference in electro-negativity between bonded atoms increase the bond becomes more polar and this increases the ionic character of the bond thus increasing the bond strength

The bond strength of the hydrides of nitrogen, oxygen and fluorine is in the order



Bond length

The larger the atoms joined by a particular bond the longer the bond length. This is because, in larger atoms there are more electrons than in smaller ones this will result in an increase in screening effect of

the nucleus and hence an increase in electron repulsion in the bonded atoms these two effects weaken the bond hence giving a low bond energy

Uses of bond energy

Strength of bonds can be compared

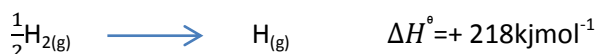
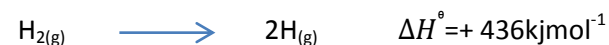
To understand the mechanism of a chemical reaction

To understand the structure and bonding of covalent compounds

Can be used to explain a number of facts from inorganic and organic chemistry

for example the increased reactivity of phosphorous compared to nitrogen,
the increased rate of substitution reactions for Iodo- Alkanes compared with other hydrogen Alkanes.

The enthalpy change for the atomization can be estimated using bond enthalpies



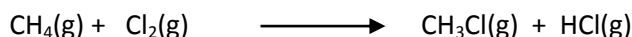
$$\text{Atomization energy} = \frac{\text{bond dissociation energy}}{2}$$

Bond enthalpies can be used to estimate likely enthalpy changes of reaction

Calculations involving bond energies

For example 1

Estimate enthalpy change for the reaction



Given the following bond enthalpies;

$$\text{C-H} = +413\text{kJmol}^{-1} \quad \text{C-Cl} = +346\text{kJmol}^{-1}$$

$$\text{Cl-Cl} = +243\text{kJmol}^{-1} \quad \text{H-Cl} = +432\text{kJmol}^{-1}$$

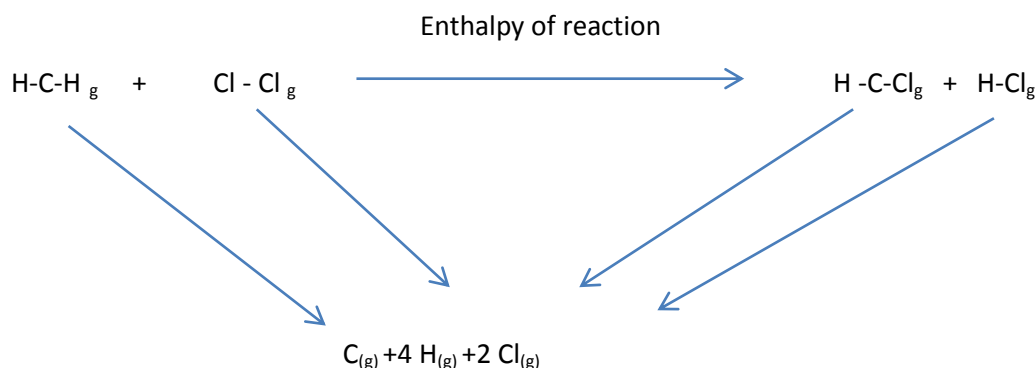
The method does require some knowledge of the bonding present in the particular molecules.

Start by writing the balance equation,

Show the structure of all the molecules to make counting bonds easier.

Draw arrows from compounds to gaseous atoms in the bottom corner.

Now find two routes around the diagram without going against the flow of an arrow and equate them according to Hess's law.



$\Delta H = (\text{the sum of the average bond enthalpies of reactants}) - (\text{the sum of the average bond enthalpies of the products})$

$$\Delta H^0 = (412 + 242) - (3 \times 412) + 338 + 431 = -115 \text{ kJ mol}^{-1}$$

Example 2

Estimate the enthalpy change for the reaction

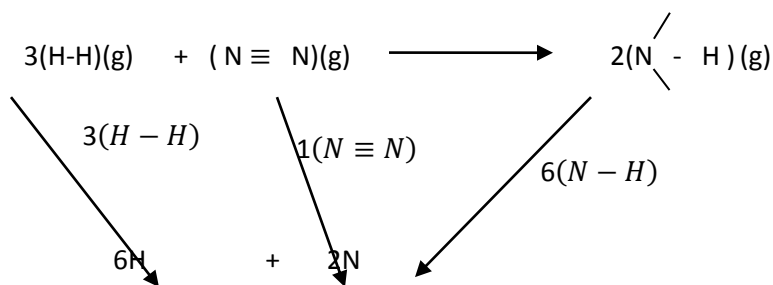


Given the following bond enthalpies;

$$\text{N-H} = +381 \text{ kJ mol}^{-1}$$

$$\text{H-H} = +436 \text{ kJ mol}^{-1}$$

$$\text{N-N} = +946 \text{ kJ mol}^{-1}$$

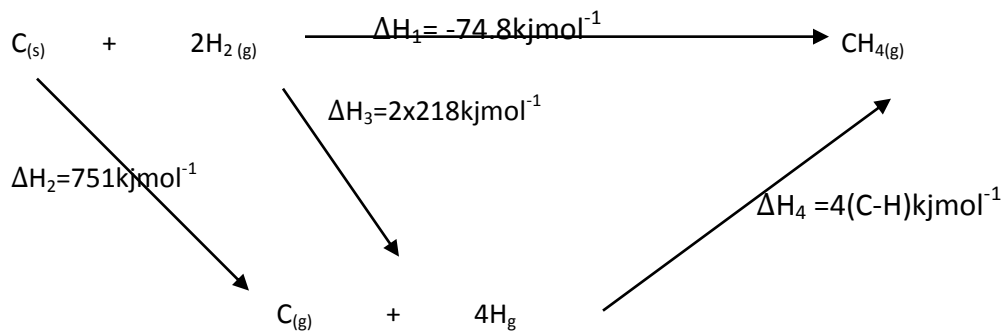


$$\Delta H = (8 \times 435) + (945.4) + (6 \times 381) = 93.3 \text{ kJ mol}^{-1}$$

Example 3

Given that the standard enthalpy of formation of methane is -74.8kJmol^{-1} and the enthalpies of atomization of graphite and hydrogen are $+751$ and $+218\text{kJmol}^{-1}$ in the gas phase.

Calculate the bond energy of C-H.

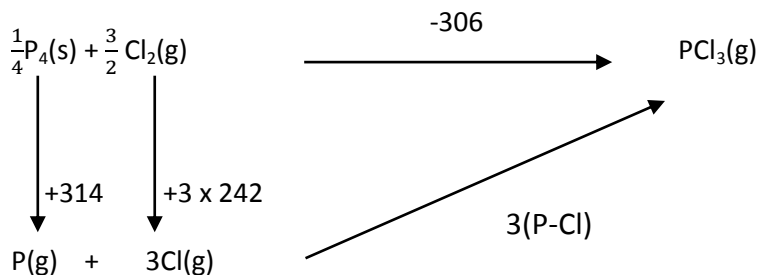


$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

Example 4

The enthalpy of formation of phosphorous tri-chloride is -306kJmol^{-1} and the enthalpy of atomization of phosphorous and chlorine are $+314$ and $+242\text{kJmol}^{-1}$ respectively. Calculate

The average the bond energy of P –Cl bond



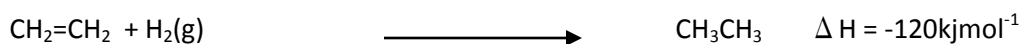
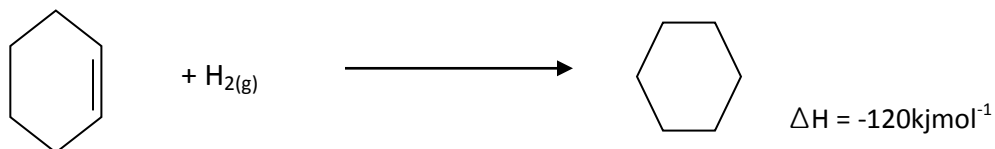
$$-306 = 314 + 3 \times 242 + 3\text{BE (P-Cl)}$$

$$\text{BE (P-Cl)} = \frac{-1346}{3} = -448.67\text{kJmol}^{-1}$$

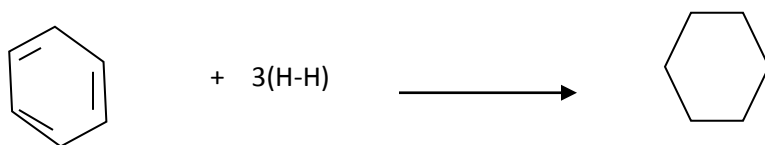
ENTHALPY OF HYDROGENATION

This is the enthalpy change when one mole of unsaturated compound is completely converted into the corresponding saturated compound by reaction with gaseous hydrogen

The hydrogenation of cyclohexene and ethene can be represented respectively by



It's possible to predict a value for standard enthalpy of hydrogenation of benzene if its structure is assumed to consist of alternate double and single carbon-carbon bonds. The reaction may be represented by the equation



The enthalpy change of hydrogenation should be $3 \times (-120) = -360 \text{ kJ mol}^{-1}$.

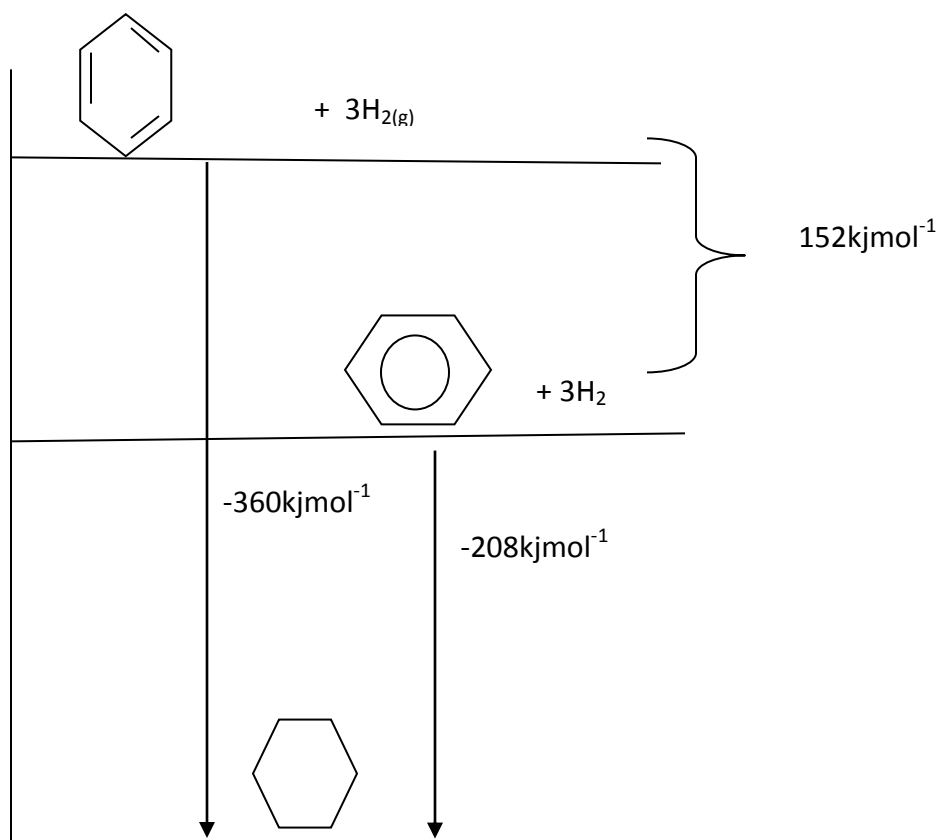
The experimental value for the enthalpy change of hydrogenation of benzene is -208 kJ mol^{-1}

The difference between these two values indicates that the actual structure of benzene is more stable than the alternate double and single bond structure by a factor equivalent to $360 - 208 = 152 \text{ kJ mol}^{-1}$

This extra stability is attributed to the delocalization of the bonding electrons over all six carbon atoms

Delocalization of energy

The sharing of electrons over more than two atoms is referred to as delocalization and the energy associated with the resulting extra stabilization is known as the delocalization energy.



Topic 5: Physical equilibrium

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

General objectives

By the end of this topic, the learner should be able to comprehend the concept of inter conversion of phases due to changes in the physical conditions and its application

System, phase and component

System

A system is the part of universe being studied, for example hot water or cold water in a beaker.

A system may be homogeneous or heterogeneous. A homogeneous system shows uniform composition or structure for example salt solution whereas a heterogeneous system is one with a mixture of state such as liquid-solid or liquid-solid-gas. There are three types of system

Open system which is a system that freely exchanges energy and matter with its surroundings for example liquid in a vessel from which vapour can escape.

Closed system is a system that exchanges only energy with its surroundings for example liquid and vapour in a sealed container.

And an isolated system is one which does not exchange energy or matter with its surroundings for example cold or hot water in a sealed thermos flask.

Phase

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

A Phase is a homogeneous part of system which is physically distinct from other parts of system and can be separated from other parts by a definite boundary surface.

Examples; **mixture of gases is one phase, Aqueous solution is one phase, Two immiscible liquids is a two phase system**

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

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

The conditions of temperature and pressure under which different phases are stable can be shown on the **phase diagram**

In a phase diagram a phase is represented by a **region** that is separated from other regions by lines or curves. The lines or curves represent the conditions under which two phases can exist in equilibrium and a **triple point** describes the conditions under which three phases can coexist.

Component

This is the number of chemical species needed to define a phase system. It can be one component system for example water system, sulphur system, two components for example solution of sodium hydroxide or three component system for example iodine in two immiscible liquids in contact.

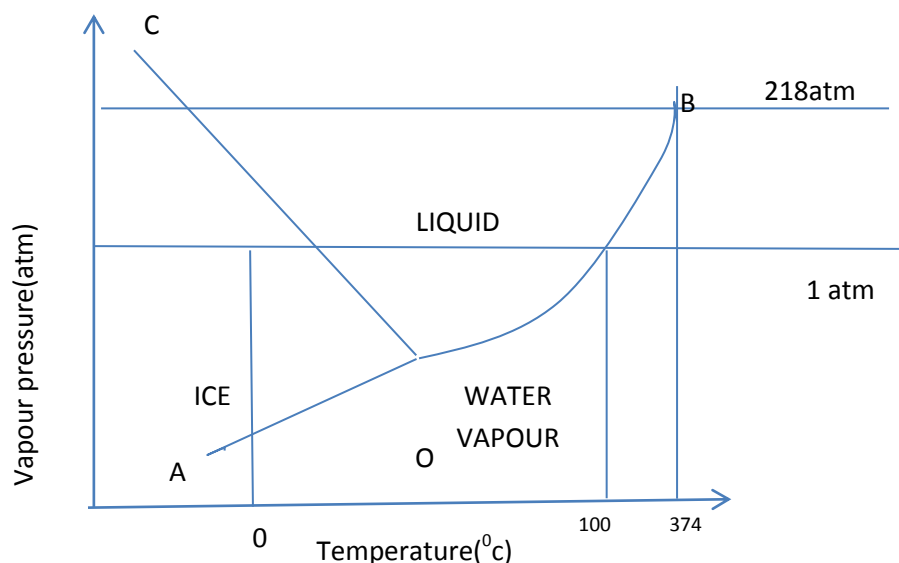
One component system

Example of one component system include; water, carbon dioxide and sulphur

Water system

Water can exist in three possible forms; ice (solid), water (liquid) and water vapour. These three forms can exist in two phase equilibria i.e solid-liquid, solid-vapour and liquid-vapour or in three phase equilibria as solid-liquid-vapour

The various equilibria which can exist when water is held at various pressures and temperatures are summarized in the pressure-temperature diagram below



Point O is called the triple point of water i.e. the temp and pressure at which all the three phases solid, liquid and vapour can co-exist in equilibrium with each other.

Point B is called the critical point of water; it corresponds to the critical temperature. critical temperature is the temperature beyond which the vapour cannot be liquefied no matter the applied pressure, the vapour and liquid become indistinguishable

Curve AO is the sublimation curve for ice. Shows the combination of temperature and pressure at which ice and its vapour are in equilibrium

Curve OB is the vapour pressure curve of liquid water or the vaporization curve of liquid water shows the combination of temperature and pressure at which liquid water and its vapour can exist in equilibrium the curves show effect of pressure on the boiling point of water

An increase in pressure causes an increase in boiling point .any temperature along this curve boiling occurs and any particular temperature along this curve gives the boiling point of liquid water at that pressure.

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

Curve OC is the melting point curve of ice or the freezing point curve of liquid water. Shows the combination of temperature and pressure at which a solid and its liquid can exist at equilibrium. The line shows the effect of pressure on the melting point of ice or the freezing point of liquid water. The curve slopes towards the pressure axis (towards the left) indicating that the melting point of ice is lowered by an increase in pressure.

Effect of change of temperature or pressure or both on the system

- (i) **suppose water at point M was cooled at constant pressure of 1 atmosphere up to point N**

The liquid continues to cool but without changes in phase until curve OC is reached at which temperature freezing starts. The temperature remains constant at the freezing point and a liquid solid equilibrium is established at the freezing point further decrease in temperature beyond curve OC, all the liquid molecules freeze forming a solid at phase N.

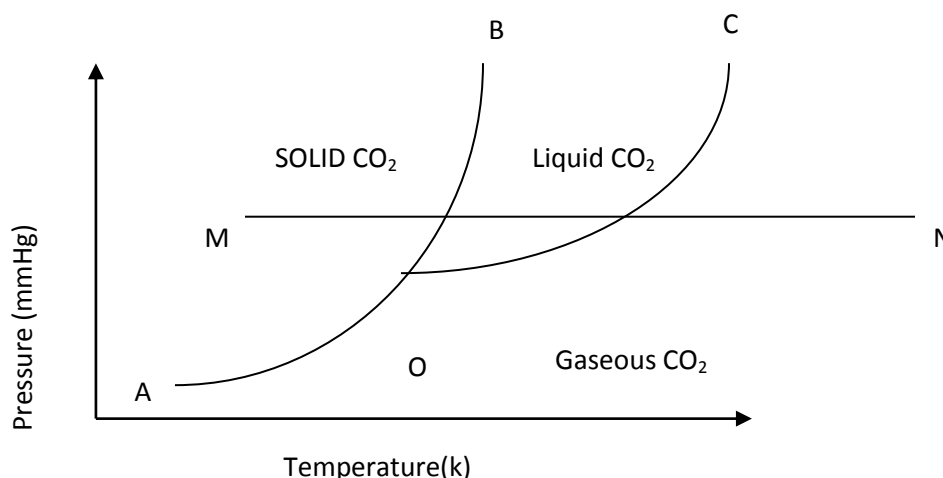
- (ii) **Suppose water vapour at point R is subjected to an increase in pressure at constant temperature up to point S**

When the pressure at point R is increased at constant temperature, the vapour is compressed causing a decrease in its volume but it remains a vapour. i.e. No change in phase occurs until the pressure on curve OB is reached at which pressure the vapour starts to change into a liquid (condensation) and the two (liquid and vapour remain in equilibrium at this pressure) further increase in pressure beyond curve OB compress the remaining vapour causing a further decrease in volume until all is a liquid at phase S

- (iii) **Suppose ice at point M is converted to vapour at point T**

ii) Carbon dioxide system

An example of a substance which melt with increases in volume



This diagram is similar to that of water though it has two important differences

(i) The line OB slopes away from the vapour pressure axis indicating that the melting point of solid carbon dioxide is increased with increase in pressure because molecules of carbon dioxide in the solid phase are parked more closely than in the liquid phase unlike in water..

(ii) the triple point of carbon dioxide occurs at a higher vapour pressure than that of water.

Describe what happens when a substance at point m is subjected to increase in temperature at constant pressure to point n

If the solid phase is heated at constant pressure, the solid expand causing an increase in its volume without a change in phase. However, further heating of the solid makes it liquefy at its melting point which occurs along curve AB. At this point the solid remains in equilibrium with liquid.

Further heating of the solid turns everything into a liquid. When the liquid is heated continuously, it begins to vaporize until curve AC at what the vapour remain equilibrium with the liquid at the boiling point.

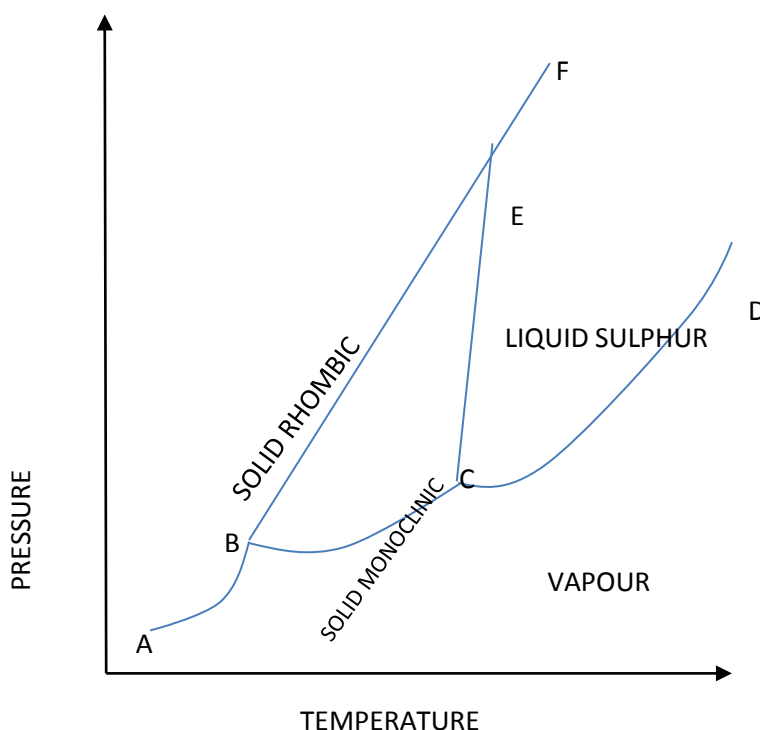
Describe what happens when a substance at point P is subjected to decrease in pressure at constant temperature to point q

The solid expands on decreasing its pressure causing an increase in its volume and it changes into a vapour i.e. it sublimates if the pressure of the liquid is decreased, the liquid changes to a vapour.

The sulphur system

Sulphur exists in two allotropic forms i.e the α -sulphur which has rhombic crystalline form and β -sulphur which has monoclinic crystalline form which are stable over different temperatures.

The temperature at which the two forms are in equilibrium is called transition temperature and it is 96°C monoclinic sulphur is stable above 96°C until a temperature of 119°C when it melt while rhombic sulphur is stable below 96°C



Curve AB; is called sublimation curve of rhombic sulphur, it shows the variation of vapour pressure of rhombic sulphur in equilibrium with its vapour with temperature.

Curve BC; is called the sublimation curve of monoclinic sulphur, it shows the variation of vapour pressure of monoclinic sulphur in equilibrium with its vapour with temperature

Curve CD; it is called vaporization curve of liquid sulphur and stable up to point D, it shows the variation of vapour pressure of liquid sulphur with temperature

Curve BF; it is called a transition curve Shows the effect of pressure on the transition point between rhombic sulphur and monoclinic sulphur along this line monoclinic sulphur is in equilibrium with rhombic sulphur.

Curve CF; is called the fusion curve of monoclinic sulphur, it shows the effect of pressure on the melting point of monoclinic sulphur

Curve EF; is called the fusion curve of rhombic sulphur, it shows the effect of pressure on the melting point of rhombic sulphur

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

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

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

Point D is called a critical point

When any of the phases is subjected to a change in temperature or pressure .it will disappear and another dominates.

When rhombic sulphur is heated, no change in phase occurs but it expands causing an increase in volume. This continues until curve EF, is reached when rhombic sulphur starts liquefying at its melting point. The solid remains in equilibrium with the liquid at the melting point.

Further heating beyond curve EF, it completely liquefies giving a liquid phase at point Y decreasing the pressure of phase Y causes no change but an increase in volume until when it vaporizes along curve CD where the liquid remains in equilibrium with the vapour.

Further decreases in pressure beyond curve CD all the liquid turns into a vapour.

When the vapour at phase Z is heated, there is no change in phase up to point W instead the vapour expands due to increase in temperature.

Decreasing the pressure of rhombic sulphur at X, there is no change in phase but an increase in volume due to a reduced pressure until curve AB is reached at which point rhombic sulphur begins to sublime. The vapour remains in equilibrium with the solid at the sublimation temperature.

Further decrease in pressure beyond curve AB all rhombic sulphur sublimates into sulphur vapour.

TWO COMPONENT SYSTEM

LIQUID-VAPOUR EQUILIBRIUM

Mixtures of two liquids

When two liquids which do not react chemically are brought together they give rise to three possibilities completely miscible, completely immiscible and partially miscible.

COMPLETELY MISCIBLE LIQUIDS

These are liquids which completely dissolve in each other in all proportions to give a homogeneous solution and have no saturation limit. Water and ethanol are completely miscible and so are methyl benzene and benzene, hexane and Heptane.

Generally it has been observed that those liquids which have similar chemical structure are completely miscible in each other while liquids which have different chemical structure are completely immiscible.

Thus water is completely miscible with alcohol because the two are chemically similar.

There are two types of solution; ideal solution and non-ideal solution

Ideal or perfect solution

This is a mixture of compatible liquids with intermolecular forces between molecules of the pure components and those intermolecular forces between the molecules of the unlike components similar and equal in strength. The solution obeys Raoult's and no heat changes or changes in volume occur when the mixture is made.

Characteristics of ideal solutions

They obey Raoult's law under all conditions

The cohesive forces between like molecules are equal to adhesive forces between unlike molecules

There is no heat change that occurs when the components of the solution are mixed. The total volume of the solution is equal to the sum of the volume of the individual components.

Pairs of liquids which act in this way are those with little or no polarity in their valency bonds or with similar degree of polarity. They include benzene and methyl benzene methanol and water and propan-1-ol and propan-2-ol.

RAOULT'S LAW

There is, in a solution, as in a pure liquid a nature tendency for some molecules to overcome the intermolecular forces of attraction and escape from solution and pass into the vapour phase.

When the solution is in equilibrium with vapour, the total vapour pressure of the solution above the mixture will depends on the partial vapour pressure of the components and on the composition of the mixture. The partial vapour pressure of each component in the mixture can be calculated using Raoult's law

Raoult's law which states that;

The partial vapour pressure of a component of an ideal solution, is equal to the vapour pressure exerted by the pure component at that temperature multiplied by the mole fraction of that component.

The assumption made here is that vapour behave as ideal gases

Mole fraction is a convenient way of expressing the composition of each component in a mixture.

The mole fraction of A in a mixture of A and B is $X_A = \frac{n_A}{n_A+n_B}$

The mole fraction of B in a mixture of A and B is $X_B = \frac{n_B}{n_A+n_B}$

The sum of the mole fraction of the components in the mixture equals to one $X_A + X_B = 1$

Raoult's can be expressed mathematically as

$$P_A = X_A P_A^O$$

$$P_B = X_B P_B^O$$

P_A and P_B are the partial vapour pressures of the components A and B over the liquid

In any mixture of gases each gas exerts its own pressure independently of the other gases in the mixture

P_A^O is the vapour pressure of A over pure A at that temperature

and P_B^O are the vapour pressure of B over pure B and B at that temperature

the total vapour pressure of the mixture (at a given temperature) over the liquid is equal to the sum of the partial pressures of the two components this is according to Dalton's law

$$\begin{aligned} P_T &= P_A + P_B \\ &= X_A P_A^O + X_B P_B^O = X_A P_A^O + (1 - X_A) P_B^O \end{aligned}$$

In the mixture of ideal solution partial vapour pressure of a component is proportional to its mole fraction. This is expressed in the figure below

VAPOUR PRESSURE- COMPOSITION DIAGRAM FOR BINARY IDEAL SOLUTION

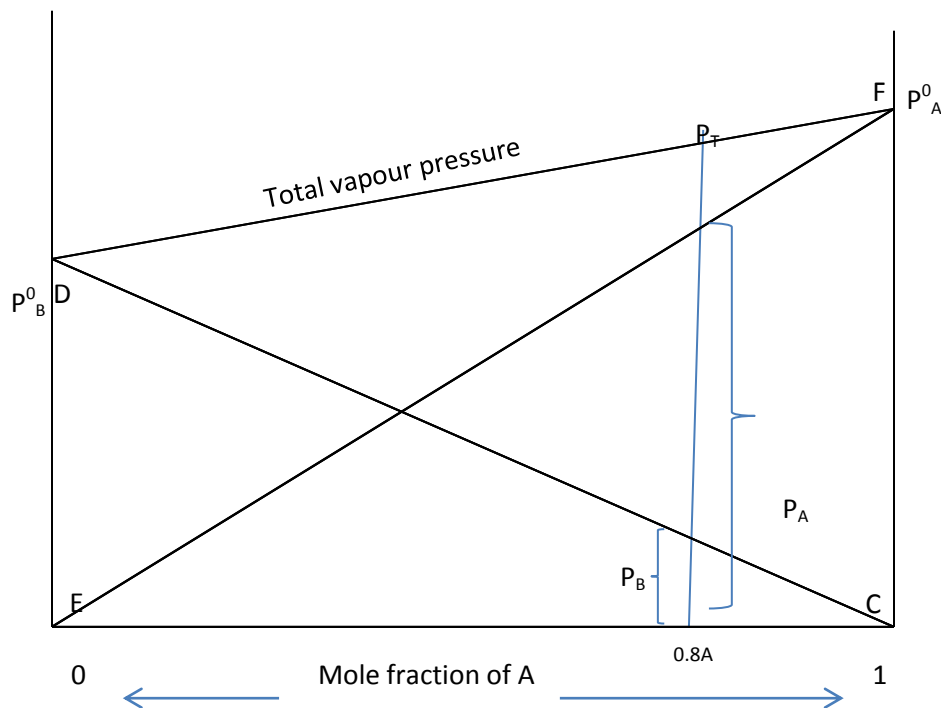


Fig 4.4 the vapour pressure composition diagram of an ideal solution

P_A^0 is the vapour pressure of pure A

P_B^0 is the vapour pressure of pure B

$P_B^0 < P_A^0$ This shows that liquid A is more volatile than liquid B

Line CD shows the variation of vapour pressure of component B with composition

Line EF shows the variation of vapour pressure of component A with composition.

Line DF shows the variation of total vapour pressure with composition

The a vertical dotted line represents a solution of composition 80%A

Beginning with pure A(100%A and 0%B) the partial vapour pressure of A decreases as B is added and it tends to zero when B is 100%. This is because the molecule of B gradually replaces the molecules of A above liquid mixture

Worked examples

Example one

At 88°C, the vapour pressure of benzene and toluene are 935 and 378 mmHg respectively.

Calculate the vapour pressure of the benzene –toluene mixture containing two moles of benzene per mole of toluene assuming ideal behavior.

Moles of benzene =2

Moles of toluene =1

$$P_{\text{Benzene}} = \frac{2}{3} \times 935$$

$$P_{\text{Toluene}} = \frac{1}{3} \times 378$$

$$P_{\text{Total}} = \frac{2}{3} \times 935 + \frac{1}{3} \times 378 = 749.333 \text{ mmHg}$$

Example 2

Calculate the vapour pressure of a solution containing 50g of Heptane and 38g of Octane at 20°C. the vapour pressure of Heptane and Octane are 473.2pa and 139.8pa respectively.

$$\text{RFM of Heptane } C_7H_{16} = 12 \times 7 + 1 \times 16 = 100$$

$$\text{RFM of Octane } C_8H_{18} = 12 \times 8 + 1 \times 18 = 114$$

$$\text{Moles of Heptane} = \frac{50}{100} = \frac{1}{2}$$

$$\text{Moles of Octane} = \frac{38}{114} = \frac{1}{3}$$

$$P_{\text{Heptane}} = \frac{2}{5} \times 473.2$$

$$P_{\text{Octane}} = \frac{1}{5} \times 139.8$$

$$P_{\text{Total}} = 283.92 + 55.92 = 339.84\text{pa}$$

NON-IDEAL SOLUTIONS OR REAL SOLUTIONS

A real solution is one which shows deviation from Raoult's law

These are deviations brought about by the difference in the intermolecular forces between the molecules of pure component and molecules of different components.

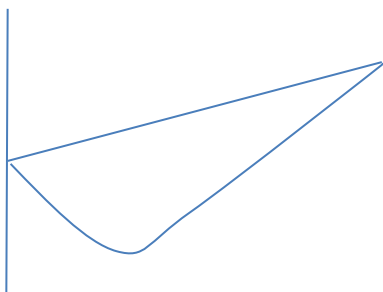
The vapour pressure of such solutions are either higher or less than that expected from Raoult's law these deviations are generally observed for systems in which the two components of liquid mixture have different molecular structure. Majority of liquid mixtures do not obey Raoult's law and exhibit either a positive or negative deviation from Raoult's law.

NEGATIVE DEVIATION FROM RAOULTS LAW

If the intermolecular forces of attraction between the different particles from the two liquids are stronger than the attractive forces in the pure liquids then the particles will be held in the liquid more strongly. There is less tendency for molecules to escape from the solution than

from the pure liquids the total vapour pressure above the liquid will be lower than that predicted by Raoult's law. In some cases the deviations are small but in others they are much greater giving a minimum value for the vapour pressure lower than that of either pure component.

Vapour pressure diagram for negative deviation from Raoult's law



Composition X, corresponding to the lowest vapour pressure, at this composition the intermolecular forces of attraction between the two liquids are strongest

Explaining the deviations

The stronger forces could be due to extra intermolecular forces which exist in the mixture but do not exist in pure liquids, which may be due to association of one or both of the components in solution via weak inter-molecular hydrogen bonding or to some degree of compound formation between the components of solution. It is recognized by the contraction in volume and evolution of heat in making the solution (heat is given out when new bonds are made)

Examples of solutions which show negative deviation from Raoult's law include;

- i) Chloroform and Propanone
- ii) Phenol and ethyl amine
- iii) Ethanol and ethyl ethanoate

This is due to hydrogen bonding formed between the two molecules; hydrogen bonds are stronger than the cohesive forces in the pure liquids

iv) Hydrochloric acid and water

v) Nitric acid and water

This is due to ionization of covalent molecules of acid in water forming the hydroxonium ions and nitrate ions or chloride ions which have a stronger ionic attraction causing low escaping tendency of the molecules into the vapour phase.



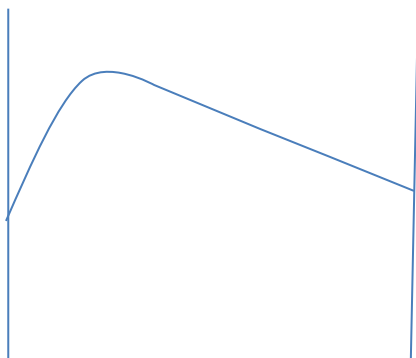
Properties of mixture that deviate negatively from Raoult's law

- i) The total volume decreases when the liquids are mixed
- ii) Heat energy is evolved
- iii) The adhesive forces between the components are stronger than the cohesive forces in the individual components

POSTIVE DEVIATION FROM RAOULTS LAW

If the intermolecular forces of attraction between the different particles from the two liquids are weaker than the attractive forces in the pure liquid then the particles will be held in the liquid less well. The molecules in the solution will have a greater tendency to escape from the solution than from pure liquids. The vapour pressure will be higher than that predicted by Raoult's law. In some cases the deviations are small but in others they are much greater giving a maximum value for the vapour pressure higher than that of either pure component

Vapour pressure composition diagram for positive deviation from Raoult's law



Composition X, corresponding to the highest vapour pressure, at this composition the inter molecular forces of attraction between the two liquids are weakest

Explaining the deviations

The weaker forces in the solution is commonly brought about by the breakdown of the hydrogen bonds in the pure liquids and replacing them with weaker intermolecular forces which make it easier for the molecules of liquid to escape from the solution into the vapour. It can also be caused by mixing a highly polar compound with a non- polar or a much less polar. This is recognized by increase in volume and absorption of heat on mixing (less heat is evolved when the new attractions are set up than was absorbed when to break the original ones).

Examples of solutions which show positive deviation from Raoult's law include;

Ethanol and water

Ethanol and water molecules associate through stronger inter molecular hydrogen bonding but when the two are mixed the hydrogen bonds break down. This causes less attraction between molecules in water –ethanol mixture than the average attraction between the molecules in the pure components of ethanol-ethanol molecules and water-water molecules hence increasing escaping tendency into the vapour phase.

Benzene and ethanol

Benzene has a non-polar structure while ethanol is polar and associates via hydrogen bonding. These two forces of attraction are different in nature and when the components are put together there will be greater repulsion between molecules of benzene and ethanol, hence a higher vapour pressure than that expected from Raoult's law. Other examples include cyclohexane and methanol, carbon disulphide and ethanol, carbon tetrachloride and methanol.

Properties of mixtures that deviate positively from Raoult's law

- i) The total volume increases when the liquids are mixed
- ii) Heat energy is absorbed
- iii) The adhesive forces between the components are weaker than the cohesive forces in the individual components.

The relationship between boiling point and vapour pressure

A liquid boils when its vapour pressure equals the atmospheric pressure.

The atmospheric pressure is frequently 1 atmosphere.

Boiling point is the temperature at which the vapour pressure becomes equal to atmospheric pressure.

Thus, a solution of two components A and B will boil when the total pressure i.e. $P_A + P_B$ becomes equal to 1 atmosphere.

The higher the vapour pressure of a liquid, the more volatile is the liquid.

A liquid with higher vapour pressure will boil at a lower temperature than a liquid with lower vapour pressure.

Thus a solution whose components have higher vapour pressure will boil at a lower temperature than the solution in which the components have lower vapour pressure, this is because solutions of higher vapour pressure can reach the external pressure at relatively lower temperature and start boiling than the solution of lower vapour pressures.

Since according to Raoult's law different compositions of solutions have different vapour pressures it follows that solutions of different composition will boil at different temperatures

Increasing temperature increases the vapour pressure of both liquids in the mixture but the vapour pressure of a more volatile component increases more rapidly

such that the graph of the temperature at which the mixture boils when plotted against composition gives a curve. For a liquid mixture of any one composition the vapour with which it is in equilibrium will be richer in the more volatile component so the composition of the vapour lies on the other side of the straight line joining the boiling point.

BOILING POINT COMPOSITION DIAGRAMS OF BINARY MISCIBLE LIQUID MIXTURES

Boiling point composition diagrams are constructed from vapour pressure composition diagram

There are three important types of boiling point-composition diagram:

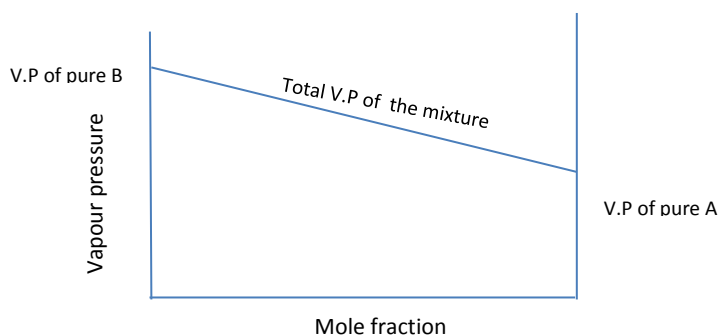
One where there is no maximum or minimum boiling point-this corresponds to the vapour pressure composition diagram for ideal and nearly ideal solution.

One where there is a maximum boiling point-this corresponds to the vapour pressure composition diagram with a minimum vapour pressure i.e. negative deviation.

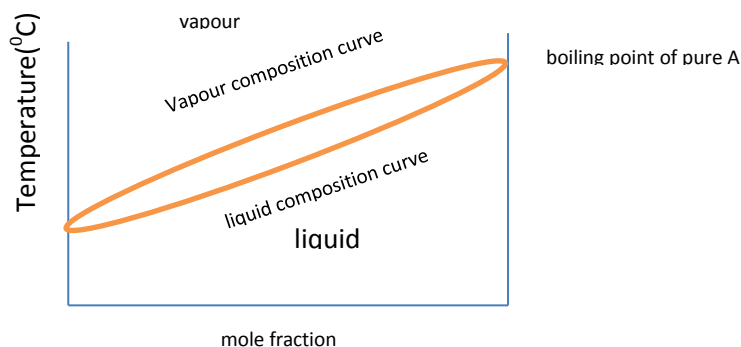
One where there is a minimum boiling point-this corresponds to the vapour pressure composition diagram with a maximum vapour pressure i.e. positive deviation.

Boiling point-composition with no maximum or minimum

Consider the vapour composition diagram of an ideal solution of A and B below



- Component B has a higher vapour pressure than component A this means component B will boil at lower temperature than component A.
- Different compositions of solution have different vapour pressure this implies that the solutions of different composition will boil at different temperature. Therefore the boiling point of the mixture will be between the boiling points of pure components.
- Increases in temperature, increases the vapour pressure of both liquids in the mixture, but the vapour pressure of a more volatile component increases more rapidly such that the graph of temperature at which the mixture boils when plotted against composition gives a curve.
- For a liquid mixture of any composition the vapour with which it is in equilibrium will be richer in the more volatile component, so the composition of the vapour lies on the other side of the straight line joining the boiling points



Separating components in an ideal solution by distillation

Components in ideal solution can be separated by fractional distillation

Distillation is the process of vaporization of one component of the mixture and then condensing the vapour back to the pure liquid. The process separates and purifies components with significantly different boiling points

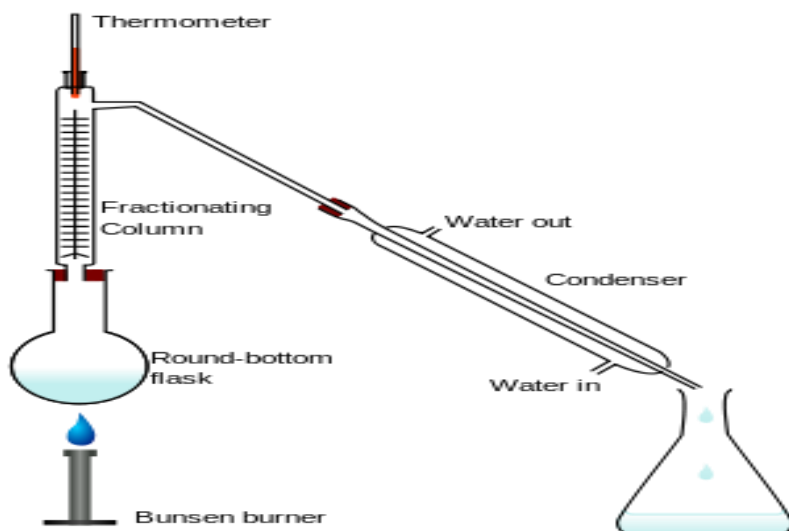
Whereas fractional distillation is the process of separating of completely miscible liquids with boiling point close to each other .

In this technique, the mixture to be separated is placed in the distillation flask and a fractionating column (long tube packed with glass beads to give the maximum possible surface area for vapour to condense on) fitted with a thermometer as shown in the diagram below.

Then liquid mixture is heated and the rising vapour passes up the fractionating column, the vapour of the less volatile component condenses on the beads as temperature fall up the column and trickles back in the distillation flask where it will meet new hot vapour rising that will cause the already condensed vapour to reboil. The vapour condenses on the beads and vaporizes again many times as it passes up the column At each condensation and vaporization the composition of the vapour changes as it becomes richer in the more volatile component .the vapour of the more volatile component continues to rise up to the top of the column

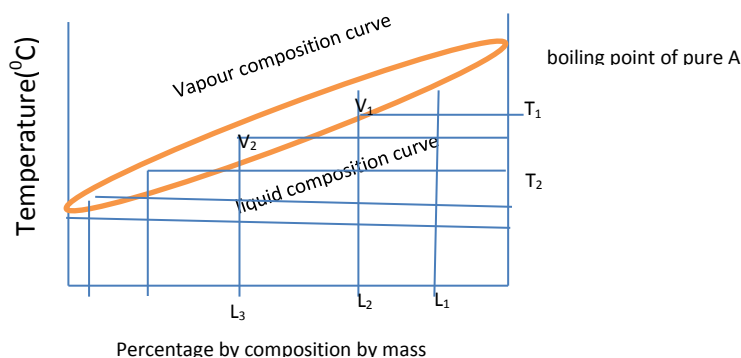
where it is cooled in the condenser and collected as the distillate the less volatile component tend to condense and fall back down the column. The first fraction to be collected is the most volatile of the mixed liquids then the next most volatile comes through and so on

All the vapour due to the more volatile component is therefore obtained at its boiling point and on cooling all the components are isolated in case of ideal solutions.



Using boiling point diagram

The boiling point composition diagram can be used to describe the changes that take place when miscible liquids are fractionally distilled



Suppose you heat a liquid mixture of composition L_1 , until it begins to boil at temperature T_1 then the vapour over the top of boiling liquid will have the composition V_2 . If the vapour is condensed by meeting the cold surface of the distillation column, it condenses to form a liquid of composition L_2 . this liquid starts to trickle down the column towards the distillation flask. If it is heated by upcoming vapour, it begins to boil at T_2 , to form a vapour of composition V_2 , if this vapour is condensed, it forms a liquid of composition L_3 . by repeated vaporization and condensation, the composition of the vapour is made to follow the curve $V_1V_2V_3$, becoming

richer in the more volatile component. The liquid is becoming richer in the less volatile component, and the composition follows the curve from L_1 towards the less volatile.

The longer the column, the more vaporization followed by condensation steps will be achieved, and the closer to pure A and pure B will the distillate and residue become.

Therefore successive boiling and cooling results in isolation of the more volatile component at its boiling point which is collected as the distillate leaving the residue in the flask as pure less volatile component

By fractional distillation it is possible to separate two components which are ideal solution

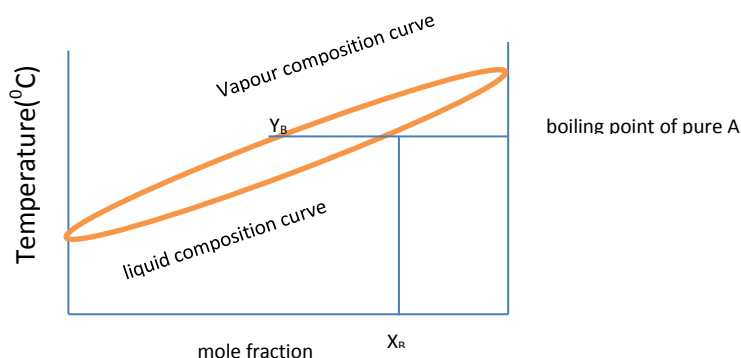
Composition of the vapour

If you boil a liquid mixture, you can find out the temperature it boils and the composition of the vapour over the boiling liquid.

Composition of the vapour ; is the fraction contributed by each component in the vapour phase

The composition of any ideal solution is governed by Raoult's law and the composition of the vapour above solution by Dalton's law of partial pressure

For example if you boil a liquid mixture of composition X_B it will boil at a temperature T_1 and the vapour over the top of the boiling liquid will have the composition Y_B



According to Daltons law

$$P_B = Y_B P_T$$

$$Y_B = \frac{P_B}{P_T} = \frac{X_B P_B^0}{X_A P_A^0 + X_B P_B^0}$$

Worked examples

The saturated vapour pressure of benzene and Toluene are 957mmHg and 378mmHg respectively

i) Calculate the composition of benzene –toluene mixture at 760mmHg

$$P_{\text{Total}} = P_B + P_T$$

$$760 = 957X_B + 378X_T$$

$$760 = 957(1-X_T) + 378X_T$$

$$X_T = 0.34$$

$$X_B = 0.66$$

ii) Calculate the composition of the vapour obtained when a liquid mixture boils

$$Y_B = \frac{X_B P_B^0}{P_{\text{Total}}}$$

$$= \frac{957 \times 0.66}{760} = 0.83$$

$$Y_{\text{Toluene}} = 1 - 0.83 = 0.17$$

iii) Which of the two liquids is more volatile

Benzene, because it has a higher vapour c

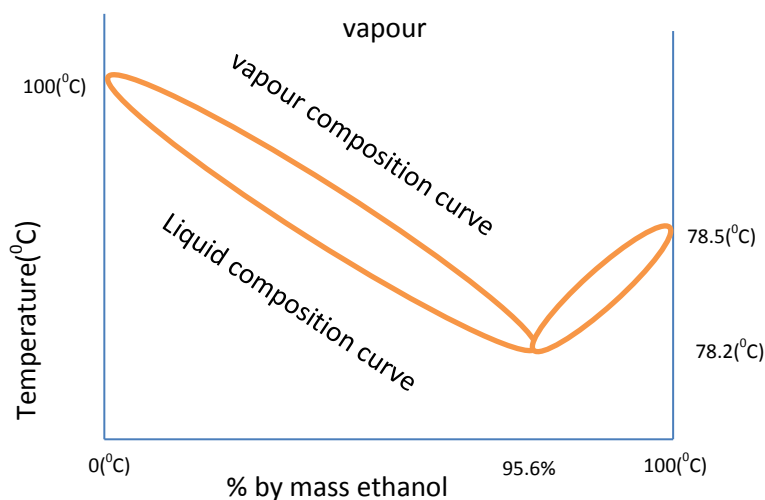
Boiling point composition diagrams for non- ideal liquid mixture

Minimum boiling point –composition diagram

A diagram of this type is given by non- ideal solution that deviates positively from Raoult's law.

A large positive deviation from Raoult's law produces a vapour pressure curve with a maximum value at some composition other than that of pure components, this implies that the boiling point composition curve will have a minimum value lower than the boiling points of either pure components

In cases of a mixture of ethanol and water which deviates positively from Raoult's law; this minimum occurs with 95.6% by mass of ethanol in the mixture. The boiling point of this mixture is 78.2°C , compared with the boiling point of pure ethanol at 78.5°C and water at 100°C



Fractional distillation of a non- ideal liquid mixture

Distilling a mixture of ethanol and water containing less than 95.6% by mass of ethanol

Suppose you heat a liquid mixture of composition C_1 as shown in the diagram above, it will boil at a temperature given by the liquid curve and produce a vapour with composition C_2 , when the vapour condenses it will of course still have the same composition C_2 . if you reboil that it will

produce a new vapour with composition C_3 much richer in the more volatile component(ethanol).repeating this process of boiling-condensing reboiling sequence you would eventually end up with a vapour with composition 95.6% by mass ethanol. If you condense that you obviously get a liquid with composition 95.6% by mass ethanol. If this liquid is reboiled it will give a vapour of the same composition and condensing it still gives a liquid of the same composition 95.6% by mass of ethanol.

Distilling a mixture of ethanol less than 95.6% by mass ethanol lets you collect a distillate containing 95.6% by mass ethanol in the collecting flask and pure water in the boiling flask.

It is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% by mass of ethanol.

This particular mixture of ethanol and water boils as if it were a pure liquid.it has a constant boiling point and the composition of liquid and vapour have fixed and exactly the same composition. It is known as a constant boiling mixture or azeotropic mixture or an azeotrope.

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

Azeotropes are not classified as compounds because; their compositions vary with pressure, they can be separated by physical means and cannot be represented by a general formula.

Distilling a mixture of ethanol and water containing more than 95.6% of ethanol

Suppose you heat a liquid mixture of composition C_4 as shown in the diagram above, it will boil at a temperature given by the liquid curve and produce a vapour with composition C_5 ,when the vapour condenses it will of course still have the same composition C_5 .if you reboil that it will produce a new vapour with composition C_5 much richer in the more volatile component(water).repeating this process of boiling-condensing reboiling sequence you would eventually end up with a vapour with composition 95.6% by mass ethanol. If you condense that you obviously get a liquid with composition 95.6% by mass ethanol. If this liquid is reboiled it

will give a vapour of the same composition and condensing it still gives a liquid of the same composition 95.6% by mass of ethanol

Distilling a mixture of ethanol more than 95.6% by mass ethanol lets you collect a distillate containing 95.6% by mass ethanol in the collecting flask and pure ethanol in the boiling flask.

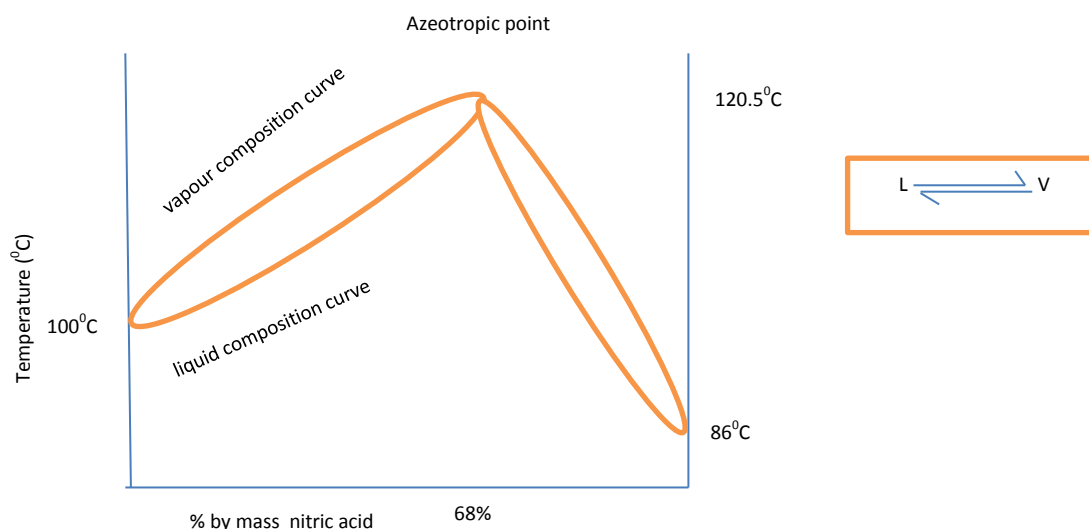
It is possible to get pure ethanol by distilling any mixture of ethanol and water containing more than 95.6% by mass of ethanol

A maximum boiling point-composition diagram

A diagram of this type is given by non-ideal mixtures that deviate negatively from Raoult's law

A large negative deviation from Raoult's law produces a vapour pressure curve with a minimum value at some composition other than that of pure components, this implies that the boiling point composition curve will have a maximum value higher than the boiling points of either pure components

In cases of a mixture of nitric acid and water which deviates negatively from Raoult's law; this maximum occurs with 68% by mass of nitric acid in the mixture. The boiling point of this mixture is 120.5°C , compared with the boiling point of pure nitric acid at 86°C and water at 100°C



Fractional distillation of a non-ideal liquid mixture

Distilling a mixture of nitric acid and water containing less than 68% by mass of nitric acid

Suppose you heat a liquid mixture of composition C_1 as shown in the diagram above, it will boil at a temperature given by the liquid curve and produce a vapour with composition C_2 , when the vapour condenses it will of course still have the same composition C_2 . If you reboil that it will produce a new vapour with composition C_3 much richer in the more volatile component (water). Repeating this process of boiling-condensing reboiling sequence you would eventually end up collecting pure water. As the acid loses water it becomes more concentrated its concentration gradually increases until it gets to 68% by mass nitric acid. At that point the vapour produced has exactly the same concentration as the liquid. The distillate will be the constant boiling mixture or azeotropic mixture this means you can't produce pure nitric acid from dilute nitric acid by distilling it.

Distilling a mixture of nitric acid and water containing more than 68% by mass of nitric acid

Suppose you heat a liquid mixture of composition C_4 as shown in the diagram above, it will boil at a temperature given by the liquid curve and produce a vapour with composition C_5 , when the vapour condenses it will of course still have the same composition C_5 . If you reboil that it will produce a new vapour with composition C_5 much richer in the more volatile component (nitric acid). Repeating this process of boiling-condensing reboiling sequence you would eventually end up with eventually end up collecting pure nitric acid.

Distilling a nitric acid-water mixtures containing more than 68% by mass nitric acid gives you pure nitric acid as the distillate and the constant boiling mixture as the residue.

Separating azeotropic mixture

Liquid mixture that deviates positively or negatively from Raoult's law cannot be separated completely by fractional distillation however such mixtures can be separated by means like

a) Azeotropic distillation (distillation by use of a third component)

An azeotrope mixture of ethanol and water can be separated by addition of benzene (the third component to be added must be readily dissolves in the components to form an ideal solution and must be immiscible with the other component such that the other two are separated using a separating funnel the third component is separated from the dissolved components by fractional distillation)

b) Solvent extraction one of the components can be extracted by use of a solvent

c)by chemical method

i)by adding another component that has a strong affinity for one of the component in the mixture

for example water and ethanol azeotrope, the liquid can be shaken with calcium oxide which reacts strongly with water to form calcium hydroxide which can be separated by filtration and the filtrate redistilled to obtain 100% pure ethanol.

ii)by addition of a compound which absorbs one of the components(adsorption)

IMMISCIBLE LIQUIDS

These are liquid which do not dissolve in each other when mixed together; they form two separate layers depending on their densities for example water and paraffin water and mercury water and carbon tetrachloride.

Generally liquids which have different chemical structure are completely immiscible. since mercury is very different chemically from water, the two are completely immiscible.

Vapour pressure of two immiscible liquids

The lack of any sort of interaction (absence of adhesive) between two immiscible liquids means that each liquid behaves almost independently of the other. If two immiscible liquids are kept agitated, the vapour pressure above the mixture is the total of the two separate vapour pressures.

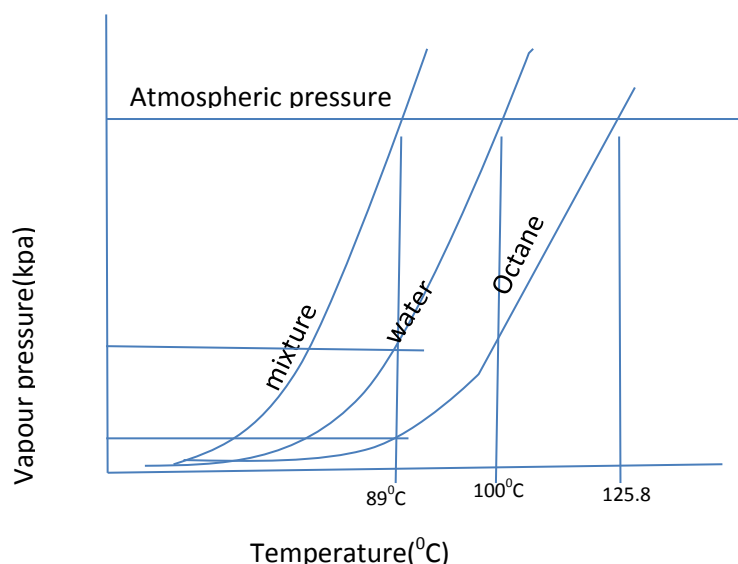
Agitation of the mixture is necessary to enable each liquid to establish its vapour pressure. Moreover, the vapour pressure above the mixture will be independent of the amount of each liquid present, so long as there is enough to give a saturated vapour

For example octane and water are immiscible, at 25°C the vapour pressure of octane and water are approximately 3.0kpa and 2.3kpa respectively the vapour pressure above the agitated mixture of them will be nearly 5.3kpa

Boiling point of the immiscible mixture

When the mixture ie of octane and water is heated the vapour pressure of both liquids will increase as shown in the figure below. the vapour pressure above the mixture is the sum of the individual vapour pressure. When the total vapour pressure equals the atmospheric pressure the mixture will boil. However this happens at a temperature lower than the boiling point of either component in the mixture

Variation of the vapour pressures of water, organic and the mixture of the two with temperature



Distilling immiscible liquids

Steam distillation

Steam distillation is a method used to separate a volatile component, which is immiscible with water, from other non-volatile impurities at a temperature less than 100°C using steam.

The processes of distillation of immiscible liquids is generally utilised in the laboratory and in the industry for the purification of those liquids which boil at too high a temperature or which decompose when heated to their normal boiling points.

It is mainly used in purification of organic substances that are immiscible with water

Principle of steam distillation

When a mixture of two practically immiscible liquids is heated, while being agitated to expose the surface of each liquid to the vapour phase. Each component contributes its own vapour pressure at a particular temperature to the total vapour pressure independent of other. Consequently, the vapour pressure of the whole system increases. Boiling begins when the sum of the vapour pressure of the two immiscible liquids just exceeds the atmospheric pressure at a temperature lower than the boiling point of either components.

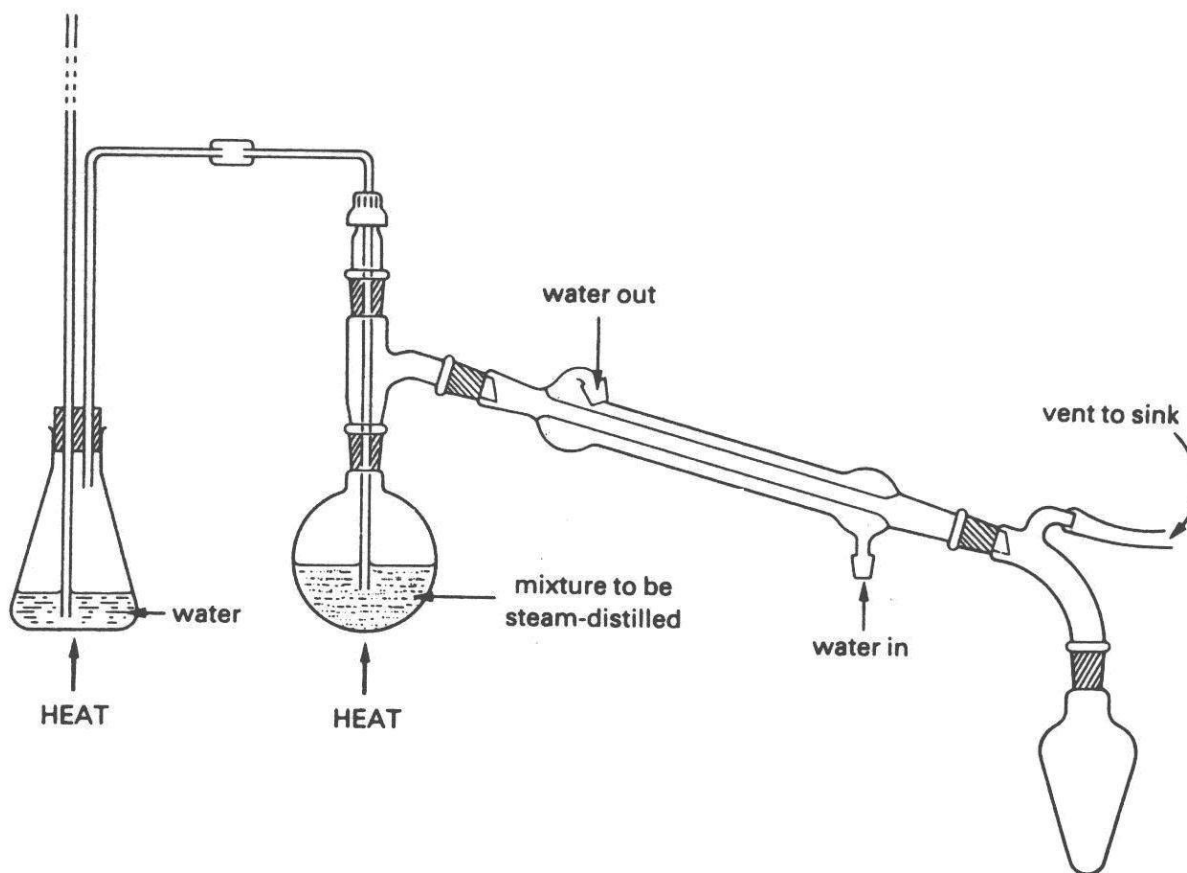
Properties of a substance to be purified by steam distilled

For the substance to be purified by steam distillation, it must;

- i) Be immiscible with water so that at a given temperature, each one of them in the mixture would produce vapour pressure independent of their proportions in the mixture as a result the mixture would have higher vapour pressure and will boil at lower temperature than that of the volatile component. The substance can easily be separated from water when it collects as a distillate using a separating funnel.
- ii) Be more volatile than the impurities so that it exerts a higher vapour pressure near the boiling point of water so that the mixture boils at a temperature below 100°C and also so that much of it is obtained with the distillate

- iii) have a high molecular mass, so that a reasonable mass of the substance is obtained in the distillate
- iv) Not react with water
- v) Exert a high vapour pressure. Near the boiling point of water. This enables a reasonable mass of the substance to be obtained in the distillate

Apparatus for steam distillation



procedure

Steam is passed through the heated mixture containing the components to be purified. The distillate collected in the receiver consists of water and the organic component (most

volatile).the organic liquid can be isolated by using a separating funnel and drying with a drying agent or by extraction with a solvent The non- volatile impurity remains in the distillation flask.

THE COMPOSITION OF THE DISTILLATE

From Dalton law the partial pressure, the partial pressure of an individual gas is equal to the total pressure multiplied by the mole fraction of that gas at constant temperature $P_i = P_T y_i$

$$\text{for water, } P_W = P_{\text{TOT}} \left(\frac{n_w}{n_w + n_o} \right) \dots\dots\dots(i)$$

$$\text{for organic, } P_O = P_{\text{TOT}} \left(\frac{n_o}{n_w + n_o} \right) \dots\dots\dots(ii)$$

Dividing equation(i)by(ii)

$$\frac{P_W}{P_O} = \frac{n_w}{n_o} = \frac{\frac{m_w}{M_w}}{\frac{m_o}{M_o}} = \frac{m_w \times M_o}{m_o \times M_w}$$

On rearranging the above equation

$$\frac{m_w}{m_o} = \frac{P_W \times M_w}{P_O \times M_o}$$

$$\frac{\text{mass of water}}{\text{mass of organic substance}} = \frac{\text{vapour pressure of water} \times \text{molecular mass of water}}{\text{vapour pressure of organic substance} \times \text{molecular mass of organic}}$$

The mass of the substance can be expressed in gram or as a percentage.

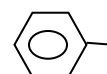
The above expression can be used to determine mass of the organic compound in the distillate or the molecular mass of the organic compound isolated

Example one

2-Aminohydroxyl benzene was steam distilled at 96°C at 760mmHg pressure. Calculate the percentage composition of the distillate.

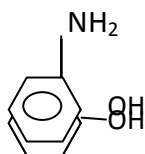
(The saturated vapour pressure. of water was 654mmHg at 96°C.)

solution



Rmm of water (H_2O) = $(1 \times 2) + (16 \times 1) = 18$

Rmm of 2-amino hydroxyl benzene



$$= (12 \times 6) + (1 \times 7) + (14 \times 1) + (16 \times 1) = 109$$

$$\frac{\text{mass of organic substance}}{\text{mass of water}} = \frac{V.P \text{ of organic substance} \times \text{molar mass of organic substance}}{V.P \text{ of water} \times \text{molar mass of water}}$$

$$\frac{\text{mass of organic substance}}{\text{mass of water}} = \frac{106 \times 109}{654 \times 18} = \frac{0.981}{1}$$

$$\text{Total mass} = 0.981 + 1 = 1.981$$

$$\% \text{ of organic substance} = \frac{0.981 \times 100}{1.981} = 49.9\%$$

$$\% \text{ of water } 100 - 49.9 = 51.1$$

Examples two

An organic compound **X** was steam distilled at 80°C at 760mmHg pressure. if distillate contained 90% by mass of X. Calculate the relative formula mass of **X**

(the saturated vapour pressure of water at 80°C is 240mmHg)

Solution

$$\frac{\text{mass of water}}{\text{mass of organic substance}} = \frac{\text{vapour pressure of water} \times \text{molecular mass of water}}{\text{vapour pressure of organic substance} \times \text{molecular mass of organic substance}}$$

$$\frac{(100-90)}{90} = \frac{240 \times 18}{(760-240) \times \text{molar mass of X}}$$

Molar mass of X is 74.8g

Example three

The following data was obtained for the steam distillation of Bromo- benzene at pressure of 760 mmHg

Temp ($^{\circ}\text{C}$)		90	92	94	96	98	100
v.p mmHg	Water	526	567	640	658	707	760
	Bromo- benzene	98	106	114	123	132	141

- Plot a suitable graph of vapour pressure against temperature.
- Use the graph to calculate the percentage by mass of Bromo- benzene that can be steam distilled.
- state the temperature of steam distillation
- Explain how Bromo- benzene can be isolated from the distillate.

Copy the above table and indicate on the column for total

Temp ($^{\circ}\text{C}$)		90	92	94	96	98	100
v.p mmHg	Water	526	567	640	658	707	760
	Bromo- benzene	98	106	114	123	132	141
	Total	624	673	725	701	839	901

ii) From the graph,

Total v.p = 760

v.p of water= 600

v.p of bromo- benzene = 108

molar mass of Bromo- benzene = C_6H_5Br = 157

Let mass of bromo- benzene in the distillate be = X %

Mass of water in the distillate will be =(100-X)%

$$\frac{\text{mass of bromo-benzene}}{\text{mass of water}} = \frac{V.P \text{ of bromo-benzene} \times \text{molar mass of bromo-benzene}}{V.P \text{ of water} \times \text{molar mass of water}}$$

$$\frac{X}{(100 - X)} = \frac{108 \times 157}{600 \times 18}$$

X=

iii)Temp of steam distillation 93°C

iv)Distillate is separated by using a separating funnel. The bromo- benzene is dried using a suitable drying agent e.g. anhydrous Calcium chloride

Advantages of using steam distillation.

1. Distillation takes place at lower temperature than the boiling point of the components of the distillate
2. It enables purification of substances that decompose at a temperature close to their boiling points

Application of steam distillation

- It is used in purification of organic compound which decomposes near their boiling points
- It is used in extraction of some natural products for example to extract eucalyptus oil from eucalyptus, citrus oils from lemons or orange peels and to extract oils used in perfumes from various plant materials
- It is used in determining relative molar mass of some compounds

exercises

THREE COMPONENT SYSTEMS.

DISTRIBUTION OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS

If a solute (solid or liquid) is shaken with two immiscible solvents or liquids in both of which it is soluble at a given temperature, then the solute distributes or partitions itself between the two solvents until equilibrium is established.

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

THE PARTITION LAW

states that “When a solute is taken up with two immiscible liquids in both of which the solute is soluble, the solute distributes itself between the two liquids in such a way that the ratio of its concentration in two liquids phases is constant at a given temperature provided the molecular state of the distributed solute is the same in both phases.”

The constant ratio is known as the partition coefficient or distribution coefficient K_D .

THE PARTITION OR DISTRIBUTION COEFFICIENT K_D

This is the constant ratio of the concentrations of the solute in one solvent to the concentration of the same solute in another solvent, when the two solvents are immiscible and in contact with each other at constant temperature.

I.e if a solute X is shaken between two immiscible liquids A and B in contact with each other at constant temperature then at equilibrium

$$\frac{\text{concentration of X in A}}{\text{concentration of X in B}} = \text{a constant} = K_D$$

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

Limitations of partition law

- Temperature must be kept constant
- The solute must be miscible in both solvents

- The solute must not dissociate or associate in either solvent i.e. it should remain the same molecular state.
- The solute must not react with either solvent.
- The solvents must be immiscible.
- Solutions used must be fairly dilute i.e. the solute should not saturate either solvent.

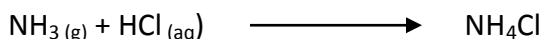
DETERMINATION OF K_D BETWEEN SOLVENTS

a) Experiment to determine of K_D of ammonia between water and trichloromethane

A given volume of a standard solution of ammonia is shaken with a given volume of a mixture of water and trichloromethane in a given temperature for about 5 minutes. This ensures that equilibrium is attained.

The mixture is allowed to stand to let the layers separate out. Equal volumes of either layer are pipette and separately titrated with standard solution of HCl using phenolphthalein indicator.

Ammonia reacts with HCl according to the equation.



The volume HCl required to reach end point is noted and the concentration of ammonia in either layer can be calculated. The value of K_D is obtained from the expression.

$$K_D = \frac{[\text{NH}_3] \text{ in water}}{[\text{NH}_3] \text{ in trichloromethane}}$$

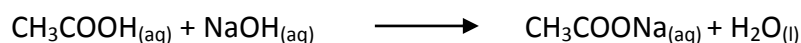
Ammonia is much more soluble in water than in trichloromethane and the partition coefficient of ammonia between the two solvents at a given temperature gives the number of times ammonia is more soluble in water than trichloromethane.

Experiment to Determine of K_D of ethanoic acid between tetra chloromethane and water.

A known volume of tetra chloromethane and a known volume of water are introduced in a separating funnel.

A known volume of standard solution of ethanoic acid added to the mixture. The funnel is stoppered and shaken for the equilibrium to be attained at a given temperature, the mixture is then allowed to stand to let the two layers separate out and equal volumes of either, layer are pipetted and titrated separately with a standard solution of NaOH using phenolphthalein as indicator.

Ethanoic acid reacts with sodium hydroxide according to the equation.



The volume of sodium hydroxide required to reach endpoint for separate layers is noted and the concentration of ethanoic acid in either layer is the determined from which the partition coefficient of ethanoic acid can be calculated.

$$K_D = \frac{[\text{CH}_3\text{COOH}]_{\text{in tetrachloromethane}}}{[\text{CH}_3\text{COOH}]_{\text{in water}}}$$

Ethanoic acid is much more soluble in tetra chloromethane than in water and the K_D value obtained is an indicator of the number of times ethanoic acid is more soluble in the organic layer than in water.

Determination of K_D of iodine between tetra chloromethane and water.

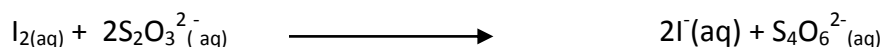
A given mass of iodine is shaken with a given volume of a mixture of tetra chloromethane and water in a stoppered separating funnel at a given temperature until the equilibrium of iodine between the two layers is attained.

The mixture is allowed to stand to let the two layers separate out.

Equal volumes of each layer are pipette in separate conical flasks and separately titrated with a standard sodium thiosulphate using starch indicator.

The volume of standard sodium thiosulphate required to reach endpoint is noted for each layer.

Sodium thiosulphate reacts with iodine according to the equation.



The concentration of iodine in either layer is then determined from which the partition coefficient of iodine can be calculated

$$K_D = \frac{[\text{I}_2]_{\text{tetrachloro methane}}}{[\text{I}_2]_{\text{water}}}$$

Worked questions and answers

1) 100cm³ of an aqueous solution of ammonia was shaken with 100cm³ of chloroform at 198k, when equilibrium was established; 25cm³ samples of each layer were titrated against 0.1M HCl. If 25cm³ of the aqueous layer required 127.5cm³ of the acid while 25cm³ of the chloroform layer required 5cm³ of the same acid.

Calculate the value of K_D for the distribution of ammonia between chloroform and water.

Solution

Organic layer

1000cm³ of solution contain 0.1mole of HCl

5cm³ of solution contains $\frac{0.1}{1000} \times 5$ moles of HCl

$\frac{0.1}{1000} \times 5$ moles of HCl reacts with $\frac{0.1}{1000} \times 5$ moles of ammonia

25cm³ of solution contain $\frac{0.1 \times 5}{1000}$ moles of NH₃

1000cm³ of solution contain $\frac{0.1 \times 5}{1000} \times \frac{1000}{25} = 2.0 \times 10^{-2} \text{ M}$

Aqueous layer

1000cm³ of solution contain 0.1 moles of HCl

127.5cm³ of solution contain $\frac{0.1}{1000} \times 127.5$ moles of HCl

$\frac{0.1}{1000} \times 127.5$ moles of HCl reacts with $\frac{0.1}{1000} \times 127.5$ moles of ammonia

25cm³ of solution contain $\frac{0.1 \times 127.5}{1000}$ moles of NH₃

1000cm³ of solution contain $\frac{0.1 \times 127.5}{1000} \times \frac{1000}{25} = 5.1 \times 10^{-1} \text{M}$

$$K_D = \frac{NH_3 \text{ in } CHCl_3}{NH_3 \text{ in } H_2O} = \frac{2.0 \times 10^{-2}}{5.1 \times 10^{-1}} = 0.04$$

2) 50cm³ of 1.5M ammonia solution were shaken with 50cm³ of trichloromethane in a separating funnel. After the layer had settled, 20cm³ of the chloroform layer were pipette and titrated with 0.05M HCl .If 23cm³ of the acid were required for neutralization,

Calculate the value of K_D of ammonia between water and chloroform at that temperature.

SOLUTION

Organic layer

1000cm³ of solution contain 0.05moles of HCl

23.0cm³ of solution contain $\left(\frac{0.05 \times 23.0}{1000}\right)$ moles of HCl

$\left(\frac{0.05 \times 23.0}{1000}\right)$ moles of HCl reacts with $\left(\frac{0.05 \times 23.0}{1000}\right)$ moles of ammonia

20cm³ of solution contain $\frac{0.05 \times 23}{1000}$ moles of NH₃

1000cm³ of solution contain $\frac{0.05 \times 23 \times 1000}{1000 \times 20} = 0.0575 \text{M}$

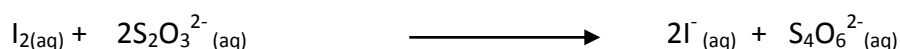
Concentration of NH₃ remaining in aqueous layer (1.5- 0.0575) =1.4425M

$$K_D = \frac{[NH_3] \text{ in water}}{[NH_3] \text{ in } CHCl_3} = \frac{1.4425}{0.0575} = 25.1$$

3) 50cm³ of an aqueous solution of iodine was shaken with an equal volume of carbon tetrachloride in a separating funnel at 290K. When equilibrium was established, the two layers were left to separate out. 25cm³ of each layer were pipetted and titrated separately against a 0.05M sodium thiosulphate solution using starch indicator. The organic layer required 47.50cm³ while the aqueous layer required 7.5cm³ of the same solutions of sodium thiosulphate.

Calculate the value of K_D of iodine between the organic layer and the aqueous layer.

Solution



Organic layer

1000cm³ of solution contain 0.05moles $\text{S}_2\text{O}_3^{2-}(\text{aq})$

47.5cm³ of solution contain $\left(\frac{0.05}{1000} \times 47.5\right)$ moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$

2 moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ react with 1 mole of I_2

$\left(\frac{0.05}{1000} \times 47.5\right)$ moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ will react with $\frac{1}{2} \left(\frac{0.05}{1000} \times 47.5\right)$ of I_2

25cm³ of solution contain $\frac{1}{2} \left(\frac{0.05}{1000} \times 47.5\right)$ moles of I_2

1000cm³ of solution contain $\frac{1}{2} \left(\frac{0.05 \times 47.5}{1000}\right) \times \frac{1000}{25}$

$$=0.0475\text{M}$$

Aqueous layer

1000cm³ of the solution contain 0.05 moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$

7.5cm³ of solution contain $\left(\frac{0.05 \times 7.5}{1000}\right)$ moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$

2moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ react with 1 mole of $\text{I}_2(\text{aq})$

$\left(\frac{0.05 \times 7.5}{1000}\right)$ Moles of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ will react with $\frac{1}{2} \left(\frac{0.05 \times 7.5}{1000}\right)$ moles of I_2

1000cm^3 of solution will contain $\frac{1}{2} \left(\frac{0.05 \times 7.5}{1000} \times \frac{1000}{25}\right)$ moles of $\text{I}_2 = 7.5 \times 10^{-3}$

$$K_D = \frac{[\text{I}_2] \text{ in } \text{CCl}_4}{[\text{I}_2] \text{ in } \text{H}_2\text{O}} = \frac{0.0475}{7.5 \times 10^{-3}} = 6.3$$

APPLICATION OF DISTRIBUTION LAW

- Solvent extraction
- Investigation of complex ions
- Distinguishing bromides from iodides
- De-silverisation of lead
- Ions exchange
- Partition chromatography

a) THE SOLVENT EXTRACTION

This involves separating one component from a mixture using a solvent in which the component is more soluble than any of the other components in the mixture.

For example, iodine is more soluble in many organic solvent than water therefore carbon tetrachloride can be used to extract iodine from aqueous solution

Solvent extraction is a process of separating a compound (mainly organic) from aqueous solution in which it is slightly soluble by adding a suitable organic solvent in which a solute is more soluble.

Solvent extraction is normally used to remove solutes from their aqueous solutions by shaking with extracting solvent in which the solute is more soluble at a given temperature.

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

Organic compounds and nonpolar substances are extracted using organic solvents such as carbon tetra chloride ethoxy ethane benzene etc

Ether is particularly used as an extracting solvent because its very volatile and therefore easily distilled off.

During solvent extraction, the process can be performed at once using all the available solvent to extract or in several small portions

Using separate portions is more economical and preferred during solvent extraction since much amount of the solute is extracted.

Worked example

Calculate the mass of Z that can be extracted from 100cm³ of aqueous solution containing 30g of Z by shaking the aqueous solution with

a) 100cm³ of ether

b) Two successive portions of 50cm³ of ether (K_D of Z between ether and water is 5)

Solution

$$K_D = \frac{\text{conc of Z ether}}{\text{conc of Z in water}}$$

$$5 = \frac{\text{mass of Z in ether/volume of ether}}{\text{mass of Z in water/volume of water}}$$

$$5 = \frac{\frac{a}{100}}{\frac{30-a}{100}} = \frac{a}{30-a}$$

$$150 - 5a = a$$

$$a = 25\text{g}$$

The mass of Z extracted by 100cm³ of ether is 25g.

c) Using first portion of 50cm³

Let b g be the mass of Z extracted by the first portion of 50 cm^3 , then mass of Z remaining in aqueous layer is $(30-b)\text{g}$.

$$K_D = \frac{\text{conc of Z ether}}{\text{conc of Z in water}}$$

$$\frac{\text{mass of Z in ether/volume of ether}}{\text{mass of Z in water/volume of water}}$$

$$\frac{\frac{b}{50}}{30 - \frac{b}{100}}$$

$$5 = \frac{2b}{30-b}$$

$$150 - 5b = 2b$$

$$b = \frac{150}{7} = 21.43\text{g}$$

Mass remaining in aqueous layer

$$= (30 - 21.43) = 8.57\text{g}$$

For the 2nd portion of 50cm^3

Let c g be the mass of Z extracted by the second portion of 50cm^3

Mass of Z remaining in the aqueous layer is $(8.57-c)\text{ g}$

$$K_D = \frac{\text{conc of Z ether}}{\text{conc of Z in water}}$$

$$5.0 = \frac{\frac{c}{50}}{8.57 - \frac{c}{100}}$$

$$5.0 = \frac{2c}{8.57 - c}$$

$$7c = 42.85$$

$$C = 6.12\text{g}$$

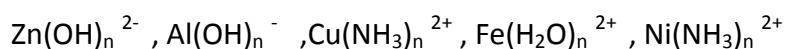
Total mass extracted using portions

$$= 21 + 3 + 6.12 = 27.55\text{g}$$

b) *Determination of formula of complex ions*

the partition law can be used to determine the number of ligands bonded to the central metal cation

for example to determine the value of n in the following complexes



Experiment to determine the formula of the complex formed between copper (ii) ions and ammonia;

procedure

A known volume of standard excess ammonia is added to standard solution of Cu^{2+} ions in a separating funnel.

The mixture is then shaken with a known volume of trichloro methane for some time, and then allowed to stand at constant temperature for the two layers to separate.

A fixed volume of each layer is pipetted in a separate conical flask and each is titrated against standard solution of hydrochloric acid using phenolphthalein indicator.

From the volume of acid that reacted with each layer, the concentration of ammonia in each layer can be determined using the equation.



Part of ammonia in aqueous layer reacted with copper (ii) ions to form a deep blue solution



The remaining part of ammonia the 'free ammonia' distributes itself between the aqueous layer and organic layer

From the known partition coefficient of ammonia between water and trichloromethane, the concentration of free ammonia in the aqueous layer can be obtained.

$$K_D = \frac{[NH_3]_{\text{free in aqueous layer}}}{[NH_3]_{\text{organic}}}$$

$$[NH_3]_{\text{free in aqueous layer}} = K_D [NH_3]_{\text{organic}}$$

$$[NH_3]_{\text{(aq) complexed}} = [NH_3]_{\text{total in aqueous}} - [NH_3]_{\text{(aq) free}}$$

$$[NH_3]_{\text{(aq) complexed}} = [NH_3]_{\text{total}} - K_D [NH_3]_{\text{organic}}$$

By comparing the concentration of Cu^{2+} and complexed ammonia in the aqueous layer the value n in the complex formed between the Cu^{2+} and NH_3 is obtained as $n = \frac{[Cu^{2+}]}{[NH_3]}$

Worked example

Excess ammonia was shaken with an aqueous solution of 0.025M Cu^{2+} and trichloromethane in a stoppered separating funnel. The separating funnel was allowed to stand for the two layers to separate out. Some ammonia reacted with the Cu^{2+} in the aqueous layer to form a complex.

At equilibrium the concentrations of ammonia in trichloromethane and the aqueous layers were 0.025 and 0.725 respectively.

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

Calculate

- The concentration of free NH_3 in the aqueous layer
- The concentration of NH_3 that formed the complex with Cu^{2+}
- The value of n in the complex and write the formula of the complex.

solution

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

$$25 = [NH_3]_{(aq) \text{ free}}$$

$$[NH_3]_{(aq) \text{ free}} = 0.021 \times 2$$

$$[NH_3]_{complexed} = [NH_3]_{(aq) \text{ total}} - [NH_3]_{(aq) \text{ free}} \\ = 0.725 - 0.625 = 0.1$$

$$[Cu^{2+}]_{(aq)} : [NH_3]_{(aq) \text{ fixed}}$$

$$\frac{0.025}{0.025} : \frac{0.1}{0.025}$$

$$n = 4.0$$

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

Alternatively the value of n in the formula of the complex $[Cu(NH_3)_n]^{2+}$ can be obtained graphically.

A known volume of standard solution of copper(ii)ions is put in a separating funnel and excess of standard solution of ammonia is added to it the solution is then vigorously shaken with known volume of trichloro methane for some time and left to stand at constant temperature for the layers to separate out.

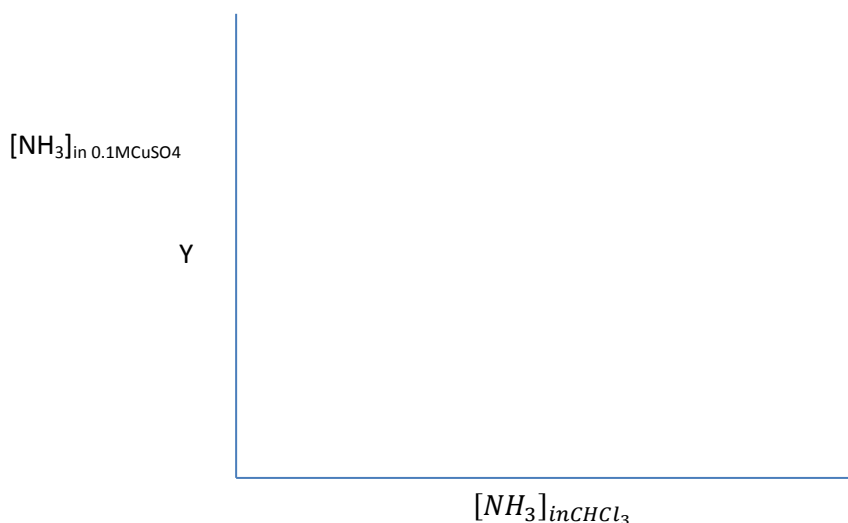
The concentration of ammonia in each layer is determined by titrating with standard hydrochloric acid using phenolphthalein indicator

The above procedure is repeated with different volumes of copper (ii) ions and trichloromethane and the concentration of ammonia determined for different volumes.

The results are tabulated in the table below

$[NH_3]_{in \ CuSO_4}$					
$[NH_3]_{in \ CHCl_3}$					

A graph of concentration of ammonia in 0.1M CuSO₄ against concentration of ammonia in trichloro methane is plotted and a typical example is shown below.



The concentration of fixed ammonia is obtained as the intercept on the y-axis from which the value of n can be obtained using the ratio,

$$\text{Cu}^{2+} : [\text{NH}_3]_{\text{fixed}} = 1 : n$$

The slope of straight line gives the partition coefficient of ammonia between water and trichloro methane

Example

The table below shows the results of partition of amino methane (CH₃NH₂)

between trichloromethane and 0.1m copper (ii) sulphate solution

$[\text{CH}_3\text{NH}_2]_{\text{in } 0.1\text{M CuSO}_4}$	0.87	1.10	1.33	1.57	1.80
$[\text{CH}_3\text{NH}_2]_{\text{in CHCl}_3}$	0.02	0.03	0.04	0.05	0.06

Represent the above data graphically and use the graph to determine the number of moles of amino methane that formed the complex with Cu^{2+}

Worked example

To a solution of 25cm^3 of 0.1M CuSO_4 was added 25cm^3 of NH_3 and the resultant solution was shaken with CHCl_3 and the mixture allowed to settle. 20cm^3 of the chloroform layer needed 10.2cm^3 of 0.05M HCl and 10cm^3 of the aqueous was titrated with 0.5M HCl and needed 16.5cm^3 of the acid to reach end point.

the K_D of ammonia between water and trichloromethane at that temperature is 25.

Calculate the value of n in the complex $\text{Cu}(\text{NH}_3)_n^{2+}$

Solution

Organic layer

1000cm^3 of solution contain 0.05 moles of HCl

10.20cm^3 of solution contain $\left(\frac{0.05}{1000} \times 10.20\right)$ moles of HCl

$\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{NH}_4\text{Cl}(\text{aq})$

$\left(\frac{0.05}{1000} \times 10.20\right)$ moles of HCl reacted with $\left(\frac{0.05}{1000} \times 10.20\right)$ moles of ammonia

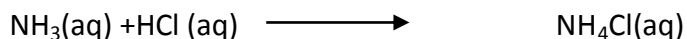
20cm^3 of solution contains 5.1×10^{-4} moles

1000cm^3 of solution contain $\frac{5.1 \times 5.1 \times 10^{-4}}{20} \times 1000 = 0.0255$ Moles

Aqueous layer (this contains complexed and free ammonia)

1000cm^3 of solution contain 0.5 moles of HCl

16.5cm^3 of solution contain $\frac{0.5 \times 16.5}{1000}$ moles of HCl



$$\frac{0.5 \times 16.5}{1000} \text{ moles of HCl reacted with } \frac{0.5 \times 16.5}{1000} \text{ moles of ammonia}$$

$$10\text{cm}^3 \text{ of solution contain } \frac{(0.5 \times 16.5)}{1000} \text{ moles of NH}_3$$

$$1000\text{cm}^3 \text{ of solution contain } 0.825$$

$$\text{But from } K_D = \frac{[\text{NH}_3]_{\text{aqueous free}}}{[\text{NH}_3]_{\text{organic}}}$$

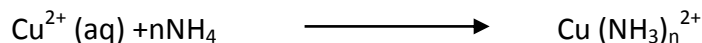
$$[\text{NH}_3]_{(\text{aq})} (\text{free}) = K_D [\text{NH}_3]_{\text{organic}}$$

$$= (25 \times 0.0255) = 0.6375 \text{ M}$$

$$[\text{NH}_3]_{(\text{aq})} \text{ complexed} = [\text{NH}_3]_{(\text{aq})} \text{ total} - [\text{NH}_3]_{(\text{aq})} \text{ free}$$

$$= 0.825 - 0.6375 = 0.1875 \text{ M}$$

From the equation leading to the formation of the complex



$$1000\text{cm}^3 \text{ of solution contain } 0.1 \text{ mole of Cu}^{2+}$$

$$25\text{cm}^3 \text{ of solution contain } \frac{0.1 \times 25}{1000} = 2.5 \times 10^{-3} \text{ moles of Cu}^{2+}$$

$$50\text{cm}^3 \text{ of solution contain } 2.5 \times 10^{-3} \text{ moles}$$

$$1000\text{cm}^3 \text{ of solution contain } \frac{2.5 \times 10^{-3} \times 1000}{50} = 0.05 \text{ Moles}$$

$$[\text{Cu}^{2+}]: [\text{NH}_3] \text{ complex}$$

$$\frac{0.05}{0.05} : \frac{0.2875}{0.05} \quad 1: 4$$

$$n = 4$$

$$\text{Hence formula} = \text{Cu}(\text{NH}_3)_4^{2+}$$

Determination of the equilibrium constant K_c

Partition can be used to determine the equilibrium constant between a covalent species and an ionic species in the equilibrium

For example to determine the equilibrium constant K_c for the reaction



Procedure;

A known volume of aqueous solution of iodine in potassium iodide is shaken with carbon tetrachloride in a separating funnel and allowed to stand at constant temperature for the two layers to separate

A fixed volume of each layer is pipetted in separate conical flask and each is titrated against standard solution of sodium thiosulphate using starch indicator.

From the volume of sodium thiosulphate that reacted with each layer the concentration of iodine in each layer is determined using the equation



Part of iodine in aqueous layer react with iodide ions to form a complex tri-iodide ion the remaining part will distribute itself between the aqueous layer and the organic layer. Only the covalent iodine molecules I_2 will dissolve in the organic solvent

From the known partition coefficient of iodine between the organic and aqueous layer the concentration of free iodine in the aqueous is determined using the expression

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

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

From the concentration of iodine in the aqueous layer which includes the free iodine and complexed iodine. The concentration of complexed iodine is obtained by subtracting the free iodine from the total iodine in aqueous

$$[I_3^-] = [I_2]_{(aq) \text{ total}} - [I_2]_{(aq) \text{ free}}$$

The concentration of iodide ions is obtained by subtracting, $[I_3^-]$ from the original iodide ions.

The equilibrium constant is calculated using the expression

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

Worked example

A known mass of iodine is dissolved in water containing 0.16 mol dm^{-3} potassium iodide and the solution is shaken with known volume of tetra chloromethane. The concentration of iodine in the aqueous layer was found to be 0.08 M and that in organic layer 0.1 M .

(The partition coefficient for iodine between tetra chloromethane and water is 85.)

Calculate the equilibrium constant for the reaction.

Solution

$$[I_2]_{CCl_4} = 0.1 \text{ M}$$

$$K_D = \frac{[I_2]_{CCl_4}}{[I_2]_{aq}}$$

$$[I_2]_{aq} = \frac{[I_2]_{CCl_4}}{K_D} = \frac{0.1}{85} = 1.176 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[I_2^-]_{(aq) \text{ total}} = 0.08 \text{ M}$$

$$[I_3^-]_{(aq)} = [I_2]_{(aq) \text{ total}} - [I_2]_{(aq) \text{ free}}$$

$$= 0.08 - 1.176 \times 10^{-3} = 0.0788 \text{ M}$$

$$\text{Initial } [I^-] = 0.16 \text{ M}$$

$[I^-]$ reacted = 0.0788

$[I^-]$ at equilibrium = 0.0812 M

$$K_C = \frac{[I_3^-]}{[I_2][I^-]} = \frac{0.0788}{0.0812 \times 1.176 \times 10^{-3}} = 825.21 \text{ mol}^{-1} \text{ dm}^3$$

d) Distinguishing bromides and iodine

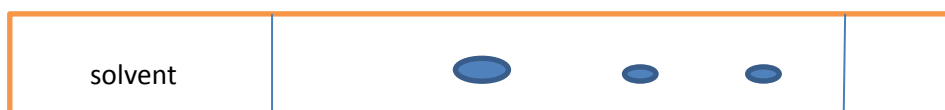
To the test solution add dilute nitric acid followed by bleaching powder then shake with tetra chloro methane and allow to stand.

Observation: brown or orange colouration in the carbon tetrachloride layer signifies bromide ion in solution and Purple colouration in carbon tetrachloride layer signifies iodide ions in solution.

e) Partition chromatography

Chromatography is the process of separating a solution containing many solutes, which are often present in very small amounts, by placing the solution on the some absorbent medium and passing yet another solvent across the medium.

Each solute in the original mixture will distribute itself between the solution on the absorbent, stationary medium and the second moving solvent in a unique way. The result is that some solute will travel across the absorbent medium faster than others leaving the individual solutes separated and spread.



Each component in the original sample can be recognized by measuring the distance it has travelled compared to the distance the solvent has travelled, this is known as retention factor

$$R_f, R_f = \frac{\text{distance travelled by solute}}{\text{distance travelled by solvent}}$$

R_f value is constant for a particular compound

Types of chromatography

Paper chromatography

The partition is between the stationary phase(water) on the paper and the mobile phase(solvent)

Column chromatography

A column of an inert material has the sample placed on top and the solvent (the eluent) washes the various components down the column at different rates

Ion exchange chromatography

The column is packed with an ion exchange resin this is made of beads of polymer that have charged groups on their surface.in anionic exchange resin the groups are negatively charged and trap positive ions in cationic exchange resin negatively charged ions will be trapped.

Application of chromatography

Separate compound in dyes

Identification of amino acids

TWO-COMPONENT SYSTEMS

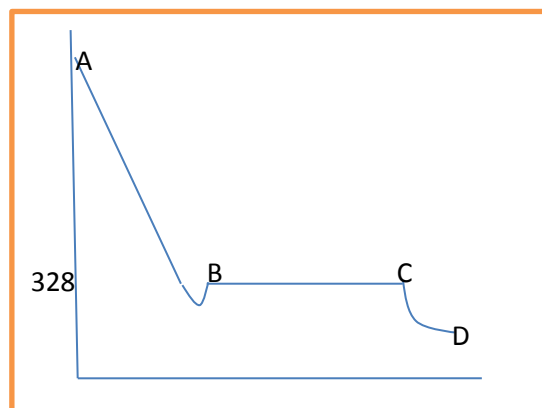
SOLID-LIQUID EQUILIBRIUM

Cooling curves for pure substances

When a molten compound is cooled, its temperature decreases but remains in the same phase until it begins to freeze then the temperature remains constant as it freezes and solid compound will be in equilibrium with its liquid. When the whole compound has frozen, the temperature of the solid then drops to the minimum. The constant temperature is referred to as the melting point.

The **melting point** is the temperature at which solid and liquid can exist in equilibrium with each other. Above the melting point, the solid will change completely into liquid. Below the melting point liquid will change completely into solid.

The diagram below shows the cooling curve of molten lead



At first the temperature decreases steadily, then it remains constant, before finally decreases again,

Point **A** is the freezing point of pure substance

AB represents the cooling curve of the hot liquid

BC is a plateau where crystals of pure solid begins to crystallize out

CD is the cooling curve of the solid

Super cooling is the cooling below the freezing point without formation of crystal

Cooling curve for mixtures

Addition of a solute to a solvent lowers the melting point of the solvent.

The decrease in melting point or freezing point is approximately proportional to the relative amount of solute added. The cooling curve is obtained by varying the amount of each component in the mixture and then determine the temperature at which the mixture begins to freeze at each composition.

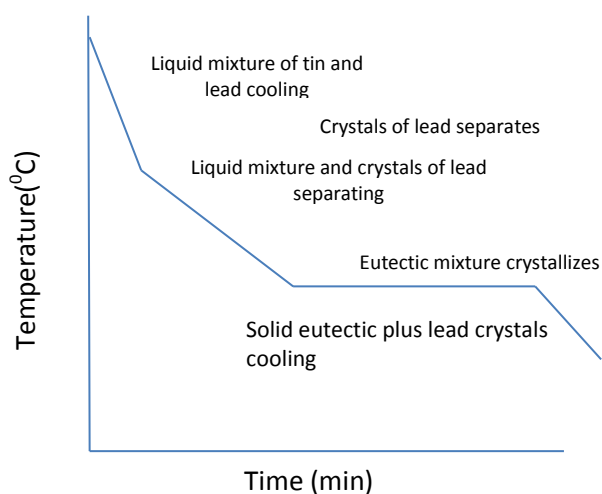
At each time the mixture freezes it's one of the components that act as the solvent that crystallizes out first until a certain composition when both components freezes out together.

Consider Tin-lead mixture

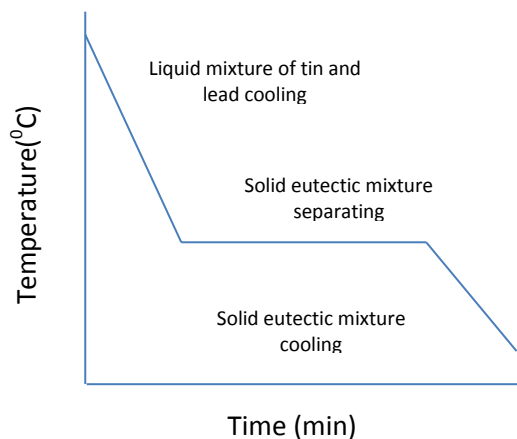
Addition of little tin to molten lead lowers the melting point of lead. On cooling pure lead separates out first. The freezing point continues to be lowered as more and more lead crystallizes out, until a certain composition (62%tin and38%lead) when both tin and lead crystallizes out

Similarly Addition of little lead to molten tin lowers the melting point of tin. On cooling pure tin separates out first. The freezing point continues to be lowered as more tin crystallizes out until a certain composition (62%tin and 38%lead) when both tin and lead crystallizes out.

This particular mixture of lead and tin has a cooling curve which looks like exactly that of a pure compound rather than a mixture, this particular mixture is known as eutectic mixture



Cooling curve for a mixture of 25% tin and 75% lead by mass



Cooling curve for a mixture of 62% tin and 38% lead by mass

Eutectic mixture is defined as a liquid mixture which at constant pressure solidifies at constant temperature to give a heterogeneous solid of the same composition

An eutectic mixture freezes at a fixed temperature (i.e. 183°C for liquid mixture of tin and lead) called eutectic temperature

Eutectic temperature is defined as the constant temperature at which a liquid mixture solidifies at constant pressure to give heterogeneous solid of the same composition.

Properties of eutectics

They have sharp melting points like a pure substance

They have a cooling curve like a pure substance

They are not compounds

Eutectic mixtures behaves as compounds but they are not because

a) they can be separated into their components by physical means whereas compounds are separated by chemical means.

b) Microscopic examination shows the presence of two kinds of crystals i.e. they are heterogeneous whereas a pure compound is homogeneous.

c) Their composition and melting points change with pressure whereas those of a compound are independent of pressure changes.

d) Their properties are simply the sum of the properties of its components whereas the properties of a compound are completely different from those of the components in it.

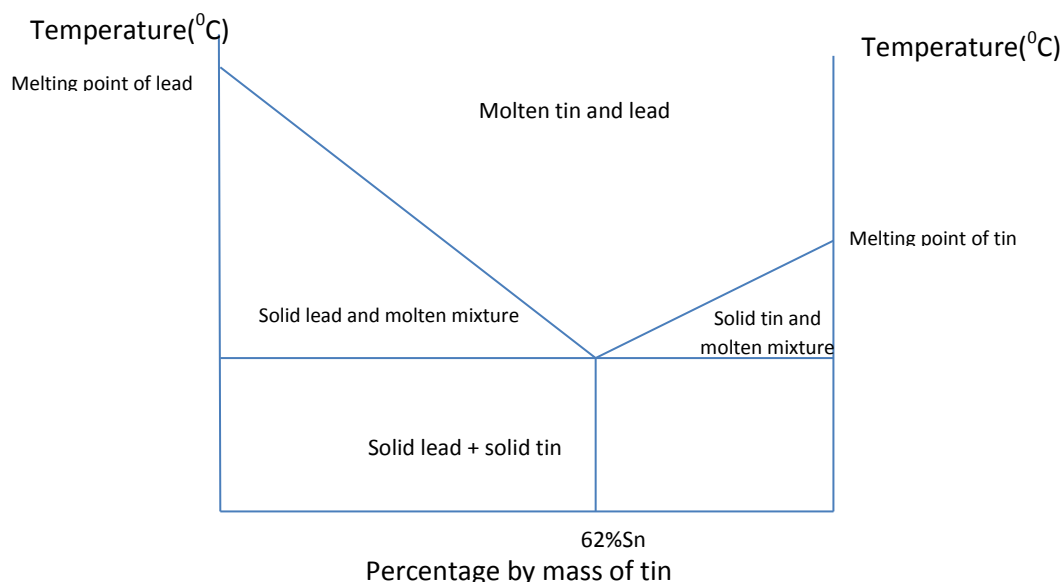
Similarity between Eutectic mixture and a compound

- I. Both have similar cooling curves
- II. Both have sharp melting point

Solid-liquid phase diagrams:

a) tin and lead mixture

Plotting temperature at which freezing starts against the proportion of tin and lead in the mixture



Point W is the eutectic mixture (36% lead and 64% tin) melts at 183°C

XY represents the solubility of tin in molten lead between 183°C and 232°C

YZ represents the solubility of lead in molten tin between 183°C and 327°C

At all points above XYZ the system is entirely liquid

In area XYR solid tin is in equilibrium with molten mixture.

In area YZS solid lead is in equilibrium with molten mixture

Below RYS the system is entirely solid

Cooling a molten mixture of tin and lead containing less than 38% of lead, no visible change occurs until a point on the curve XY is reached when pure tin begins to solidify, further decrease in temperature more tin is formed and the composition of solution follows curve XY when point Y is reached both tin and lead solidifies as eutectic mixture

Cooling a molten mixture of tin and lead containing more than 38% of lead, no visible change occurs until a point on the curve ZY is reached when pure lead begins to solidify, further decrease in temperature more lead is formed and the composition of solution follows curve ZY when point Y is reached both tin and lead solidifies as eutectic mixture

Cooling a molten mixture of tin and lead containing 38% of lead, no separation of solid occurs at all until the temperature reaches 183°C , then the temperature remains constant while a eutectic mixture crystallize out.

b) SALT SOLUTION:

solution of sodium nitrate

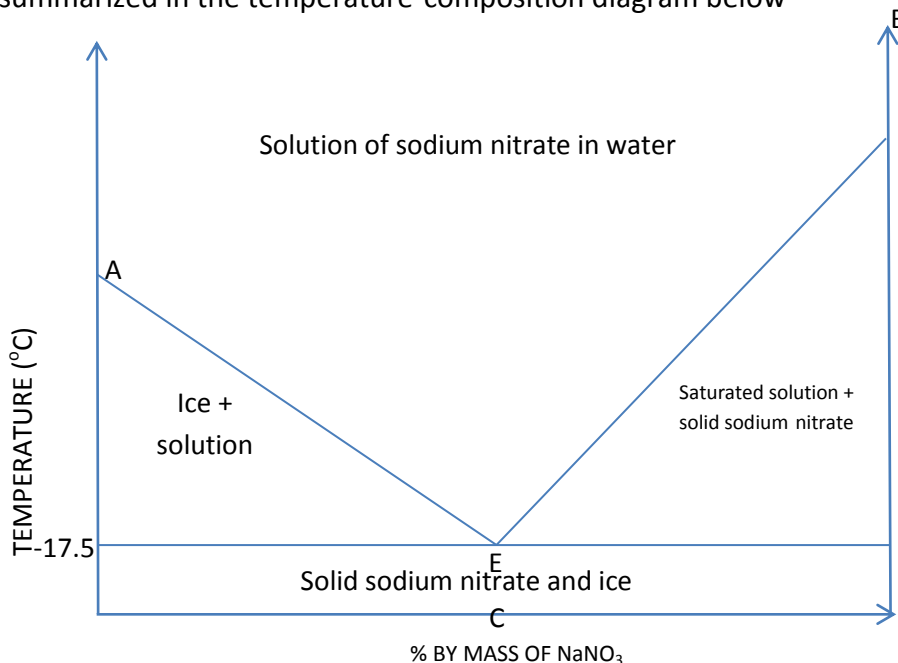
if a dilute solution of sodium nitrate is cooled below 0°C , pure ice will form when the freezing point of the solution is reached. This freezing point will be less than 0°C , because the added solute lowers the freezing point of water.

As ice is formed, the solution become more concentrated so that its freezing point becomes lower still, but further cooling will deposit more ice. Eventually, at -17.5°C , the solution remaining will become saturated, and any further cooling will deposit a mixture of ice and solid sodium nitrate, the temperature remaining constant at -17.5°C until whole system solidifies.

If a concentrated solution of sodium nitrate is cooled, crystals of pure sodium nitrate will be deposited until at a temperature of -17.5°C , a mixture of ice and sodium nitrate will again crystallize out at constant temperature

Crystallization will occur at lower temperature for more dilute solutions and at higher temperature for more concentrated solutions

This is summarized in the temperature-composition diagram below



The line BE describes the solubility curve of sodium nitrate in water.

The line AE describes the way in which the freezing point of water is lowered as more and more sodium nitrate is added to it. Along this curve equilibrium is established between the liquid mixture and ice.

Point E is known as the **eutectic point**; it corresponds to the lowest temperature which must be reached before the whole system solidifies.

At this point the crystals deposited from solution have the same composition as the solution. This composition is given by **C** i.e. 38.6% by mass of sodium nitrate and the mixture of this composition is known as the **eutectic mixture**

It is also the only point at which the three phase's ice, solid sodium nitrate and saturated solution of sodium nitrate in water are in equilibrium.

Application of eutectic mixtures

1-are used in the formation of alloys eg solder , brass

2-are used in industries where it is desirable to lower the melting point of a substance e.g in extraction of aluminium from bauxite; cryolite is added to bauxite to lower its melting point.

3-are used in safety appliances as plugs

Examples of mixtures which form eutectics include;

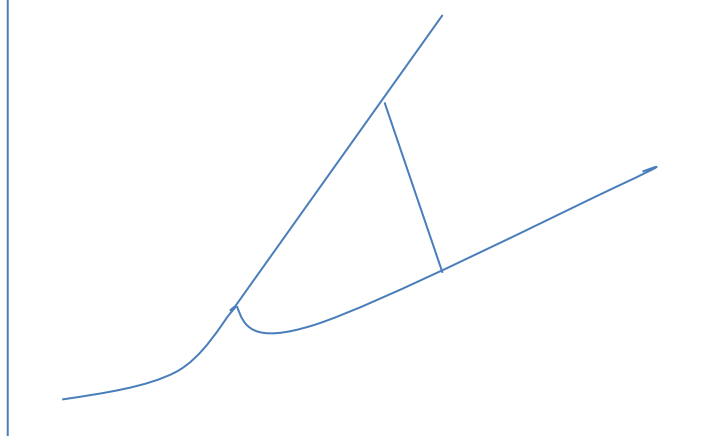
Zinc and cadmium

Bromo- benzene and benzene

Silver chloride and potassium iodide.

Benzene and naphthalene

Qn. The phase diagram for a certain substance is shown below.



a) Label the following on the diagram

- (i) The axes.
- (ii) The phase present.
- (iii) The critical temperature.
- (iv) The triple point.

b) Define the terms;

- (i) Critical point.
- (ii) Triple point.

c) Explain what would happen when the substance in point X changes to point B.

Solution .

b) (i) Critical point is the temperature and pressure beyond which the vapour cannot be liquefied no matter the applied pressure.

(ii) Triple point is the temperature and pressure where all the three phases co-exist in equilibrium with each other.

c) When the phase at point X has its pressure reduced with a slight increase in temperature, no change in phase occurs but there is an increase in volume due to expansion of rhombic

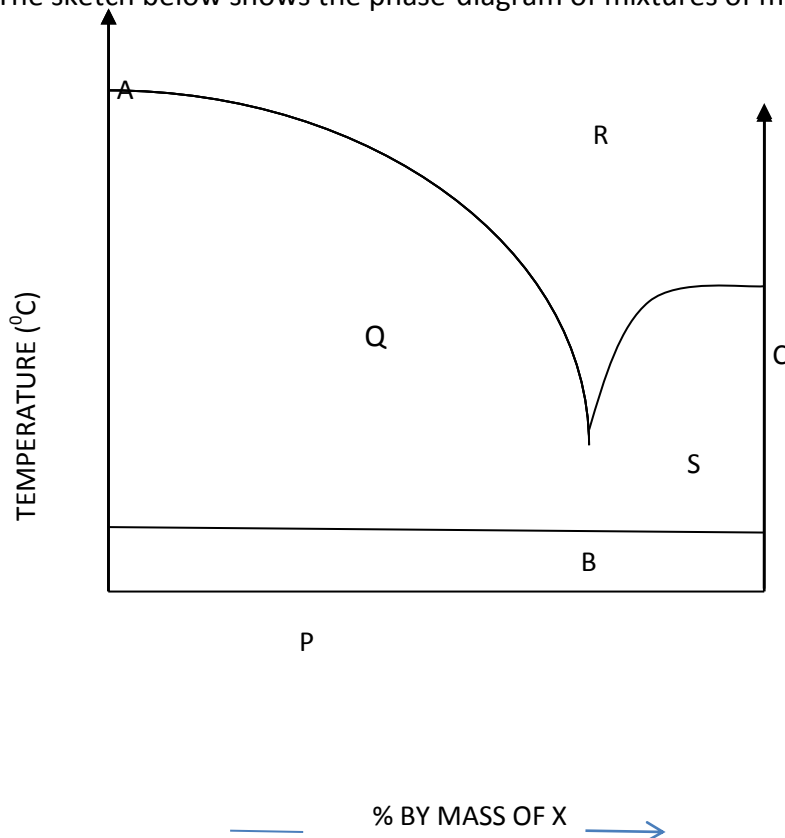
sulphur when the curve EF is reached, rhombic sulphur turns into monoclinic sulphur and the two remain in equilibrium at the transition temperature.

- d) Further decrease in pressure with slight increase in pressure with slight increase in temperature all the rhombic sulphur turns into monoclinic sulphur. when the pressure of monoclinic sulphur is reduced, it continues to expand with no change due to an increase in volume until when curve ED is reached at which point monoclinic sulphur turns into a vapour and the two remain in equilibrium with the vapour at a given temp and pressure.

Further decrease in pressure with slight increase in temperature all solid monoclinic turns into sulphur vapour

Question

The sketch below shows the phase-diagram of mixtures of metals X and Y



- a) State how above curve was obtained.

By cooling molten metals X and Y.

b) Identify the regions P, Q, R and S.

i) **P** Liquid mixture of x and y

ii) **Q** Solid **Y** and is liquid mixture of x and y

iii) **R** Solid x and solid y

iv) **S** Solid x and liquid mixture of x and y

c) State what the following points represent

B It represents the eutectic point.

A melting point of pure X

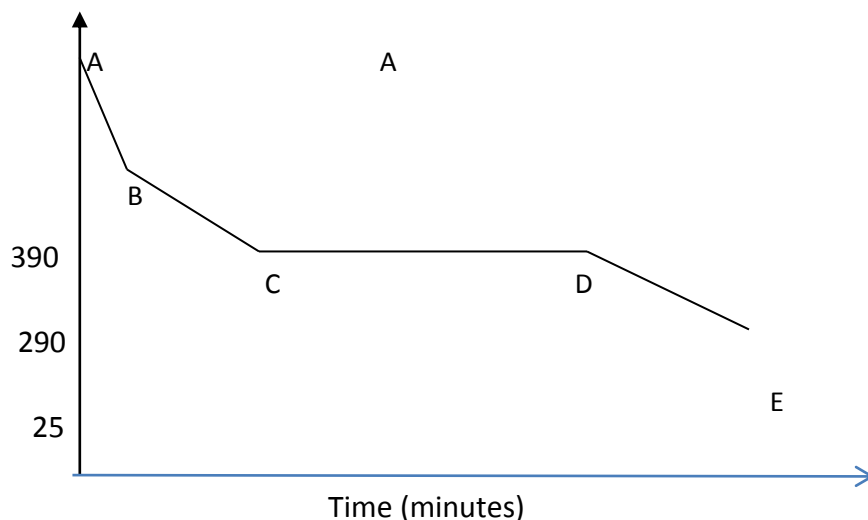
C melting point of pure Y

Describe what would happen if a mixture containing 50% by mass of X and Y is cooled from 410°C to 270°C.

Using points L and v as shown on the graph:

The mixture would remain in liquid state during the cooling, until point v on the curve AB where compound y begins to solidify out. It would continue to solidify along curve VB until point B, the eutectic point where both compounds x and y solidify out together. Solidification would continue until all is solid.

Draw a cooling curve to represent the above changes in part(d)



AB represent cooling of the hot liquid mixture

BC represents cooling of the liquid mixture as Y crystallize out

CD show the constant temperature when both components solidifies

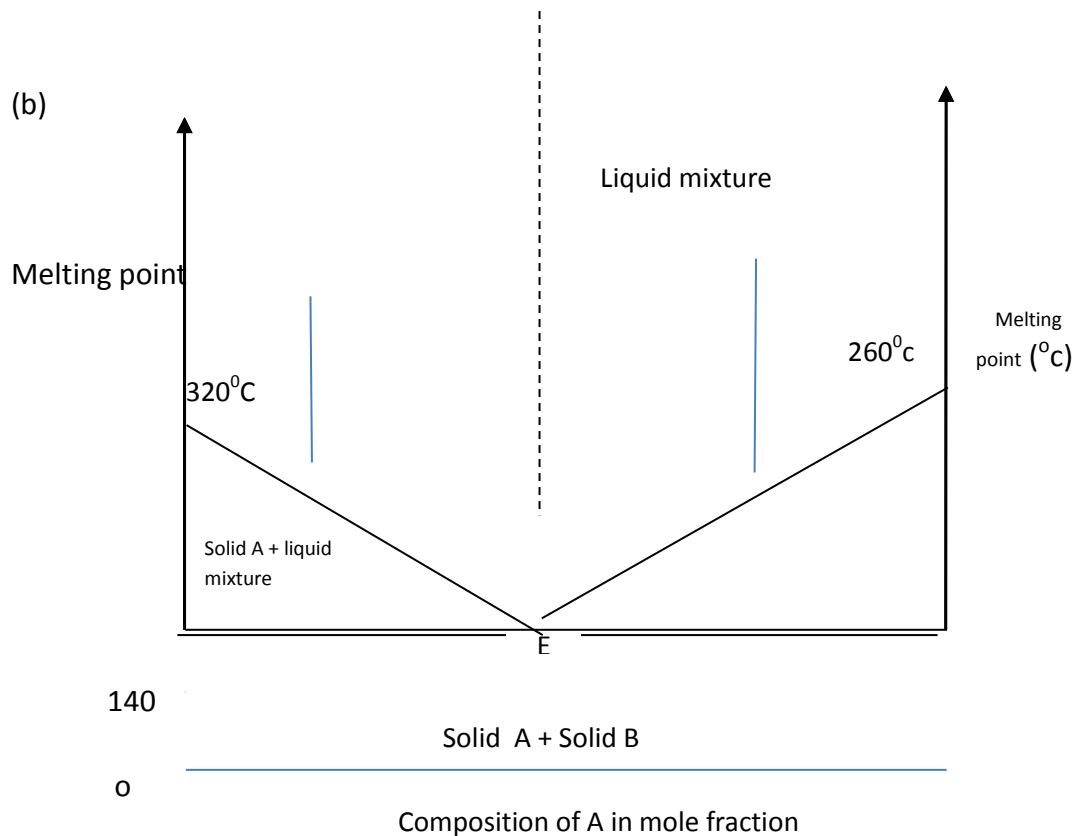
DE shows the cooling curve of the eutectic mixture

Question two

a) Explain what is meant by the term eutectic mixture.

Eutectic mixture is a liquid mixture which at constant pressure solidifies at constant temperature to give a heterogeneous solid of the same composition.

b) Two components A and B form eutectic mixture of composition 0.75A. The melting points of pure A, B and eutectic are 320, 260 and 140°C respectively. Using the above information sketch a fully labeled phase diagram for the mixture A and B.



c) Explain what happens if a liquid mixture of 40% B at 400 $^{\circ}\text{C}$ cooled to room temperature.

If the mixture at 400 $^{\circ}\text{C}$ is cooled, no visible change along xc, at point c freezing of B starts and solid B remains in equilibrium with the liquid mixture. Further cooling along CE more solid B is formed leaving the mixture richer in A, At point E, solid B and A solidify out together as an eutectic and they do so at a constant temperature until when all is converted into a solid which is left to cool to room temperature.

Question three

The melting point of pure Cadmium and pure bismuth are 321°C and 271°C respectively. The table below shows the melting point of the various compositions of the two metals.

Percentage of cadmium	21	35	50	65	80	95
Melting point in($^{\circ}\text{C}$)	216	190	156	184	242	300

a) Draw a fully labeled phase diagram for the mixture and explain the shape of the graph.



The graph is V-shaped. Pure bismuth has a high freezing point of 271°C but the freezing point lowers along AE due to the increase in the amount of cadmium which acts a solute responsible for lowering the freezing. Pure cadmium has a high freezing point which similarly decreases along BE due to the increase in the amount of bismuth which acts as a solute. Point E is the Eutectic mixture which freezes at a constant temperature and cooling beyond the eutectic mixture both solids solidify out.

b) Using the graph, explain what would happen if a liquid mixture containing 25% Cd at 350°C was gradually cooled.

No change in state is observed when the mixture is cooled from 350°C until a temp lower than 271°C at point x along curve AE, At this point pure bismuth starts solidifying out and remains in equilibrium with the liquid mixture. It continues solidifying out as temp is lowered until the eutectic temp is reached at point E when both Cadmium and bismuth start solidifying out together as eutectic and they do so at a constant temperature until when all is converted into a solid.

worked questions and answers

1. At 100.3 kN m⁻², the steam distillation of Nitro benzene takes place at 98°C. If the vapour pressure of water at the same temperature is 93.6 kN m⁻², Calculate the Composition of the distillate as a percentage by mass of 67.16%
2. At 1732 mmHg, the steam distillation of compound x takes place at 98°C.

The ratio of the mass of the Compound to the mass of water in the distillate is 0.188. If the vapour pressure of water at the same temp is 712 mmHg, calculate the relative formula mass of X.

During steam distillation, the distillate obtained consists of the substance being isolated and water

separation of miscible liquids which have boiling points that differ greatly from each other for example

A mixture of 2-nitro phenol and 4-nitrophenol can be separated by steam distillation because 2-nitrophenol and 4-nitro phenol are miscible, but 2-nitrophenol is immiscible with water while 4-nitrophenol is miscible with water when steam is passed through a heated mixture of 2-nitro phenol and 4-nitro-phenol the mixture will boil at a temperature lower than that of water such that 4-nitrophenol with a much higher boiling point will remain in the flask and the distillate will be a mixture of 2-nitrophenol and water the vapour is condensed to give a distillate which contains 2-nitrophenol

A mixture of phenyl amine (b.p.=184⁰C) and water (b.p.=100⁰C),for example will boil at 98⁰C under a pressure of 760mmHg

Reason:

Water and phenyl amine are immiscible liquids and each of the liquids exerts its own vapour pressure independent of the vapour pressure of other liquid at a given temperature. Each liquid evaporates independently of the other such that the total vapour pressure above the mixture is equal to atmospheric pressure at a temperature below the boiling point of the pure liquid.

The above principle of immiscible liquids is the basis of steam distillation (distillation under reduced pressure

SUB-TOPIC3 :COLLIGATIVE PROPERTIES OF SOLUTION

When a non- volatile solute is added to a solvent to form a solution, this solution will exhibit four properties namely

Vapour pressure lowering of solvent

Freezing point depression of solution

Boiling point elevation of solution

Osmosis and osmotic pressure of solution

These four properties are collectively known as the colligative properties of solution.

A colligative property is a physical property of dilute solution which depends on the number of nonvolatile solute particles dissolved in a fixed amount of solvent but is independent of their chemical nature.

The solute present should not undergo any association or dissociation

If there is association of solute particles the number of particles actually added will become small. And correspondingly the properties mentioned above will be lowered similarly if the solute particles are dissociated as in case of electrolytes the numbers of particles become larger than the original number and the value of the colligative property becomes higher.

The solutions are assumed to be very dilute and the solute should not react with the solvent.

The study of these properties has proved very helpful in the determination of molecular mass of the dissolved substances which are non-volatile.

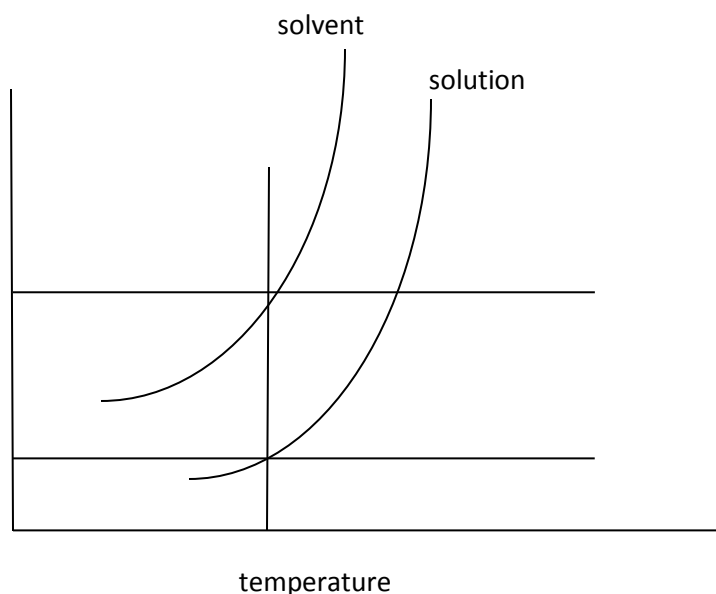
LOWERING OF VAPOUR PRESSURE

Vapour pressure of a liquid at a given temperature is the pressure exerted by the vapour when it is in equilibrium with its liquid.

Whenever some non-volatile solute is added to a liquid solvent vapour pressure of the solvent is lowered.

This because the molecules of solute on the surface of the solution tend to hinder the escape of the molecules into the vapour phase leading to a lower vapour pressure.

This can be shown by drawing a graphs of vapour pressure of solvent and solution against temperature



The vapour pressure of the solvent or solution increases with increase in temperature however the vapour pressure of pure solvent is always greater than that of solution

P° is the vapour pressure of the pure solvent

P is the vapour pressure of the solution at the same temperature.

Raoult's law of vapour pressure

It states that; the relative lowering of vapour pressure of a solvent is equal to the mole fraction of non-volatile solute dissolved in the solvent

$$\frac{P^0 - P}{P^0} = \frac{n}{n + N}$$

Where n is the number of moles of the solute

N is the number of moles of the solvent.

If the solution is very dilute n is negligibly small compared to N such that $n + N \sim N$

And the Raoult's law in approximate form is $\frac{P^0 - P}{P^0} = \frac{n}{N}$

$$\frac{P^0 - P}{P^0} = \frac{\frac{\text{mass of solute}}{\text{relative molecular mass of solute}}}{\frac{\text{mass of solvent}}{\text{relative molecular mass of solvent}}}$$

$$\frac{P^0 - P}{P^0} = \frac{\text{mass of solute} \times \text{relative molecular mass of solvent}}{\text{mass of solvent} \times \text{relative molecular mass of solute}}$$

Note the relative lowering of vapour pressure

- i) is independent of temperature
- ii) proportional to concentration of solute
- iii) Constant if the same numbers of moles of different solutes are dissolved in the same mass of the same solvent.

Worked examples

Example one

A solution of 100g of a solute in 1000g of water has a vapour pressure of $2.27 \times 10^{-3} \text{ Nm}^{-2}$ at 20°C if the saturated vapour pressure of water is $2.34 \times 10^{-3} \text{ Nm}^{-2}$ calculate the molecular mass of a solute.

.....

.....

.....

.....

.....

Example two

The vapour pressure of benzene is 9970 Nm^{-2} at 20°C calculate the vapour pressure of solution if 1.8g of naphthalene (C_{10}H_8) are dissolved in 100g of benzene (C_6H_6)

.....

.....

.....

.....

.....

.....

Example three

The vapour pressure of water at 100°C is 94200pa the vapour pressure of 1% solution of sucrose is 94150pa calculate the molecular mass of a solute.

.....

.....

.....

.....

.....

.....

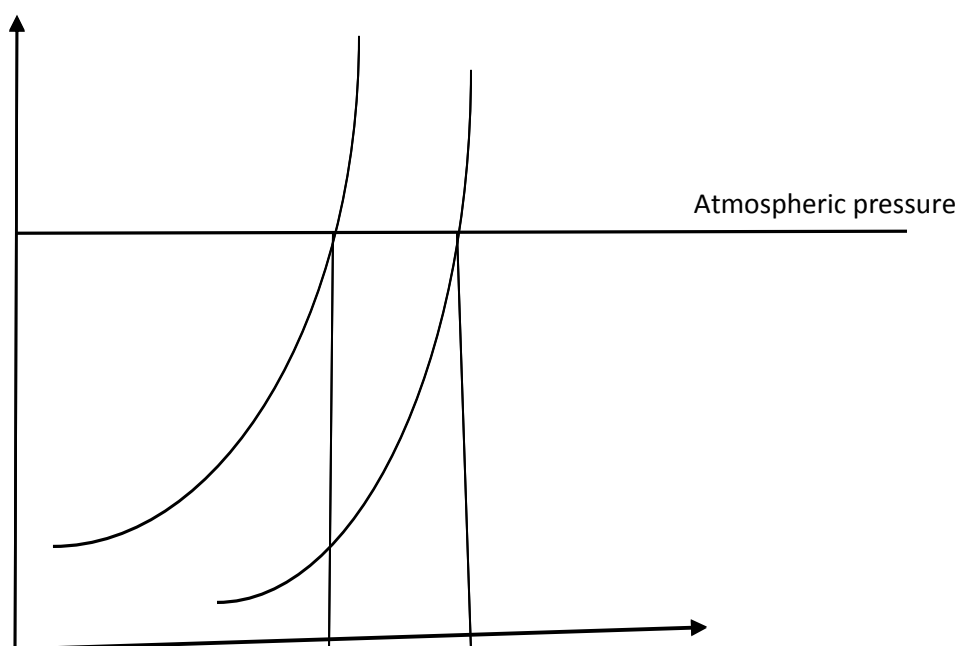
ELEVATION OF BOILING POINT

Boiling point of a liquid is the temperature at which the vapour pressure above the liquid is equal to that of external atmospheric pressure.

Dissolving a non-volatile solute in a solvent increases or elevates the boiling point of a solvent this is because:

When a non-volatile solute is added to the solvent to form a solution the solute particles introduced in the solvent tend to hinder or prevent the molecules of the solvent from escaping into the vapour phase hence there will be a few solvent molecules in the vapour exerting a low vapour pressure on the surface of the solution. Consequently, this solution, has to be heated to much higher temperature in order for the vapour pressure to be equal to atmospheric pressure for boiling to occur.

The vapour pressure curve for the solution and the solvent are shown below



The vapour pressure of solution is less than the vapour pressure of the pure solvent at all temperatures.

Where T_2 is boiling point of solution

T_1 is the boiling point of solvent

For dilute solutions, the elevation of boiling point ($T_2 - T_1$) is proportional to the lowering of vapour pressure

$$\Delta T \propto P^o - P$$

$$\Delta T = k(P^o - P) \dots\dots\dots(i)$$

From Raoult's law $\frac{P^o - P}{P^o} = \frac{n}{N}$

$$P^o - P = \frac{n P^o}{N}$$

Substituting in equation (i)

$$\Delta T = \frac{n K P^o}{N}$$

The vapour pressure of a solvent is constant at particular temperature therefore $K P^o$ is constant let it be equal to K^1

$$\Delta T = \frac{w M K^1}{m W}$$

If one mole of solute is dissolved in 1000g of solvent ie

$$\frac{w}{W} = 1 \text{ and } m = 1000\text{g}$$

$$\Delta T = \frac{M K^1}{1000} = K_b$$

$$M K^1 = 1000 K_b$$

$$\Delta T_b = \frac{K_b 1000 x w}{W X M}$$

Where w is the mass of solute

M is the mass of solvent

W is the molecular mass of the solute

K_b is the elevation in boiling point constant or ebullioscopic constant

Definition

EBULLIOSCOPIC constant is the elevation in boiling point caused when one mole of a solute is dissolved in 1000g of the pure solvent.

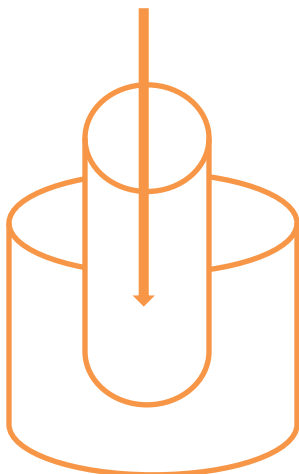
For example the K_b for water is $0.52\text{Kmol}^{-1}\text{Kg}^{-1}$ which means that when one mole of non-volatile solute is dissolved in 1000g of water the boiling point is raised by 0.52K

NOTE

The elevation in boiling point is directly proportion to the mass of solute dissolved and inversely proportional to the molecular mass of the non-volatile solute

EXPERIMENT TO DETERMINE THE RELATIVE MOLECULAR MASS OF A SOLUTE USING THE BOILING POINT ELEVATION METHOD

Using cottrells apparatus



Procedure

- A known mass of pure solvent ($a\text{g}$) is put in the tube and heated until it starts to boil.
- The temperature of boiling pure solvent (T_0) is recorded.
- A known mass of the solute ($b\text{g}$) is introduced into the solvent through the side arm
- The solution is heated until it starts to boil and the boiling point of solution T_1 is recorded when temp remains constant.

Treatment of results

Let the boiling point constant of the solvent be $K_b \text{ } ^\circ\text{C mol}^{-1} \text{ kg}^{-1}$

Elevation of boiling point be $\Delta T_b = (T_1 - T_0)^\circ\text{C}$

If (a)g of solvent is dissolves (b)g of solute

1000g of solvent will dissolve $\left(\frac{1000xb}{a}\right)$ g of a solute

ΔT_b is the elevation in b.p caused by *dissolving* $\left(\frac{1000xb}{a}\right)$ g of a solute in 1000g of solvent

K_b is the elevation in b.p caused by dissolving $\left(\frac{1000xb \times K_b}{a \times \Delta T_b}\right)$ g of a solute in 1000g of solvent

Hence the molar mass of a solute is $\frac{1000xb \times K_b}{a \times T}$

Worked examples

Example one

A solution of 5.0g of compound X in 100g of water boiled at 100.42°C calculate the relative molecular mass of X. (K_b for water is $0.520^\circ\text{C mol}^{-1} \text{ kg}^{-1}$)

.....

.....

.....

.....

.....

Example two

The boiling point of ethanol is 78°C . Calculate the boiling point of a solution containing 2.7g of ethanamide CH_3CONH_2 in 75 g of ethanol (K_b for ethanol is $1.15^\circ\text{C mol}^{-1} \text{ kg}^{-1}$)

.....

.....

.....

.....

.....

.....

.....

Example three

The addition of 2.01g of glucose $C_6H_{12}O_6$ to 25g of benzene caused the boiling point elevation of $1.204^{\circ}C$ while the boiling point elevation caused by 2.04g of X in 20g of benzene was $2.413^{\circ}C$ calculate the

- i) K_b for benzene (ii) Molecular mass of X

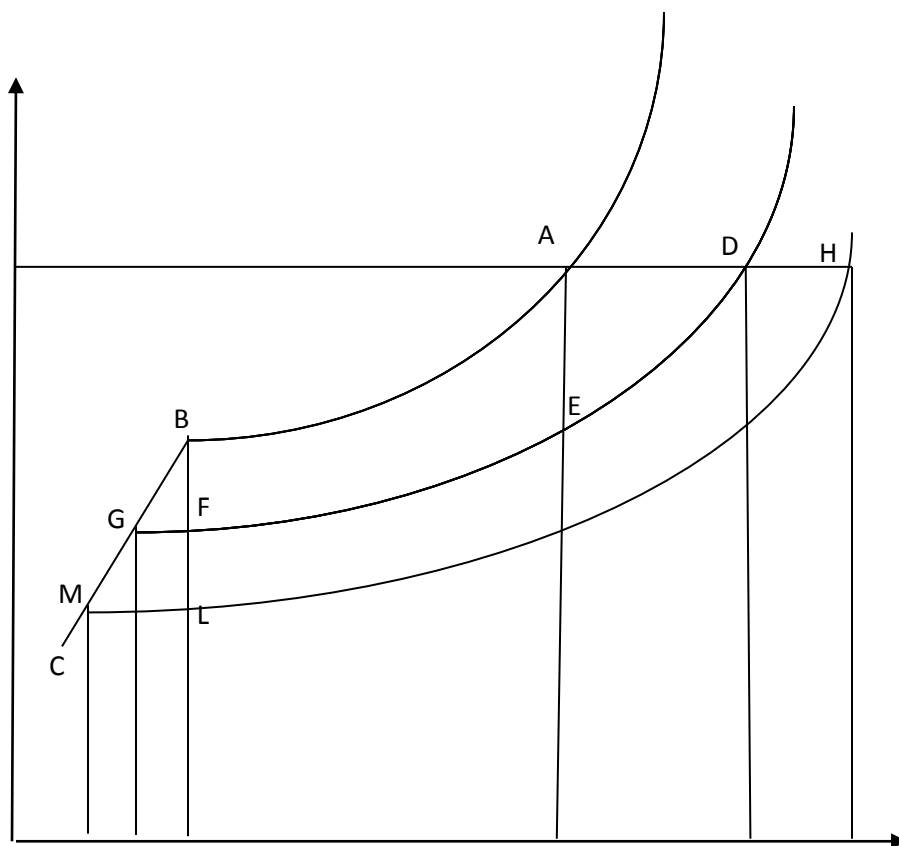
DEPRESSION IN FREEZING POINT

The freezing point of a substance is defined as constant temperature at which the solid solvent is in equilibrium with the liquid solvent at constant pressure.

Dissolving a non-volatile solute in a solvent lowers the vapour pressure of the pure solvent leading to a decrease of the freezing point of a solution. This is because

For a solvent to solidify the intermolecular forces should be strong enough to hold solvent molecules in a fixed position, a non- volatile solute added lowers the freezing point of pure solvent because the solute molecules weaken the intermolecular forces of attraction between the solvent molecules therefore much lower temperature is required for freezing to occur.

Variation of vapour pressure of a solvent or solution with temperature



CURVE BC is the sublimation curve for the solid solvent along which the solid solvent is in equilibrium with its vapour.

Curve BA is the vapour pressure curve for the liquid solvent along which the liquid solvent is in equilibrium with its vapour.

Curve GD is the vapour pressure curve of solution A ,Along which the solution is in equilibrium with its vapour

Curve MH is the vapour pressure curve of solution B, Along which the solution is in equilibrium with its vapour.

T_0 is the freezing point of the solvent because

T_1 is the freezing point of solution A

T_2 is the freezing point of solution B

Solution A more dilute than solution B

For dilute solution the depression in freezing point ($T_0 - T_1$) is proportional to the lowering of vapour pressure

$$\Delta T \propto (P^0 - P)$$

$$\Delta T = k(P^0 - P)$$

From Raoult's law $\frac{P^0 - P}{P^0} = \frac{n}{N}$

$$P^0 - P = \frac{nP^0}{N}$$

$$\Delta T = \frac{KnP^0}{N}$$

The vapour pressure of a solvent is constant at particular temperature therefore KP^0 is constant let equal to K^1

$$\Delta T = \frac{wMk^1}{mW}$$

If one mole of solute is dissolved in 1000g of solvent i.e.

$$\frac{w}{W} = 1 \text{ and } m = 1000\text{g}$$

$$\Delta T = \frac{Mk^1}{1000} = K_f$$

$$MK^1 = 1000K_f$$

$$\Delta T_f = \frac{K_f 1000xw}{Wxm}$$

Where w is the mass of solute

M is the mass of solvent

W is the molecular mass of the solute

K_f is the depression in freezing point constant or cryoscopic constant

Definition

CRYOSCOPIC constant is the depression in freezing point caused when one mole of a solute is dissolved in 1000g of the pure solvent.

For example the K_f for water is $1.86\text{Kmol}^{-1}\text{Kg}^{-1}$ which means that when one mole of non-volatile solute is dissolved in 1000g of water the freezing point is lowered by 1.86K

NOTE

The depression in freezing point is directly proportion to the mass of solute dissolved and inversely proportional to the molecular mass of the non-volatile solute.

One advantage of freezing point depression over boiling point elevation is that it is not affected much by pressure changes unlike boiling point elevation method which depends on atmospheric pressure.

Its unsuitability is due to the polymers having very large relative molecular masses. In dilute solutions there are fewer particles of the polymer and causes very small depression of freezing point which are difficult to measure

EXPERIMENT TO DETERMINE THE RELATIVE MOLECULAR MASS OF A SOLUTE BY DEPRESSION IN FREEZING POINT METHOD.

Apparatus set up

- a) Using Beckmann's method

Procedure

- A known mass of a pure solvent is put in the freezing tube fitted with a stirrer and Beckmann's thermometer.
- The freezing tube is then put in the air jacket to prevent rapid cooling of the content below its freezing point and to ensure uniform cooling.
- The whole assembly is placed in a larger outer vessel which contains the freezing mixture.
- The solvent is stirred until when freezing just starts and the freezing temperature of the pure solvent is recorded at a steady state.
- The freezing tube is then removed and warmed on the Bunsen burner to melt the crystals.
- Its then re inserted in the air jacket and freezing mixture
- A known mass of the solute under investigation is then introduced through the side arm stirred completely to form a uniform solution.
- The temperature of solution is noted until when freezing just starts and the freezing point of solution is recorded at steady state.

Treatment of results

Let the mass of solvent be	a g
Mass of solute be	b g
Freezing Temperature of solvent be	$T_1^{\circ}\text{C}$
Freezing temperature of solution be	$T_2^{\circ}\text{C}$
Freezing depression	$(T_1 - T_2)^{\circ}\text{C}$
Cryoscopic constant of solvent be	$K_f^{\circ}\text{Cmol}^{-1}\text{Kg}^{-1}$

a g solvent dissolves b g of solute

1000 g of solvent will dissolve $\frac{1000xb}{a}$ g of solute

$(T_1 - T_2)^{\circ}\text{C}$ is the depression caused by $\frac{1000xb}{a}$ g of solute

$K_f^{\circ}\text{C}$ is the depression caused by $\frac{1000xbxK_f}{a(T_1 - T_2)}$ g of solute

The molecular mass of solute is $\frac{1000xbxK_f}{a(T_1 - T_2)}$ g

Alternatively

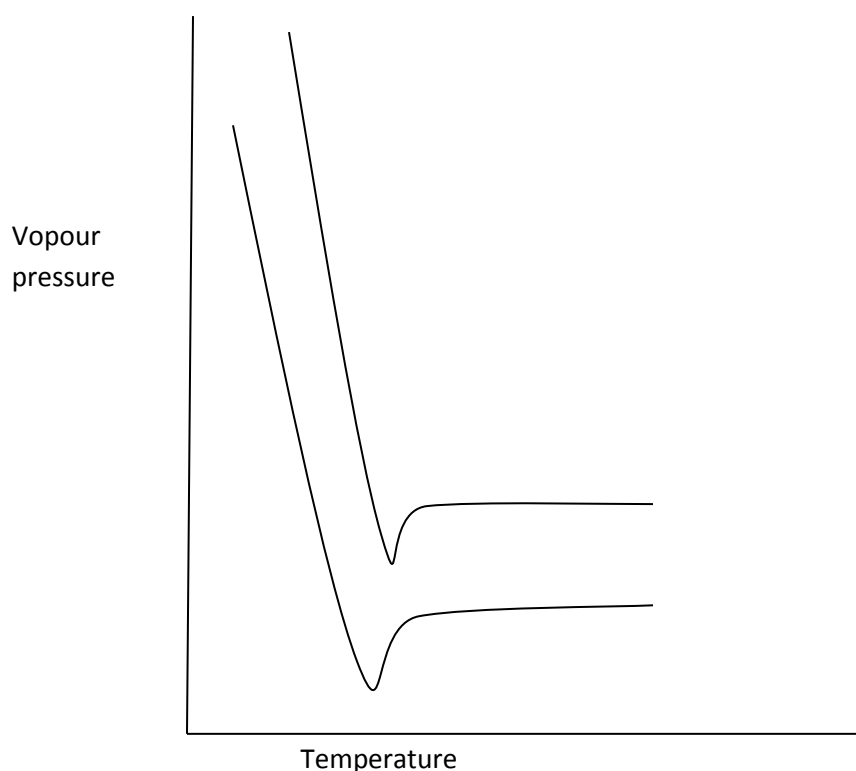
The depression in freezing point can be determined from the cooling curves of the solvent and solution.

- In this case a known mass of the solvent is placed in the tube and is then placed in the freezing mixture.
- The solvent is then stirred continuously and its temperature recorded after a known interval of time until solidification occurs

- Its then removed and melted and a known mass of the solute introduced in the solvent stirred to dissolve the placed back in the freezing mixture.
- The temperature of solution is recorded for the same interval of time as for the solvent until solidification occurs

Graphs of temperature against time are plotted

The graphs have the shapes below



b)by Rasts method

this method is based on the use of melted camphor as the solvent

Experiment to determine the molecular mass of naphthalene using camphor as the solvent

Procedure

- A known mass of pure camphor is put in a boiling tube and a thermometer inserted.
- The boiling tube and its contents are transferred into a beaker containing water and the water heated on the burner.
- Camphor is continuously stirred as boiling occurs until when all the crystals have melted.
- The flame is removed and camphor is allowed to cool in the water bath.
- The freezing temperature of pure camphor is noted when crystals begin to form.

- The flame is put back to melt the crystals and a known mass of naphthalene is introduced into the boiling tube and stirred to form a solution, the heating is continued until the whole mixture is a solution.
- The flame is removed and the solution is allowed to cool in a water bath the temperature at which the crystals begin to form is noted.

Treatment of results

Let the mass of camphor be a g
 Mass of naphthalene be b g
 Freezing Temperature of camphor be T_1 °C
 Freezing temperature of solution be T_2 °C
 Freezing depression $(T_1 - T_2)$ °C
 Cryoscopic constant of solvent be K_f °C mol⁻¹ Kg⁻¹
 a g camphor dissolves b g of naphthalene

1000 g of camphor will dissolve $\frac{1000xb}{a}$ g of naphthalene

$(T_1 - T_2)$ °C is the depression caused by $\frac{1000xb}{a}$ g of naphthalene

K_f °C is the depression caused by $\frac{1000xbxK_f}{a(T_1 - T_2)}$ g of naphthalene

The molecular mass of is naphthalene $\frac{1000xbxK_f}{a(T_1 - T_2)}$ g

Worked examples

Example one

0.55g of nitro benzene in 22 g of ethanoic acid depressed the freezing point of ethanoic acid by 0.78°C. Calculate the relative formula mass of nitrobenzene

(K_f of ethanoic acid is 3.9Kmol⁻¹ Kg⁻¹)

.....

.....

.....

.....

Example two

Calculate the freezing point of a solution of 28 g of ethanamide(CH_3CONH_2) in 500 g of water given that the cryoscopic constant of 100 g of water is 1.86°C

.....

.....

.....

.....

Example three

1.5 g of compound Q of molecular mass 90 g on dissolving in 30 g of water produced a freezing point of -1.04 calculate the freezing point constant of water

.....

.....

.....

.....

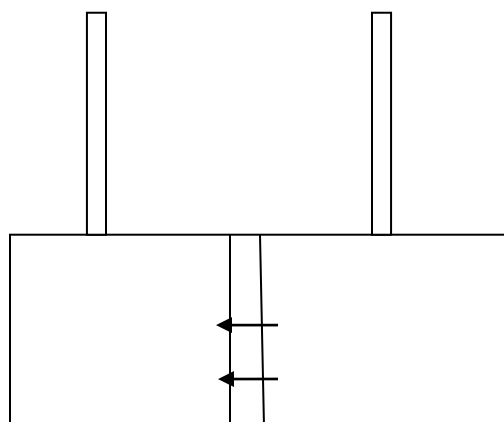
OSMOSIS AND OSMOTIC PRESSURE

OSMOSIS is the movement of solvent molecules move from a region where they are highly concentrated to region where their concentration is low across a semi-permeable membrane.

OSMOTIC PRESSURE of solution is the pressure that must be applied to the solution side to balance the tendency of the solvent molecules to flow from the solvent side to the solution side across a semi-permeable membrane.

Note the **semi-permeable membrane** allows only solvent molecules and not the solute molecules to pass through it freely. This membrane can be obtained from pig's bladder, cellulose membrane or a film of cupric ferrocyanide.

EXPERIMENT TO DEMONSTRATE OSMOTIC PRESSURE



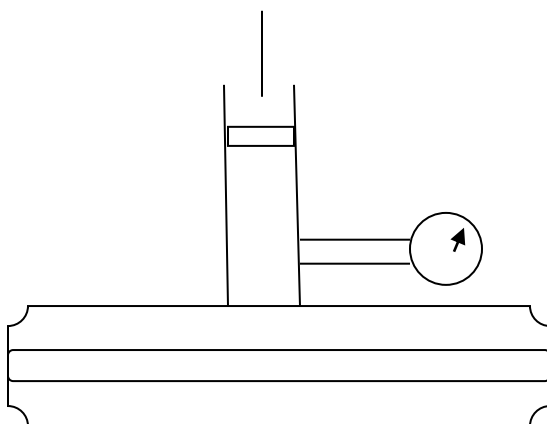
If a cell is set up so that the liquid level is initially the same in both compartment you will soon notice that the liquid rises in the left compartment and falls in the right side

Indicating that solvent molecules from the right compartment are migrating through the Semi-permeable membrane into the left compartment. This migration of solvent molecules is known as osmosis

When the level in the tube no longer rises, the pressure of this column of solution is equal to the osmotic pressure.

EXPERIMENT TO MEASURE OSMOTIC PRESSURE

(Berkeley and Hartley method)



Procedure

A known mass of solute is dissolved in a known volume of a solvent and the solution formed is placed in the outer tube connected to the pressure gauge.

A pure solvent is placed in the inner tube containing a porous pot to act as a semi-permeable membrane.

Osmosis is allowed to take place at a given temperature $T^{\circ}\text{C}$ and the level of the solvent in the capillary tube is seen to drop below mark **x**

Pressure is applied on the solution to force back the solvent molecules to the solvent side.

The pressure is adjusted until the liquid level in the capillary tube is maintained at point **x**

This is the osmotic pressure of the solution at $T^{\circ}\text{C}$ which can be registered by the pressure gauge.

FACTORS THAT AFFECTS OSMOTIC PRESSURE

1. Concentration

Osmotic pressure increases with concentration this is because more solvent molecules will move into the solution to reduce on the concentration gradient a higher osmotic pressure is required to force back the many solvent molecules.

2 temperatures

Osmotic pressure increase with increase in temperature this because more solvent molecules will gain more kinetic energy and move faster and can easily diffuse through the semi-permeable

LAWS OF OSMOTIC PRESSURE

These two laws apply to un ionized solutes only

First law

It states that at a given temperature, the osmotic pressure π of a dilute solution is directly proportional to concentration C .

$$\pi \propto C$$
$$\frac{\pi}{C} = \text{Constant}$$

Since concentration is inversely proportional to the volume of the solution, this law can also be written as

$$\pi V = \text{constant} \dots\dots\dots(i)$$

This is analogous to Boyle's law for gases, expressed in the form $PV = \text{constant}$

Second law

It states that at a given concentration, the osmotic pressure π of a dilute solution, is directly proportional to its absolute temperature

$$\pi \propto T$$

$$\frac{\pi}{T} = (\text{Constant}) \dots\dots\dots(ii)$$

This is analogous to Charles law for gases $\frac{P}{T} = K$ (if V is constant)

OSMOTIC PRESSURE AND THE IDEAL GAS EQUATION

Combining law 1 and law 2

$$\pi \propto CT$$

$$\frac{\pi}{CT} = \text{constant}(K) \quad \text{or} \quad \frac{\pi V}{T} = \text{constant}(K)$$

For n moles of the solute $\pi V = nKT$

Vant Hoff said that if the pressure is in standard units, solutions are dilute, temperature is absolute and volume is in dm^3 the value of K is universal for all solutions and is approximately equal to the ideal gas constant R

Therefore the expression $\pi V = nKT$ can be written as $\pi V = nRT$

This expression $\pi V = nRT$ is similar to the expression $PV = nRT$ for ideal gases

Vant Hoff came up with a gaseous theory which states that the pressure a dilute solution exerts is the same pressure it would have exerted if it were a gas under identical conditions of temperature and pressure.

For $\pi V = nRT$

$$n = \frac{\text{mass of solute } (m)}{\text{molar mass of solute } (M)}$$

$$\pi V = \frac{mRT}{M}$$

$$\pi = \frac{mRT}{VM}$$

$$\pi = C \frac{RT}{M} \quad \text{Where } C \text{ is concentration in g per dm}^3$$

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ or $0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ is gas constant

$$M = \frac{mRT}{\pi V}$$

LIMITATION OF OSMOTIC PRESSURE LAWS

- i) The solution must be very dilute
- ii) The solute particles must not react with solvent molecules
- iii) The solute particles must not dissociate or associate in solvent
- iv) The solute must be non-volatile

SIGNIFICANCE OF OSMOSIS

- 1 it is used in determining of relative molecular mass of polymers
2. it is used in process of excretion e.g filtration in kidney gaseous exchange in lungs
3. up take of water by plants through the roots

WORKED EXAMPLES

Example one

20g of cane sugar in 2 dm^3 of solution at 283K produced an osmotic pressure of 0.68 atmospheres. Calculate the relative molecular mass of cane sugar

Using $\frac{\pi_1}{C_1 T_1} = \frac{\pi_2}{C_2 T_2}$

$$\frac{0.68}{\frac{20}{2} \times 283} = \frac{1}{\frac{M}{22.4} \times 273} \quad M = 341$$

OR 2 dm^3 of solution contains 20 g of a solute

22.4 dm^3 of solution will contain $\frac{20}{2} \times 22.4 \text{ g}$ of a solute

At 283K the osmotic pressure of solution was 0.68 atm

At 273K the osmotic pressure of solution will be $\frac{0.68 \times 273}{283} \text{ atm}$

$$\frac{0.68 \times 273}{283} \text{ atm is caused by } \frac{20 \times 22.4}{2} \text{ g of cane sugar}$$

$$1 \text{ atm is caused by } \frac{20 \times 22.4 \times 283}{2 \times 0.68 \times 273} \text{ g of cane sugar} = 341 \text{ g}$$

OR

Direct application of the gas equation (SI units must be used in this case)

$$\text{The volume of solution containing 1 mole is given by } V = \frac{RT}{\pi} = \frac{8.31 \times 283}{0.68 \times 101325} = 3.414 \times 10^{-2} \text{ m}^3$$

$2 \times 10^{-3} \text{ m}^3$ Contains 20 g of cane sugar

$$3.414 \times 10^{-2} \text{ m}^3 \text{ will contain } \frac{20 \times 3.414 \times 10^{-2}}{2 \times 10^{-3}} = 341 \text{ g}$$

EXAMPLE TWO

The osmotic pressure of solution containing 1.24% of a polymer is 3.1×10^{-3} atmosphere, at 25°C . Determine the relative molecular mass of the polymer. ($R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$)

.....

.....

.....

.....

.....

.....

.....

note

Advantage of osmotic pressure over the elevation in boiling point and depression in freezing point method is that it can be used to determine molecular mass of polymers

Since molecular mass of polymers are very high they produce very small depression in freezing point or elevation in boiling point which cannot be read on the thermometer.

Exercises

TOPIC6: CHEMICAL EQUILIBRIUM:

CHEMICAL EQUILIBRIUM:

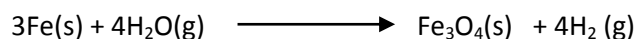
Deals with the study of reversible reactions

Reversible reactions

A reversible reaction is one in which the reaction can go either forwards or backwards depending on the conditions of the reaction.

Reversible reactions make products which themselves react to give back the products. These reactions never stop because once some products is made it can regenerate the reactants from which it came. In equation the symbol \rightleftharpoons (double headed arrow) is used to show that the reaction is reversible.

For example; When steam is passed over heated iron, hydrogen and tri- iron tetra oxide are produced

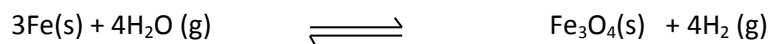


During this reaction, the concentration of reactants decrease and this is the forward reaction.

Also when dry hydrogen gas is passed over heated tri- iron tetra oxide, the reverse reaction takes place and tri- iron tetra oxide is reduced to iron



If the four chemicals are sealed in the container, the iron would react with steam to form hydrogen and tri- iron tetra oxide, but at the same time hydrogen would be reacting with tri- iron tetra oxide to produce iron and steam. The forward and reverse reaction together form a reversible reaction



Both forward and reverse reaction proceeds indefinitely in a reversible reaction up to the point when there is no further observable change. At this point the rate of the forward reaction equals the rate of the backward reaction and thus a reaction never goes to completion, and the reaction is said to have reached a chemical equilibrium a state at which the concentration of reactants and products get fixed and the reaction appears to come to standstill thus chemical equilibrium is dynamic in nature.

A dynamic equilibrium occurs when

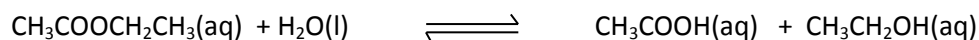
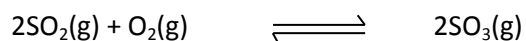
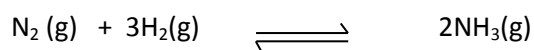
- You have a reversible reaction in a closed system (A **closed system** is one in which no substances are either added to the system or lost from it)
- The concentration of all reactants and products remain constant although the reaction is still continuing.
- The rate of the forward reaction is equal to the rate of the back ward reaction

In chemical reaction ,Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time.

Equilibria are of two types:

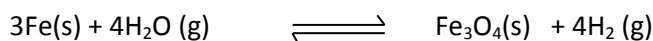
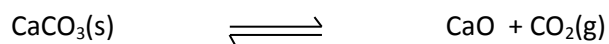
Homogeneous equilibria

Is a type of equilibrium in which all the products and reactants are in the same physical state e.g



Heterogeneous equilibria

Is the type of equilibrium in which all the products and reactants have different physical states e.g



The equilibrium law

Equilibrium law states that; for any system at equilibrium, there is a numerical relationship between the concentration of products, raised to the power of their stoichiometric numbers and the concentration of the reactants raised to the powers of their stoichiometric numbers. The numerical relationship is called the equilibrium constant.

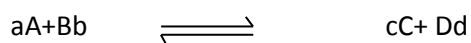
The equilibrium constant

This is the ratio of the product of the concentration of products to the product of the concentration of reactants when each is raised to an appropriate power according to the balanced chemical equation at a given temperature. The equilibrium constant is normally expressed as K_c or K_p

The equilibrium constant K_c for homogeneous systems

Homogeneous system is a type of equilibrium in which all the products and reactants are in the same physical state. Here K_c is the equilibrium constant when concentration is measured in mol dm^{-3}

Consider a homogeneous equation below



$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

i) K_c is only equal to $\frac{[C]^c [D]^d}{[A]^a [B]^b}$ when the system is at equilibrium

ii) the square brackets [] means concentration in mol dm^{-3} of whatever is inside them.

iii) it's the product of products raised to their Stoichiometric numbers divided by products of reactants raised to their Stoichiometric number

The table below contains the expressions for K_c for some common equilibrium reactions

reactions	Equilibrium constant K_c	units
$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$	Mol dm^{-3}
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$	No units
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	$\frac{[\text{SO}_3]^2}{[2\text{SO}_2]^2 [\text{O}_2]}$	Mol dm^{-3}
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$	$\text{Mol}^{-2} \text{dm}^6$
$\text{CH}_3\text{CH}_2\text{OH}(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$\frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]}$	No units
$\text{Cu}^{2+}(\text{aq}) + 4\text{Cl}^{-}(\text{aq}) \rightleftharpoons \text{CuCl}_4^{2-}(\text{aq})$	$\frac{[\text{CuCl}_4^{2-}]}{[\text{Cu}^{2+}][\text{Cl}^{-}]^4}$	$\text{Mol}^{-3} \text{dm}^9$

The equilibrium constant K_c for heterogeneous systems

Many systems contain more than one phase and so are heterogeneous. If one of the phases is pure solid or liquid, then although the amount of the solid or liquid may change, its concentration will not. In these cases it is usual to write an equilibrium law expression that does not contain the pure solid or liquid phase's concentration (which is actually included in the modified equilibrium constant).

reactions	Equilibrium constant K_c	units
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	$K_c = [\text{CO}_2]$	Mol dm^{-3}
$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightleftharpoons 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$	$K_c = \frac{[\text{CO}_2]^3}{[\text{CO}]^3}$	No units

Equilibrium constant K_p for gaseous systems

K_p is the equilibrium constant when concentration is expressed in terms of partial pressure and this applies only in gaseous systems. For gases it is usually more convenient to measure the pressure of the gas than its concentration.

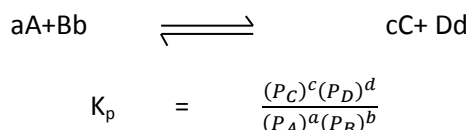
The partial pressure of a gas A, P_A in a mixture is the pressure that a gas would exert if it alone filled the container.

It is calculated from the expression partial pressure = mole fraction x total pressure

Where mole fraction = $\frac{\text{number of moles of that gas}}{\text{total number of moles of gases in the container}}$

Total pressure P is equal to the sum of the partial pressure of each gas in the mixture.

Consider a homogeneous gaseous equation below



Where P_A is the partial pressure of gas A

Where P_B is the partial pressure of gas B

Where P_C is the partial pressure of gas C

Where P_D is the partial pressure of gas D

The table below contains expression for K_p for some common equilibrium reactions

Reactions	Expression of equilibrium constant K_p	units
$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$	$\frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})}$	
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	$\frac{(P_{\text{HI}})^2}{(P_{\text{I}_2})^1 (P_{\text{H}_2})}$	
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$	$\frac{(P_{\text{SO}_3})^2}{(P_{\text{H}_2})^2 (P_{\text{O}_2})}$	
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	$\frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3 (P_{\text{N}_2})}$	
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(P_{CO_2})	
$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$	$\frac{P_{\text{CO}} P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$	

$3\text{Fe(s)} + 4\text{H}_2\text{O (g)} \rightleftharpoons \text{Fe}_3\text{O}_4\text{(s)} + 4\text{H}_2\text{(g)}$	$\frac{(\text{H}_2)^4}{(\text{H}_2\text{O})^4}$	
--	---	--

Experimental determination of equilibrium constant K_c

a) experiment to determine the equilibrium constant K_c for the reaction between ethanol and ethanoic acid to form ethylethanoate

Procedure

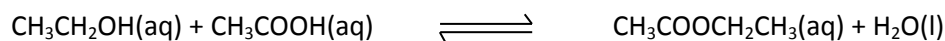
- A known amount of ethanoic acid, a moles is mixed with a known amount of ethanol, b moles
- The mixture is heated under reflux in a thermostatically controlled bath at say 60°C for several hours in order to achieve equilibrium.
- The mixture is rapidly cooled by placing it in large bath of cold water containing ice.
- The amount of ethanoic acid remaining can then be determined by titrating with standard solution of sodium hydroxide using phenolphthalein indicator.
- The concentration of other substances in the equilibrium mixture need not be experimentally determined since they can be deduced from the stoichiometry of the reaction.

Treatment of results

Let the x be the moles of ethanoic acid remaining at equilibrium

$V\text{dm}^3$ be the Volume of the container

	$\text{CH}_3\text{CH}_2\text{OH(aq)}$	$\text{CH}_3\text{COOH(aq)}$	$\text{CH}_3\text{COOCH}_2\text{CH}_3\text{(aq)}$	H_2O
Moles at start	b	a	0	0
change	$-(a-x)$	$-(a-x)$	$+(a-x)$	$+(a-x)$
Moles at equilibrium	$b-(a-x)=(b-a+x)$	$a-(a-x)=x$	$(a-x)$	$(a-x)$
Concentration at equilibrium (mol dm^{-3})	$\frac{b-a-x}{V}$	$\frac{x}{V}$	$\frac{a-x}{V}$	$\frac{a-x}{V}$



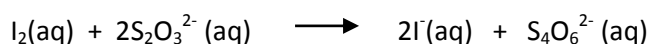
From the equation

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]} = \frac{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}{\left(\frac{b-a+x}{V}\right)\left(\frac{x}{V}\right)} = \frac{(a-x)^2}{x(b-a+x)}$$

b) Experiment to Determine the equilibrium constant K_c for the reaction between iodine and hydrogen to form hydrogen iodide.

Procedure

- A known amount of hydrogen, a mole is mixed with a known amount of iodine b moles in a bulb of known volume $V \text{ dm}^3$.
- The mixture is heated under reflux in a thermostatically controlled bath at say 450°C for several hours in order to achieve equilibrium.
- The bulb is rapidly cooled to room temperature and broken under potassium iodide solution to dissolve the iodine.
- The aqueous potassium iodide solution containing the dissolved iodine is titrated against standard sodium thiosulphate solution using starch indicator
- The concentration of iodine can be calculated from the equation



Treatment of results:

Moles of iodine at equilibrium = x

Moles of iodine at equilibrium = b-x

	$\text{H}_2(\text{g})$	$\text{I}_2(\text{g})$	$2\text{HI}(\text{g})$
Moles at start	a	b	0
change	-(b-x)	-(b-x)	+2(b-x)
Moles at equilibrium	$a-(b-x)=(a-b+x)$	$b-(b-x)=x$	$2(b-x)$
Equilibrium concentration in mol dm^{-3}	$\frac{a-b+x}{V}$	$\frac{x}{V}$	$\frac{2(b-x)}{V}$

From the equation $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2(b-x)}{V}\right)^2}{\left(\frac{a-b+x}{V}\right)\left(\frac{x}{V}\right)} = \frac{(2(b-x))^2}{(a-b+x)(b-x)}$$

Calculations involving equilibrium constant

Example one

A mixture containing 0.25 moles of nitrogen and 0.40 moles of hydrogen was allowed to reach equilibrium at a temperature $T^{\circ}\text{C}$ in a vessel of volume 0.5dm^3 . At equilibrium; it was found that 0.075 moles of ammonia had been produced. Calculate the value of the equilibrium constant K_c

Equation of reaction

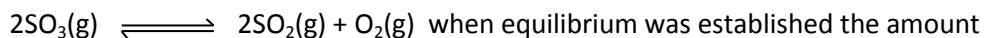


	$\text{N}_2(\text{g})$	$3\text{H}_2(\text{g})$	$2\text{NH}_3(\text{g})$
Moles at start	0.25	0.400	0.0
change	$\frac{1 \times 0.075}{2} = -0.0375$	$\frac{3}{2} \times 0.075 = -0.1125$	+0.075
Moles at equilibrium	$0.25 - 0.0375 = 0.2125$	$0.400 - 0.1125 = 0.2875$	0.075
Concentration in mol dm^{-3}	$\frac{0.2125}{0.5} = 0.425$	$\frac{0.2875}{0.5} = 0.575$	$\frac{0.075}{0.5} = 0.1500$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{0.15^2}{(0.425)(0.575)^3} = 0.278 \text{ mol}^{-2} \text{ dm}^6$$

Example two

3.4 moles of sulphur trioxide were decomposed at 60°C in 5.0dm^3 container in the reaction



Of sulphur dioxide formed was 0.060 moles. calculate the equilibrium constant at 60°C .

	$2\text{SO}_3(\text{g})$	$2\text{SO}_2(\text{g})$	$\text{O}_2(\text{g})$
Moles at start	3.4	0	0
change	-0.06	+0.06	$+\frac{1}{2} \times 0.06 = +0.03$
Moles at equilibrium	$3.4 - 0.06 = 3.34$	0.06	0.03
Concentration in mol dm^{-3}	$\frac{3.34}{5} = 0.668$	$\frac{0.06}{5} = 0.012$	$\frac{0.03}{5} = 0.006$

$$K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{(0.012)^2(0.006)}{(0.668)^2} = 1.936 \times 10^{-6} \text{ mol dm}^{-3}$$

Example three

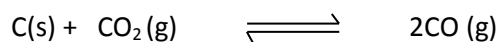
In an experiment 10g of methane CH_4 and 54g of water H_2O were heated in a container of volume 4.0dm^3 . at equilibrium 2.0moles of hydrogen, H_2 had formed. Calculate the value of K_c from the equation of reaction. $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g})$

	$\text{CH}_4(\text{g})$	$2\text{H}_2\text{O}(\text{g})$	$\text{CO}_2(\text{g})$	$4\text{H}_2(\text{g})$
Moles at start	$\frac{10}{16}=0.625$	$\frac{54}{18}=3.0$	0	0
change	$-\frac{1}{4}\times 2.00 = -0.50$	$-\frac{1}{2}\times 2.00 = -1.00$	$+\frac{1}{4}\times 2.00 = +0.5$	+2.00
Moles at equilibrium	$0.625-0.50=0.125$	$3.0-1.00= 2.00$	0.5	2.00
Concentration in mol dm^3	$\frac{0.125}{4}=0.03125$	$\frac{2.0}{4}=0.5$	$\frac{0.5}{4}=0.125$	$\frac{2.0}{4.0}=0.5$

$$K_c = \frac{[\text{H}_2]^4[\text{CO}_2]}{[\text{CH}_4][\text{H}_2\text{O}]^2} = \frac{(0.5)^4(0.125)}{(0.5)^2(0.03125)} = 1.0 \text{ mol}^2\text{dm}^{-6}$$

Example four

When 1.0moles of carbon dioxide was heated with excess carbon to a temperature of 70°C in a vessel of volume 20dm^3 , 95% of carbon dioxide reacted to form carbon monoxide. Calculate K_c for the reaction



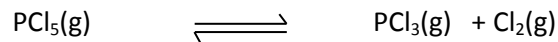
	$\text{CO}_2(\text{g})$	$2\text{CO}(\text{g})$
Initial moles	1.0	0
change	-0.95	+0.95x2 = 1.9
Moles at equilibrium	$1.0-0.95=0.05$	1.9
Concentration at equilibrium in mol dm^3	$\frac{0.05}{20}=0.0025$	$\frac{1.9}{20}=0.095$

$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.095)^2}{(0.0025)} = 3.6 \text{ mol dm}^{-3}$$

Note $\text{C}(\text{s})$ does not appear in the K_c expression because it is a solid.

Example five

0.080 moles PCl_5 was placed in a vessel and heated to 175°C when equilibrium had been reached. It was found that the total pressure was 2.0 atmospheres and that 40% of PCl_5 had dissociated. Calculate K_p for the reaction.

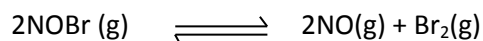


	$\text{PCl}_5(\text{g})$	$\text{PCl}_3(\text{g})$	$\text{Cl}_2(\text{g})$	total
Initial moles	0.080	0	0	
change	$-\frac{40}{100} \times 0.08 = -0.032$	+0.032	+0.032	
Moles at equilibrium	$0.08 - 0.032 = 0.048$	0.032	0.032	0.112
Mole fraction	$\frac{0.048}{0.112} = 0.429$	$\frac{0.032}{0.112} = 0.286$	$\frac{0.032}{0.112} = 0.286$	
Partial pressure in atmospheres	$0.429 \times 2 = 0.857$	$0.286 \times 2 = 0.571$	$0.286 \times 2 = 0.571$	

$$K_p = \frac{(P_{\text{PCl}_3})(P_{\text{Cl}_2})}{(P_{\text{PCl}_5})} = \frac{0.571 \times 0.571}{0.857} = 0.38 \text{ atm}$$

Example six

Nitrosylbromide decomposes according to the following equation.



In closed vessel at 25°C , it is 24% dissociated resulting in a total pressure of 4.0 atm calculate the value of K_p

(Assume that there was 1.0 moles of Nitrosylbromide.)

	$2\text{NOBr}(\text{g})$	$2\text{NO}(\text{g})$	$\text{Br}_2(\text{g})$	total
Initial moles	1.0	0	0	
change	$-\frac{24}{100} \times 1.0 = -0.24$	+0.24	$+\frac{1}{2} \times 0.24 = 0.12$	
Moles at equilibrium	$1.0 - 0.24 = 0.76$	0.24	0.12	1.12
Mole fraction	$\frac{0.76}{1.12} = 0.679$	$\frac{0.24}{1.12} = 0.214$	$\frac{0.12}{1.12} = 0.107$	
Partial pressure	$0.679 \times 4 = 2.72$	$0.214 \times 4 = 0.856$	$0.107 \times 4 = 0.428$	

$$K_p = \frac{(P_{\text{NO}})^2 (P_{\text{Br}_2})}{(P_{\text{NOBr}})^2} = \frac{(0.856)^2 (0.428)}{2.72^2} = 0.0424 \text{ atm}$$

Example seven

Thionyl chloride decomposes according to the equation $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

At a pressure of 1.0atm and temperature of 100°C a sample of SO_2Cl_2 in the gas phase was found to contain 34% of chlorine calculate the value of K_p

Let a be the moles of chlorine at equilibrium

	$\text{SO}_2\text{Cl}_2(\text{g})$	$\text{SO}_2(\text{g})$	$\text{Cl}_2(\text{g})$	total
Moles at start	1.00	0	0	
change	-a	+a	+a	
Moles at equilibrium	1-a	a	a	1+a
Mole fraction	$\frac{1-a}{1+a}=0.32$	$\frac{a}{1+a}=0.34$	$\frac{a}{1+a}=0.34$	
Partial pressure	$0.32 \times 1 = 0.32$	$0.34 \times 1 = 0.34$	$0.34 \times 1 = 0.34$	

34% of chlorine means $\frac{a}{1+a} = \frac{34}{100}$, $a=0.515$

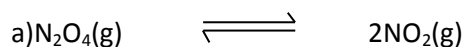
$$K_p = \frac{(P_{\text{Cl}_2})(P_{\text{SO}_2})}{(P_{\text{SO}_2\text{Cl}_2})} = \frac{0.34 \times 0.34}{0.32} = 0.36 \text{ atm}$$

Exercises

RELATIONSHIP BETWEEN K_p AND K_c

K_p and K_c for a given reaction are not same numerically. It is possible to obtain a relationship between these two constants at any temperature provided the gases in the reaction obey the ideal gas laws

Consider the reactions



$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})}$$

But $PV=nRT$ where V is the volume occupied by n moles of a gas at temperature T

$P = \frac{n}{V}RT$ but $\frac{n}{V}$ is equal to the molar concentration C therefore $P = CRT$, substituting this value of P

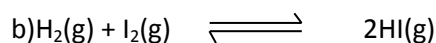
$$P_{\text{NO}_2} = [\text{NO}_2]RT$$

$$P_{\text{N}_2\text{O}_4} = [\text{N}_2\text{O}_4]RT$$

$$K_p = \frac{[\text{NO}_2]^2(RT)^2}{[\text{N}_2\text{O}_4]RT}$$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$K_p = K_c RT \quad \text{This implies that } K_p > K_c$$



$$P_{\text{HI}} = [\text{HI}]RT$$

$$P_{\text{H}_2} = [\text{H}_2]RT$$

$$P_{\text{I}_2} = [\text{I}_2]RT$$

$$K_p = \frac{[\text{HI}]^2 (RT)^2}{[\text{I}_2]RT[\text{H}_2]RT} = \frac{[\text{HI}]^2}{[\text{I}_2][\text{H}_2]} = K_c$$

$$K_p = K_c$$



$$P_{\text{NH}_3} = [\text{NH}_3]RT$$

$$P_{\text{H}_2} = [\text{H}_2]RT$$

$$P_{\text{N}_2} = [\text{N}_2]RT$$

$$K_p = \frac{[\text{NH}_3]^2 (RT)^2}{[\text{N}_2]RT[\text{H}_2]^3 (RT)^3} = \frac{[\text{NH}_3]^2 (RT)^{-2}}{[\text{N}_2][\text{H}_2]^3}$$

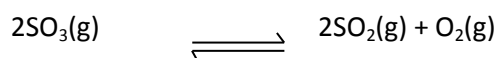
$$K_p = K_c (RT)^{-2}$$

$$\text{Generally for any reaction } K_p = K_c (RT)^{\Delta n}$$

Where Δn = total number of moles of product – total number of moles of reactant

Example

Calculate the value of equilibrium constant K_p for the reaction



Given that K_c at 60°C is $1.936 \times 10^{-6} \text{ mol dm}^{-3}$

Factors affecting equilibrium reactions include;

i) concentration

ii) Temperature

iii) Pressure of gaseous equilibrium

iv) Catalyst

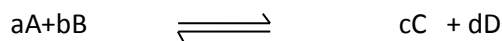
v) Presence of an inert gas (argon or helium)

A change in the conditions of the above factors may affect the following

a) Position of equilibrium

Position of equilibrium: this refers to proportion of products to reactants at equilibrium.

Consider a general equation



If the conversion of A and B into C and D is small or slow then the equilibrium position is said to shift from right to left and if the conversion of A and B is large or fast the equilibrium position is said to shift from left and right.

The equilibrium position of the system may be altered by the following changes

i) Changing Concentration of products and reactants.

ii) Changing the equilibrium Temperature

iii) Changing Pressure of gaseous equilibrium

iv) Adding an inert gas.

The likely effect on the position of equilibrium can be predicted by le'chatelier's principle;

The principle states that: When a system is in equilibrium and one of the factors holding the system in equilibrium is altered, the system will adjust itself in order to nullify the effect of change.

b) Rate of attainment of equilibrium

This refers to how fast equilibrium concentrations are attained

the rate of attainment of equilibrium may be altered by

i) Changing Concentration of products and reactants.

ii) Changing the equilibrium Temperature

iii) Changing Pressure of gaseous equilibrium

c) The equilibrium constant

This refers to the ratio of concentration of products raised to appropriate powers to products of concentration of reactants raised to appropriate powers

This is affected by changes in temperature only

1)Effect of concentration on

a) the position of equilibrium

For a system at equilibrium, when the concentration of the reactants is increased, the reaction will proceed in the direction that will reduce the concentration of the reactants.

Consider the equation $aA + bB \rightleftharpoons cC + dD$

When the concentration of A is increased the equilibrium position shifts to the right more A or B react to produce C and D similarly when the concentration of C or D is increased the equilibrium position shifts from left to right ie more C or D react to produce A and B.

b)on the rate of attainment of equilibrium

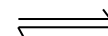
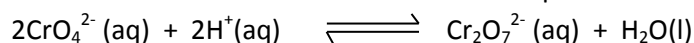
increase in concentration increases the number of particles and hence the number of collision which increases the rate of reaction.

c) on the equilibrium constant (K_c or K_p)

A change in the concentration of one of the substance in the equilibrium mixture will not alter the value of equilibrium constant, but it will alter the value of the quotient. Therefore the reaction will no longer be at equilibrium. It will react until the value of the quotient once again equals K_c or K_p

For example

Sodium chromate reacts with dilute acids to produce sodium dichromate according to the equation.



State what is observed and explain your observation when

i) dilute sulphuric acid is added to the equilibrium mixture

ii) dilute is added to the equilibrium mixture

iii) water is added to the equilibrium mixture

2)effect of temperature on

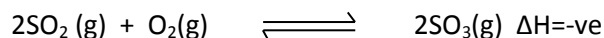
a) the position of equilibrium

The effect of temperature on the equilibrium position depends on whether the forward reaction is exothermic or endothermic.

For exothermic reactions increase in temperature favours the backward reaction ie the position of equilibrium shifts in the direction which absorbs heat from right to left



For endothermic reactions increase in temperature favours the forward reaction ie the position of equilibrium shifts in the direction which absorbs heat from left to right



b) on the rate of attainment of equilibrium

Increase in temperature leads to an increase in the rate of attainment of equilibrium because of the increase in the frequency of collision of the reacting particles. However, a decrease in temperature lowers the rate of attainment of equilibrium.

c) On the equilibrium constant

This is the only factor that alters the value of equilibrium constant

If a reaction is exothermic left to right, an increase in temperature will lower the value of equilibrium constant. This means that the position of equilibrium will shift to the left (the endothermic direction).

If a reaction is endothermic left to right, an increase in temperature will increase the value of equilibrium constant. This means that the position of equilibrium will shift to the right (the exothermic direction).

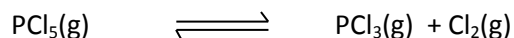
3) Effect of pressure on reactions

Pressure has generally little or no effect on equilibrium reactions involving solids and liquids.

a) on the position of equilibrium

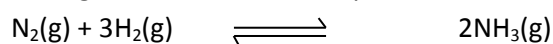
The effect of pressure on a reversible reaction depends on whether a reaction occurs with volume change (change in number of molecules)

for a gaseous reaction that proceeded with an increase in volume or number of molecules such as



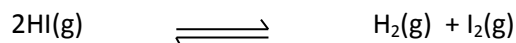
Increase in pressure favours the backward reaction ie when pressure increases the equilibrium position shifts to the left.

For a gaseous reactions that proceeds with a decrease in volume or number of molecules such as



Increase in pressure shifts the equilibrium position to the right ie as pressure increases nitrogen and hydrogen molecules collide more often to produce more ammonia.

For a gaseous reactions that proceeds with no change in volume or number of molecules such as



Change in pressure does not affect the equilibrium position.

b) On the rate of attainment of equilibrium. if there is more gas molecules on one side than the other, the value of the quotient will be altered by a change

Increase in pressure increases the rate of attainment of equilibrium because of decrease in volume the particle will be closer and collide more often.

c) On the equilibrium constant.

A change in pressure does not change equilibrium constant

4)Effect of a catalyst on reactions

a)On the rate of attainment of equilibrium

This neither alters the value of K nor the position of equilibrium. It speeds up the forward and reverse reactions equally by providing a new route for the reaction, of lower activation energy.

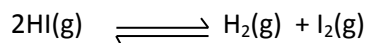
Thus it causes equilibrium to be reached more quickly.

5)Effect of adding an inert gas or noble gas on

a) the position of equilibrium

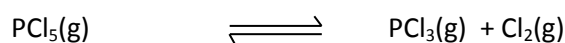
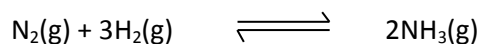
the effect adding an inert gas to a system in equilibrium depends on the type of reaction.

i)for reaction which proceed with no change in volume for example



Addition of inert gas will simply increase the total pressure of the system without changing the partial pressure of reactants and products, hence no effect on the position of equilibrium since they are not affected by pressure changes.

ii)For reactions which proceed with change in volume for example



addition of an inert gas is at constant volume,

The various equilibrium concentration terms involved are not changed. Since the concentration of an inert gas is not involved in the equilibrium expressions. Therefore the equilibrium remains un- changed.

Addition of inert gas is at constant pressure,

Introduction of an inert gas causes an increase in volume leading to a dilution or reduction in the partial pressure of the system therefore the system will adjust itself to the direction that leads to the increase in the number of molecules in order to maintain the partial pressure constant

APPLICATION OF LE CHATELIERS PRINCIPLE

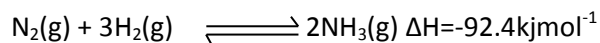
This principle is widely applied in the manufacturing industry to choose conditions necessary to give a high yield of a given product at a reasonable rate

The principle is used in;

- a) Manufacture of ammonia by Haber process
- b) Manufacture of sulphuric acid by contact process.

Manufacture of ammonia (Haber process)

Ammonia is synthesized from nitrogen obtained from the atmosphere by fractional distillation of liquid air and hydrogen obtained from natural gas according to the equation



Because this reaction, left to right is exothermic and the number of gas molecules decrease the yield and kinetic are affected. The following conditions are found to be the most economical for the high yield of ammonia

- Low temperature of about 400°C since the forward reaction is exothermic, high temperature reduces the yield of ammonia
- High pressure of about 200 atmospheres because the reaction proceeds with a decrease in volume
- iron catalyst to speed up the rate of attainment of equilibrium. Because at low temperature the reaction rate would be very slow and hence the reaction would take long to attain equilibrium and the process become economically unviable,
- Constantly removing ammonia as soon as it had been produced
- Increasing the concentration of either hydrogen or nitrogen but excess nitrogen is preferred since its cheaply obtained from atmosphere

Uses of ammonia

- Manufacture of fertilizers eg ammonium sulphate
- Manufacture of explosives
- Manufacture of nitric acid ammonia solution is used in laundry
- Liquid ammonia is used in refrigeration

Manufacture of nitric acid

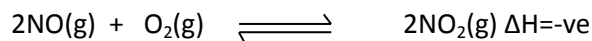
The process involves the following stages

- i) catalytic oxidation of ammonia to nitrogen monoxide.

The catalyst used is platinum at about 700°C and a pressure of 9 atmospheres



ii) oxidation of nitrogen monoxide to nitrogen dioxide.



iii) nitrogen dioxide obtained is reacted with water to form nitric acid.



In presence of oxygen the nitrous acid formed is oxidised to nitric acid



Uses of nitric acid

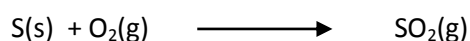
- Manufacture of fertilizers especially ammonium nitrate
- Manufacture of explosives eg trinitrotoluene (TNT)
- Manufacture of dyes

Manufacture of sulphuric acid (contact process)

Three stages are involved

i) Formation of sulphur dioxide

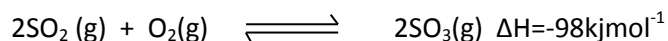
Sulphur dioxide can be obtained by burning sulphur in air or roasting metallic sulphides in air



The sulphur dioxide formed is purified and dried to remove any impurities like arsenic (iii) oxide that would otherwise poison the catalyst as sulphur dioxide reacts in air to form sulphur trioxide

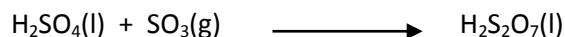
ii) Conversion of sulphur dioxide to sulphur trioxide.

Sulphur dioxide and excess oxygen are passed over finely divided vanadium (v) oxide at a temperature of 400-500°C and a pressure of less than 10 atmospheres.

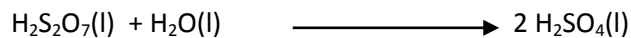


iii) Conversion of sulphur trioxide to sulphuric acid

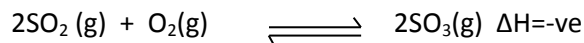
Concentrated sulphuric acid is fast used to absorb sulphur trioxide to form oleum



Oleum is then converted into ordinary sulphuric acid by adding a calculated amount of water.



The amount of sulphuric acid produced depends on the amount of sulphur trioxide formed from the reaction.



A high yield of sulphur trioxide is favored by

- Use of low temperature since the forward reaction is exothermic
- Use of high pressure of about 150-250 atmospheres since the forward reaction occurs with a decrease in volume.
- Vanadium (v) oxide catalyst to speed up the rate of attainment of equilibrium. Because at low temperature the reaction rate would be very slow and hence the reaction would take long to attain equilibrium and the process become economically unviable,
- Constantly removing sulphur trioxide as soon as it had been produced
- Use of excess oxygen since it is cheaply obtained from air.

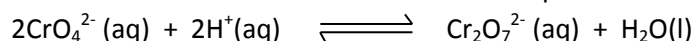
Uses of sulphuric acid

- Manufacture of fertilizers e.g calcium dihydrogen phosphate
- Manufacture of pigments, detergents, plastics fibres, dyes etc

worked examples

example one

Sodium chromate reacts with dilute acids to produce sodium dichromate according to the equation.



State what is observed and explain your observation when

- dilute sulphuric acid is added to the equilibrium mixture
- dilute is added to the equilibrium mixture
- water is added to the equilibrium mixture

CHAPTER SEVEN; IONIC EQUILIBRIA

OBJECTIVE; by the end of this topic, the learner should be able to describe the behavior of acids, bases and salts in aqueous solutions.

The equilibrium established between the unionized molecules of the electrolyte and the ions produced by the electrolyte in the solution is called ionic equilibrium.

Terms used in ionic equilibria

Electrolyte: is a chemical substance which can conduct electricity in aqueous state or in molten state

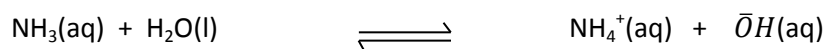
There two types of electrolytes, strong electrolyte and weak electrolyte.

Strong electrolyte: This is the electrolyte which dissociate almost completely into its constituent ions in aqueous solution.

Weak electrolyte: This is the electrolyte which dissociate to lesser extent into its constituent ions in aqueous solution.

Dissociation; is a physical process in which ions of an ionic compound are separated by dissolving the compound in water e.g $\text{NaCl(s)} + \text{aq} \longrightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Ionization is a reaction between a covalent compound and water to form ions eg



Degree of dissociation or ionization α ; It is a fraction of the total number of molecules which ionise (or dissociate) into constituent ions. Or is a fraction of each mole of an electrolyte that exist as free ions

For strong electrolytes $\alpha=1$ for weak electrolyte $\alpha<1$ values of degree of dissociation depends upon the following facts: nature of solvent, concentration and temperature.

Acid-Base theory

Acids and bases were first defined in several ways depending upon easily recognizable chemical and physical properties e.g taste, change in colour of litmus etc.

According to Arrhenius theory (1887);

An acid is defined as a substance which when dissolved in water dissociates to form hydrogen ions (H^+) or hydroxonium ions (H_3O^+).

A base is defined as a substance which when dissolved in water dissociate to form hydroxyl ions ($\bar{\text{O}}\text{H}$)

Arrhenius theory fails to explain the acidic and basic behavior in non-aqueous solution.

According to Bronsted-Lowry theory(1923)

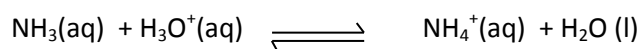
An acid is a chemical substance that can donate a proton (H^+) to some other substance.

A base is a chemical substance that can accept a proton from other substance.

Thus an acid is a proton donor where as a base is a proton acceptor

It applies to both aqueous and non-aqueous systems and bases which do not contain the hydroxyl group.

All neutralization reactions may be regarded as equilibria involving proton transfer. For example the reaction between ammonia and hydrochloric acid in aqueous solution can be described by the reaction.



In the forward reaction, the base NH_3 accepts a proton from the acid H_3O^+ . In the reverse reaction, the base H_2O accepts a proton from the acid NH_4^+ .

The acid NH_4^+ and the base NH_3 are conjugate acid-base pair because they are related by transfer of a proton. Similarly, the acid H_3O^+ and the base H_2O are conjugate acid-base pair.

The conjugate acid is the species that results when a base accepts a proton, e.g. the ammonium ion $\text{NH}_4^+(\text{aq})$ is the conjugate acid of the base ammonia $\text{NH}_3(\text{aq})$

The conjugate base is the species that results when an acid donates a proton, e.g. water $\text{H}_2\text{O}(\text{l})$ is the conjugate base of the oxonium ion H_3O^+ .

Thus the equilibrium mixture consists of two acids and two bases and this must always be the case.

Shortcomings of Bronsted definition

-For an acid to behave as a proton donor, a base must be present to accept a proton from it. This is why a solution of hydrogen chloride in water is acidic because water acts as a base to accept a proton but a solution of the same gas in benzene is not acidic because there are no molecules present that can accept a proton.

-For a base to behave as a proton acceptor, an acid must be present to donate protons to it

-Some substances, which are considered to be acidic such as SO_3 or BCl_3 are excluded due to lack of hydrogen.

According to Lewis theory

An acid is a chemical substance which can accept a lone pair of electrons from another substance

A base is a chemical substance which can donate a lone pair of electrons so as to form a covalent bond with another substance

The definition applies to aqueous, non-aqueous species and species with or without protons.

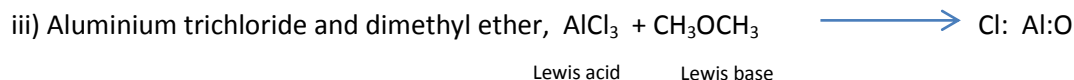
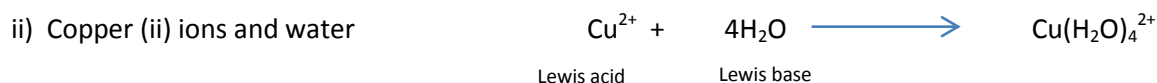
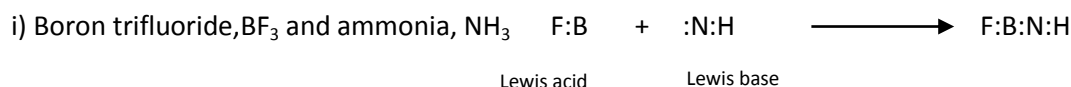
In this system, an acid does not exchange atoms with a base, but combines with it. for example consider the reaction between hydrochloric acid and sodium hydroxide:



The definition regards the acid to be the H^+ itself and the base to be OH^- ion, which has unshared electron pair. The donation of electron pair from OH^- to the H^+ ions results in formation of a covalent bond between H^+ and OH^- thus producing water molecule H_2O



- Also The reaction between



Lewis acids and bases take part in many reactions including redox reactions the formation of complex ions by transition element ions and as electrophiles and nucleophiles in organic chemistry

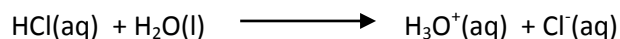
Strengths of acids and bases

Strong and weak acids

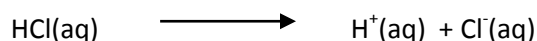
The strength of an acid is a term used to indicate the amount of ionization which occurs when the acid is dissolved in water.

A strong acid is one that fully ionises in aqueous solution producing its constituent ions.

All mineral acids are strong acids

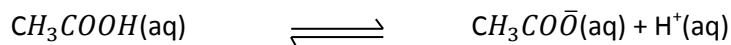
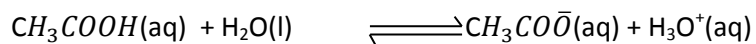


Or



A weak acid is one that partially ionises in solution producing very few of its constituent ions

eg organic acids.



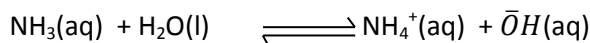
Strong and weak bases

The strength of a base is a term used to indicate the amount of ionization which occurs when the base is dissolved in water.

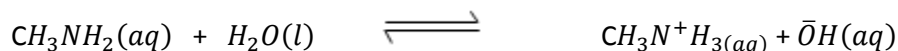
A strong base is one which is fully ionized in its aqueous solution producing hydroxyl ions as part of its constituent ions for example sodium hydroxide



A weak base is one which partially ionises in its aqueous solution producing hydroxyl ions as part of its constituent ions for example ammonia solution



Methyl amine



Comparing the strength of acids and bases under similar conditions

The strength of acids or bases can be compared by

a) Degree of ionization or dissociation α

It shows the extent to which an acid is dissociated or ionized

The higher the degree of ionization or dissociation, the more hydrogen ions concentration or hydroxyl ion concentration in solution.

The degree of dissociation α is determined by measuring the molar conductivity of solution at a given concentration (λ_c) and the molar conductivity of solution at infinity dilution (λ_∞)

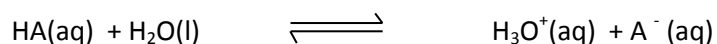
$$\alpha = \frac{\lambda_c}{\lambda_\infty}$$

b) Dissociation constant or ionization constants of acids and bases

The equilibrium law cannot be applied to the ionization of strong acids and bases in a solvent like water because they are completely ionized. But ionization equilibria of weak electrolytes can be easily studied in water as they are feebly dissociated.

i) Weak acids

the equilibrium set up when a weak monobasic acid HA dissolves in water is



Applying the equilibrium law

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

the concentration of water is essentially constant because it is so large compared to the concentration of other species present. Concentration of water can be incorporated into the value of K_c so that it becomes a new constant $K_c[\text{H}_2\text{O}]$ which is given the symbol K_a

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

K_a is the acid dissociation constant

It is temperature dependant and its value depends on the position of equilibrium

The greater the value of, K_a value, the stronger the acid HA

Thus a quantitative comparison of the strengths of acids when dissolved in water can be made.

A weak acid strength can also be measured using its $\text{p}K_a$ value

$$\text{p}K_a = -\log K_a$$

the lower the $\text{p}K_a$ value, the stronger the weak acid

some values of K_a for some common acids are given in table 7.1

Table 7.1 K_a and $\text{p}K_a$ values for some weak acids

Acid	formula	K_a	$\text{p}K_a$
Ethanoic acid	CH_3COOH	1.7×10^{-5}	4.77
Chloro ethanoic acid	ClCH_2COOH	1.38×10^{-3}	2.86
Dichloro ethanoic acid	Cl_2CHCOOH	5.13×10^{-2}	1.29
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	6.30×10^{-5}	4.20
Nitrous acid	HNO_3	5.00×10^{-4}	3.30

The acid strength is in the order $\text{C}_6\text{H}_5\text{COOH} < \text{CH}_3\text{COOH} < \text{ClCH}_2\text{COOH} < \text{Cl}_2\text{CHCOOH}$ explain

In dichloroethanoic acid, the chlorine atom is more electronegative than the carbon atom it therefore withdraws electrons from the carbon. i.e the chlorine atoms have a negative inductive effect; they therefore pull electrons towards themselves increasing the partial positive charge on the hydrogen

atom. This weakens the hydrogen-oxygen bond making the proton more easily lost. The more the chlorine atoms bonded to the carbon atom adjacent to the carbonyl carbon of the carboxylic acid the higher the negative inductive effect, so dichloroethanoic acid is stronger acid than chloro ethanoic acid.

In ethanoic acid, the methyl group which is bonded to the carbonyl group has a positive inductive effect. The methyl group therefore pushes electrons towards the oxygen-hydrogen bond which reduces the partial positive charge on the hydrogen atom. This strengthens the oxygen hydrogen bond making the proton less readily to released, so ethanoic acid is weaker acid than chloro ethanoic acid.

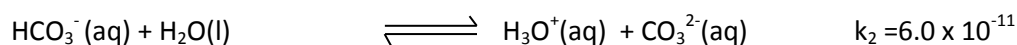
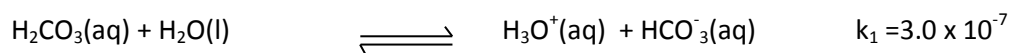
In benzoic acid

For weak polyprotic acids (these are acids which contains two or more ionizable hydrogen ions)

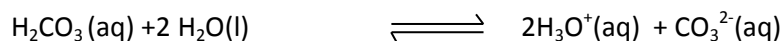
They do not ionise in a single step but in successive stages depending on the number of protons

For example

Carbonic acid which is dibasic has two dissociation constants



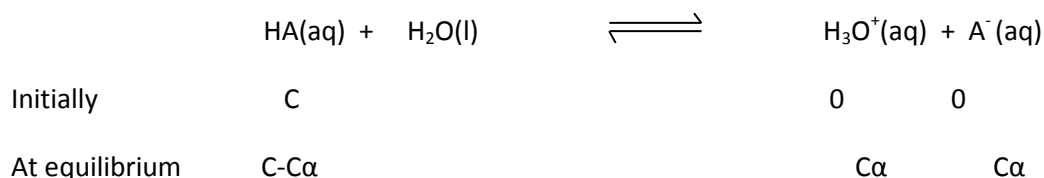
Over all equation



$$K_a = \frac{[\text{H}_3\text{O}^+]^2 [\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]} = K_1 \times K_2$$

Relationship between degree of dissociation and acid dissociation constant K_a

Consider the ionization of a weak mono basic acid HA whose original concentration is $C \text{ mol dm}^{-3}$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$= \frac{(C\alpha)(C\alpha)}{(C - C\alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

For a dilute solution of a weak acid α is much smaller than 1 such that $1 - \alpha \approx 1$ therefore $K_a = C\alpha^2$

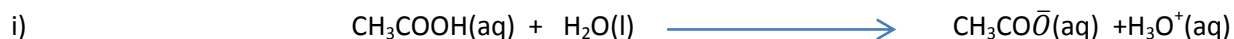
Worked example

The dissociation constant K_a of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ethanoic acid is $1.8 \times 10^{-5} \text{ mol dm}^{-3}$. find

i) the degree of dissociation

ii) the concentration of hydrogen ions and ethanoic molecules at equilibrium.

Solution



Initially c $-$ $-$

Conc at equilibrium $C - C\alpha$ $C\alpha$ $C\alpha$

$$\text{From } K_a = C\alpha^2 \quad \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{1.0 \times 10^{-4}}} = 0.42$$

$$\text{ii) } [\text{H}_3\text{O}^+] = C\alpha = 1.0 \times 10^{-4} \times 0.42 = 4.2 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COOH}] = C - C\alpha = 1.00 \times 10^{-2} (1 - 0.424) = 5.76 \times 10^{-3} \text{ mol dm}^{-3}$$

Question

A solution containing $0.001 \text{ mol dm}^{-3}$ of methanoic acid is 1% ionised calculate

i) the acid dissociation constant K_a of the acid

.....

.....

.....

.....

.....

ii) determine the hydrogen ion concentration.

.....

.....

.....

.....

.....

Factors which determines the strength of acid

Strength of the bond holding ionizable hydrogen

The acidic strength of group(vii) hydrides is shown below

Halogen acid	Bond length	Bond strength(KJmol ⁻¹)	Acid strength
H—F		562	5.62 x10 ⁻⁴
H—Cl		431	1.0 x10 ⁻⁷
H—Br		366	1.0 x10 ⁻⁹
H—I		299	1.0 x10 ⁻¹¹

Acidic strength is in the order $HI > HBr > HCl > HF$

Fluorine being the most electronegative and iodine being the least electronegative, the bond strength of the hydrides is in the order $H-F > H-Cl > H-Br > H-I$

In solution-F bond is not easily broken and hence, there will be low concentration of hydrogen ions in solution while H-I bond, being the weakest is easily broken and thus will have a very high concentration of hydrogen ions in solution. This makes HI the most acidic; hence the acidic strength of the hydrides is in the order $HI > HBr > HCl > HF$

Nature of solvents

The more basic the solvent the stronger will be the acid in the solvent e g ethanoic acid is a stronger acid in liquid ammonia than in water because ammonia is more basic than water.

Nature of the substituent group

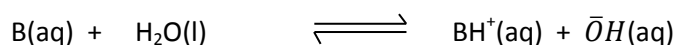
Electron withdrawing groups attached to carbon atoms increases the acidic strength and electron releasing groups' decreases acidity by inductive effect

For example chloro ethanoic acid $ClCH_2COOH$ is 80 times stronger than ethanoic acid CH_3COOH this is because the chlorine nucleus in the anion $ClCH_2CO_2^-$ attracts the electrons in the Cl-C bond, enabling the charge to be spread through the anion more than it is in $CH_3CO_2^-$

The reduction of the charge located on the oxygen atoms makes $ClCH_2CO_2^-$ a weaker proton acceptor

ii)Weak bases

the equilibrium set up when a weak base acid B dissolves in water is



Applying the equilibrium law

$$K_c = \frac{[BH^+][\bar{O}H]}{[H_2O][B]}$$

the concentration of water is essentially constant because it is so large compared to the concentration of other species present. Concentration of water can be incorporated into the value of K_c so that it becomes a new constant $K_c[H_2O]$ which is given the symbol K_b

$$K_b = \frac{[BH^+][\bar{O}H]}{[B]}$$

Where K_b is the dissociation constant

The greater the value of K_b the stronger the weak base

The strength of the weak base can also be determined using its P^{Kb} value

$$P^{Kb} = -\log K_b$$

The lower the P^{Kb} value the stronger the weak base

some values of K_b for some common bases are given in table 7.2

Table 7.2 K_b and P^{Kb} values for some weak bases

base	formula	K_a	P^{Kb}
Ammonia	NH_3	1.81×10^{-5}	
Methyl amine	CH_3NH_2	4.38×10^{-4}	
Dimethyl amine	$(CH_3)_2NH$	5.12×10^{-4}	
Trimethyl amine	$(CH_3)_3N$	5.12×10^{-5}	
Amino benzene	$C_6H_5NH_2$	3.83×10^{-10}	

The order of increasing basic strength is $C_6H_5NH_2 < (CH_3)_3N < NH_3 < CH_3NH_2 < (CH_3)_2NH$ explain

Phenyl amine is less basic compared to trimethyl amine this is because the basic strength of an amine depends on the availability of the lone pairs of electrons on the nitrogen atom.

In phenyl amine, the lone pair of electrons on the nitrogen atom interacts with the delocalized π electrons of the benzene ring. The lone pair is therefore not readily available



The hydrogen atoms bonded to nitrogen in ammonia have no effect on the availability of the lone pair of electrons on nitrogen. They have neither positive nor negative inductive effect

In methyl amine the methyl group has a positive inductive effect releasing bonding electrons to the nitrogen atom this increases the electron density on the nitrogen atom of methyl amine making the molecules more basic

Factors which determines the strength of bases

The strength of a base depends on how readily it accepts a proton and this depends on the availability of lone pairs

Relationship between degree of dissociation and base dissociation constant K_b

Consider the ionization of a weak base B whose original concentration is $C \text{ mol dm}^{-3}$

	$B(aq) + H_2O(l)$	\rightleftharpoons	$BH^+(aq) + \bar{O}H(aq)$
Initially	C		0 0
At equilibrium	$C - C\alpha$		$C\alpha$ $C\alpha$

$$K_b = \frac{[BH^+][\bar{O}H]}{[B]}$$

$$= \frac{(C\alpha)(C\alpha)}{(C - C\alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

For a dilute solution of a weak acid α is much smaller than 1 such that $1 - \alpha \approx 1$ therefore $K_b = C\alpha^2$

Question

At 25°C , 0.01 mol dm^{-3} ammonia NH_3 is 4.5% ionised

a) write the

i) equation for the ionization of ammonia

.....

ii) expression for ionization constant K_b for ammonia

.....

b) calculate the

i) ionization constant K_b for ammonia

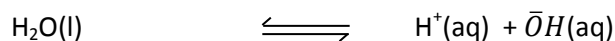
.....
.....
.....

ii) concentration of hydroxyl ions at equilibrium

.....
.....

IONIZATION OF WATER

Water, no matter how pure it is made, always ionises to a very small extent



And this is itself an acid-base equilibrium. Water produces its own conjugate acid and its own conjugate base at the same time.

Application of the equilibrium law to this leads to the following expression for the equilibrium constant K_c .

$$K_c = \frac{[\text{H}^+][\bar{\text{O}}\text{H}]}{[\text{H}_2\text{O}]}$$

However, since water is dissociated to a very small extent, its concentration in aqueous solution may be regarded as constant. Including this constant in K_c

$$K_c[\text{H}_2\text{O}] = [\text{H}^+][\bar{\text{O}}\text{H}]$$

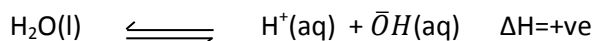
$$K_w = [\text{H}^+][\bar{\text{O}}\text{H}]$$

K_w is called the ionic product of water and has units of $\text{mol}^2\text{dm}^{-6}$

Since K_w is equilibrium constant it is temperature dependent its numerical value at 0°C is about $1 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$ at 298K its value is $1 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$

and at 100°C is about $5.4 \times 10^{-13} \text{ mol}^2\text{dm}^{-6}$

This implies that K_w increases with increase in temperature because the dissociation of water is endothermic



Increase in temperature increases the concentration of H^+ ions and $\bar{\text{O}}\text{H}$ ions and therefore K_w

In water the concentration of H^+ ions must be the same as that of $\bar{\text{O}}\text{H}$ ions thus

$$[\text{H}^+] = [\bar{\text{O}}\text{H}] = 1 \times 10^{-7} \text{ mol dm}^{-3} \text{ at } 298\text{K}$$

When acids or alkalis are dissolved in water there will be different concentration of H^+ ions and $\bar{\text{O}}\text{H}$ ions but the product of these two concentrations is always equal to the value of K_w at that temperature

If the solution has $[\text{H}^+] = [\bar{\text{O}}\text{H}]$ it is said to be neutral

THE HYDROGEN ION INDEX pH

By definition P^H is the negative logarithms to base ten of the concentration of hydrogen ions in mol dm^{-3}

i.e $P^H = -\text{Log}[H^+]$ the relationship between the quantities is shown below.

P^H	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[H^+]\text{mol dm}^{-3}$	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}

Note that P^H rises as $[H^+]$ falls

Calculating pH of water at 298k

The hydrogen ion concentration pure water, $[H^+] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ at 298k

$$\text{pH} = -\text{Log}(1 \times 10^{-7}) = 7$$

since pure water is the end product of neutralization of a strong acid and a strong base, a P^H of 7 is regarded as defining a neutral solution at 25°C . solution with a P^H of less than 7 are therefore acidic and those with a P^H greater than 7 are alkaline, but at 25°C . neutral solution in general (i.e at any temperature) are those where $[H^+] = [OH^-]$

Calculating pH of strong acids

For purpose of calculation, it is assumed that all strong acids are completely ionised hence the hydrogen ion concentration is obtained directly from the molarity of the acid.

Example 1;

Calculate the P^H of 0.1 mol dm^{-3} hydrochloric acid solution

The acid ionises completely as



$$0.1 \qquad \qquad \qquad 0.1 \qquad \qquad 0.1$$

$$[H^+] = 0.1 \text{ mol dm}^{-3}$$

$$P^H = -\text{Log}(0.1) = 1.0$$

Example 2

Calculate the of 0.01 mol dm^{-3} sulphuric acid.

Each mole of sulphuric acid produces 2 moles of hydrogen ions in solution



The concentration of the hydrogen ions is therefore twice the concentration of the acid

$$[H^+] = 2 \times 0.01 = 0.02 \text{ mol dm}^{-3}$$

$$p^H = -\log_{10}(0.02) = 1.70$$

Example 3

Calculate the concentration of sulphuric acid whose p^H is 2.5

$$[H^+] = 10^{-2.5} =$$

Concentration of the acid is half the concentration of hydrogen ions $= \frac{\quad}{2} = \dots \text{mol dm}^{-3}$

Calculating pH of strong bases

Strong bases are also assumed to be completely ionised. The hydroxide ion concentration is therefore easily obtained from the molarity of the base

Example 4

Calculate the P^H of a solution of 0.3 mol dm^{-3} sodium hydroxide.

Sodium hydroxide ionises completely as



$$0.3 \qquad \qquad \qquad 0.3 \qquad \qquad 0.3$$

$$[H^+] = \frac{K_W}{[\bar{O}H]} = \frac{1 \times 10^{-14}}{0.3} = 3.33 \times 10^{-14} \text{ mol dm}^{-3}$$

$$pH = -\log(3.33 \times 10^{-14}) = 13.50$$

$$\text{Or from } K_W = [H^+][\bar{O}H] = 1 \times 10^{-14}$$

$$-\log(K_W) = -\log([H^+][\bar{O}H])$$

$$14 = -\log[H^+] + -\log[\bar{O}H]$$

$$= p^H + p^{OH}$$

$$pH = 14 - pOH$$

$$pOH = -\log(0.3) = 0.523$$

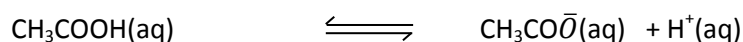
$$pH = 14 - 0.523 = 13.477$$

Calculating pH of weak acids

Weak acids are slightly ionised in aqueous solution and thus the degree of ionization and the dissociation constant must be known

Example 5

Calculate the pH of 0.1 mol dm⁻³ ethanoic acid at 298K given that its K_a value is 1.7 × 10⁻⁵ mol dm⁻³ at this temperature



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Assumption; ethanoate ions and hydrogen ions must be produced in equal concentrations such that $[\text{CH}_3\text{COO}^-] = [\text{H}^+]$

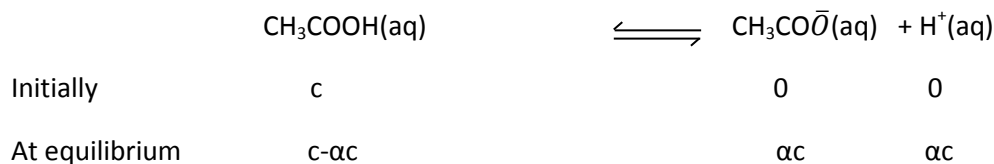
$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{0.1} = 1.7 \times 10^{-5}$$

$$[\text{H}^+] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.3 \times 10^{-3}) = 2.88$$

Example 6

Calculate the pH of 0.1 mol dm⁻³ solution of ethanoic acid for which the acid is 2.5% ionised



$$[\text{H}^+] = \alpha c = \frac{2.5}{100} \times 0.1 = 0.025 \text{ mol dm}^{-3}$$

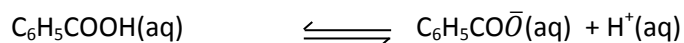
$$\text{pH} = -\log(0.025) = 2.6$$

Example 7

The pH of 0.001M solution of benzoic acid is 3.59 calculate the

- Dissociation constant of the acid
- Degree of dissociation of the acid

solution



$$\text{pH} = -\log[\text{H}^+] = 3.59$$

$$[H^+] = 10^{-3.59} = 2.57 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Assumption } [C_6H_5COO^-] = [H^+]$$

$$K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]} = \frac{(2.57 \times 10^{-4})^2}{0.001} = 6.6 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[H^+] = \alpha c = 2.57 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\alpha = \frac{2.57 \times 10^{-4}}{0.001} = 0.257$$

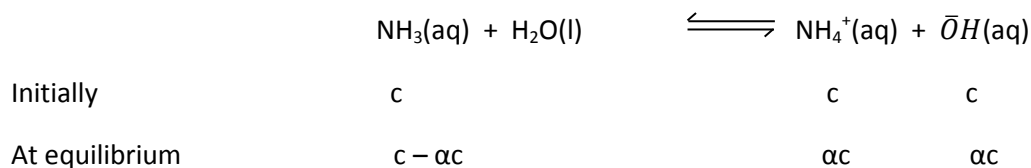
calculating the pH of weak bases

Weak bases are slightly ionised in aqueous solution and thus the degree of ionization and the dissociation constant must be known.

Example 8

Calculate the pH of 0.01 mol dm^{-3} ammonia solution in which the degree of dissociation is 0.043

Equation of reaction



$$[OH^-] = \alpha c = 0.043 \times 0.01 = 4.3 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pOH = -\log(4.3 \times 10^{-4}) = 3.37$$

$$pH = 14 - 3.37 = 10.63$$

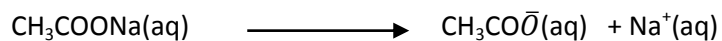
Factors which affect pH of solution

1. concentration of H^+ ions the higher the concentration of hydrogen ions the lower the p^H

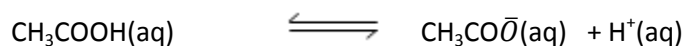
2. Addition of a common ion

Consider addition of sodium ethanoate to ethanoic acid

Sodium ethanoate is a strong electrolyte completely ionizes producing excess ethanoate ions



where as ethanoic acid is a weak electrolyte that partially ionizes



Excess ethanoate ions react with H^+ ions to form undissociated ethanoic acidic molecules reducing concentration of H^+ ions, shifting the equilibrium to the left increasing pH of solution

BUFFER SOLUTIONS

When an acid is added to a neutral solution, the pH of the solution falls, and when an alkali is added to such a solution, its pH rises.

Some solutions resist pH changes when small quantities of an acid or alkali are added to them such solutions are known as buffer solutions.

A buffer solution is a solution that resists pH changes, when a small amount of acid or alkali is added to it.

There are two types of buffer solutions

Acidic buffer (a buffer solution with pH less than seven)

This is a solution which contains a weak acid and its salt from a strong base. Eg

Ethanoic acid and sodium ethanoate

Benzoic acid and sodium benzoate

Phosphoric acid and sodium phosphate

Basic buffer (a buffer solution with pH greater than seven)

This is a solution which contains a weak base and its salt with a strong acid. eg

Ammonium hydroxide and ammonium chloride

Ammonium hydroxide and ammonium sulphate

Action of acid buffer solution

We will take ethanoic acid and sodium ethanoate as a typical example. The ethanoic acid is a weak acid, and so it partially ionizes as

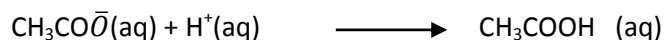


Sodium ethanoate is an ionic salt, and in solution consists of free sodium and ethanoate ions.

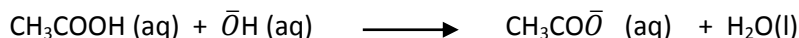


This mixture therefore contains a relatively high concentration of undissociated acid molecules, ethanoate ions and a small amount of hydrogen ions formed by the original ionization of ethanoic acid.

When a small amount of acid is added to such a solution, these will nearly all combine with the ethanoate ions to form ethanoic acid molecules and so the pH will hardly change at all.



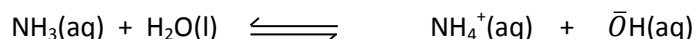
When small amount hydroxyl ions are added to this solution, almost all of these will react with the un-ionised ethanoic acid to make ethanoate ions and water. So the pH will hardly change at all.



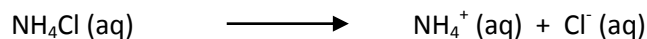
In other words, trying to alter the pH of the solution by increasing the concentration of H^+ or $\bar{\text{O}}\text{H}$ largely fails.

Action of basic buffer solution

We will take ammonia and ammonium chloride as a typical example. The ammonia is a weak base and so it partially ionises as

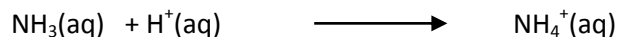


Ammonium chloride is an ionic salt, and so its solution consist of free ammonium and chloride ions:

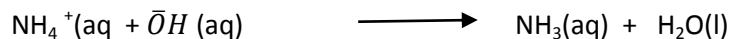


The mixture therefore contains a relatively high concentration of undissociated ammonia molecules and ammonium ions and enough hydroxyl ions to make the solution alkaline.

When a small amount of hydrogen ions are added to such a solution, these will nearly all combine with the ammonia present to make more ammonium ions, and so the pH hardly changes at all.



When a small amount of hydroxyl ions are added to such a solution, most of them react with ammonia ions to produce ammonia molecules and water.



Once again, trying to change the pH by increasing the concentration of H^+ or $\bar{\text{O}}\text{H}$ largely fails.

CALCULATING pH OF A BUFFER SOLUTION

The pH of a buffer solution can be calculated using the dissociation constant of the weak acid or base

For an acidic buffer containing ethanoic acid and its salt with a strong base, the dissociation of ethanoic acid is considered.



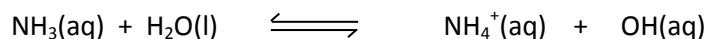
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Assumption: ethanoate ions are produced by the dissociation of the salt, sodium ethanoate. Therefore $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COONa}]$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$$

$$pH = -\log[H^+] = -\log\left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]}\right)$$

For an alkaline buffer containing ammonia and ammonium chloride, the ionization of ammonia molecules is considered.



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Assumption: ammonium ions are produced by the dissociation of the salt, ammonium chloride. Therefore $[NH_4^+] = [NH_4Cl]$

$$[OH^-] = \frac{K_b \times [NH_3]}{[NH_4Cl]}$$

$$pOH = -\log[OH^-] = -\log\left(\frac{K_b \times [NH_3]}{[NH_4Cl]}\right)$$

$$pH = 14 - pOH$$

Worked examples

Example one

A buffer solution was made by dissolving 18.5g propanoic acid, CH_3CH_2COOH , and 12.0g of sodium propanoate, CH_3CH_2COONa , in water and then making the volume up to 250cm^3 .

(pK_a for propanoic acid = 4.87, C=12, O=16, Na=23, H=1)

a) calculate the pH of a buffer solution

b) what will be the effect of adding

i) 1.00cm^3 of 10mol dm^{-3} hydrochloric acid.

ii) 1.00cm^3 of 10mol dm^{-3} sodium hydroxide solution to 1000cm^3 of the buffer solution.

Solution

Molar mass of $CH_3CH_2COOH = 12 \times 3 + 6 \times 1 + 16 \times 2 = 74\text{g}$

$$\text{Moles of } CH_3CH_2COOH \text{ in } 250\text{cm}^3 = \frac{18.5}{74}$$

$$\text{Moles of } CH_3CH_2COOH \text{ in } 1000\text{cm}^3 = \frac{18.5 \times 1000}{74 \times 250} = 1.00\text{mol dm}^{-3}$$

Molar mass of $CH_3CH_2COONa = 12 \times 3 + 5 \times 1 + 16 \times 2 + 23 \times 1 = 96\text{g}$

$$\text{Moles of CH}_3\text{CH}_2\text{COONa in 250cm}^3 = \frac{12}{96}$$

$$\text{Moles of CH}_3\text{CH}_2\text{COONa in 1000cm}^3 = \frac{12 \times 1000}{96 \times 250} = 0.50 \text{ mol dm}^{-3}$$

$$\text{pK}_a = 4.87$$

$$\text{K}_a = 1.35 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{K}_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

assumption

Because virtually all the propanoate ions $\text{CH}_3\text{CH}_2\text{COO}^-$ are coming from the sodium propanoate, and almost none from propanoic acid, the propanoate concentration is also equal to 0.50 mol dm^{-3} and that so little of propanoic acid ionizes that its equilibrium concentration is 1.00 mol dm^{-3}

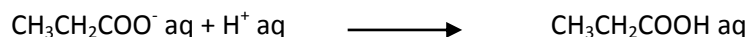
$$1.35 \times 10^{-5} = \frac{0.500x[\text{H}^+]}{1.00}$$

$$[\text{H}^+] = 2.70 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = 4.57$$

b i) the buffer solution works by combining the hydrogen ions from the added acid with propanoate ions from the sodium propanoate, turning them into propanoic acid. This means that the concentration of the propanoate ions will fall, while that of the propanoic acid will rise.

$$\text{Number of moles of H}^+ \text{ ions added} = \frac{1 \times 10}{1000} = 0.010 \text{ mol}$$



$$\text{New moles of CH}_3\text{CH}_2\text{COO}^- = 0.5 - 0.01 = 0.49$$

$$\text{New moles of CH}_3\text{CH}_2\text{COOH} = 1.00 + 0.01 = 1.01$$

$$\text{K}_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

$$1.35 \times 10^{-5} = \frac{0.49x[\text{H}^+]}{1.01}$$

$$[\text{H}^+] = 2.78 \times 10^{-5}$$

$$\text{pH} =$$

the pH falls by

ii) the buffer solution works by reacting the hydroxide ions from the sodium hydroxide with propanoic acid, producing more propanoate ions. This means that the concentration of the propanoate ions will rise, while that of the propanoic acid will fall.

$$\text{Number of moles of } ^-\text{OH ions added} = \frac{1 \times 10}{1000} = 0.010 \text{ mol}$$



$$\text{New moles of CH}_3\text{CH}_2\text{COO}^- = 0.5 + 0.01 = 0.51$$

$$\text{New moles of CH}_3\text{CH}_2\text{COOH} = 1.00 - 0.01 = 0.99$$

$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

$$1.35 \times 10^{-5} = \frac{0.51 \times [\text{H}^+]}{0.99}$$

$$[\text{H}^+] = 2.62 \times 10^{-5}$$

$$\text{pH} =$$

the pH rise by

Example two

Calculate the pH of a buffer solution made by mixing 50 cm³ of 0.300 mol dm⁻³ ethanoic acid with 100 cm³ of 0.600 mol dm⁻³ sodium ethanoate. (K_a for ethanoic acid = 1.75 × 10⁻⁵ mol dm⁻³)

$$\text{Total volume } 100 + 50 = 150 \text{ cm}^3$$

$$\text{Moles of ethanoic acid in the total volume of } 150 \text{ cm}^3 = \frac{0.300 \times 50}{1000} = 0.015$$

$$\text{Moles of ethanoic acid in } 1000 \text{ cm}^3 = \frac{0.015 \times 1000}{150} = 0.100 \text{ mol dm}^{-3}$$

$$\text{Moles of sodium ethanoate in the total volume of } 150 \text{ cm}^3 = \frac{0.600 \times 100}{1000} = 0.0600$$

$$\text{Moles of sodium ethanoate in } 1000 \text{ cm}^3 = \frac{0.0600 \times 1000}{150} = 0.400 \text{ mol dm}^{-3}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{1.75 \times 10^{-5} \times 0.100}{0.400} = 4.375 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(4.375 \times 10^{-6})$$

=

Example three

A solution was made by mixing 30cm³ of a 0.1M ethanoic acid and 20cm³ of 0.1M sodium hydroxide solution. Calculate the P^H of the resultant solution

State any assumption made. (K_a for ethanoic acid = 1.8 x 10⁻⁵ moldm⁻³)

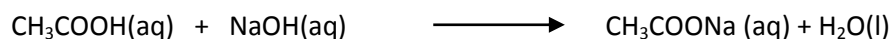
Solution

1000cm³ of ethanoic acid solution contains 0.1 moles

30cm³ of ethanoic acid solution contains $\frac{0.1 \times 30}{1000} = 3 \times 10^{-3}$ moles

1000cm³ of sodium hydroxide solution contains 0.1 moles

20cm³ of sodium hydroxide solution contains $\frac{0.1 \times 20}{1000} = 2 \times 10^{-3}$ moles



One mole of sodium hydroxide reacts with one mole of ethanoic acid

Therefore moles of ethanoic acid reacting = 2 x 10⁻³ moles

Excess moles of ethanoic acid in solution = 3 x 10⁻³ - 2 x 10⁻³ = 1 x 10⁻³ moles

The resultant solution is a buffer containing excess ethanoic acid and the salt sodium ethanoate formed

Total volume of the mixture (30+20) = 50cm³

Concentration of ethanoate ions in the mixture = $\frac{2 \times 10^{-3} \times 1000}{50} = 0.04 \text{ moldm}^{-3}$

Concentration of ethanoic acid in the mixture = $\frac{1 \times 10^{-3} \times 1000}{50} = 0.02 \text{ moldm}^{-3}$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Assumption: ethanoate ions are produced by the dissociation of the salt, sodium ethanoate. Therefore $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COONa}]$.

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{1.8 \times 10^{-5} \times 0.02}{0.04} = 9.0 \times 10^{-6} \text{ moldm}^{-3}$$

$$\text{pH} = -\text{Log}(9.0 \times 10^{-6}) = 5.0$$

Example four

Calculate the mass of sodium ethanoate that should be added to 1dm³ of 0.1 M ethanoic acid at 25⁰ C to give a solution whose pH is 5.5 State any assumption made

(K_a for ethanoic acid = 1.8 x 10⁻⁵ mol dm⁻³)

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Assumption: ethanoate ions are produced by the dissociation of the salt, sodium ethanoate. Therefore
 $[CH_3COO^-] = [CH_3COONa]$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$$

$$pH = -\log[H^+]$$

$$[H^+] = 10^{-5.5} = 3.16 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[CH_3COO^-] = \frac{K_a [CH_3COOH]}{[H^+]} = \frac{1.8 \times 10^{-5} \times 0.1}{3.16 \times 10^{-6}} = 0.5696 \text{ mol dm}^{-3}$$

Molar mass of CH₃COONa = (12x2) + (1x3) + (16x2) + (23x1) = 82

0.5696 moles of CH₃COONa weighs (0.5696 x 82) = 46.71g

Example five

A buffer solution was made by mixing 0.1 M ammonia solution and 0.025 ammonium chloride in 1.0dm³

a) Calculate the pH of this solution.

b) calculate the pH of the above solution when

i) 10cm³ of 0.1 M NaOH was added

ii) 10cm³ of 0.1M HCl was added .(K_b for ammonia = 1.8 x 10⁻⁵ mol dm⁻³)

solution

$$a) K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$[OH^-] = \frac{K_b [NH_3]}{[NH_4^+]}$$

Assumption: $[NH_4^+] = [NH_4Cl]$

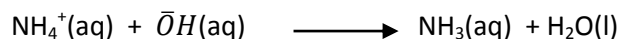
$$[\bar{O}H] = \frac{1.8 \times 10^{-5} \times 0.1}{0.025} = 7.2 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[H^+] = \frac{K_W}{[\bar{O}H]} = \frac{1 \times 10^{-14}}{7.2 \times 10^{-5}} = 1.389 \times 10^{-10}$$

$$\text{pH} = -\log(1.389 \times 10^{-10}) = 9.857$$

$$\text{b) moles of NaOH in } 10\text{cm}^3 = \frac{0.1 \times 10}{1000} = 1 \times 10^{-3}$$

after the addition of sodium hydroxide concentration of NH_3 increases by 0.001 while concentration of NH_4Cl decreases by 0.001 moles.



$$\text{New concentration of } \text{NH}_3 = 0.1 + 0.001 = 0.101 \text{ moles}$$

$$\text{New concentration of } \text{NH}_4^+ = 0.025 - 0.001 = 0.024 \text{ moles}$$

$$\text{a) } K_b = \frac{[\text{NH}_4^+][\bar{O}H]}{[\text{NH}_3]}$$

$$[\bar{O}H] = \frac{K_b[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$\text{Assumption: } [\text{NH}_4^+] = [\text{NH}_4\text{Cl}]$$

$$[\bar{O}H] = \frac{1.8 \times 10^{-5} \times 0.101}{0.024} = 7.515 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[H^+] = \frac{K_W}{[\bar{O}H]} = \frac{1 \times 10^{-14}}{7.515 \times 10^{-5}} = 1.320 \times 10^{-10}$$

$$\text{pH} = -\log(1.320 \times 10^{-10}) = 9.879$$

$$\text{ii) b) moles of HCl in } 10\text{cm}^3 = \frac{0.1 \times 10}{1000} = 1 \times 10^{-3}$$

after the addition of hydrochloric acid concentration of NH_4Cl increases by 0.001 while concentration of NH_3 decreases by 0.001 moles.



$$\text{New concentration of } \text{NH}_3 = 0.1 - 0.001 = 0.099 \text{ moles}$$

$$\text{New concentration of } \text{NH}_4^+ = 0.025 + 0.001 = 0.026 \text{ moles}$$

$$K_b = \frac{[\text{NH}_4^+][\bar{O}H]}{[\text{NH}_3]}$$

$$[\bar{O}H] = \frac{K_b[\text{NH}_3]}{[\text{NH}_4^+]}$$

Assumption: $[NH_4^+] = [NH_4Cl]$

$$[\bar{O}H] = \frac{1.8 \times 10^{-5} \times 0.099}{0.026} = 6.854 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[H^+] = \frac{K_W}{[\bar{O}H]} = \frac{1 \times 10^{-14}}{6.854 \times 10^{-5}} = 1.459 \times 10^{-10}$$

$$P^H = -\log (1.459 \times 10^{-10}) = 9.834$$

Example six

Calculate the pH of a solution obtained when 25cm³ of 0.02 M HCl are added to 25cm³ of 0.04M NH₄OH. (pK_b of ammonia is 4.76 at 25°C).

Solution

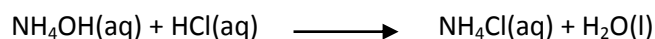
1000cm³ of hydrochloric acid contains 0.02 moles

25cm³ of hydrochloric acid contains $\frac{0.02 \times 25}{1000} = 5 \times 10^{-4}$ moles

1000cm³ of ammonia solution contains 0.04 moles

25cm³ of ammonia solution contains $\frac{0.04 \times 25}{1000} = 10 \times 10^{-4}$ moles

Equation of reaction



One mole of HCl reacts with one mole of NH₄OH

Therefore moles of ammonia reacting = 5×10^{-4}

Excess moles of ammonia = $10 \times 10^{-4} - 5 \times 10^{-4} = 5 \times 10^{-4}$

The buffer formed is composed of excess NH₄OH and the salt formed NH₄Cl

Total volume of the mixture = (25 + 25) = 50cm³

Concentration of ammonium ions in the mixture = $\frac{5 \times 10^{-4} \times 1000}{50} = 0.01 \text{ mol dm}^{-3}$

Concentration of ammonia in the mixture = $\frac{5 \times 10^{-4} \times 1000}{50} = 0.01 \text{ mol dm}^{-3}$

$$K_b = \frac{[NH_4^+][\bar{O}H]}{[NH_3]}$$

$$K_b = 10^{-4.76} = 1.738 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\bar{O}H] = \frac{K_b[NH_3]}{[NH_4^+]} = \frac{1.738 \times 10^{-5} \times 0.01}{0.01} = 1.738 \times 10^{-5} \text{ moles}$$

$$K_w = [H^+][\bar{O}H]$$

$$1 \times 10^{-14} = [H^+] \times 1.738 \times 10^{-5}$$

$$[H^+] = 5.754 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(5.754 \times 10^{-10}) = 9.24$$

Example seven

In what proportions should ammonia and ammonium chloride be mixed in solution to give a buffer solution of pH 10.0? pKa for NH_4^+ is 9.25

Solution

$$\text{pH} = 10$$

$$[H^+] = 1.00 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\text{pKa} = 9.25$$

$$K_a = 5.62 \times 10^{-10} \text{ mol dm}^{-3}$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.62 \times 10^{-10}$$

$$\frac{[NH_3]}{[NH_4^+]} = \frac{5.62 \times 10^{-10}}{1.00 \times 10^{-10}} = \frac{5.62}{1}$$

The concentration of ammonia to ammonium chloride should be 5.62 to 1.0

Application of buffer solutions

- in medicine, injections into blood stream given for medical reasons should be buffered. the pH of living cells and blood must be maintained at its value of pH 7.4 any variation of about 0.5 in this pH could prove fatal.
- In agriculture, specific plants grow in specific soil pH and therefore the pH of the soil has to be maintained. Fertilizers applied must be well buffered
- In industrial process, for example in fermentation process any change in pH would cause death of the fermentation organisms. Fermentation process must be buffered.
- In Preservation of food
- In Preparation of standard solutions of definite pH
- In electroplating processes must be buffered

SALT HYDROLYSIS

SALTS

A salt; is an ionic compound formed when the hydrogen of an acid is partially or totally replaced by a metal(or ammonium ion)

A salt is an ionic compound formed by the reaction of an acid and a base

Salts are strong electrolyte and are completely dissociated in water.

Types of salts

Normal salts; these are salts obtained by complete neutralization of an acid with a base eg NaCl and K_2SO_4 .

Acidic salts; these are salts formed by incomplete neutralization of polybasic acids eg $NaHCO_3$ and Na_2SO_4 .

Basic salts; these are salts formed by incomplete neutralizations polybasic bases e.g $Mg(OH)Cl$

Double salts; these are salts containing more than one cation or anion and are formed by the combination of two simple salts eg $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$.

Hydrolysis: is a reaction involving the breaking of a bond in a molecule using water. The reaction mainly occurs between an ion and water molecules and often changes the pH of solution.

There three types of hydrolysis; salt hydrolysis, acid hydrolysis and base hydrolysis

SALT HYDROLYSIS

When an acid reacts with a base in aqueous solution neutralization takes place.

This neutralization is complete only in case of a reaction between strong acid like hydrochloric acid and a strong base like sodium hydroxide and the final solution will be neutral ie containing equal moles of hydrogen ions and hydroxide ions.

In all other cases, the final solution will not be neutral and is either acidic or basic

The acidity or basicity of a final solution is due to the tendency of the salt formed by neutralization to react with water thereby partially reversing the process of neutralization. Therefore

Salt hydrolysis is the partial reversal of neutralization due to reaction of the salt with water to form either acidic or alkaline solution.

When the solvent is not water the phenomenon is generally referred to as solvolysis

When a salt is dissolved in water, water spontaneously ionizes into hydroxide anions and hydronium cations. The salt also dissociates into its constituent anions and cations. The cation or anion may react with water.

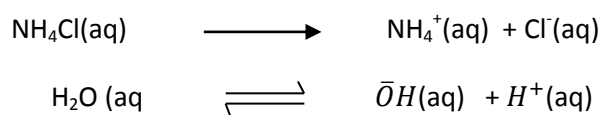
There are **four** types of salt to consider.

a) salt of strong acid and a weak base

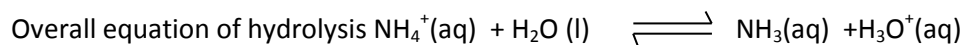
Salts of strong acids and weak bases such as NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, $\text{C}_6\text{H}_5\text{NH}_3$ undergo hydrolysis to give acidic solution.

Consider for example the hydrolysis of NH_4Cl

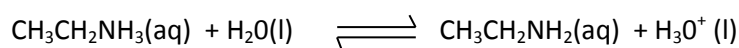
Ammonium chloride dissociates completely into ions in solution whereas water partially ionises



Chloride ions will not undergo hydrolysis because HCl is a strong acid so there is no formation of HCl molecules, however the ammonium ions react with hydroxyl ions from water to form feebly ionised NH_4OH molecules and this increases the concentration of hydrogen ions in solution. The removal of OH^- ions by ammonium ions causes water to ionise further to keep K_w constant. This leads to the accumulation of hydrogen ions in solution, the pH of solution falls below 7 and it reacts acidic.



Further examples include

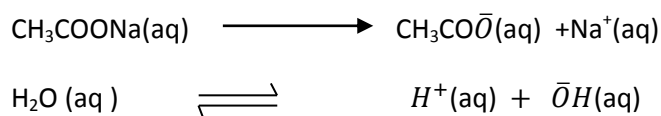


b) Salt of strong base and weak acid

Salts of weak acids and strong bases such as sodium ethanoate, sodium carbonate, sodium cyanide etc. undergo hydrolysis to give basic solutions.

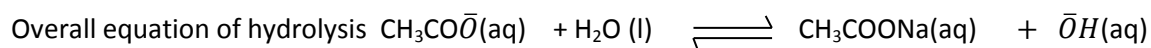
Consider for example the hydrolysis of sodium ethanoate.

Sodium ethanoate dissociates completely into ions in solution whereas water partially ionises



Sodium ions will not undergo hydrolysis because NaOH is a strong base so there is no formation of NaOH molecules, however the ethanoate ions react with hydrogen ions from water to form feebly ionised CH_3COOH molecules and this increases the concentration of hydroxyl ions in solution. The

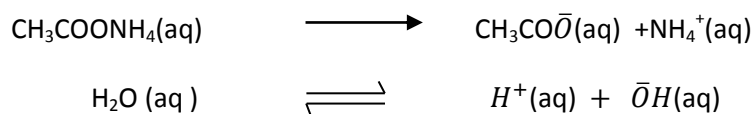
removal H^+ of ions by ethanoate ions causes water to ionise further to keep K_w constant this lead to the accumulation of hydroxyl ions in solution, the P^H of solution increases above 7 and it reacts alkaline



c)a salt of weak acid and weak base

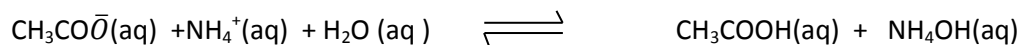
salt of weak acids and weak bases such as ammonium ethanoate undergo hydrolysis to give either acidic or alkaline or neutral solution depending on

consider for example ammonium ethanoate in aqueous solution the equilibrium



Since the acid and base are both weak unionized molecules of ethanoic acid and ammonium hydroxide are formed by utilizing the hydrogen and hydroxyl ions derived from water the removal of these ions disturbs the equilibrium of water, to restore K_w water ionises further. in this particular case the acid and base are about equally weak so that the concentration of hydrogen ions and hydroxyl ions remains about equal in solution in spite of hydrolysis ammonium ethanoate is strongly hydrolysed in solution but the solution remains almost neutral.

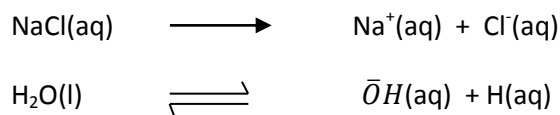
Equation of hydrolysis



In general a salt formed from a weak acid and a weak base will hydrolyse but the acidity or basicity depends on the equilibrium constants K_a and K_b if K_a value is greater than K_b value the resultant solution will be acidic or if K_a is less than K_b the resultant solution will be basic or if K_a is equal to K_b the resultant solution will be neutral.

d)a salt of a strong acid and a strong base

a typical case of this kind is sodium chloride the situation in a solution of this salt is



The acid and base are both strong so that no formation of molecules, NaOH or HCl, occurs. The ionic equilibrium of water remains undisturbed, there is no hydrolysis, and the solution remains neutral. The salt of sodium and potassium hydroxide with any of the three mineral acids show this situation.

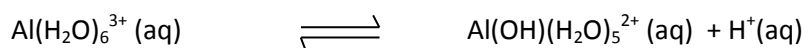
e) salts involving ions with a high charge density

Ionic compounds dissociate 100% into ions in solution. These ions become solvated by water molecules (the water molecules bond to the ions- this is one of the driving forces behind dissolution)

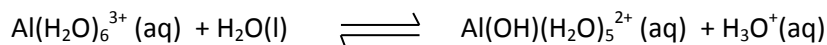
the polar water molecules use the lone pairs on the oxygen of the water to coordinate to the positive metal ion. The ions are then enclosed by a cage of water molecules usually in an octahedral

arrangement. I.e $\text{Al}(\text{H}_2\text{O})_6^{3+}$ $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ $\text{Cr}(\text{H}_2\text{O})_6^{3+}$

the high charge density of the ions polarizes the water molecules surrounding the ion in solution this results in weakening of the O-H bonds within water molecules allowing the hydrogen ions to be released into solution hence the solution is acidic.

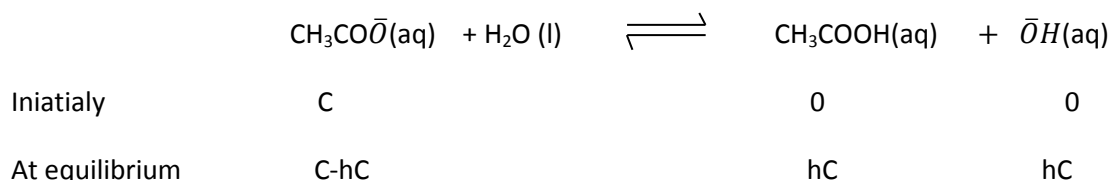


or



Quantitative treatment of hydrolysis

a) Consider hydrolysis of a salt of weak acid and a strong base e.g sodium ethanoate



Where C is the original concentration

h degree of hydrolysis (fraction of the total salt that under goes hydrolysis when equilibrium has been established)

K_h is hydrolysis constant (this gives the extent to which the salt under goes hydrolysis)

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \dots\dots\dots(1)$$

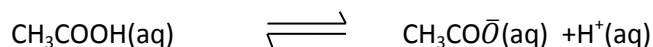
$$= \frac{hc \cdot hc}{c-hc} = \frac{h^2c}{1-h}$$

Assuming the concentration of water is virtually constant.

If h is very small compared to 1 then $K_h = h^2C$

Relationship between K_h and K_w

Consider the ionization of the conjugate acid CH_3COOH formed from hydrolysis of sodium ethanoate



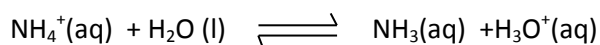
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \dots\dots\dots(2)$$

Multiplying expressions (1) and (2)

$$K_h \times K_a = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = [\text{OH}^-][\text{H}^+] = K_w$$

For a salt of a weak acid $K_h = \frac{K_w}{K_a}$

b) consider the hydrolysis of a salt of weak base and a strong acid eg ammonium chloride



Initially $\qquad\qquad\qquad \text{C} \qquad\qquad\qquad 0 \qquad\qquad\qquad 0$

At equilibrium $\qquad\qquad\qquad \text{C}-h\text{C} \qquad\qquad h\text{C} \qquad\qquad h\text{C}$

$$K_h = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \dots\dots\dots(4)$$

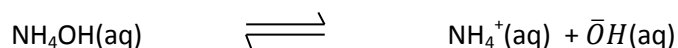
$$= \frac{hc \cdot hc}{c-hc} = \frac{h^2c}{1-h}$$

Assuming the concentration of water is virtually constant.

If h is very small compared to 1 then $K_h = h^2C$

Relationship between K_h and K_w

Consider the ionization of the conjugate base NH_4OH formed from hydrolysis of ammonium chloride



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \dots\dots\dots(4)$$

Multiplying expressions (3) and (4)

$$K_h \times K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

For a salt of a weak base and a strong acid, $K_h = \frac{K_w}{K_b}$

It can also be shown that if the salt is derived from a weak base and a weak acid its hydrolysis constant is given by $K_h = \frac{K_w}{K_a K_b}$

ACID- BASE INDICATORS

Theory of acid-base indicators

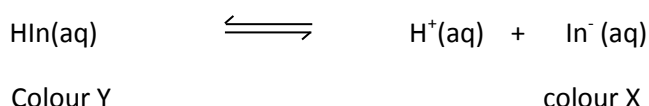
Indicators are used to detect the equivalence point or end point in titration of solutions of unknown concentration with a standard solution.

An acid -base indicator is either a weak organic acid or weak organic base which change colour according to the hydrogen ion concentration of the solution in which it is added.

It is a vital feature of an indicator that there should be a marked difference of colour between the undissociated molecule and the dissociated form of an indicator.

Consider a weak organic acid indicator represented by HIn

In a solution, the indicator partially ionizes according to the equation



The undissociated form of phenolphthalein indicator is colourless while the dissociated form is pink.

The colour change is used to indicate the end point of the titration.



The equivalence point (the point at which stoichiometrically equivalent amount of acid and base have been added together) can be determined accurately with an indicator when the end point coincides with the equivalent point. At the equivalent point of an acid base titration, the pH changes rapidly through several units of pH

HOW ACID-BASE INDICATOR WORK

i) addition of an acid(H^+)

The extra hydrogen ions of the acid will combine with the ionised species In^- to form the unionized molecule HIn. The equilibrium will shift from the right to the left reducing the amount of In^- species while increasing the amount of HIn molecules. The predominant HIn molecule will then show its colour in solution i.e. the solution becomes colourless for phenolphthalein



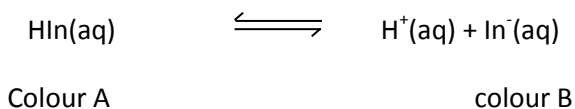
Addition of a base (OH^-)

The hydroxyl ions from the base combines with the hydrogen ions to form water molecules which reduces the amount of hydrogen ions in the equilibrium therefore more HIn molecules will ionise to produce more hydrogen ions which shifts the equilibrium from the left to right the amount of HIn molecules reduces while that of the In^- species increases consequently the predominant In^- will show its colour for the case of phenolphthalein it becomes pink.

THE INDICATOR DISSOCIATION CONSTANT; K_{in}

The strength of an indicator as an acid will depend on the K_a value for the indicator. This is called indicator dissociation constant K_{in}

For acid indicator, HIn , this partially ionizes in aqueous solution.



$$K_{in} = \frac{[H^+][In^-]}{[HIn]}$$

The indicator will show an intermediate colour when colour A and colour B are present in equal concentration ie when $[HIn]=[In^-]$

And therefore $K_{in} = [H^+]$

$$-\log K_{in} = -\log [H^+]$$

$$pK_{in} = pH$$

The indicator will show its intermediate colour at a pH value which is determined by the K_{in} value for the indicator.

Since indicators have different K_{in} values, they will change colour at different p^H value.

For phenolphthalein $K_i = 7 \times 10^{-10}$

$$[H^+] = 7 \times 10^{-10}$$

$$pH = 9.15$$

Phenolphthalein will show its intermediate colour at $pH=9.15$

The complete colour change from colour A to colour B, or vice versa requires a change of about 1.5 to 2.0 units of pH. This range is the working range of the indicator.

The working range of an indicator

is the pH range over which an indicator changes colour effectively in a solution.

The pH of the intermediate colour is at the midpoint of this range.

The following table shows the pH range and colours shown by some commonly used indicators.

indicator	pH range	$p^{K_{in}}$	Colour in	
			Acid	Alkali
Thymol blue	1.2-2.8	1.5	Red	Yellow
Methyl orange	2.9-5.0	3.7	Pink	Yellow
Congo orange	3.0-5.0		red	yellow
Methyl red	4.8-6.3	5	Pink	Yellow
Litmus	5.0-8.0	6.4	Red	Blue
Bromothymolblue	6.0-7.6		yellow	blue
Phenol red	6.8-8.4		yellow	red
Thymolblue	8.0-9.0		yellow	blue
phenolphthalein	8.3-10.0	9.15	Colourless	Pink
Alizarin yellow	10.1-13.0		yellow	orange

note

It will be seen that Thymol blue undergoes two colour change at different pH values this is true for mixed indicators.

A mixture of carefully selected indicators which gives a gradual change in colour over a wide range of pH is known as a universal indicator

Choice of indicator in titration

The indicator to be chosen for any titration should be one whose p^H at neutral point is almost the same as the p^H of the neutralized mixture at the end point i.e. the pH of the mixture at the end point must fall within the working range of the indicator to be chosen

The choice of indicators depends on the pH of the end point of the reaction and on the pH range over which the indicator changes colour.

A suitable choice of indicators for different types of acids and bases is shown in the table below.

Reactants	Suitable acid – base indicator	Reason
Strong acid Vs strong base e.g NaOH and HCl	Methyl orange Phenolphthalein litmus	When a strong acid H^+ is titrated against a strong base, the salt formed does not undergo hydrolysis the resultant solution is neutral within $pH = 7$. There is a sharp pH change from 3 – 10 when the acid is in the flask. The working range of phenolphthalein (8.2 – 10) methyl orange (3.2 – 4.4) litmus (5 – 8) are within this sharp pH change and either can therefore be used in locating the end point.
Strong acid Vs weak base e.g HCl and NH_3	Methyl orange	When a strong acid H^+ is titrated against a weak base eg NH_3 , the product cat ion NH_4^+ hydrolyses to give an acidic solution With pH less than seven $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ The is sharp a pH change from approximately 3 to 7 This is within the working range of methyl orange 3.2 – 4.6 hence methyl orange can be used to locate end point.
Weak acid Vs strong base eg CH_3COOH and NaOH	Phenolphthalein indicator	When a weak acid H^+ is titrated against a strong base eg NaOH the anion product CH_3COO^- hydrolyses to give base solution $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ the resultant solution has a pH above 7. There is remarkable pH change from approximately 7 – 10. This is within the working range of phenolphthalein (8.2 – 10) hence can be used to locate the end point.
Weak acid Vs weak base	No indicator	An acid base indicator cannot be used to locate the end point of the titration between a weak acid and a weak base because there is no sharp pH change at the end point to cause a colour change.

TITRATION CURVES

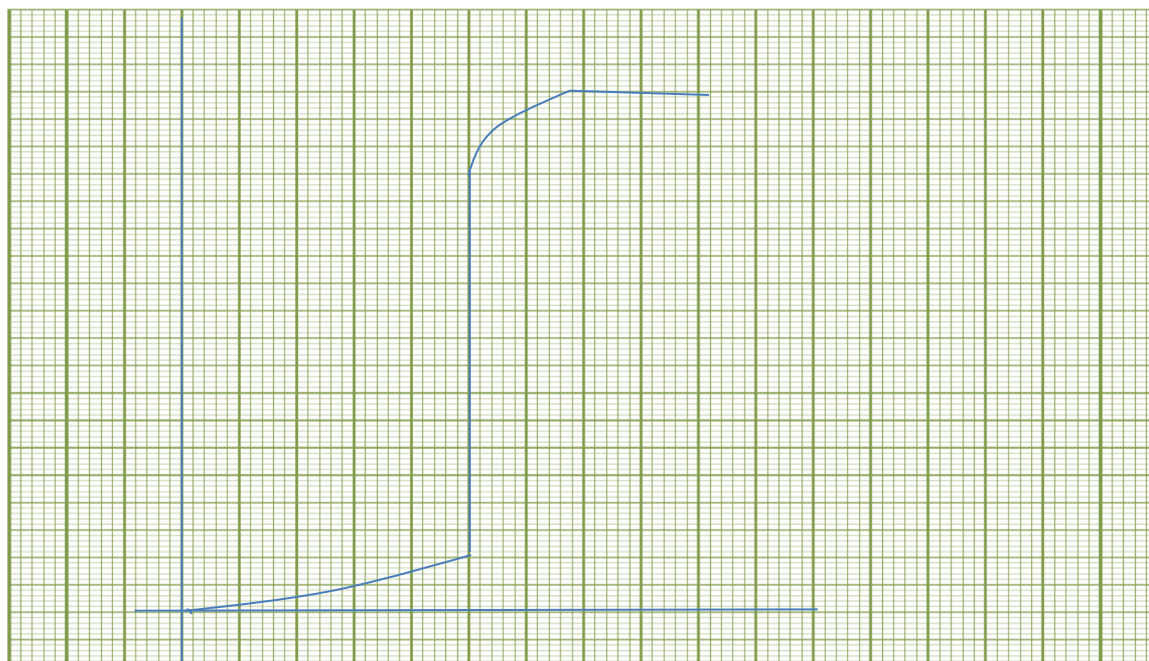
These are graphs showing how the pH of acid or base changes as it is neutralized. The curves usually obtained by placing a glass electrode into the titration flask and recording the pH as the alkali is run in.

Characteristics of titration curves

- At the end point, a small addition of the base or acid produces a sharp change in pH
 - The end point corresponds to the vertical or nearly vertical portion.
 - The pH of the mixture at the end point lies in the middle part of the vertical length of the curve.
 - The strength of acid added to the base is shown by the pH value from where the curve starts on the vertical axis
 - The strength of the base is shown by the height of the vertical part of the curve above 7
- the shape of the P^H curve depends on the strength of the acid and alkali used.

a) Titration curve for a strong base added to a strong acid

This curve shows what happens when 1.0mol dm^{-3} sodium hydroxide is added to 50cm^3 of 1.0mol dm^{-3} hydrochloric acid.



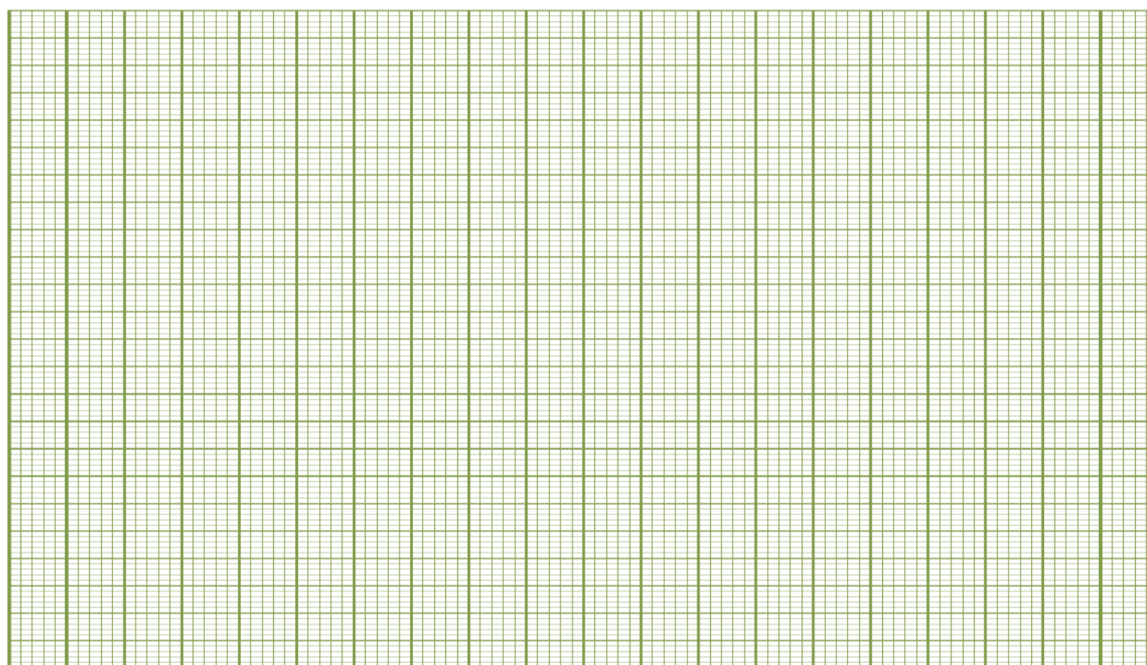
Explanation of the shape of the curve

- initially at A, before the addition of the base, pH of the acid is very low because of the high concentration of H^+ ions produced by the complete ionization of HCl which is a strong acid.
- Along AB, pH gradually rises as the base is added because the acid is still in excess and the hydrogen ions are being neutralized by the hydroxyl ions from the base.

- At B, a small amount of sodium hydroxide added gives a sharp rise in PH indicating that the end point has been reached or neutralization is complete
- pH at the endpoint is 7 because the strong salt formed can't undergo hydrolysis.
- Along CD, Beyond endpoint, the PH rises gradually due to excess sodium hydroxide adde

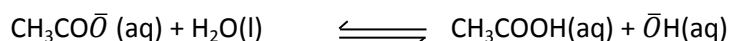
b) Titration of a strong alkali against a weak acid

This curve shows what happens when 1.0mol dm^{-3} sodium hydroxide is added to 50cm^3 of 1.0mol dm^{-3} ethanoic acid



Explanation of the shape of the curve

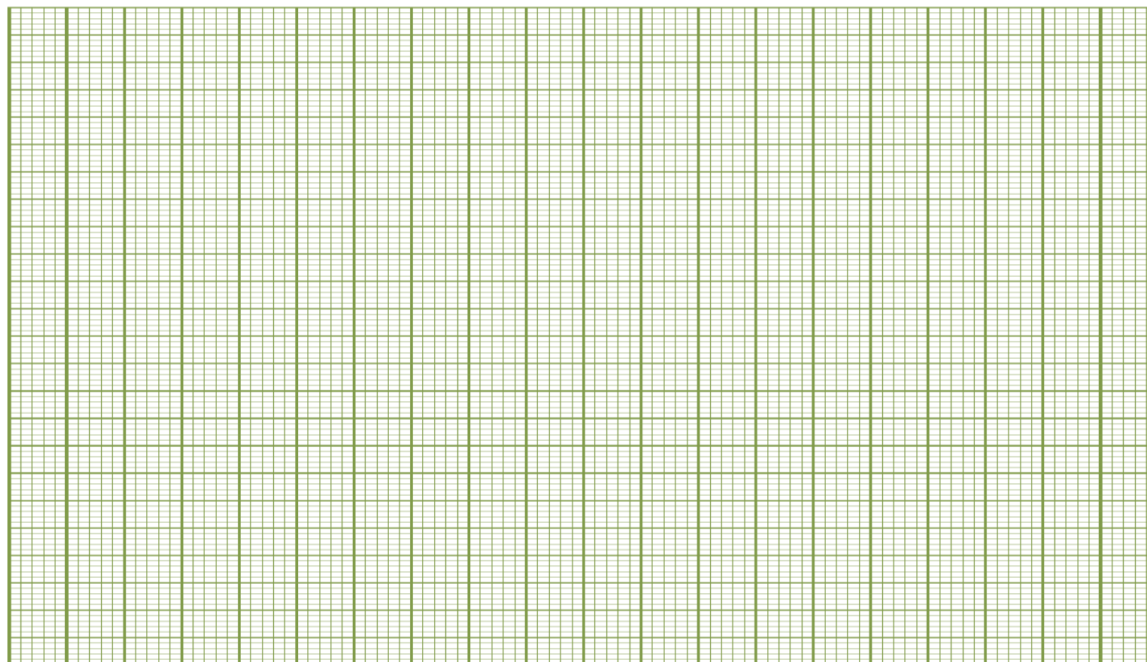
- Initially pH of the acid is a bit high because the acid is weak and thus partially ionises in solution producing few hydrogen ions.
- The pH gradually rises as the base is added because the acid is still in excess which together with the salt formed constitute a buffer solution that resist change in pH.
- At the end point, a very small amount of sodium hydroxide added gives a sharp rise in pH since the alkali is strong
- The pH at the end point is greater than 7 because the salt formed undergoes hydrolysis producing hydroxyl ions that make the solution alkaline.



- Beyond the end point, the pH rises gradually due to excess sodium hydroxide added.

c) Titration curve for a weak base added to a strong acid

this curve shows what happens when 1.0mol dm^{-3} ammonia solution is added to 50cm^3 of 1.0mol dm^{-3} hydrochloric acid



Explanation of the shape of the curve

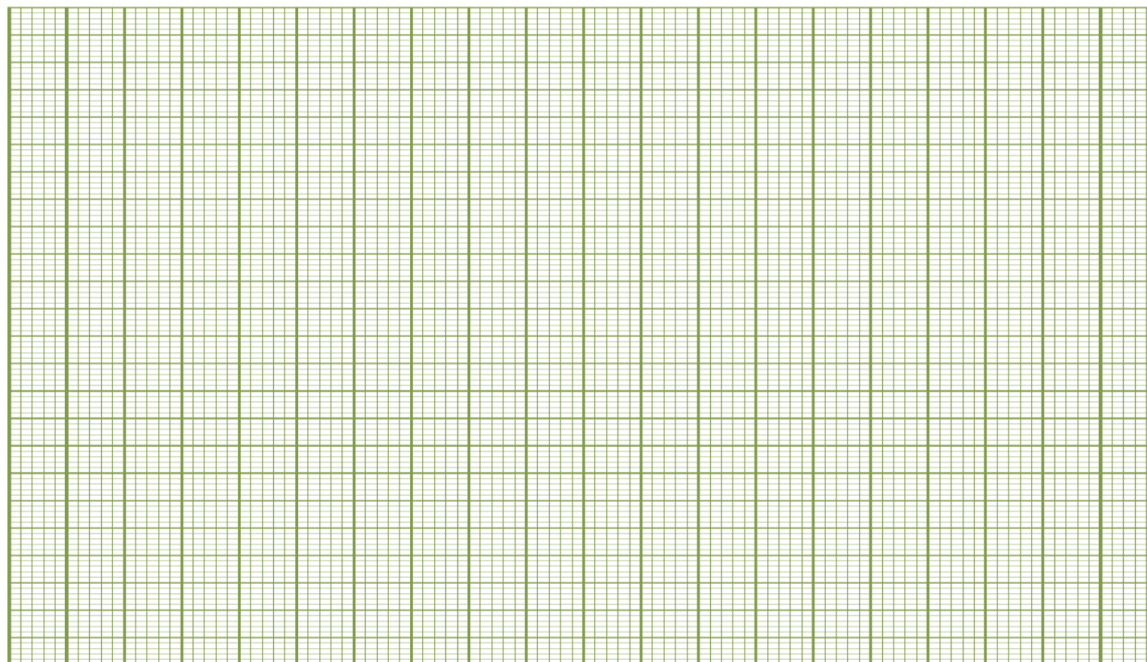
- Initially, the pH is very low because of the high concentration of H^+ ions produced by the complete ionization of HCl which is a strong acid.
- pH gradually rises as the base is added because the acid is still in excess and the hydrogen ions are being neutralized by the hydroxyl ions from the base.
- At the end point, a small amount of ammonium hydroxide added gives a sharp rise in pH
- pH at the end point is less than 7 because the salt formed is hydrolyses to form a slightly acidic solution.



- Beyond endpoint, the pH increases gradually due to excess sodium hydroxide added.

d) Titration curve for a weak base added to a weak acid.

This curve shows what happens when 1.0 mol dm⁻³ ammonia is added to 50 cm³ of 1.0 mol dm⁻³ ethanoic acid.

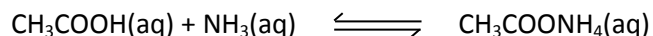


Explanation of the shape of the curve

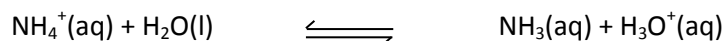
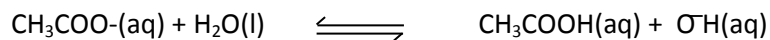
The above curve does not show a significant change at the end point i.e. there is no sharp rise in pH at the end point.

Therefore pH measurements are not suitable for such a titration.

Ammonia solution reacts with ethanoic acid to give ammonium ethanoate.



The salt hydrolyses in water



The acid and acid formed from hydrolysis have the same strength

i.e. K_a of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$, and K_b for $\text{NH}_3 = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$

Therefore, the pH of the resultant solution at the end point

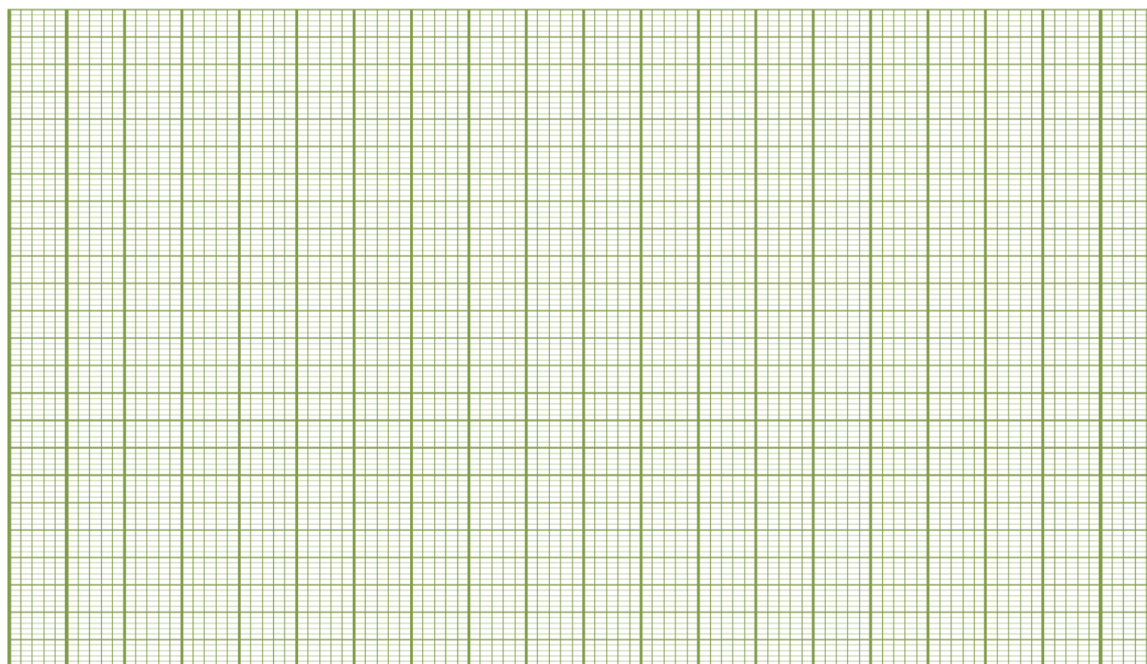


Question

25cm³ of a weak acid HX of concentration 0.01mol dm⁻³ was titrated with 0.10mol dm⁻³ sodium hydroxide solution, and the pH measured at intervals. the results are set out below

Volume of sodium hydroxide(cm ³)	5	10	12	20	23	24	25	26	30
pH	4.5	4.8	4.9	5.5	6.5	7.0	9.0	12.0	12.5

a)Plot a graph of p^H against volume of the base added



b)Determine the p^H at the end point

.....

c)Explain the shape of the graph

.....
.....
.....
.....
.....
.....
.....

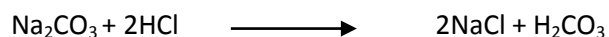
Two-indicator titrations

Titration of alkali carbonate.

A cold solution of sodium carbonate can be titrated with a strong acid

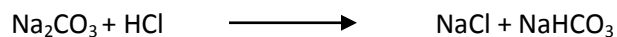
if methyl orange is the indicator since the indicator is not affected by carbonic acid ($\text{pH} = 6.3$)

The solution appears to be alkaline and the indicator remains yellow as soon as all the carbonate has reacted and a slight excess of HCl appears pH decreases rapidly covering the change point of methyl orange which alters its colour to orange (or pink) to give the end point.

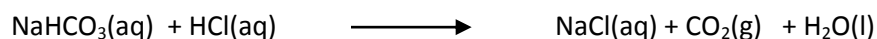


On the other hand litmus and phenolphthalein indicator are both sensitive to carbonic acid and can only be used when the solution is kept boiling to decompose off the carbonic acid.

However if phenolphthalein indicator is used without boiling it changes colour from purple to colourless when sodium carbonate is only half neutralized.

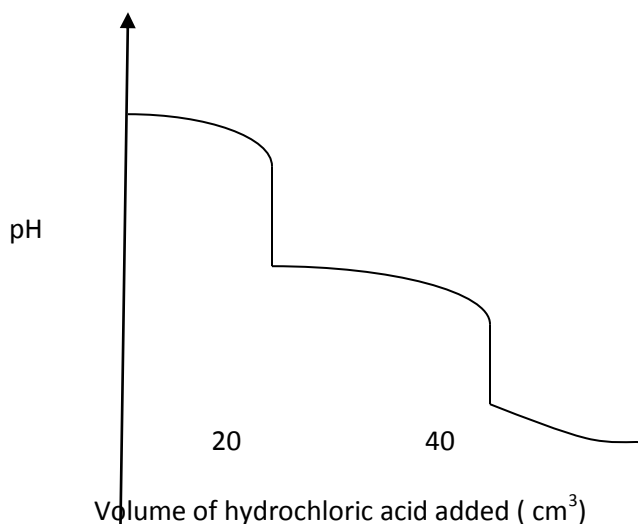


But when methyl orange is used as the indicator, complete neutralization of the sodium carbonate takes place via two stages.



Titration of 0.1 M Na_2CO_3 with 0.1M HCl

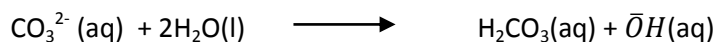
50 cm^3 of 0.1M HCl added to 20 cm^3 of 0.1M Na_2CO_3



Explanation of the shape of the curve

- There are two stages to this reaction, which correspond to two equivalence points at 20cm³ and 40cm³

- Initially pH is 11 corresponds to the pH of sodium carbonate solution



- pH decreases slowly as hydrochloric acid is added the H⁺ ions react with hydroxyl ions to form water.
- There is a rapid change in pH when small amount of acid are added corresponding to the first end point which is due to the reaction



- The pH is 8.3 at the first end point so it can be detected by phenolphthalein indicator since its within its range.
- The pH continues to decrease on addition of the acid.
- There is a rapid change in pH when small amount of acid is added corresponding to the second endpoint which marks complete neutralization.



- The pH is 3.7 at the second endpoint so it can be detected by methyl orange indicator since its within its range.
- After the end point pH decreases because excess acid added.

APPLICATION

used in the estimating the amount of sodium hydroxide and sodium carbonate in the mixture or sodium carbonate and sodium hydrogen carbonate in the mixture or sodium hydroxide and sodium hydrogen carbonate

Such Mixtures are analyzed by titrating the mixture with standard mineral acid using both phenolphthalein and the methyl orange indicators either by two step method or by a continuous method

SOLUBILITY AND SOLUBILITY PRODUCTS

When a certain solute is continuously added to a given solvent at constant temperature a point is reached when the solvent cannot dissolve any more solute. The solution obtained at this point is called a saturated solution.

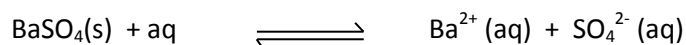
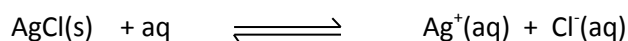
A saturated solution is one which cannot dissolve any more solute at a given temperature in presence of undissolved solute.

The amount of solute in grams or in moles that dissolves in specific amount of solvent at a given temperature to form a saturated solution is called solubility.

Some solutes do not easily dissolve in water. Such solutes are said to be sparingly soluble.

A sparingly soluble salt or solute is one which dissolves up to a certain extent beyond which it cannot dissolve at that temperature.

When a sparingly soluble salt such as silver chloride or barium sulphate is added to water and vigorously shaken, it is found that after some time a little of the salt dissolves in water to give a saturated solution at this point an equilibrium is established between the undissolved salt and the ions produced. I.e



In general for a sparingly soluble salt A_xB_y dissolved in water



Applying the equilibrium law(law of mass action)

$$K = \frac{[\text{A}^{y+}]^x [\text{B}^{x-}]^y}{[\text{A}_x\text{B}_y]}$$

$$K[\text{A}_x\text{B}_y] = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

Since the concentration of solid remains constant at constant temperature we have

$$[\text{A}^{y+}]^x [\text{B}^{x-}]^y = \text{a constant (K}_{\text{SP}}) \text{ or}$$

$$\text{K}_{\text{SP}} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y \dots\dots\dots(\text{ii})$$

The constant K_{SP} is the solubility product of the salt A_xB_y

Solubility product is the product of the molar concentration of the ions of a saturated solution of a sparingly soluble salt or electrolyte raised to appropriate powers according to the stoichiometry of the solubility equation.

Note:

- Equation (i) is the solubility equation for the salt A_xB_y
- Equation (ii) is called the solubility product expression for the salt A_xB_y
- $[A^{y+}]$ and $[B^{x-}]$ are the ionic concentration in mol dm^{-3} in the saturated solution
- $[A^{y+}]^x[B^{x-}]^y$ is called the ionic product of the salt A_xB_y
- A solution of A_xB_y is saturated if the solubility product is equal to the ionic product i.e.

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

- A solution of A_xB_y is unsaturated if the solubility product is greater than ionic product i.e

$$K_{sp} \gg [A^{y+}]^x[B^{x-}]^y$$

- A solution of A_xB_y will be precipitated out of solution if the solubility product is much less than the ionic product i.e $K_{sp} \ll [A^{y+}]^x[B^{x-}]^y$

Examples of sparingly soluble salts include Ag_2CrO_4 , PbCl_2 , $\text{Ca}(\text{OH})_2$, $\text{Ca}_3(\text{PO}_4)_2$

Write the i) equation of dissolution of each of the salts

ii) Expression for the solubility product of each of the salt.

Experimental determination of solubility products

The following methods are used to experimentally determine solubility products

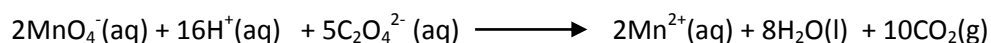
- Volumetric analysis or titration method
- Precipitation method
- Conductivity measurements
- Ion exchange method

a) Experiment to determine the solubility product of silver oxalate by volumetric method

Procedure;

A saturated solution of silver oxalate is prepared by adding excess of oxalate to water and shaken strongly for some time and left for a period of time so as to reach equilibrium at a fixed temperature.

A fixed/known volume of the saturated solution is pipetted, acidified with sulphuric acid, warmed and titrated with standard solution of potassium permanganate to determine the concentration of oxalate ions according to the equation.



The results of the titration are used to determine the concentration of oxalate ions

If the concentration of oxalate ions is $X \text{ mol dm}^{-3}$ that of silver ions is $2X \text{ mol dm}^{-3}$



$$K_{\text{SP}} = [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}]$$

$$= (2x)^2 x = 4x^3 \text{ mol}^3 \text{ dm}^{-9}$$

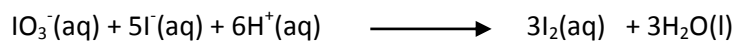
b) Experiment to determine the solubility product of calcium iodate

Procedure;

A saturated solution of calcium iodate is prepared by adding excess of iodate to water and shaken strongly for some time and left for a period of time so as to reach equilibrium at a fixed temperature.

After equilibrium has been established a fixed/known volume of the saturated solution is pipetted into a conical flask containing excess potassium iodide and dilute sulphuric acid

The acidified iodate reacts with iodide ion according to the equation



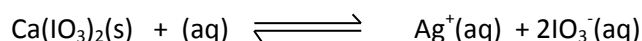
The iodine liberated is titrated with standard solution of sodium thiosulphate using starch indicator.



The titration is repeated and the average volume of sodium thiosulphate calculated

Knowing the volume of sodium thiosulphate that reacted and using the equations above the concentration of iodate ions in the saturated solution can be calculated

If the concentration of iodate ion is $2x \text{ mol dm}^{-3}$ from the solubility equation that of calcium will be $x \text{ mol dm}^{-3}$



$$K_{SP} = [Ca^{2+}][IO_3^-]^2$$

$$=(x)(2x)^2 = 4x^3 \text{mol}^3 \text{dm}^{-9}$$

Precautions

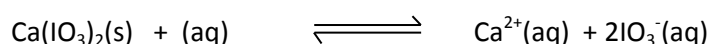
- Pipette after equilibrium has been established
- Pipette only saturated solution
- Maintain a constant temperature

c) Determining of solubility product of calcium iodate by conductivity measurement

Procedure;

- to a known volume of distilled water in a clean beaker excess calcium iodate is added and the mixture vigorously shaken to reach equilibrium and allowed to stand at constant temperature
- the mixture is filtered and the conductivity of the filtrate is measured using a conductivity meter
- the molar conductivities of calcium and iodate ions are obtained
- the concentration of calcium iodate in a saturated solution

$$x = \frac{\text{conductivity of the filtrate}}{\text{molar conductivity at infinite dilution}}$$
- From the solubility equation



$$K_{SP} = [Ca^{2+}][IO_3^-]^2$$

$$=(x)(2x)^2 = 4x^3 \text{mol}^3 \text{dm}^{-9}$$

Calculations involving solubility and solubility product

Example one

The solubility of silver oxalate $Ag_2C_2O_4$, at 25°C is $3.344 \times 10^{-2} \text{ gdm}^{-3}$. calculate the solubility product at this temperature. ($Ag=108, C=12, O=16$)

Solution

Molar mass of $Ag_2C_2O_4 = (108 \times 2) + (12 \times 2) + (16 \times 4) = 304 \text{ g}$

$$\text{Solubility of } Ag_2C_2O_4 = \frac{3.344 \times 10^{-2}}{304} = 1.1 \times 10^{-4} \text{ moldm}^{-3}$$

Each mole of silver oxalate that dissolves produces 2 mole of Ag^+ and 1 mole of $\text{C}_2\text{O}_4^{2-}$ ions in solution.

$$[\text{C}_2\text{O}_4^{2-}] = 1.1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{Ag}^+] = 2 \times 1.1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_{\text{SP}} = [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}]$$

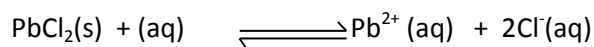
$$K_{\text{SP}} = (2.2 \times 10^{-4})^2 (1.1 \times 10^{-4}) = 5.3 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

Example two

Calculate the solubility in g dm^{-3} of lead(ii) chloride, PbCl_2 at 25°C if its solubility product is $1.6 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$ ($\text{Pb}=207$, $\text{Cl}=35.5$)

Solution

Let the solubility of lead(ii) chloride be $S \text{ mol dm}^{-3}$



$$S \qquad \qquad \qquad S \qquad \qquad 2S$$

$$K_{\text{SP}} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = (S)(2S)^2 = 4S^3 = 1.6 \times 10^{-5}$$

$$S = \frac{\sqrt[3]{1.6 \times 10^{-5}}}{4} = 1.587 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{Molar mass of lead (ii) chloride} = 207 + (2 \times 35.5) = 278 \text{ g}$$

$$\text{Solubility of lead (ii) chloride} = 1.587 \times 10^{-2} \times 278 = 4.412 \text{ g dm}^{-3}$$

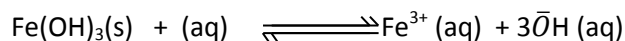
Example three

The solubility product of iron (iii) hydroxide $\text{Fe}(\text{OH})_3$ at 25°C is $8 \times 10^{-40} \text{ mol}^4 \text{ dm}^{-12}$

Calculate the solubility of iron (iii) hydroxide in mol dm^{-3}

Solution;

Let the solubility of iron (iii) hydroxide be S



$$S \qquad \qquad \qquad S \qquad \qquad 3S$$

$$K_{\text{SP}} = [\text{Fe}^{3+}][\text{OH}^-]^3$$

$$K_{SP} = (S)(3S)^3 = 27S^4 = 8 \times 10^{-40} \text{ mol}^4 \text{ dm}^{-12}$$

$$S = \sqrt[4]{(8 \times 10^{-40})} = 0.74 \times 10^{-10} \text{ mol dm}^{-3}$$

Limitations of solubility products

- Solubility products only apply to saturated solution at equilibrium.
- Solubility products only apply to sparingly soluble ionic compounds
- Solubility products are only constant at a particular temperature

Significancy

It reveals the point at which the compound is to precipitate

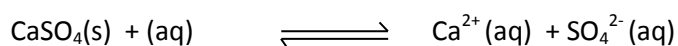
Factors that affects the solubility of a sparingly soluble salt at constant temperature

a) Common ion effect

Adding a strong electrolyte or an ionic salt that contains a common ion to a sparingly soluble salt at equilibrium reduces the solubility of the salt and this effect is called common ion effect.

Common ion effect is the precipitation of a sparingly soluble compound/salt/electrolyte from its saturated solution by adding a soluble ionic compound containing one of the ions released by the sparingly soluble salt.

Suppose you had a saturated solution of calcium sulphate:



$$K_{SP} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^\circ \text{C}$$

Now suppose you added sodium sulphate solution to this which contained an ion in common with it (sulphate ions).

Increasing the concentration of sulphate ions will cause the position of equilibrium to move to the left according to Le Chatelier's principle, and so more of the calcium sulphate will precipitate out. i.e. The calcium sulphate becomes less soluble. The value of solubility product cannot be exceeded it must remain at $2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$, because it is an equilibrium constant. Increasing the concentration of the sulphate ions by adding more of them must be compensated for by lowering the concentration of calcium ions. The only way that can be done is to turn them into solid calcium sulphate.

Therefore; Addition of a common ion reduces the solubility of a sparingly soluble salt.

Worked examples

Example one

The solubility product of calcium iodate (v) is $1.69 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ at 25°C

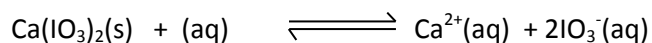
a) calculate the solubility of calcium iodate (v) in mol dm^{-3} in

i) water.

ii) sodium iodate solution of concentration 0.2 mol dm^{-3}

b) Calculate the mass of calcium iodate(v) precipitated out due to addition of 0.1 mol dm^{-3} calcium nitrate solution. (Ca=40, I=127, O=16)

Solution



Let the solubility of $\text{Ca}(\text{IO}_3)_2$ in water be $y \text{ mol dm}^{-3}$

$$[\text{Ca}^{2+}] = y \text{ mol dm}^{-3}$$

$$[\text{IO}_3^-] = 2y \text{ mol dm}^{-3}$$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^-]^2 = (y)(2y)^2 = 4y^3 = 1.69 \times 10^{-9}$$

$$y = 7.50 \times 10^{-4}$$

ii) let the solubility of $\text{Ca}(\text{IO}_3)_2$ in 0.2 M sodium iodate be S

$$[\text{Ca}^{2+}] = S \text{ mol dm}^{-3}$$

$$[\text{IO}_3^-] = (2S + 0.2) \text{ mol dm}^{-3}$$

But Solubility of $\text{Ca}(\text{IO}_3)_2$ is very small compared to solubility of 0.2 M NaIO_3

Such that $(2S + 0.2) \approx 0.2$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{IO}_3^-]^2 = (s)(0.2)^2 = 1.69 \times 10^{-9}$$

$$s = 4.225 \times 10^{-8} \text{ mol dm}^{-3}$$

b) let the solubility of $\text{Ca}(\text{IO}_3)_2$ in 0.1 M calcium nitrate be $w \text{ mol dm}^{-3}$

$$[\text{Ca}^{2+}] = (w + 0.1) \text{ mol dm}^{-3}$$

$$[\text{IO}_3^-] = 2w \text{ mol dm}^{-3}$$

But Solubility of $\text{Ca}(\text{IO}_3)_2$ is very small compared to solubility of $0.1 \text{ M Ca}(\text{NO}_3)_2$

Such that $(W+0.1) \approx 0.1$

$$K_{sp} = [Ca^{2+}][IO_3]^{-2} = (0.1)(2w)^2 = 1.69 \times 10^{-9}$$

$$w = 6.5 \times 10^{-5}$$

Moles of $Ca(IO_3)_2$ precipitated = solubility in water – solubility in calcium nitrate

$$= 7.50 \times 10^{-4} - 6.5 \times 10^{-5} = 6.85 \times 10^{-4} \text{ mol dm}^{-3}$$

Molar mass of $Ca(IO_3)_2 = 40 + (127 \times 2) + (16 \times 6) = 390 \text{ g}$

Mass of $Ca(IO_3)_2$ precipitated = $390 \times 6.85 \times 10^{-4} = 0.267 \text{ g}$

Deciding whether or not precipitate will form when solutions are mixed.

Will a precipitate of calcium hydroxide form if

a) 5.0 cm^3 of $0.050 \text{ mol dm}^{-3}$ sodium hydroxide solution, NaOH , is added to 5 cm^3 of 0.05 mol dm^{-3} calcium chloride CaCl_2 .

b) 5.0 cm^3 of ammonia solution containing OH^- ions with concentration $0.002 \text{ mol dm}^{-3}$ is added to 5.0 cm^3 of 0.05 mol dm^{-3} calcium chloride solution, CaCl_2

$$K_{sp}(\text{Ca}(\text{OH})_2) = 5.5 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9} \text{ at } 298 \text{ K}$$

Solution

$$\text{Moles of hydroxide ions in } 1000 \text{ cm}^3 = \frac{5 \times 0.05 \times 1000}{1000 \times 10} = 0.025 \text{ mol dm}^{-3}$$

$$\text{Moles of calcium ions in } 1000 \text{ cm}^3 = \frac{5 \times 0.05 \times 1000}{1000 \times 10} = 0.025 \text{ mol dm}^{-3}$$

$$\text{ionic product } [Ca^{2+}][OH^-]^2 = 0.025 \times (0.025)^2 = 1.6 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

This value is greater than the solubility product of calcium hydroxide $5.5 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$ calcium ions and hydroxide ions will precipitate out as calcium hydroxide until the ion concentrations are sufficiently reduced.

$$\text{b) Moles of hydroxide ions in } 1000 \text{ cm}^3 = \frac{5 \times 0.002 \times 1000}{1000 \times 10} = 0.001 \text{ mol dm}^{-3}$$

$$\text{Moles of calcium ions in } 1000 \text{ cm}^3 = \frac{5 \times 0.05 \times 1000}{1000 \times 10} = 0.025 \text{ mol dm}^{-3}$$

$$\text{ionic product } [Ca^{2+}][OH^-]^2 = 0.025 \times (0.001)^2 = 2.5 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}$$

This value is less than the solubility product of calcium hydroxide $5.5 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$

The solution is not saturated with calcium hydroxide so no precipitate will form

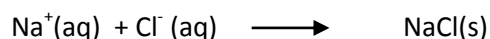
Application of common ion effect

i) Purification of common salt (sodium chloride)

Common salt or sodium chloride contains calcium chloride and magnesium chloride as impurity which make it appear damp.

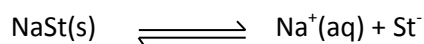
Pure common salt may be obtained by bubbling hydrogen chloride gas into saturated solution of impure sodium chloride since the solution is saturated with sodium chloride.

Addition of hydrogen chloride gas provides chloride ions which precipitate only pure sodium chloride and not magnesium chloride or calcium chloride i.e



ii salting out soap

Ordinary soap is a sodium salt stearic acid; a saturated solution of soap has equilibrium



In the manufacture of soap, a concentrated solution of sodium chloride added provides sodium ions and this increases the concentration of sodium ions making the solubility product of soap to exceed K_{sp} of soap.

Therefore the soap precipitates out in order to maintain the K_{sp} value.

iii) Determining the percentage of the chloride ion in solution by volumetric analysis

iv) In extraction of aluminium

b) Complex ion formation

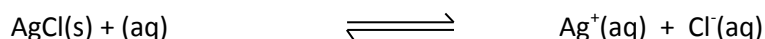
A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contains at least one lone pair of electron .

a sparingly soluble salt will dissolve in a solution if it has the ability to form a complex.

For example;

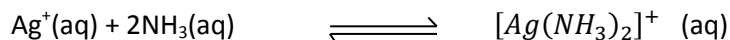
Silver chloride is sparingly soluble in water but readily dissolves in ammonia solution

In water silver chloride ionizes according to the equation.



The solubility product of silver chloride is very small and is easily reached when negligible amount of silver chloride dissolves in water.

in ammonia solution, silver ions react with ammonia solution to form a soluble complex cation diammonia silver(I) ion.

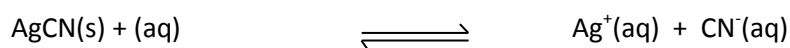


The withdrawal of silver ion decreases their solubility at equilibrium and therefore more silver chloride dissolves to restore the equilibrium constant no longer participates in the solubility product equilibrium of silver chloride. This continues if sufficient ammonia is present until all the silver chloride precipitate has dissolved and the concentration of Ag^+ in the solution is so small that the solubility product of silver chloride cannot be reached.

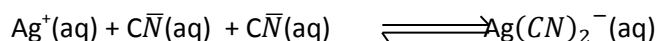
Similarly

Silver cyanide is almost insoluble in water but readily soluble in potassium cyanide solution.

The solubility product of silver cyanide in water is very small and is easily reached when negligible amount of silver cyanide dissolves in water

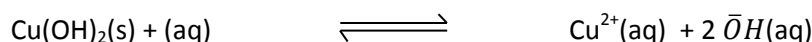


In potassium cyanide, cyanide ions react with potassium cyanide solution to form a soluble complex anion

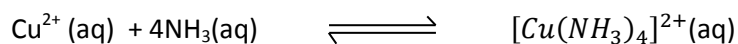


Copper (II) hydroxide, almost insoluble in water; readily soluble in excess aqueous ammonia solution

The solubility product of copper hydroxide is very small and is easily reached when negligible amount of copper hydroxide dissolves in water.

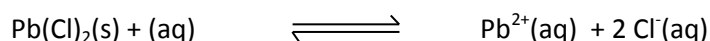


in ammonia solution, copper(II) ions react with ammonia solution to form a soluble complex cation tetra amminecopper(II) ion.



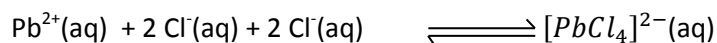
Lead (II) chloride is sparingly soluble in cold water but considerably soluble in concentrated hydrochloric acid.

In water lead(II) chloride ionizes according to the equation.

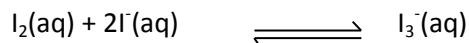


The solubility product of lead(II) chloride is very small and is easily reached when negligible amount of lead(II) chloride dissolves in water.

in concentrated hydrochloric acid solution, lead chloride reacts with concentrated hydrochloric acid solution to form a soluble complex anion.



Iodine is sparingly soluble in water because it is covalent, but readily soluble in concentrated potassium iodide due to formation of a soluble complex.



Therefore formation of soluble complex ion results into increase in solubility of a sparingly soluble salt

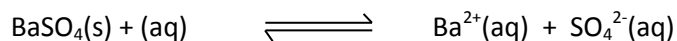
Note adequate presentation of each of these cases requires a full argument on the lines shown for the case of silver chloride in ammonia solution.

c) addition of soluble salt that doesn't contain the common ion but forms a precipitate with one of the ions

Addition of a soluble salt, which does not contain a common ion but reacts with one of the ions in solution increases solubility of sparingly soluble salt.

Example; barium sulphate is more soluble in calcium nitrate than in water

In water barium sulphate ionizes according to the equation.



The solubility product of barium sulphate is very small and is easily reached when negligible amount of barium sulphate dissolves in water.

In calcium nitrate solution, calcium ions reacts with sulphate ions at equilibrium to form calcium sulphate precipitate. $\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{CaSO}_4(\text{s})$

This disturbs the equilibrium of barium sulphate and therefore more barium sulphate dissolves to restore the equilibrium thus increase in solubility of barium sulphate.

Application of the concept of solubility product

1. Solubility product is applied in qualitative analysis in

a) precipitation of sulphides in qualitative analysis

Sulphides with low solubility product eg copper sulphide and lead sulphide are precipitated in acidic media while those with high solubility product eg nickel sulphide and manganese sulphides are precipitated in alkaline media.

Hydrogen sulphide is a weak electrolyte and is used for precipitation of various sulphides in qualitative analysis, it ionizes to a small extent as $\text{H}_2\text{S}(\text{aq}) \rightleftharpoons 2\text{H}^{+}(\text{aq}) + \text{S}^{2-}(\text{aq})$

In acidic medium the ionization of hydrogen sulphide is suppressed due to common ion, the concentration of S^{2-} is so low that the ionic product of sulphide of group (ii) can exceed their solubility product and get precipitated.

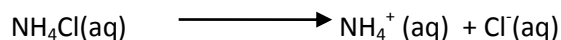
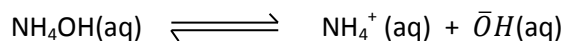
While in alkaline medium, $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + \bar{O}H(aq)$

the OH^- ions furnished by NH_4OH removes H^+ ions from solution in form of water. more of the ionization of H_2S occurs and thus the concentration of S^{2-} ions increases it becomes so high that the ionic product of the sulphides of group (iv) exceed their solubility product and get precipitate

b) Precipitation of metallic hydroxides in qualitative analysis

the hydroxides of Fe^{3+} , Al^{3+} , and Cr^{3+} are precipitated by ammonia solution in presence of ammonium chloride because they have low solubility product while Zn^{2+} , Fe^{2+} and Co^{2+} are not precipitated by ammonia solution in presence of ammonium chloride because they have a high solubility product.

Aqueous ammonia is a weak electrolyte producing few $\bar{O}H$ ions where as ammonium chloride is a strong electrolyte ionizing completely.



In presence of ammonium chloride the concentration of NH_4^+ ions is high and due to common ion effect the equilibrium is displaced to the left ie the ionization of ammonia is suppressed. Therefore the low concentration of $\bar{O}H$ ions exceeded the low K_{sp} value of $Fe(OH)_3$ $Al(OH)_3$ hence precipitated while for $Zn(OH)_2$ $Fe(OH)_2$ the low concentration of $\bar{O}H$ ions cannot be exceed the K_{sp} of these hydroxides

TOPIC 8:CHEMICAL KINETICS

8.1 INTRODUCTION

Is the study of speed with which a chemical reaction occurs, the factors that affect this speed ie temperature, concentration of reactants in solution, pressure of gaseous reactants, particle size of solid reactants, presence of light ,addition of catalyst and the mechanisms by which reactants are converted to products.

Speed of a reaction is the rate at which the concentration of reactants and products change

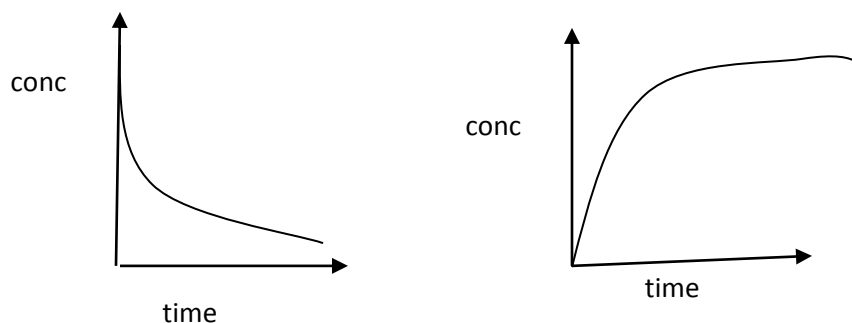
Reaction rates

Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time

Reaction rate is the measure of change in the concentration of reactants or products with time

$$\text{Rate} = \frac{\text{change in concentration of products or reactants}}{\text{time taken}}$$

A plot of concentration of reactant or product against time yields a curve like this



The slope of a line tangent to the curve at any point is the instantaneous rate at that time

The reaction for the reactant slows down with time because the concentration of reactants decrease . Therefore rate can be written as $\text{rate} = \frac{\Delta[\text{reactant}]}{\Delta t} = - \frac{d[\text{reactant}]}{dt}$

The reaction for products increase with time because the concentration of products increases

Therefore rate can be written as $\text{rate} = \frac{\Delta[\text{products}]}{\Delta t} = + \frac{d[\text{products}]}{dt}$

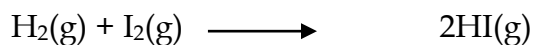
The steeper the gradient, the faster the rate of the reaction.

The reaction is fastest at the start when the concentration of reactant is greatest.

When the reaction is complete, the graph levels off and the gradient becomes zero.

Reaction rates and stoichiometry

For the reaction



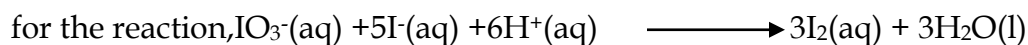
The rate of disappearance of $\text{H}_2 = - \frac{d[\text{H}_2]}{dt}$

The rate of disappearance of $\text{I}_2 = - \frac{d[\text{I}_2]}{dt}$

The rate of formation of $\text{HI} = + \frac{d[\text{HI}]}{dt}$

Since one mole of hydrogen combines with one mole of iodine to form two moles of hydrogen iodide the rate of decrease of concentration of hydrogen and concentration of iodine must be equal and should be half the rate of increase of concentration of hydrogen iodide so that we have.

$$\text{Rate} = - \frac{1}{2} \frac{d[\text{H}_2]}{dt} = - \frac{1}{2} \frac{d[\text{I}_2]}{dt} = + \frac{d[\text{HI}]}{dt}$$



$$\text{Rate} = - \frac{d[\text{IO}_3^-]}{dt} = - \frac{1}{5} \frac{d[\text{I}^-]}{dt} = - \frac{1}{6} \frac{d[\text{H}^+]}{dt} \quad (\text{reactants})$$

$$= + \frac{1}{3} \frac{d[\text{I}_2]}{dt} = + \frac{1}{3} \frac{d[\text{H}_2\text{O}]}{dt} \quad (\text{products})$$

Measuring reaction rate

The rate of reaction is found by measuring some property of reactant or product proportional to concentration such as gas volume, gas pressure, colour change, electric properties e t.c at various times after the start of reaction.

Then the property is plotted against time elapsed since the start of a reaction.

The rate of reaction is the gradient of the tangent to the curve at that point

Some of the methods of following the reaction include;

a)chemical methods

i) By recording the time for the reaction to reach a certain stage

Examples of this method are

-classic iodine-clock experiment, in which the time for the iodine-starch colour to appear is recorded

-the acid-thiosulphate reaction in which the time for the sulphur precipitate to reach a certain density is recorded.

ii) By following the progress of a reaction

Known volumes are withdrawn from the reaction mixture at regular intervals of time. Each sample is quickly run into excess of a reagent which will arrest the reaction or the reaction is stopped by rapid cooling the sample.

The sample is then analyzed usually by titration to determine the concentration of either a reactant or a product present.

Example of these include

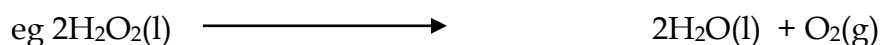
-Reaction between iodine and Propanone

-Catalyzed decomposition of hydrogen peroxide

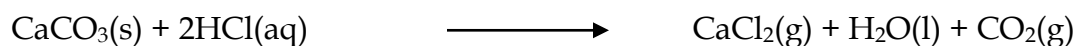
b)physical methods

This is done by

i) Measuring the volume of a gas produced by using a graduated syringe in a given time



ii) Measuring the loss in mass of a reaction mixture due to the loss of gaseous products



iii) Measuring the change in conductivity of liquid due to the change in number of ions

e.g in the hydrolysis of halogen alkane



LAW OF MASS ACTION

According to the law of mass action

The rate of any chemical reaction at constant temperature is directly proportional to the concentration of the reacting species with each concentration term raised to a power equal to the number of molecules of each reacting species.

For the reaction



$$\text{Rate} \propto [\text{A}]^m[\text{B}]^n$$

$$\text{Rate} = K [\text{A}]^m[\text{B}]^n$$

Where: K is the rate constant

The above expression is called the rate equation for the reaction

RATE EQUATION OR RATE LAW

The rate equation or the rate law shows the relationship between the reaction rate and the concentration of reactants involved in the rate determining step.

Rate determining step refers to the slowest stage in a chemical reaction through which a reactant is converted into products.

The rate equation of any given chemical reaction must be experimentally determined; it can't be deduced from a given chemical equation

Rate constant K;

This is the ratio of the rate of a chemical reaction to the product of concentration of its reactants raised to an appropriate power as in the experimentally determined rate equation.

- K is unique for each reaction
- K is constant at constant temperature
- Its magnitude determines whether the reaction is slow or fast
- Its value depends on the activation energy (E_a) and temperature of reaction
 $(K = Ae^{\frac{-E_a}{RT}})$
- The units of K must always be worked out from the rate equation

Order of reaction

This is the sum of the powers to which the concentrations of the reactants in the experimentally determined rate equation are raised.

For example from the rate equation $\text{Rate} = K [A]^m[B]^n$

The exponent's **m** and **n** which are usually integers tell the order of reaction with respect to each reactant.

m is the order of reaction with respect to A

It's the power to which the concentration of A is raised in the rate equation

n is the order of reaction with respect to B

It's the power to which the concentration of B is raised in the rate equation

m+n is the overall reaction order

its the sum of the powers to which the concentration terms of the reactants are raised in the rate equation

NOTE

- M and n bears no relationship to the coefficients a and b
- M and n are determined experimentally
- The exponents in the rate law are not equal to the Stoichiometric coefficients unless the reaction actually occurs via a single step mechanism however the coefficients are equal to the Stoichiometric coefficient of the rate determining step

TYPES OF ORDER OF REACTION

Zero order

An order of 0 is called zero order. If a reaction is zero order with respect to a particular reactant, it means that the concentration of that substance does not affect the rate of reaction. It would be written in the rate equation as for example

$$\text{Rate} = k[A]^0 = K$$

First order

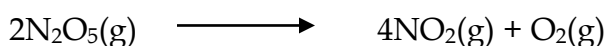
An order of 1 is called first order. If a reaction is first order with respect to a particular reactant, it means that the concentration of that substance is proportional to the rate of reaction. Doubling the concentration doubles the rate of reaction tripling the concentration triples the rate and so on. It would be written into the rate equation as for example

$$\text{Rate} = k[A]$$

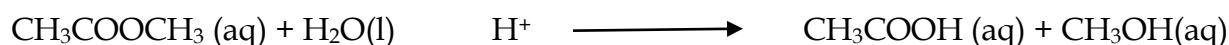
Examples of first order reaction

a) all radioactive decays

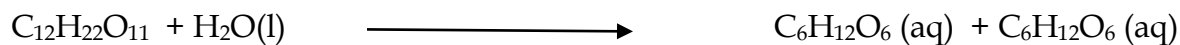
b) Decomposition of nitrogen pent oxide



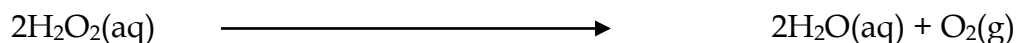
c) Hydrolysis of methyl acetate in aqueous solution



d) hydrolysis of sucrose (sugar)



e) Decomposition of hydrogen peroxide



Second order

An order of 2 is called second order. If a reaction is second order with respect to a particular reactant, it means that the square of the concentration of that substance is proportional to the rate of reaction. Doubling the concentration the rate will increase

four times (2^2), tripling the concentration of the reactant the rate goes up nine times (3^2). It would be written into the rate equation as, for example $\text{rate} = k[A]^2$

DETERMINING THE OVERALL ORDERS OF REACTION

a) From initial rate method

In this method, series of experiments with different initial concentrations are carried out separately and their initial rate of reaction measured. the order with respect to a given reactant is done by comparing the initial rate for two experiments in which the concentration of only the reactant whose order is to be determined is changing while the concentration of other reactants are kept constant. The initial rate is the gradient of the tangent to the concentration vs time curve at $t=0$.
(This method requires more than one reactant.)

If doubling the concentration of A has no effect on the rate, the reaction is zero order with respect to A: $\text{rate} = k[A]^0$ i.e $\text{rate} = k$

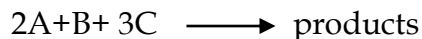
If doubling the concentration of A doubles the rate, the rate and the concentration are directly proportional, and the reaction is first order with respect to A: $\text{rate} = k[A]^1$ i.e $\text{rate} = k[A]$

If doubling the concentration of A increases the rate by a factor of four, the reaction is second order with respect to A: $\text{rate} = k[A]^2$

In general, if the concentration of a reactant A is increased or decreased by X and the initial rate increases or decreases by X^n the order of reaction with respect to that reactant A is n. and $\text{rate} = k[A]^n$

Example one

The table below shows some kinetic data for the following reaction



experiment	Initial concentration of A (mol dm^{-3})	Initial concentration of B (mol dm^{-3})	Initial concentration of C (mol dm^{-3})	Initial rate $\text{Mol dm}^{-3} \text{ s}^{-1}$
1	0.1	0.1	0.1	2.0×10^{-4}
2	0.2	0.1	0.1	4.0×10^{-4}
3	0.2	0.2	0.1	1.6×10^{-3}
4	0.1	0.1	0.2	2.0×10^{-4}

(a) Determine the order of reaction with respect to A,B and C

i) By inspection

Look for two experiments where the concentration of everything else have remained unchanged, but the concentration of A is different. in this case experiment 1 and 2

The concentration of A has doubled and so has the initial rate of reaction.

The reaction is therefore **first order** with respect to A

Look for two experiments where the concentration of everything else have remained unchanged, but the concentration of B is different. in this case experiment 2 and 3

Doubling concentration of B has caused the rate to go up four times (2^2).

The reaction is **second order** with respect to B

Look for two experiments where the concentration of everything else have remained unchanged, but the concentration of C is different. in this case experiment 1 and 4

Doubling concentration of C the initial rate remain the same (2^0).

the reaction is zero order with respect to C

ii) by calculation

$$\text{let rate} = k[A]^x[B]^y[C]^z$$

using experiment 1 and 2

$$\text{rate}_1 = k(0.1)^x(0.1)^y(0.1)^z = 2.0 \times 10^{-4} \dots\dots\dots \text{(i)}$$

$$\text{rate}_2 = k(0.2)^x(0.1)^y(0.1)^z = 4.0 \times 10^{-4} \dots\dots\dots \text{(ii)}$$

equation (ii) divide by equation (i)

$$\frac{(0.2)^x}{(0.1)^x} = \frac{4.0 \times 10^{-4}}{2.0 \times 10^{-4}}$$

$$2^x = 2^1 \quad x=1$$

Using experiment 2 and 3

$$\text{Rate}_3 = k(0.2)^x(0.2)^y(0.1)^z = 1.6 \times 10^{-3} \dots\dots\dots \text{(iii)}$$

$$\text{rate}_2 = k(0.2)^x(0.1)^y(0.1)^z = 4.0 \times 10^{-4} \dots\dots\dots \text{(ii)}$$

equation (iii) divide by equation (i)

$$\frac{(0.2)^y}{(0.1)^y} = \frac{1.6 \times 10^{-3}}{4.0 \times 10^{-4}}$$

$$2^y = 2^2 \quad y=1$$

using experiment 1 and 4

$$\text{rate}_1 = k(0.1)^x(0.1)^y(0.1)^z = 2.0 \times 10^{-4} \quad \dots\dots\dots(i)$$

$$\text{rate}_4 = k(0.1)^x(0.1)^y(0.2)^z = 2.0 \times 10^{-4} \quad \dots\dots\dots(iv)$$

equation (iv) divide by equation (i)

$$\frac{(0.2)^z}{(0.1)^z} = \frac{2.0 \times 10^{-4}}{2.0 \times 10^{-4}}$$

$$2^z = 2^0 \quad z=0$$

b) write the rate equation for the reaction

$$\text{rate} = k[A][B]^2$$

c)state the overall order of reaction

The overall order of reaction is 3 (because the sum of the individual orders 1+ 2+0,is3)

d)Calculate the rate constant and give its units

Rearranging the rate expression gives

$$K = \frac{\text{rate}}{[A][B]^2}$$

Substituting in the numbers for the first experiment gives:

$$K = \frac{2.0 \times 10^{-4}}{(0.1)(0.1)^2} = 0.2$$

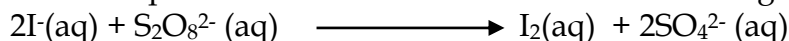
Units for k

$$K = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^2} = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$$

Exercises

The table below shows the experimental data for the reaction between

Peroxodisulphate ion $\text{S}_2\text{O}_8^{2-}$ and iodides ions according to the reaction:



Experiment no	Initial concentration(moldm ⁻³)		Initial rate of reaction(moldm ⁻³ s ⁻¹)
	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	
1	0.038	0.030	7.0×10^{-6}
2	0.076	0.030	14.0×10^{-6}
3	0.076	0.060	28.0×10^{-6}

a)find the order of reaction with respect to I^- and $\text{S}_2\text{O}_8^{2-}$

b)state the overall order of reaction

c)write the rate equation

d) calculate the value of the rate constant and state its units

FINDING ORDERS OF REACTION GRAPHICALLY

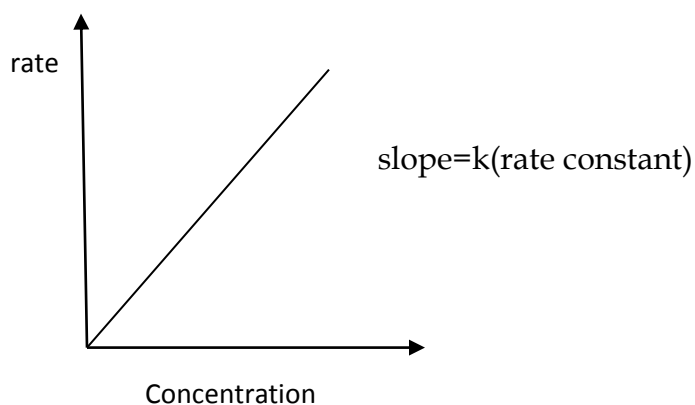
First order with respect to A

Consider the reaction $A \longrightarrow B$

Rate concentration- graphs

$$\text{Rate} = K[A]^1$$

If a reaction is first order a plot of rate against concentration gives a straight line through the origin with positive gradient k



Concentration-time graphs

From First order differential form $-\frac{d[A]}{dt} = K[A]$

$$-d[A] = k[A]dt$$

$$\frac{d[A]}{[A]} = -Kdt \quad (\text{separating variables})$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t -Kdt \quad (\text{integrating})$$

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad [A]_t = [A]_0 e^{-kt}$$

$$\log_{10} \frac{[A]_t}{[A]_0} = -\frac{kt}{2.303} \quad (\text{converting to base ten})$$

$$\log[A]_t = \frac{-kt}{2.303} + \log [A]_0$$

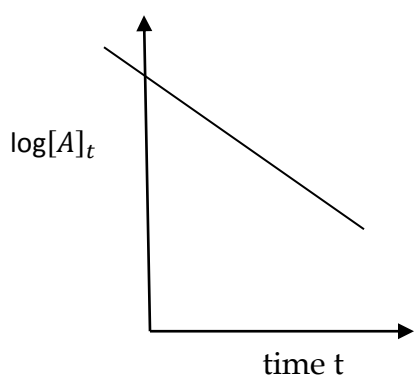
where $[A]_0$ is the initial concentration of A, at $t=0$,

$[A]_t$ is the concentration of A at some time, t during the course of the

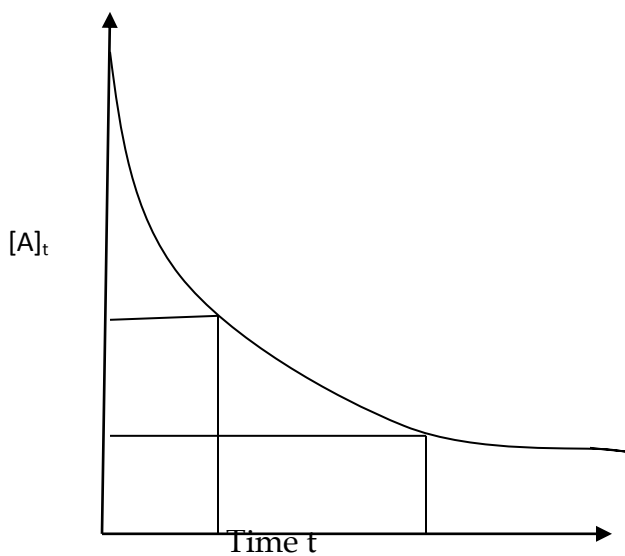
If a reaction is first order a plot

i) $\log[A]_t$ against time gives

a straight line graph with a negative gradient and intercept on the y -axis



i) $[A]_t$ against time t gives a curve with constant half life



For first order reaction $(t_1-0) = (t_2-t_1) = (t_3-t_2)$

HALF LIFE ($t_{\frac{1}{2}}$)

Half life is defined as the time it takes for the concentration of a reactant to fall to half of its initial value

HALF LIFE OF FIRST ORDER REACTION

From the equation $\log_{10} \frac{[A]_t}{[A]_0} = -\frac{kt}{2.303}$

$$\text{At } t = t_{\frac{1}{2}} \quad [A]_t = \frac{[A]_0}{2}$$

$$\log_{10} \left(\frac{\frac{[A]_0}{2}}{[A]_0} \right) = -\frac{kt_{\frac{1}{2}}}{2.303}$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

This shows that first order reaction is independent of the initial concentration of the Reactant

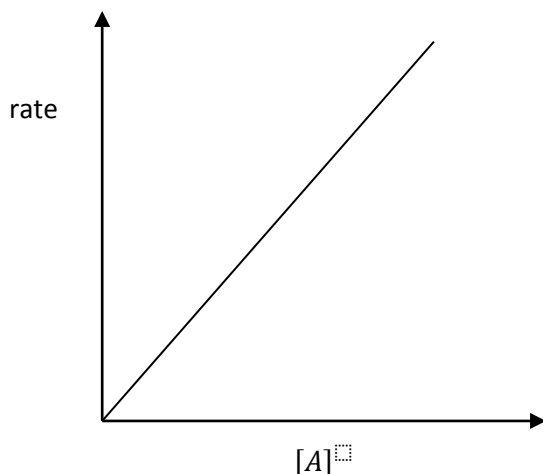
a) Second order reaction

Consider the reaction $A \longrightarrow \text{products}$

Rate-concentration graphs

$$\text{Rate} = K[A]^2$$

A plot of rate against the square of concentration gives a straight line graph



Concentration-time graphs

From second order differential form $-\frac{d[A]}{dt} = K[A]^2$

$$-d[A] = k[A]^2 dt$$

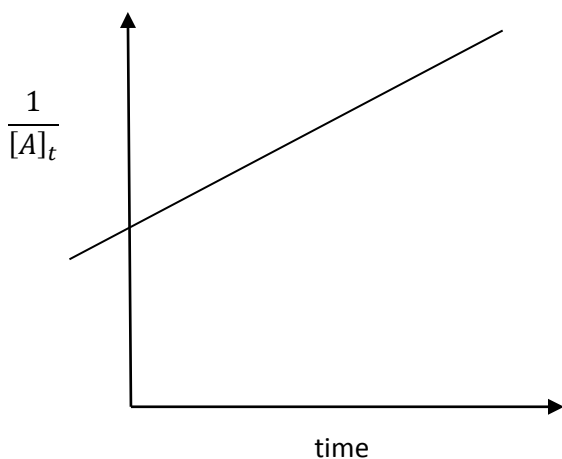
$$\frac{d[A]}{[A]^2} = -K dt \quad (\text{separating the variables})$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_0^t -K dt$$

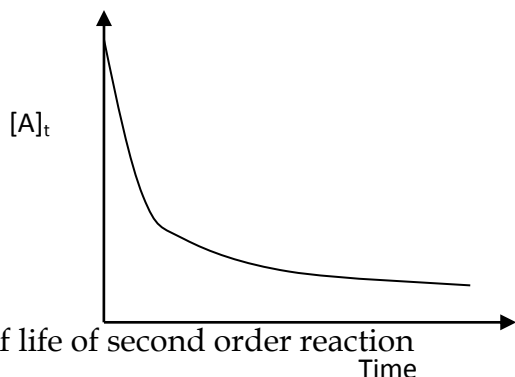
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

A reaction is said to be second order if a plot of

$\frac{1}{[A]_t}$ against time Gives straight line with positive gradient and intercept on y-axis



ii) $[A]_t$ against time t gives a curve with non-constant half life(doubles)



Half life of second order reaction

from the equation $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

$$\text{At } t = t_{\frac{1}{2}}, [A]_t = \frac{[A]_0}{2}$$

$$\frac{1}{0.5[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}, \quad t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

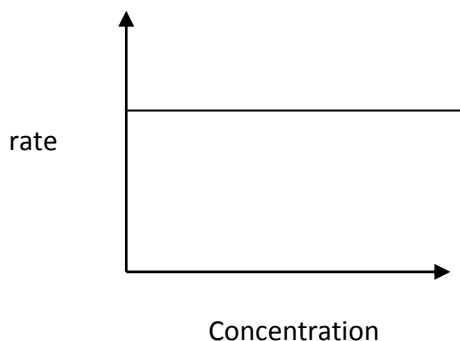
c) zero order reaction

Consider the reaction $A \longrightarrow B$

rate- concentration graphs

$$\text{Rate} = k[A]^0 = K$$

A reaction is said to be zero order reaction if the rate of reaction is independent of the concentration of reactants



Concentration-time graph

From zero order differential form $-\frac{d[A]}{dt} = K$

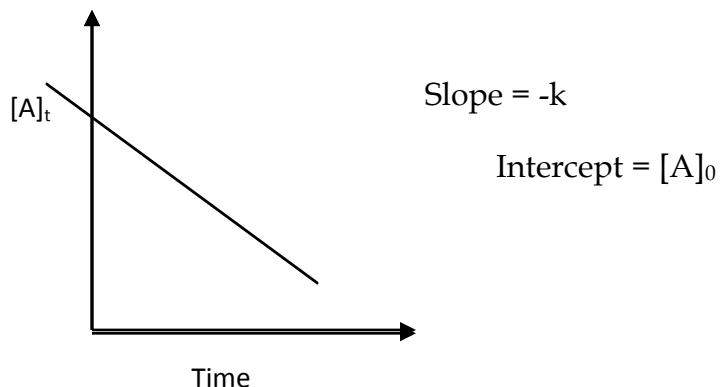
$$-d[A] = kdt \quad (\text{separating the variables})$$

$$\int_{[A]_0}^{[A]_t} d[A] = \int_0^t -kdt \quad (\text{integrating})$$

$$[A]_t = -kt + [A]_0$$

A reaction is said to be zero order if:

a plot of $[A]_t$ against time t gives a straight line with negative gradient and intercept on the y-axis



Half life of zero order reaction

From the equation $[A]_t = -kt + [A]_0$

$$\text{At, } t = t_{\frac{1}{2}} \quad [A]_t = \frac{[A]_0}{2}$$

$$\frac{[A]_0}{2} = -kt_{\frac{1}{2}} + [A]_0$$

$$t_{\frac{1}{2}} = \frac{1}{2k}[A]$$

d) Pseudo first order reactions

Some reactions which may appear to be second order overall may be first order, if one of the reactants is in excess or a solvent

In hydrolysis of methyl ethanoate



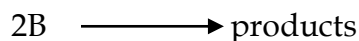
The reaction is very slow it is studied in presence of a small amount of mineral acid which acts as a catalyst

The concentration of water is in large excess and its concentration is therefore almost constant as the reaction proceeds the rate equation therefore reduces to

$$\text{Rate} = k[\text{CH}_3\text{COOCH}_3]$$

Exercises

A compound B decomposes according to the following equation



The table below shows the concentration of B at various times

Time (min)	2.0	4.0	7.0	10.0	14.0	20.0
$[B]\text{mol dm}^{-3}$	0.820	0.670	0.490	0.372	0.240	0.141

(a) draw the graph of $\log_{10}[B]$ against time

(b) using the graph determine the

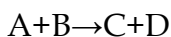
i) original concentration of B

ii)order of reaction

iii)rate constant for the reaction

iv)half life for the reaction

1 Given the data below, find the rate law for the following reaction at 300K.



exp	initial[A] (Moldm ⁻³)	initial[B] (Moldm ⁻³)	Initial rate (Moldm ⁻³ s ⁻¹)
1	0.010	0.010	1.0x10 ⁻⁵
2	0.010	0.030	1.0x10 ⁻⁵
3	0.030	0.030	9.0 x 10 ⁻⁵

a) Find the orders of reaction with respect to A and B

b) Write the rate equation

c) Calculate the rate constant including its units

3.The rate equation for the reaction



$$\text{Rate} = k[A] [X^-] [B]^2$$

Where k is the rate constant

How would the rate of the reaction alter

If (i) [B] and [X⁻] were kept constant but [A] doubled

i) [X⁻] and [A] are kept constant but [B] halved

ii) [X⁻] and [A] were kept constant but [B] doubled

i)From the rate equation Rate = k[A] [X⁻] [B]²

$$\text{Rate} = k[2A] [X^-] [B]^2$$

$$\text{Rate} = 2 k[A] [X^-] [B]^2$$

Therefore The rate would be doubled

ii)from the rate equation Rate = k[A] [X⁻] [B]²

$$\text{Rate} = k[A] [X^-] \left[\frac{B}{2}\right]^2$$

$$\text{Rate} = \frac{1}{4} k[A][X^-][B]^2$$

Hence the rate reduces by $\frac{1}{4}$

iii) From the rate equation $\text{Rate} = k[A][X^-][B]^2$

$$\text{Rate} = k[A][X^-][2B]^2$$

$$\text{Rate} = 4 k[A][X^-][B]^2$$

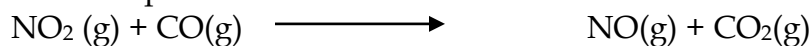
Hence the rate increases by 4

REACTION MECHANISMS

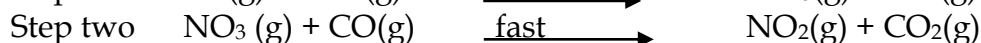
A reaction mechanism is a detailed step-by-step account of how an overall reaction happens. It specifically states all intermediate stages and mentions all intermediate species formed, even though some do not appear as products.

A suggested mechanism must be consistent with the order of reaction. The partial order of any species which occurs in the mechanism after the rate determining step will be zero. A chemical reaction proceeds through several steps, but the slowest step is the rate determining step.

for example



Suggested mechanism



$$\text{Rate} = k[\text{NO}_2]^2[\text{CO}]^0$$

MOLECULARITY OF A REACTION

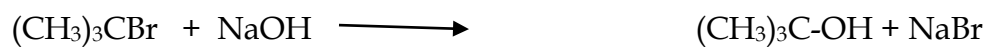
This is the number of ions, molecules or atoms which take part in the rate determining step of a reaction.

Molecularity is a theoretical postulate (believed to be true) and not an experimentally measured quantity. Unlike the order of reaction, molecularity must be a whole number.

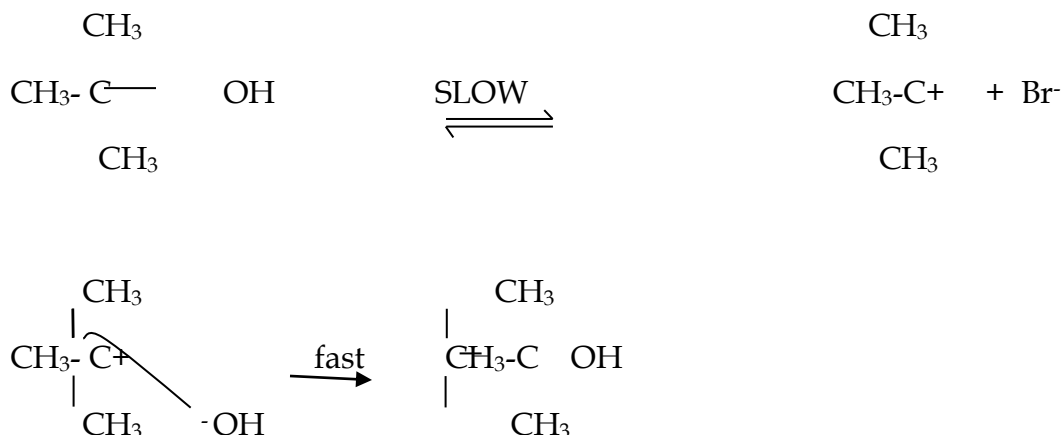
Types of Molecularity

Unimolecular is a reaction where one molecule is involved in the reaction.

for example; **Hydrolysis of tertiary alkyl halide**

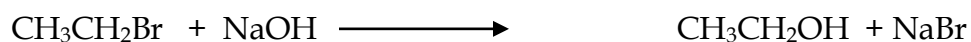


Suggested mechanisms



Bimolecular is a reaction where two molecules are involved in the reaction for example

Hydrolysis of primary alkyl halide



Suggested mechanisms



THEORIES RESPONSIBLE FOR OCCURANCE OF CHEMICAL REACTIONS

There are two theories responsible for occurrence of chemical reactions

The collision theory and the transition state theory

The collision theory

This is based on kinetic theory of gasses that assumes that before particles can react

- i) They must collide

(old bonds may break and new bonds form during collision.)

- ii) they must have a certain minimum amount of energy often referred to as the activation energy E_a for the bonds within the reactant molecules to break and become sufficiently activated for products to be formed

ACTIVATION ENERGY: is the minimum energy which reactant molecules must absorb before a reaction can take place.

Or this is the energy barrier which must be overcome before a reaction can take place

iii) reactant molecules must collide in the correct position

The transition state theory

this theory considers the details of the actual collision between two molecules

according to this theory reactants are not directly converted into products the molecules first absorb energy to form highly unstable species in which bonds are partially broken and others partially formed this unstable species is known as the transition state or activated complex

ACTIVATED COMPLEX is an unstable intermediate state in which the bonds between the molecules of reactants are partially broken and the bonds between products are partially formed.

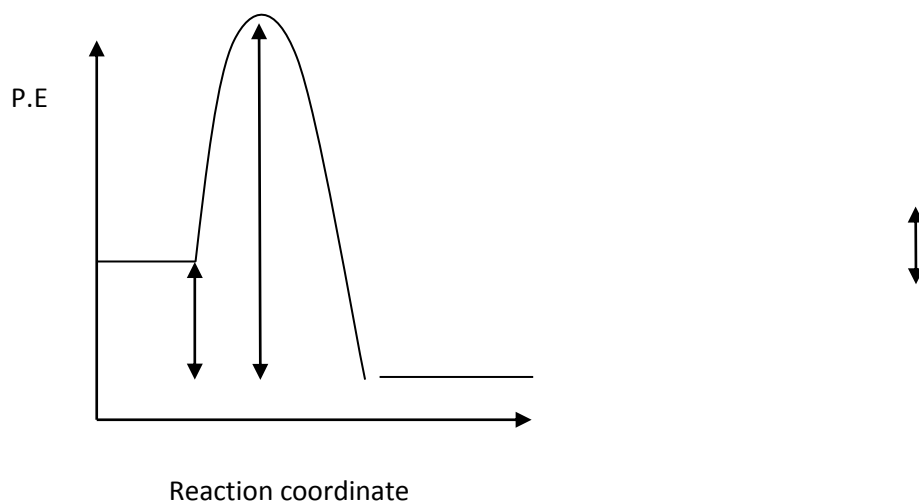


During this process, the kinetic energy of the collision is converted into potential energy which can be shown on an enthalpy diagram usually referred to as the reaction profile and the energy gap between the reactants and this peak is known as the activation energy for the reaction

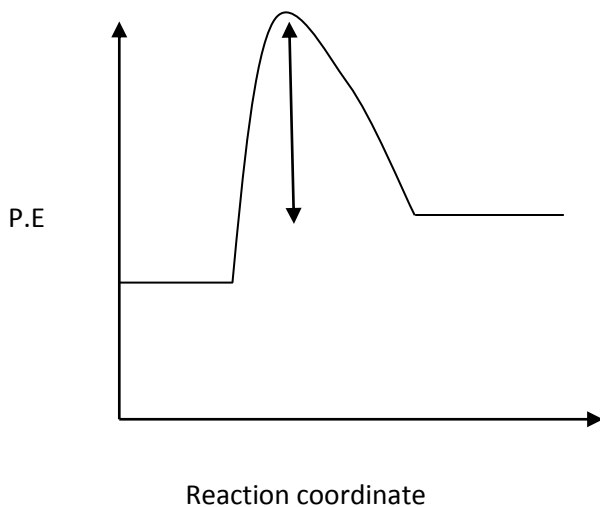
When the activated complex decomposes into products energy is released

The difference in the energy ΔH is equal to the activation energy of forward reaction minus the activation energy of the reverse process

The reaction profile for an exothermic reaction



The reaction profile for an endothermic reaction



Factors which influence rates of reaction

Any factor which increases frequency of collision lowers the activation energy for the reaction.

Or any factor which increases the number of molecules with energy equal to or greater than the activation energy of the reaction increases the rate of reaction. These factors include;

Concentration

If concentration of a reactant in solution is increased, The ions will be closer together, the closer together they are the more frequently do the ions collide ,the more they collide the greater is their chance of reacting and this results in increased reaction rate therefore rate of reaction is proportional to concentration of reactant except for zero order reaction

Pressure of gaseous reactants

If the pressure of gaseous reactants is increased the molecules of gases are pushed closer together as a result they collide more frequently and react more rapidly

Physical state of reactants or surface area

The rate of chemical reaction involving a solid reactant is increased by increasing the surface area of the solid. in such reactions collisions occur between moving molecules and the solid reactants it follows that the greater the surface area of reactants the greater the surface area available for collisions and the greater the reaction rate

Increase in surface area increase the rate of reaction because the amount of contact or surface area for contact between the reactant molecules or particles do increase and hence the rate or frequency of collision increases

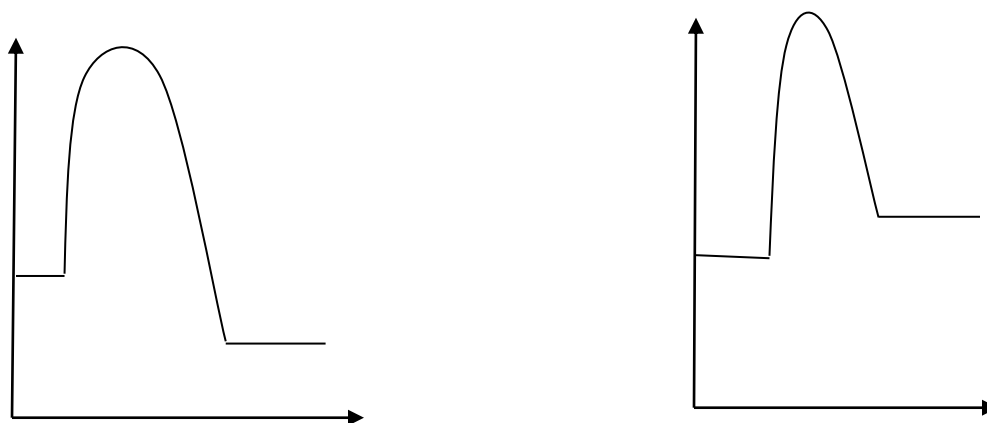
The effects of a Catalyst on the rate of reaction

A catalyst is a substance which alters the rate of chemical reaction without undergoing any chemical change and can be recovered at the end of reaction.

it may be a positive or a negative catalyst

A positive catalyst increases the rate of chemical reaction by providing an alternate path way with lower activation energy while a negative catalyst decreases the rate of chemical reaction by providing an alternate path way with higher activation energy

Below are energy diagrams showing positive and negative catalyzed reactions



Types of catalyst.

There are generally two types of catalyst

- i) homogeneous catalyst and
- ii) heterogeneous catalyst

Homogeneous catalyst

This is when the catalyst and reactants exist in the same phase during a reaction .

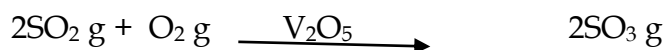
These can be gaseous or liquid phase

Examples of homogeneous catalyst



Heterogeneous catalyst

This is when the catalyst and reactants are in different phases during reaction for example vanadium (v) oxide is a solid catalyst that catalyses a reaction between sulphur dioxide and oxygen to form sulphur trioxide which are gases



Auto catalyst

In some reactions one of the products of the reaction acts as a catalyst for the reaction for example in the reaction of ethane dioate with acidified potassium manganate (vii) the reaction has to be heated to 60°C to get the reaction to start but the reaction manganese (ii) ions produced catalyses the reaction and reaction continues even if the solution is cooled to room temperature.



Essential properties of a catalyst

- It should remain chemically unchanged at the end of the reaction
- It alters the rate of reaction
- Only small amount of the catalyst is required to bring about a change
- Its specific in action ie it catalyses only particular reaction
- It has optimum temperature. (the temperature at which the catalyst is most active)
- It catalyses both forward and back ward reaction to the same extent this explains why a catalyst has no effect on the value of equilibrium constant but increase the rate of attainment of equilibrium
- A catalyst provides an alternative route with lower activation energy barrier for the reaction more molecules possess the lower activation energy and so the reaction is speeded up
- The enthalpy values are the same for catalyzed and uncatalyzed reaction
- A catalyst can be poisoned by presence of impurities(catalyst poison) they form strong bonds with active sites of the catalyst to make the surface unavailable for chemisorption's for example platinum is poisoned by arsenic (iii) oxide in the Haber process.
- Its activity can be enhanced by a catalyst promoter a material added to a catalyst to increase its activity but not to catalyze the reaction for example iron in Haber process is enhanced by aluminium(iii) oxide

Mechanism of a catalyst

THE EFFECTS OF TEMPERATURE ON THE RATE OF REACTION AND RATE CONSTANT

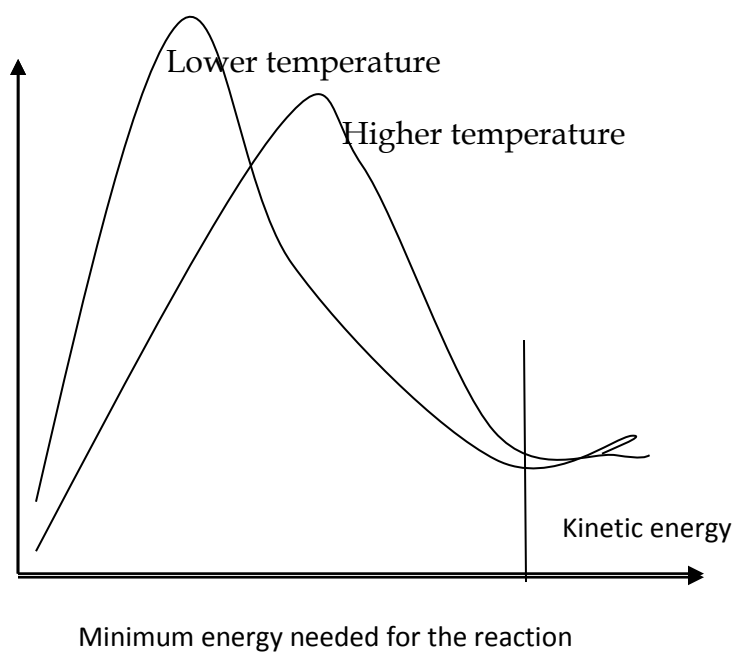
Increase in temperature increases the average kinetic energy of the reacting particles therefore

- the molecules move faster and have more kinetic energy

- there are more collision each second
- the increased kinetic energy produces more energetic collisions
- a greater proportion of molecules exceed the activation energy hence the rate of reaction increases.

The increased energy means more particles now exceeds the energy of activation so there are many more successful collisions this leads to a dramatic increase in the rate of reaction

This can be shown on the Maxwell-Boltzmann distribution of molecular energies



As temperature increases the curve flattens and broaden thus at higher temperature a larger population of molecules has higher energy and the number of molecules that can overcome the activation energy barrier increases as a result the reaction rate increases

For some chemical reactions the reaction rate increases approximately two folds for every 10°C rise in temperature.

From the simple collision theory, the rate of reaction is proportional to the number of molecules possessing energy greater than or equal to

The effect of temperature on reaction rate

An increase in temperature increases the rate of a reaction by increasing the rate constant.

The variation of rate constant with temperature was studied by Arrhenius and found to fit the equation $k = Ae^{\frac{-E_a}{RT}}$ this equation is known as the Arrhenius equation.

K is the rate constant

E_a is the activation energy

T is the temperature(in kelvin)

R is the gas constant (8.31JK⁻¹ mol⁻¹)

A is approximately constant and is taken as constant over small temperature ranges. The constants can be found by using the equation in logarithmic form.

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{in log}_{10},$$

$$\log k = \log A - \frac{E_a}{2.303RT}$$

A plot of $\log k$ against $\frac{1}{T}$ is a straight line of gradient $-\frac{E_a}{2.303R}$ and the intercept is $\log A$.

The rate constant of a reaction was found to vary with temperature as follows

T(K)	290	310	330	350
k x10 ⁻³	1.01	5.04	20.7	72.2

By plotting a suitable graph, find the activation energy of reaction.

(R=8.31JK⁻¹mol⁻¹)

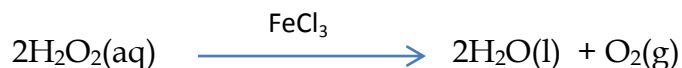
EXERCISE

The following data was obtained from the reaction between hydrogen and iodine at different temperature use the given data to determine the activation energy of the reaction

TEMP(K)	RATE CONSTANT k(mol ⁻¹ dm ⁻³)
678	4.32 x 10 ⁵
727	43.07x10 ⁵
761	177.8x10 ⁵
816	1432x10 ⁵
855	5012x10 ⁵

EXPERIMENTAL DETERMINATION OF ORDER OF REACTION

1) Experiment to determine the order of reaction with respect to hydrogen peroxide



Procedure

- A known volume of hydrogen peroxide is placed in a conical flask, small amount of dilute sodium hydroxide added
- Iron (iii) chloride (a catalyst) added to the mixture and a stop clock simultaneously started.
- After certain time ie two minutes a fixed volume is pipetted into a conical containing a known volume of dilute sulphuric acid (to stop the reaction and prevent further decomposition of hydrogen peroxide).
- The amount of hydrogen peroxide left undecomposed after two minutes is determined by titrating with standard potassium permanganate solution
- $2\text{MnO}_4^-(\text{aq}) + 5\text{H}_2\text{O}_2(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow 2\text{Mn}^{2+}(\text{aq}) + 5\text{O}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$
- The volume of potassium permanganate is proportional to the concentration of hydrogen peroxide present after time t.
- The procedure is repeated after a given interval for at least five intervals
- a graph of log(volume of potassium permanganate) against time is plotted
- if it gives a straight line with negative gradient and an intercept on the y-axis the reaction is first order with respect to hydrogen peroxide.

2) iodination of Propanone

Iodine reacts with propanone in acidic medium according to the equation



Procedure

- A known volume of propanone and dilute sulphuric acid are measured into a conical flask.
- A known volume of iodine is added to the mixture above and the stop clock simultaneously started.
- After a given time a fixed volume of the mixture is pipetted into a conical flask containing aqueous sodium hydrogen carbonate(to stop the reaction and prevent further decomposition of iodine).
- The amount of iodine left undecomposed after a given time is determined by titrating with standard sodium thiosulphate solution

- $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \longrightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{I}^-(\text{aq})$
- The volume of sodium thiosulphate solution is proportional to the concentration of iodine present after time t .
- The procedure is repeated after a given interval for at least five intervals
- a graph of (volume of sodium thiosulphate solution) against time is plotted
- if it gives a straight line with negative gradient and an intercept on the y -axis the reaction is zero order with respect to iodine.

3.Experiment to determine the order of reaction with respect to sodium thiosulphate.

Sodium thiosulphate react with dilute hydrochloric acid slowly according to the equation $\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) + \text{S}(\text{s})$

Procedure

- A known volume of known concentration of sodium thiosulphate is placed in a beaker and placed on a piece of paper marked with cross.
- A known volume of hydrochloric acid is added and a stop clock simultaneously
- Started.
- The time taken for the cross to disappear when view from above the beaker is noted.
- The procedure is repeated for different concentration of sodium thiosulphate which is varied by adding a known volume of water
- A graph of reciprocal of time taken for the cross to disappear is plotted against concentration of sodium thiosulphate.
- If a straight line graph passing through the origin with positive gradient is obtained then its first order with respect to sodium thiosulphate.

Exercises

1) The table below shows variation in concentration of sodium thiosulphate with time when a fixed volume of hydrochloric acid was added to sodium thiosulphate of various concentrations.

Concentration of sodium thiosulphate(mol dm^{-3})	0.2	0.16	0.12	0.08	0.04
Time, t(s)	24	29	39	60	138

- Plot a graph of $\frac{1}{t}$ against concentration of sodium thiosulphate.
- state the order of reaction and Give a reason for your answer.
- Calculate the rate constant of the reaction and indicate its units.
- Determine the time taken for the concentration of sodium thiosulphate to decrease from 0.2 mol dm^{-3}

2. The table below shows the kinetic data obtained for hydrolysis of methyl ethanoate in acidic media.

$[\text{CH}_3\text{COOCH}_3](\text{mol dm}^{-3})$	0.241	0.161	0.109	0.073	0.046	0.034
Time(minutes)	0	60	120	180	240	320

- Plot a graph of concentration of methyl ethanoate against time
- Using the graph determine the:
 - Half-life of the reaction
 - Order of the reaction with respect to $\text{CH}_3\text{COOCH}_3$. Give a reason for your answer.
 - Calculate the rate constant and indicate its units.

2. (a) Distinguish between activation energy and rate constant.

(b) Briefly explain how activation energy and rate constant affect the rate of reaction

(c) Hydrogen reacts with iodine according to the following equation



The table below shows the rate constant for the reaction varying with temperature.

Temperature, T (K)	556	629	700	7.81
Rate constant, k($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	7.04×10^{-7}	6.04×10^{-5}	2.32×10^{-3}	7.90×10^{-2}

- i. Plot a graph of $\log(k)$ against $\frac{1}{T}$
- ii. Use the graph to determine the activation energy of the reaction from Arrhenius equation

$$K = A e^{-E_a/RT} \quad (R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

(d) Draw an energy level diagram for the reaction in (c) above and use it to determine the activation energy for the backward reaction.

e) Briefly explain how temperature affects the activation of the reaction.

3.(a) describe briefly how you determine the rate of reaction of the following reactions

- i) Decomposition of hydrogen peroxide
- ii) Iodination of propanone
- iii) Reaction of sodium thiosulphate and dilute hydrochloric acid

END

3.(a) What is meant by the following terms?

- i. Saturated solution
- ii. Solubility of a salt
- iii. Solubility product

(b) The solubility product of silver phosphate at 25°C is $1.4 \times 10^{-21} \text{ mol}^4 \text{ dm}^{-12}$.

Calculate the

- i. Solubility of silver phosphate in g dm^{-3} at 25°C .
- ii. Molar concentration of silver ions in the saturated solution of silver phosphate at 25°C .

(c) Describe an experiment to determine the solubility product of strontium hydroxide in the laboratory at 25°C .

25 cm^3 of a saturated solution of strontium hydroxide at 25°C were mixed with 50 cm^3 of 0.2 M hydrochloric acid. The resultant solution was diluted to 250 cm^3 . 20 cm^3 of this solution required 12.55 cm^3 of 0.025 M sodium hydroxide solution using phenolphthalein indicator. Calculate the solubility product of strontium hydroxide at 25°C

TOPIC 9: ELECTRO CHEMISTRY

This is the branch of chemistry which explains the inter conversation between chemical energy and electrical energy in a chemical reaction.

ELECTROLYSIS

Definition:

This is the decomposition of a substance when in solution or molten state by passing an electric current through it.

Terms used in electrolysis

ELECTROLYTE

This is an ionic compound which when in solution or molten state allows a current to go through it and become decomposed.

Types of electrolytes

a)Strong electrolytes

these are electrolytes which completely dissociate or ionize in dilute solution and readily conducts electricity . example include; all strong mineral acids ,all strong alkalis while in solution and all aqueous solution of soluble ionic salts.

b)Weak electrolytes

These are electrolytes which partially ionize in aqueous solution producing few free mobile ions. These allow small current to pass through them. Example include all weak acids and weak alkalis ions.

Conductors

This is a solid substance which allows an electric current to go through it e,g all metals and graphite. These conduct electricity because they have delocalized electrons which transmit the electric current.

Electrodes

These are terminals through which current enters or leaves the electrolyte or terminal of conductors through which electrons enter or leave the electrolyte. , electrodes are usually made of unreactive metals such as platinum or non-metal carbon which do not take part in the chemical change occurring in electrolysis or active metals like copper which take part in the chemical change occurring in electrolysis

Types of electrodes

Anode

This is the positive terminal through which current enters the electrolyte or the positive terminal through which electrons leave the electrolyte. it is connected to the positive terminal of the battery, negatively charged ions are attracted to this terminal.

Cathode,

This is the negative terminal through which current leaves the electrolyte or the negative terminal through which electrons enter the electrolyte. it is connected to the negative terminal of the battery, positively charged ions are attracted to this terminal.

Ion

This is a charged atom which has either gained or lost an electron.

Types of ions

Cations these are positively charged ions which migrate to the cathode

Anions these are negatively charged ions which migrate to the anode.

Discharge

Discharge is the process by which ions gain or lose electrons during electrolysis and become atoms or molecules i.e. they lose their charge.

Cations are discharged at the cathode by gaining electrons and are deposited there for example

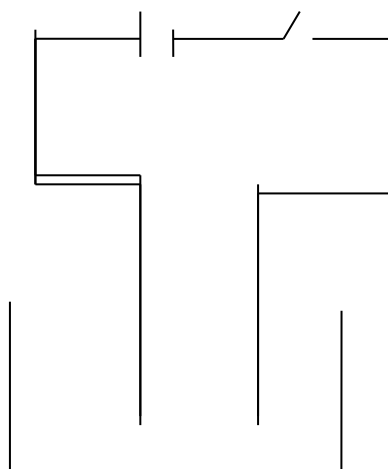


Anions are discharged at the anode by losing electrons and are liberated there for



ELECTROLYTIC CELL

This is the apparatus in which electrolysis is carried out



Current flows through the electrolyte from the positive terminal through the electrolyte then to the negative terminal. Electrons flow from the negative terminal through the electrolyte then to the positive terminal. When the circuit is complete the bulb light.

Process of electrolysis

It involves two stages

Stage one: Movement of ions to electrodes

During electrolysis the electrolyte is first dissociated into cations and anions, when current is passed through an electrolyte, the anions move towards the anode and the cations move towards the cathode.

Stage two: discharge of ions

At the anode anion loses electrons and form a neutral atom or molecule. Oxidation occurs at the anode



At the cathode, the cations gain electrons and form neutral atoms or molecules. Reduction occurs at the cathode.



the electrons lost at the anode enter the external circuit and re-enter the electrolytic cell at the cathode.

The migration of ions results in conduction of electricity

Selective or preferential discharge of ions at the electrode

When two or more ions of similar charge are present in solution under similar conditions for example OH^- and Cl^- or H^+ and Na^+ , one is preferentially selected for discharge depending on the following factor

Position of the ion in the electro chemical series

An electro chemical series is an arrangement of ions in the order of decreasing reactivity

Cations	anions
K^+	
Ca^{2+}	
Na^+	
Mg^{2+}	
Zn^{2+}	SO_4^{2-}
Fe^{2+}	NO_3^-
TO CATHODE \leftarrow Pb^{2+}	Cl^- \rightarrow TO ANODE
H^+	Br^-
Cu^{2+}	I^-
Ag^+	OH^-

If all factors below are constant, any ion will be discharged from the solution in preference to those above it. Lower cations are preferentially selected at the cathode and lower anions are preferentially selected at the anode.

Concentration of the electrolyte

Irrespective of the position of the ion in the electrochemical series, there is a tendency to promote the discharge of the most concentrated ion present in solution.

Nature of electrodes

Some electrodes are reactive while others are inert.

Inert electrodes: these are electrodes which do not react with electrolytes or products during electrolysis. Examples include platinum and graphite.

Active electrodes: these are electrodes which react with product of electrolysis affecting the course of electrolysis and the products of electrolysis e.g. mercury and copper.

Quantitative aspect of electrolysis

Faraday first law of electrolysis:

It states that the amount of any substance deposited, evolved or dissolved at the electrode is directly proportional to the quantity of electricity passing through the electrolytic cell.

$$M \propto C$$

Where C = quantity of electricity in coulomb

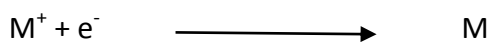
$$\text{One coulomb} = \text{one ampere} \times \text{one second} = I \times t$$

I = current strength in amperes

t = time in seconds

Experimentally, it has been found that one mole of electrons has a charge of 96500C.

Therefore, when one mole of a singly-charged ion is discharged at an electrode this happens:



This process requires the passage of 96500C (or the addition or removal of one mole of electrons).

Similarly, in the discharge of one mole of a doubly charged ion at an electrode this happens:



This process requires the passage of 2 x 96500C (or the addition or removal of two moles of electrons).

In general, then, to discharge one mole of an ion, M^{n+} or X^{n-} , at the electrode $n \times 96500C$ of electricity must be passed through the electrolyte.

Worked example one

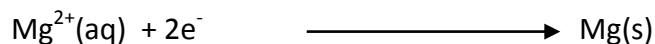
What mass of magnesium is deposited at the cathode by the passage of 2.00 amperes through molten magnesium chloride for 30 minutes?

solution

Quantity of electricity passed in coulombs = amperes x time in seconds

$$= 2 \times 30 \times 60 = 3600C$$

From the equation for the discharge of magnesium



2 x 96500C are required for the formation of one mole of magnesium (24g)

3600C will be required for formation of $\frac{24 \times 3600}{96500} = 0.45\text{g}$ of magnesium.

Faraday second law of electrolysis

It states that the quantity of electricity required to liberate one mole of any element is proportional to the charge number

Application of electrolysis

1. Extraction of sodium by electrolysis of molten sodium chloride in the downs process
2. Manufacture of sodium hydroxide by electrolysis of aqueous sodium chloride in a diaphragm cell.
3. Manufacture of sodium chlorate (i) and sodium chlorate (v) by electrolysis of aqueous sodium chloride.
4. Manufacture of hydrogen by the electrolysis of sodium chloride as in 1 and 2 above.
5. Manufacture of hydrogen by the electrolysis of brine (aqueous sodium chloride) as in 2 above.
6. Extraction of magnesium and calcium by electrolysis of the molten chlorides .
7. Extraction of aluminium by the electrolysis of molten aluminium oxide
8. Anodisation and dyeing of aluminium.
9. Purification of copper by electrolysis, using a lump of impure copper as the anode.
10. Electroplating, e.g chromium plating.

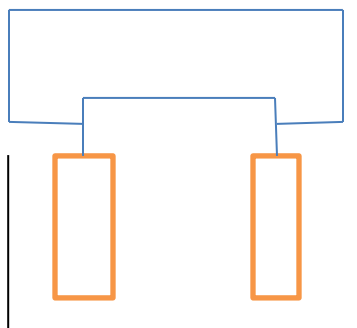
SUB-TOPIC 2: ELECTROLYTIC CONDUCTION

Electrolytes conduct electricity in molten or in liquid state by movement of ions

Conductivity (or specific conductance) of electrolytic solution is a measure of its ability to conduct electricity

Conductivity measurements are used in many industry and environmental application in measuring the ionic content in solution. for example drinking water must have a conductivity in the range $5\text{-}50\text{msm}^{-1}$

The electrical conductivity of a solution of an electrolyte is measured by determining the resistance of solution between two flat electrodes separated by a fixed distance by electrical conductivity meter.



The resistance, R is proportional to the distance L between electrodes and inversely proportional to the cross-sectional area, A of solution between the electrode

$$R \propto \frac{l}{A}$$

$$R = \rho \frac{l}{A}$$

Where R is the electric resistance measured in ohms (Ω)

L is the distance between electrodes measured in meters or centimeters

ρ (rho) = resistivity of the material

A = cross-section area of the electrode measured in metres squared or centimeter squared

When $L = 1\text{cm}$ and $A = 1\text{cm}^2$

$R = \rho$ in this case ρ is known as the specific electrolytic resistance

By definition

Specific electrolytic resistance is the resistance of a given volume of electrolyte between two electrodes of cross-sectional area 1cm^2 placed between two electrodes 1cm apart at constant temperature.

Causes of resistance in an electrolyte

- Presence of unionized water molecules which abstract conducting ions
- Collision between opposite charged ions as they migrate
- Viscosity of water due to the bonding and vander-waals forces of attraction
- Hydration which makes ions heavier
- Attraction between opposite charged ions.

In dealing with solutions of electrolytes it is more convenient to use the quantities conductance and electrical conductivity than resistance and resistivity to minimize the contribution of each of the factors above which can't be easily quantified.

Conductance of solution is

The reciprocal of resistance of solution of an electrolyte is called conductance. ($C = \frac{1}{R}$)

This implies high resistance means low conductance. units are per ohm Ω^{-1} or Siemens(s)

The electrical conductance of an electrolyte is due to the ions it contains, the greater the concentration of ions the higher will be the conductance

Electrolytic conductivity (k)

Is the reciprocal of the resistivity of an electrolyte.

$K = \frac{1}{\rho} = \frac{l}{AR}$ units of k are per ohm per meter or per ohm per centimeter

Experiment to determine electrolytic conductivity of an electrolyte

The electrical conductivity of a solution of an electrolyte is measured by determine the resistance of a solution between two electrodes separated by a fixed distance.



- A solution of electrolyte is prepared using conductance water
- The electrolyte is placed in a conductivity cell
- The sliding contact is connected to a cathode ray oscilloscope and moved along resistance wire AB until a point when no signals are registered.
- At the balance point $\frac{R_{cell}}{AE} = \frac{R_{known}}{EB}$, $R_{cell} = \frac{R_{known}}{EB} \times AE$
- The procedure above is repeated using another electrolyte of known electrolytic k in order to determine the cell constant
- The procedure the repeated using pure conductivity water to obtain its electrolytic conductivity.
- The conductivity of the electrolyte is given by $k_{\text{electrolyte}} = k_{\text{electrolyte in solution}} - k_{\text{water}}$

Note

an alternating voltage is used in order to avoid electrolysis.

Factors that affect the electrolytic conductivity of solution

in general conductance of an electrolyte depends upon the number of ions present in the solution, therefore the greater the number of ions in the solution the greater is the conductance. conductance depends upon the following factors

1) nature of electrolyte (type of electrolyte (weak or strong))

The number of ions produced by the electrolyte depends upon its nature

Strong electrolytes have high electrolytic conductivity because they undergo complete ionization producing a very high concentration of ions in solution such that the resistance to conduction is low.

Weak electrolytes have low conductivity because they undergo partial ionization producing few ions in solution making the resistance to conduction to increase

b) Temperature

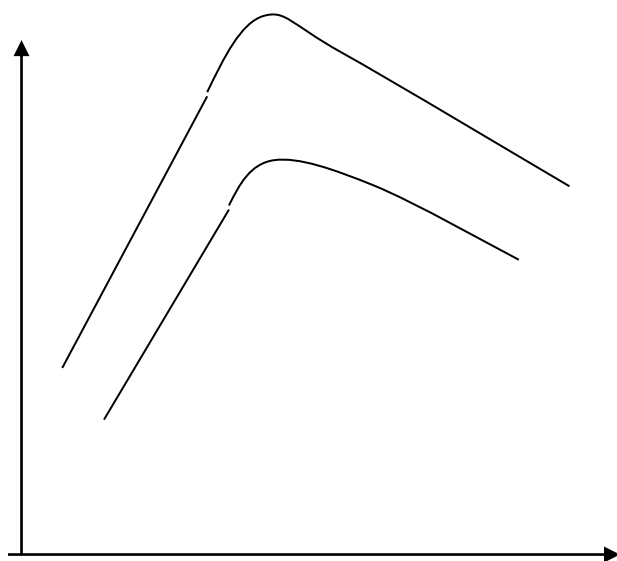
For strong electrolyte, increase in temperature increases electrolytic conductivity because since they are completely ionized in water increase in temperature decreases viscosity of water since heat weakens the hydrogen bonds and the vander-waals forces of attraction.

For weak electrolytes which ionizes endothermically, increases in temperature increases the degree of ionization of electrolytes. Hence, producing many conducting ions resulting in increased conductivity.

e) concentration of ions in solution

The higher, the concentration of ions in solution the higher the conductivity.

A graph of variation of electrical conductivity k with concentration



Explanation of the shape of the graph

Strong electrolytes have higher conductivity than weak electrolytes because they are considered to be fully ionized in solution yet weak electrolytes are considered to be partially ionized in solution

For strong electrolyte:

Conductivity increases with increase in concentration at first because the number of conducting particles per unit volume of solution increases with concentration and ions in electrolyte are still at

maximum distance apart. Beyond a certain concentration of electrolyte further increase in concentration leads to a decrease in conductivity this is because at higher concentration ions of opposite charges are close to each other and exert a dragging effect (inter ionic interferences) which lowers the mobility of the ions hence the decrease in conductivity

For weak electrolyte:

Conductivity increases with increase in concentration at first because the number of conducting particles per unit volume of solution increases with concentration and the degree of dissociation is still high beyond a certain concentration of electrolyte further increase in concentration leads to a decrease in conductivity this is because at higher concentration the degree of dissociation decreases this leads to a decrease in number of conducting ions per unit volume hence conductivity decreases

MOLAR CONDUCTIVITY(λ)

This is the conductance of one mole of an electrolyte in a given volume of a solution which is placed or enclosed between two electrodes with unit cross-section area and unit length apart.

Mathematically; molar conductivity $\lambda = \frac{k}{C}$ or kV

where k is the electrolytic conductivity

C is concentration of the electrolyte

$V = \text{Dilution} = \frac{1}{C}$ is the volume of electrolyte containing one mole .

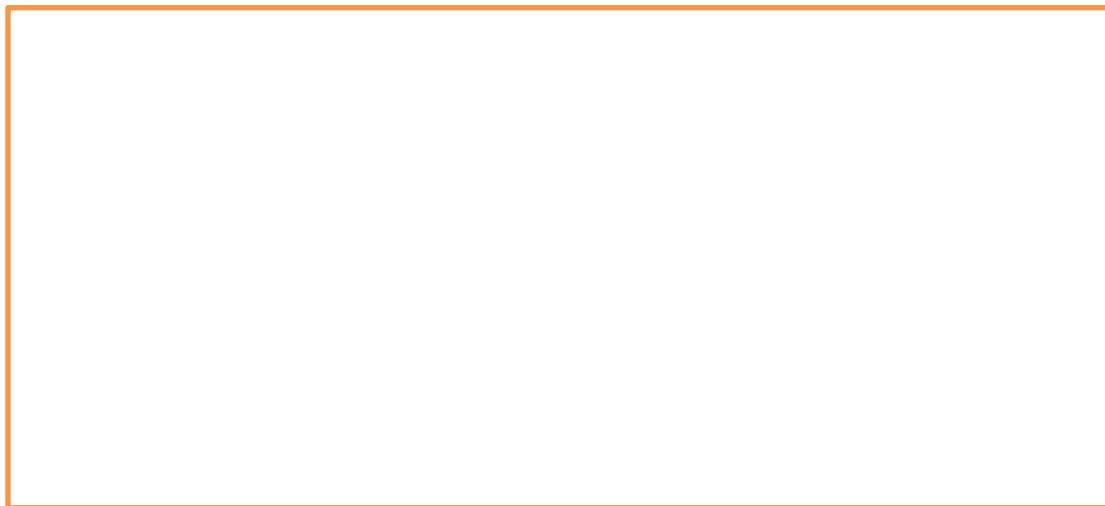
Units of molar conductivity

If concentration is expressed in mol m^{-3} and electrolytic conductivity in $\Omega^{-1}\text{m}^{-1}$ units of molar conductivity λ will be $\Omega^{-1} \text{mol}^{-1} \text{m}^2$

If concentration is expressed in mol cm^{-3} and electrolytic conductivity in $\Omega^{-1}\text{cm}^{-1}$ units of molar conductivity λ will be $\Omega^{-1} \text{mol}^{-1} \text{cm}^2$

If concentration is expressed in mol dm^{-3} and electrolytic conductivity in $\Omega^{-1}\text{cm}^{-1}$ units of molar conductivity λ will be $1000\Omega^{-1} \text{mol}^{-1} \text{cm}^2$ ie molar conductivity will be expressed as $\lambda = \frac{1000k}{C}$

A graph of variation of molar conductivity with dilution



Explanation of the shape of the graph

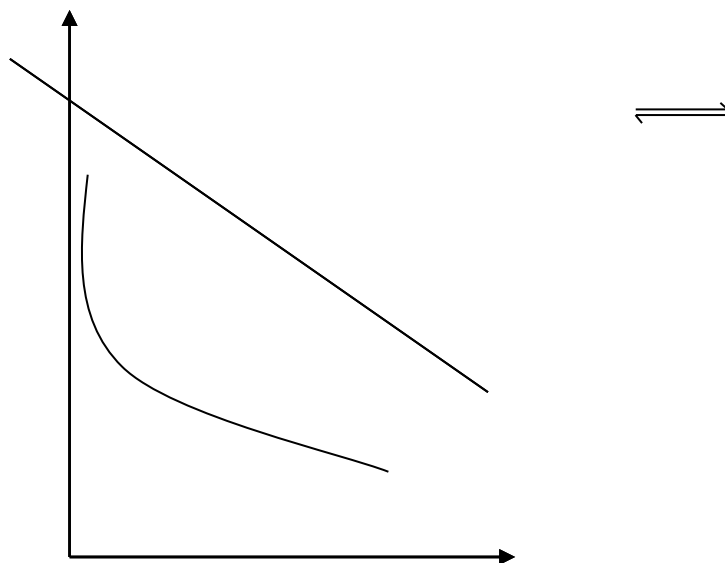
For strong electrolyte

At low dilution or high concentration the molar conductivity is low this is because the ions of opposite charge are close and exert a dragging effect on each other (inter-ionic interferences) with increase in dilution the separation of ions increases and the dragging effect decreases. Molar conductivity therefore increases up to a limiting value beyond which further dilution has no effect. At this point the ions can move independently without exerting a drag on each other. The molar conductivity is the molar conductivity at zero concentration or infinite dilution.

For weak electrolyte

At low dilution (or high concentration) the molar conductivity is low this is because the electrolyte is less dissociated /ionized with increase in dilution degree of dissociation of electrolyte increases therefore the number of ions per unit volume increases hence molar conductivity increases. It is not possible to get molar conductivity at infinity dilution using this method because molar conductivity continues to increase drastically at high dilution without reaching a limiting value.

A graph of variation of molar conductivity with concentration



Explanation of the shape of the graph

For strong electrolytes

At low concentration there are few ions per unit volume and ionic interferences are low, therefore the speed of the ions is high hence high molar conductivity at low concentration.

As concentration increases ions per unit volume increases ionic interferences increases and therefore ionic mobility decreases hence the decrease in molar conductivity at high concentration.

By extra-polating this graph to the axis the intercept is the molar conductivity at infinity dilution

For weak electrolytes

At low concentration molar conductivity is high due to the high degree of dissociation which results into increase in number of ions.

As concentration increases degree of dissociation decreases and the number of ions per degree therefore molar conductivity decreases with increase in concentration.

Factors affecting molar conductivity

b)charge on the ion

the higher the charge on the ion the greater the conductivity.

e.g the electrical conductivity of magnesium chloride is greater than that of sodium chloride with both at the same concentration because the magnesium Mg^{2+} gives a higher charge and higher number of ions in solution than sodium ion Na^+

c) Ionic radius

Increase in ionic radius decreases the ionic mobility and hence the decreases in conductivity.

For example in molten state the conductivity of lithium salts are greater than those of cesium salts since the ionic radius of Li^+ ion is smaller than that of Cs^+

However in aqueous solution the extent of hydration affects the mobility of the ion, which in turn affects the conductivity.

In aqueous solution Li^+ ion with high charge density is heavily hydrated than Cs^+ ion with low charge density hence hydrated Li^+ ion is bigger than hydrated Cs^+ . As a result lithium salts show lower conductivities compared to those of cesium salts in water.

Explain each of the following observations

1. The electrical conductivity of a 0.01M solution of hydrochloric acid is greater than that of 0.001M solution of hydrochloric acid. But the molar conductivity of 0.001M hydrochloric acid is greater than that of a 0.01M hydrochloric acid.
2. The molar conductivity of 0.5M ethanoic acid is less than that of 0.5M hydrochloric acid.

KOHLRAUSCHS LAW OF INDEPENDENT MIGRATION OF IONS

It states that the molar conductivity of an electrolyte at infinity dilution is equal to the sum of the molar ionic conductivities at infinity dilution of the ions produced by the electrolyte at a given temperature.

For example $\lambda_{\infty} \text{NaOH} = \lambda_{\infty} \text{Na}^+ + \lambda_{\infty} \text{OH}^-$

$$\lambda_{\infty} \text{BaCl}_2 = \lambda_{\infty} \text{Ba}^{2+} + 2\lambda_{\infty} \text{Cl}^-$$

Note

This law can be used to determine the molar conductivities at infinite dilution for weak electrolytes whose molar conductivities cannot be determined experimentally.

For example to determine the molar conductivity at infinity dilution of ethanoic acid which ionises as follows $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$

We require the value of the molar conductivity of sodium ethanoate, hydrochloric acid and sodium chloride which are strong electrolyte.

Worked example

1.9.05g of anhydrous magnesium chloride was dissolved in water and the solution made up to one litre. The electrolytic conductivity of the solution of the solution was found to be $2.58 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 25°C . calculate the molar ionic conductivity of the chloride ions at this temperature.
(RFM of $\text{MgCl}_2 = 95, \lambda_{\infty} \text{Mg}^{2+} = 106 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$)

2. calculate the molar conductivity of water at infinity dilution given that

$$\lambda_{\infty} NaCl = 126 \Omega^{-1} mol^{-1} cm^2 \quad \lambda_{\infty} NaOH = 248.4 \Omega^{-1} mol^{-1} cm^2 \text{ and } \lambda_{\infty} HCl = 426.2 \Omega^{-1} mol^{-1} cm^2$$

3. Calculate the molar conductivity of ammonia solution at infinite dilution given

$$(\lambda_0 Ba(OH)_2 = 497.6 \quad \lambda_0 BaCl_2 = 240.6 \quad \lambda_0 NH_4Cl = 129.8$$

APPLICATION OF CONDUCTIVITY

1. In determination of molar conductivity at infinity of strong electrolyte.

From the graph of molar conductivity against the square root of concentration after an experiment.

Worked example

The molar conductivity of sodium hydroxide solution at different concentration is shown below

Concentration(moldm ⁻³)	0.01	0.04	0.09	0.16	0.25	0.36
Molar conductivity($\Omega^{-1} mol^{-1} cm^2$)	238	230	224	217	210	202

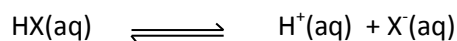
i) draw a graph of molar conductivity against the square root of concentration

ii) explain the shape of the graph

iii) determine the value λ_{∞} of sodium hydroxide

2. In determination of molar conductivity at infinity dilution for weak electrolyte using the Kohlrausch law of independent migration of ions.

3. It can be used to determine the dissociation constant of a weak electrolyte HX



$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{\alpha^2 c}{1 - \alpha}$$

$$\alpha = \frac{\lambda_c}{\lambda_0}$$

Worked example

Calculate the equilibrium constant K_a of 0.1M ethanoic acid given that the molar conductivity of 0.1 M ethanoic acid is $5.2 \times 10^{-4} \Omega^{-1} mol^{-1} cm^2$ and is $3.9 \times 10^{-2} \Omega^{-1} mol^{-1} cm^2$ at infinity dilution.

$$\alpha = \frac{\lambda_c}{\lambda_0} = \frac{5.2 \times 10^{-4}}{3.9 \times 10^{-2}} =$$

$K_a =$ —

4. In Determining the solubility of a sparingly soluble salt.

Worked example

A saturated solution of silver chloride has a conductivity of $1.89 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 298K the electrical conductivity of water is $5.5 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ ($\lambda_{\infty} \text{AgNO}_3 = 133.4$, $\lambda_{\infty} \text{KCl} = 149.9$, $\lambda_{\infty} \text{KNO}_3 = 145$)

a) Calculate the solubility of silver chloride

$$K_{\text{AgCl}} = K_{\text{solution}} - K_{\text{water}}$$

$$= 1.89 \times 10^{-6} - 5.5 \times 10^{-8} = 1.835 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$$

$$\lambda_{\infty} \text{AgCl} = \lambda_{\infty} \text{AgNO}_3 + \lambda_{\infty} \text{KCl} - \lambda_{\infty} \text{KNO}_3$$

$$= 133.4 + 149.9 - 145 = 138.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$$

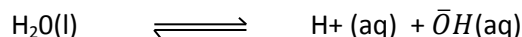
Since concentration of silver chloride is very small its concentration is taken as concentration at infinity dilution

$$C = \frac{K}{\lambda_{\infty}} = \frac{1.835 \times 10^{-6}}{138.3} = 1.33 \times 10^{-8} \text{ mol cm}^{-3} = 1.33 \times 10^{-5} \text{ mol dm}^{-3}$$

b) hence determine the solubility product of silver chloride

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (1.33 \times 10^{-5})(1.33 \times 10^{-5}) = 1.77 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

In determining the ionic product of water



$$K_{\text{w}} = [\text{H}^+][\bar{\text{O}}\text{H}] = C_{\text{H}} C_{\bar{\text{O}}\text{H}} = C^2$$

$$C = \frac{1000K}{\lambda_{\text{H}^+} + \lambda_{\bar{\text{O}}\text{H}}}$$

5. In Conductrimetric titration

This involves the determination of the end point during titration by measurement of conductivity other than by use of an indicator

Experimental determination of end point by conductivity measurement

Apparatus set up

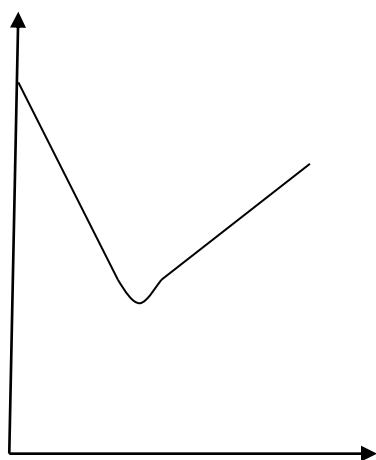


a known volume of strong acid is placed in a conductivity cell the solution is stirred magnetically, small volumes of strong base e.g. 1.0 M sodium hydroxide solution are added from the micro burette and the resistance of the solution is measured after each addition. It is important that the acid is much more dilute than the alkali in order to minimize dilution effects which will tend to mask any conductivity. The graph of $1/R$ or conductivity K against volume of base added is plotted.

The end point of the titration is obtained from the intersection of the straight line portion of the graph.

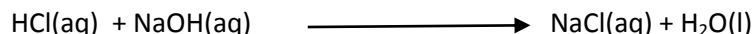
Conductimetric titration curves for acid-base reactions depend on the relative strength of the acids and bases used.

a) Strong acid vs strong base e.g. HCl and NaOH



Initially conductivity is high because HCl is a strong electrolyte which completely ionises into many highly conducting H⁺ ions.

Along AB conductivity decreases with addition of the base because the highly conducting H⁺ ions are being neutralized by hydroxide ions to form water and are being replaced by less conducting Na⁺ ions due to the reaction

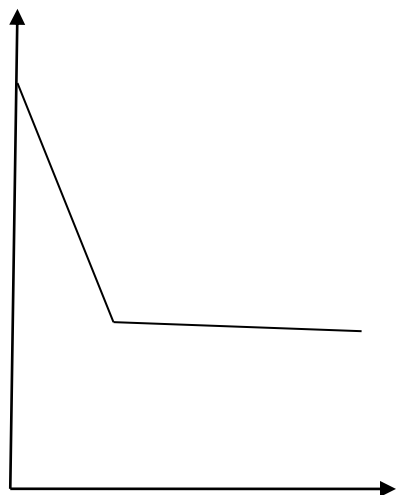


At B It's the end point indicated by a minimum conductivity due to the conductivity of Na⁺ and Cl⁻ ions only

Beyond the end point conductivity increases due to the addition of excess sodium ions and hydroxide ions

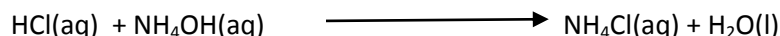
Note the rise is not as steep as the fall in AB because the sodium ions and hydroxide ions added are less conducting than the hydrogen ions.

b)strong acid vs a weak base e.g HCl and NH₃



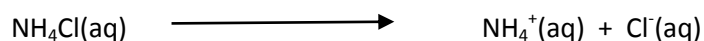
Initially conductivity is high because HCl is a strong electrolyte which completely ionises into many highly conducting H⁺ ions.

Along AB conductivity decreases with addition of the base because the highly conducting H⁺ ions are being neutralized by hydroxide ions to form water and are being replaced by less conducting NH₄⁺ ions due to the reaction



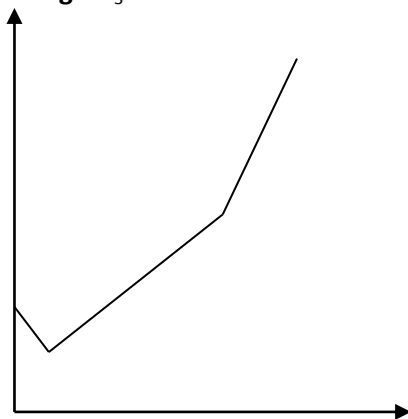
At the end point indicated by a minimum point conductivity due to the conductivity of NH₄⁺ and Cl⁻ ions only.

After the end point the ionisation of a weak base added is suppressed by ammonium ions from the salt NH_4Cl formed.



The equilibrium lies to the left consequently conductivity of the few OH^- is negligible leading to a constant conductivity

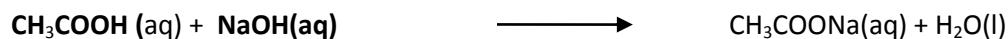
c) weak acid vs strong base e.g CH_3COOH and NaOH



Initially conductivity is low because ethanoic acid is a weak electrolyte that partially ionises into few H^+ ions

Along AB conductivity falls slightly as the base is added because the few H^+ ions from the ionisation of ethanoic acid is/are being neutralized.

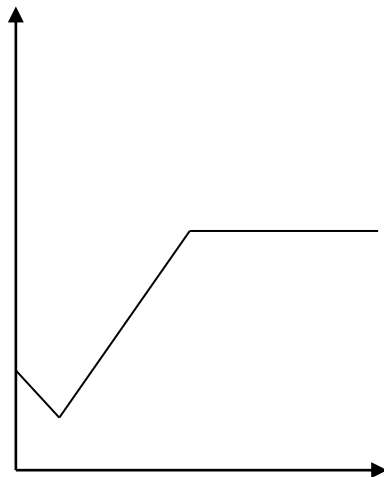
Along BC conductivity gradually increases due to increase in number of ions CH_3COO^- and Na^+ from the completely ionised salt CH_3COONa formed during neutralization



At C conductivity is due to CH_3COO^- and Na^+ ions only

After the end point conductivity increases further due to excess hydroxyl ions added from sodium hydroxide.

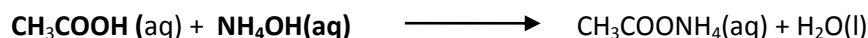
d) weak acid vs a weak base e.g CH_3COOH and NH_4OH



Initially conductivity is low because ethanoic acid is a weak electrolyte that partially ionises into few H^+ ions

Along AB conductivity falls slightly as the base is added because the few H^+ ions from the ionisation of ethanoic acid is/are being neutralized.

Along BC conductivity gradually increases due to increase in number of ions CH_3COO^- and NH_4^+ from the completely ionised salt $\text{CH}_3\text{COONH}_4$ formed during neutralization



At C conductivity is due to CH_3COO^- and NH_4^+ ions only after complete neutralization.

Along CD conductivity remains constant because the ammonia solution added is suppressed by the ammonium ions from the salt formed.

QUESTIONS

The table below shows the variation of conductivity with volume of ammonia when inert electrodes connected to a conductivity meter were immersed in 50cm^3 of 0.025M zinc nitrate solution and 2cm^3 portions of 0.5M ammonia added at intervals.

Volume of ammonia solution added cm^3	0	2	4	6	8	10	12	14
Conductivity of resultant solution $\Omega^{-1}\text{cm}^{-1}$	1.2	1.16	1.12	1.08	1.05	1.045	1.06	1.10

i) draw a graph of conductivity of solution against volume of ammonia

ii) determine the volume of ammonia solution that gave the lowest conductivity.

iii) determine the formula of the species present in the solution.

SUB-TOPIC 3 ELECTROCHEMICAL CELLS

ELECTROCHEMICAL CELLS

An electrochemical cell is a device capable of generating electrical energy from chemical reactions.

An electrochemical cell can be created by placing metallic rod into an electrolyte where a chemical reaction generates an electric current. Electrochemical cells which generates an electric current are called voltaic cells or galvanic cell

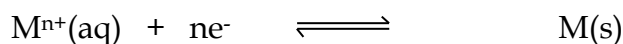
When a metal rod is dipped in solution containing its ions an equilibrium is set up. There is a tendency for metal ions from the metal lattice to pass into solution and form hydrated metal cations leaving electrons on the metal strip, therefore the metal strip becomes negatively charged.



there is also a tendency for the hydrated metal ions in solution to gain electrons from the metal and form metal atoms which are then deposited on a metal strip in this case the metal will become positively charged.



A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again.



The difference is that for some metals the equilibrium lies to the left(these give extra positive ions into the solution),while for others it lies to the right(these take positive ions out of solution)

The metal, therefore acquire a negative or positive charge respectively depending upon which process predominates.

The difference between the negativeness of the metal and the positiveness of the solution around it, called potential difference could be recorded as voltage. The bigger the difference, the bigger the voltage

The potential difference generated between the metal and solution of its ions when they are in contact is called electrode potential (E).

The value of the electrode potential for a particular metal depends on

- the concentration of the metal ions,
- temperature,
- charge on the ions and
- pressure of gas electrode.

The absolute value of the potential difference cannot be measured since the measurement would mean inserting another electrode into the electrolyte and this leads to formation of another potential difference.

A metal dipping into a metal salt solution is called a **half cell** / electrode
a metal strip or rod which is dipped into the electrolyte is called an electrode.

Types of Half cells/electrodes

a-metal-metal ion electrode

This is made up of a metal rod dipped into solution of its ions

For example zinc metal dipping into a solution of zinc sulphate Zinc

Half cell symbol $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq})$

Half cell equation $\text{Zn}^{2+}(\text{aq}) + 2\bar{e} \rightleftharpoons \text{Zn(s)}$

b-Gas electrode

This consist of a gas under pressure on the surface of a catalyst

For example hydrogen in contact with platinum electrode in the hydrogen electrode

Half cell symbol $\text{Pt}/\text{H}_2(\text{g}),\text{H}^+(\text{aq})$

Half cell equation $2\text{H}^+(\text{aq}) + 2\bar{e} \rightleftharpoons \text{H}_2(\text{g})$

c-Ion-ion electrode

This consists of an inert metal in contact with a solution containing ions in two different oxidation states.

For example a platinum electrode dipped into a solution containing Fe^{2+} and Fe^{3+}

Half symbol $\text{Pt}/\text{Fe}^{2+}(\text{aq}),\text{Fe}^{3+}(\text{aq})$

Half cell equation $\text{Fe}^{3+}(\text{aq}) + \bar{e} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$

d-Metal- metal sparingly soluble salt electrode

This is made up of a piece of metal coated with the desirable sparingly soluble salt then the set up immersed into a solution with an anion common to that of the sparingly soluble salt of the metal.eg

Silver metal coated with silver chloride immersed in a chloride solution.

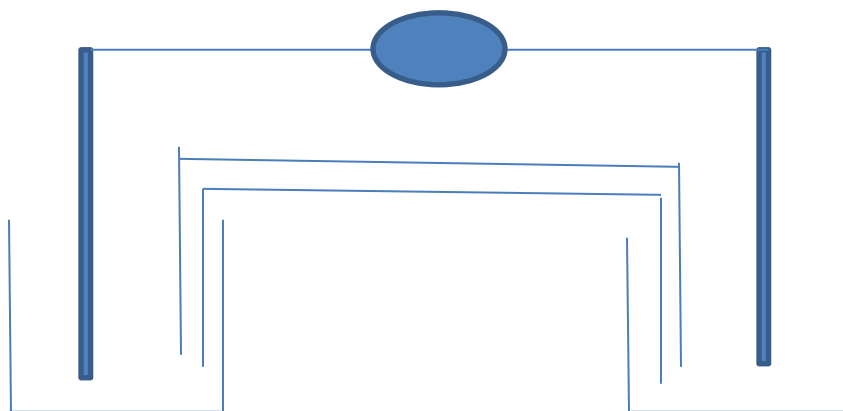
Half- cell symbol $\text{Ag(s)}/\text{AgCl(s)},\text{Cl}^{-}(\text{aq})$

Half- cell equation $\text{AgCl(s)} + \bar{e} \rightleftharpoons \text{Ag(s)} + \text{Cl}^{-}(\text{aq})$

Electrochemical cell/galvanic cell

For relative measurements of potentials of various metals in various solutions two half cells are connected together to make galvanic cell

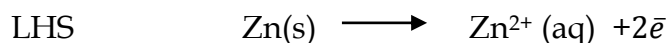
Typical galvanic cell consists of two metallic electrodes e.g zinc and copper immersed into different solutions i.e zinc sulphate and copper sulphate respectively. The solutions are electrically connected by a salt by a salt bridge. The metallic electrodes are connected to high resistance voltmeter.as illustrated in the diagram below.



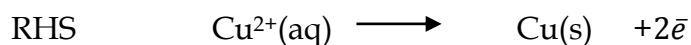
Electrons will flow along the wire from the electrode with higher concentration of electrons to the one with lower electron concentration

By convention; the negative electrode is put on the left and the positive electrode on the right of the diagram

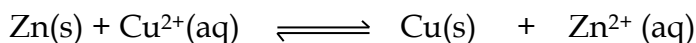
In the daniell cell, the zinc is the negative electrode because it has the more negative electrode potential; it constitutes the left hand electrode (the anode) and the electrons travel from the zinc through the wire to the positive copper electrode. This means the reaction in the zinc half-cell must be



The copper is the positive electrode because it has a more positive electrode potential, it constitutes the right hand electrode (cathode) and the reaction in copper half-cell is the one that absorbs the electrons travelling round the circuit.



The overall equation



If the value of the current is negligible (high resistance voltmeter is used) the measured potential difference between the electrodes is equal to the electromotive force (EMF) of the galvanic cell.

The measurements of electromotive force are usually made under standard conditions:

- Temperature of 25°C or 298K
- Pressure of gasses at 1.0 atm
- Electrolyte solution of 1.0 mol dm⁻³

Electromotive force measured under standard conditions has a notation E^{\ominus}

EMF of galvanic cell is a resulting sum of potential difference of the anode and cathode:

$$E^{\ominus} = E_{\text{cathode}} - E_{\text{anode}}$$

A cell diagram

The galvanic cell is schematically described by the cell notation or cell diagram

this is an agreed way of depicting cells on paper for example, in the galvanic cell above



By convention:

- The two parallel lines represent the salt bridge.
- Each single line represents the change of phase between aqueous ions and solid metal
- Broken line represents a porous partition (for some cell)
- A comma represents separation between two elements in different oxidation state
- Pt represent platinum electrode

- The electrode through which electrons flow are placed at the start and the finish of the cell diagram.
- The half-cell undergoing oxidation is written on the left of the diagram.
- The half-cell undergoing reduction is written on the right of the diagram.
- Oxidation will take place in the half-cell with the more negative standard electrode potential
- Reduction will take place in the half-cell with the less negative (more positive) standard electrode potential.
- The electrode where reduction takes place is called the cathode and where oxidation takes place is the anode
- The e.m.f of a combination of two half-cells is the difference between the e.m.f of the half cell on the right-hand side minus the e.m.f of the half-cell on the left-hand side, ie

$$E_{\text{cell}} = E^{\theta}_{\text{right}} - E^{\theta}_{\text{left}}$$

Note

The salt bridge

The salt bridge is included to complete the electrical circuit but without introducing any more bits of metal into the system it is just a glass tube filled with an electrolyte like potassium nitrate solution. The ends are stoppered by bits of cotton wool. This stops too much mixing of the contents of the salt bridge with contents of the two beakers. The electrolyte in the salt bridge is chosen so that it does not react with the contents of either beaker.

The voltmeter

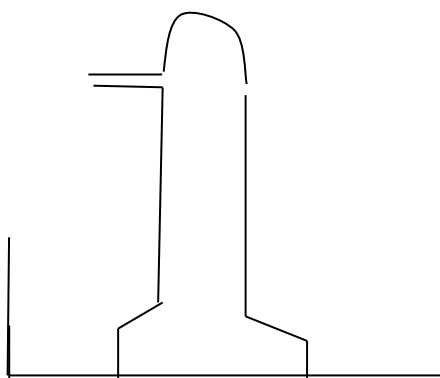
High resistance voltmeter is used to avoid any flow of current through the circuit such that maximum possible voltage is measured. This is called the electromotive force e.m.f. the e.m.f measured under standard conditions is given the symbol E^{θ}_{cell}

STANDARD ELECTRODE POTENTIAL

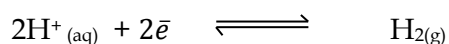
Standard electrode potential is the electromotive force measured in the galvanic cell consisting of the half cell with the electrode under standard conditions and half -cell with the standard hydrogen electrode

THE STANDARD HYDROGEN ELECTRODE

Standard hydrogen electrode(SHE) consists of platinum foil coated by platinum black, which is dipped into an acidic solution with concentration of hydrogen ions(H^+) 1.0mol dm^{-3} at 298k and which is in contact with gaseous hydrogen bubbling at 1.0 atmospheres around the electrode.



As the hydrogen gas flows over the platinized platinum, equilibrium is set up between hydrogen molecules and hydrogen ions in solution. The reaction is catalyzed by platinum



This is the equilibrium that we are going to compare all the others with.

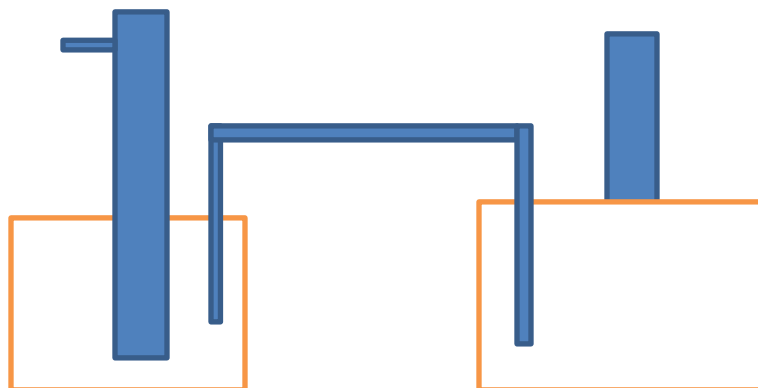
Platinum does not take part in the reaction but it serves as a catalyst for oxidation-reduction reaction of hydrogen

- It acts as an inert connection to the H_2/H^+ system because there is no tendency of platinum to form ions
- It allows hydrogen gas to get adsorbed on its surface
- Being platinized, the surface area for the establishment of equilibrium between hydrogen gas and hydrogen ions is increased.

Standard electrode potentials are measured relatively to the standard hydrogen electrode, potential of which is defined as 0.0volts

Measuring the standard electrode potential of a metal in a solution of its ions.

The metal plate is dipped in a solution containing 1.0mol dm^{-3} solution of the metal ions. The electrode is connected to the positive terminal of the voltmeter and the standard hydrogen electrode is connected to the negative terminal of the voltmeter and the two solutions by means of a suitable salt bridge, as shown below.



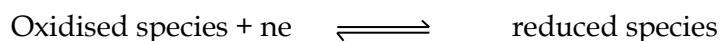
The maximum potential difference, known as the e.m.f of the cell is then measured by a high-resistance voltmeter in volts (because it withdraws negligible current from the cell set up). Since the standard hydrogen electrode has a potential of 0.00V , the reading on the voltmeter is the standard electrode potential of the metal.

Standard electrode potential E^θ is the potential value measured with respect to a standard hydrogen electrode at conditions of 1 atmosphere, 298K and 1.0mol dm^{-3} concentration of ions in the solution. **or**

The e.m.f measured when the metal is in solution of its ions coupled to a standard hydrogen electrode is called the standard electrode potential for the metal/metal ion combination. The hydrogen electrode must be the left-hand electrode, and everything must be under standard conditions (all ion concentration 1.0mol dm^{-3} , temperature of 298K , and gas pressure of 1.0 atmosphere).

By convention, standard electrode potentials are recorded as standard reduction potentials. this is because the second electrode on the right is being reduced by gaining electrons from the standard hydrogen electrode As $E^\theta \text{M}^{n+}/\text{M} = __ + x\text{V}$

The reaction is written with the reduced species on the right i.e



The sign of the standard electrode potential E^θ value

When the metal M is above hydrogen in the reactivity series e.g Zinc or Magnesium or Aluminium, electrons will flow from the metal rod to the standard hydrogen electrode and

hence the metal electrode becomes negative with respect to the hydrogen electrode. The minus (-) sign signifies that the electric potential on the electrode is more negative than the potential on the standard hydrogen electrode.

When the metal M is below hydrogen in the reactivity series e.g copper or gold or silver electrons will flow from the standard hydrogen electrode to the metal electrode and the electrode potential will be registered as positive. The plus (+) sign signifies that the standard hydrogen potential has the more negative potential

Electro-chemical series

Standard electrode potentials of metals are arranged in electrochemical(galvanic)series

The arrangement of elements according to their electrode potentials gives rise to the electro-chemical series in which the most reactive metals has the most negative reduction potential and it is the one the top.

The more negative a reduction potential is the easier it is for the oxidation process to take place and the more difficult it is for the reduction process to take place.

The elements or species with the greatest negative electrode potentials have a greater tendency to donate electrons and therefore exist as the anode. Therefore these metals are strong reducing agents.

Consider the potential of the following electrodes

electrode	$E^\theta\text{V}$
$\text{Li}^+(\text{aq})/\text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq})/\text{K}(\text{s})$	-2.92
$\text{Na}^+(\text{aq})/\text{Na}(\text{s})$	-2.82
$\text{Ca}^{2+}(\text{aq})/\text{Ca}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq})/\text{Mg}(\text{s})$	-2.31
$\text{Al}^{3+}(\text{aq})/\text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$	-0.44
$\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$	-0.13

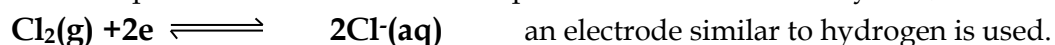
$\text{H}^+(\text{aq})/\text{H}_2(\text{s})$	0.00
$\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$	+0.34
$\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$	+0.80
$\text{Au}^{2+}(\text{aq})/\text{Au}(\text{s})$	+1.50

Measuring redox potentials for other systems

Since the electrochemical series is essentially about redox reactions, it would make sense to include reducing agents and oxidizing agents other than metals and their ions-for example, oxidizing agents like chlorine, acidified potassium dichromate(vi) or acidified potassium manganate(vii).all of these have measurable E^θ often called redox potentials rather than electrode potentials

a)Systems involving gases

For example to measure the electrode potential for the chlorine system,

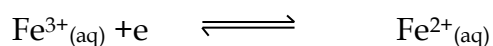


Chlorine gas is bubbled over platinum electrode which is immersed in a solution containing chloride ions with concentration 1.0mol dm^{-3} and coupled this to standard hydrogen electrode.

b)Redox ions

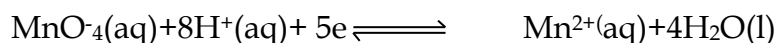
The $\text{Fe}^{2+}/\text{Fe}^{3+}$ system

Iron(ii) ions are easily oxidised to iron(iii) ions and iron(iii) are fairly easily reduced to iron(ii) ions.



To measure the redox potential of this you would simply insert a platinum electrode into a beaker containing a solution containing both iron(ii) and iron(iii) ions of concentration 1.0mol dm^{-3} with respect to both and coupled this to a hydrogen standard electrode.

c)In acidified potassium manganate(vii)



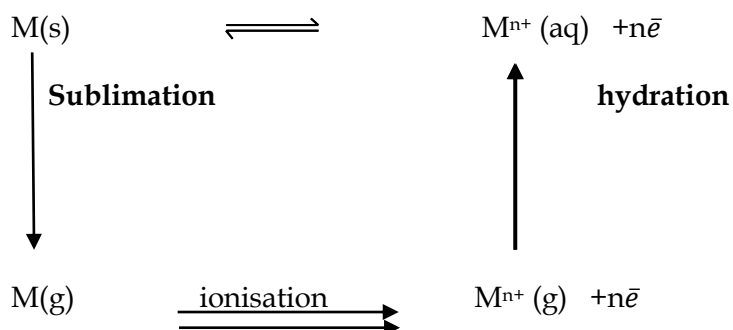
To measure the redox potential of this you would simply insert a platinum electrode in the a beaker containing all the ions MnO_4^- , $\text{H}^+(\text{aq})$ and Mn^{2+} all at 1.0mol dm^{-3}

An updated electrochemical series looks like this

electrode	$E^{\circ}\text{V}$
$\text{Li}^+(\text{aq})/\text{Li}(\text{s})$	-3.04
$\text{K}^+(\text{aq})/\text{K}(\text{s})$	-2.92
$\text{Na}^+(\text{aq})/\text{Na}(\text{s})$	-2.82
$\text{Ca}^{2+}(\text{aq})/\text{Ca}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq})/\text{Mg}(\text{s})$	-2.31
$\text{Al}^{3+}(\text{aq})/\text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$	-0.44
$\text{Pb}^{2+}(\text{aq})/\text{Pb}(\text{s})$	-0.13
$\text{H}^+(\text{aq})/\text{H}_2(\text{s})$	0.00
$\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$	+0.34
$\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$	+0.80
$\text{Au}^{2+}(\text{aq})/\text{Au}(\text{s})$	+1.50
$\text{MnO}_4^-(\text{aq}), \text{H}^+(\text{aq}), \text{Mn}^{2+}(\text{aq})$	+1.52
$\text{F}_2(\text{g})/2\text{F}^-(\text{aq})$	+2.87

Factors which affects the magnitude of standard electrode potential of a metal and hence the overall e.m.f of a cell

The factors are generated from the process that occurs when a metal dipped into solution containing its ions ionises to produce electrons hence generate electrode potential



The value of standard electrode potential depends on the overall enthalpy change which depends on sublimation energy, ionization energy and hydration energy.

Sublimation energy

This is the energy required to convert one mole of a solid metal into one mole of gaseous atom the process is endothermic the higher the sublimation energy, the more positive the electrode potential

Ionization energy

This is the energy required to convert one mole of gaseous atom into one mole of gaseous ions the process is endothermic, the higher the sublimation energy the more positive the electrode potential.

Hydration energy

This the energy liberated when one mole of gaseous ions is complexly surrounded by water molecules the process is exothermic the more negative the hydration energy the more negative the electrode potential.

note

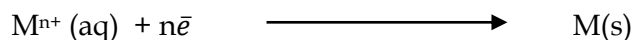
if $\Delta H_{\text{sub}} + IE > \Delta H_{\text{hydration}}$ then E^θ is positive

if $\Delta H_{\text{sub}} + IE < \Delta H_{\text{hydration}}$ then E^θ is negative

if $\Delta_{\text{sub}} + IE = \Delta H_{\text{hydration}}$ then E^θ is zero(only possible for standard hydrogen electrode.

Standard electrode potential and standard free energy change

There is a relationship between electro chemistry and thermo chemistry. In the electrode reaction



If the standard electrode potential is E^θ then the value of the standard free energy change ΔG^θ

At the same temperature is given by $\Delta G^\theta = -nFE^\theta$

Where n is the number of electrons transferred in the electrode reaction

F is the faradays constant

E^θ overall emf of the cell

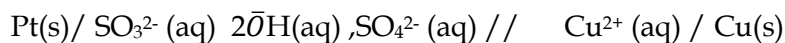
Example

The equation for some half-cell conventions are given below

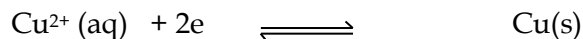
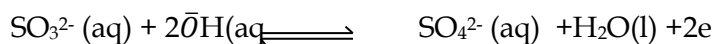


a)write the

i)convention for the combined cells



ii) Overall cell equation



b) calculate the

i) emf of the cell

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = 0.337 - (-0.90) = +1.237\text{V}$$

ii) the maximum work done by the cell

$$\Delta G^\theta = -nFE^\theta$$

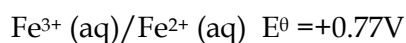
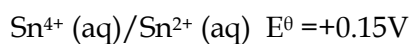
$$= -2 \times 96500 \times 1.237 = -238.741 \text{ kJ mol}^{-1}$$

Application of standard redox potentials

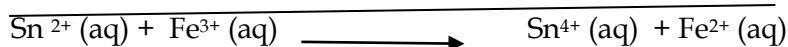
1-Predicting an e.m.f value of a cell

example

Predict the cell reaction and calculate E_{cell} given that



From the size of the E^θ values for the half-cells it is apparent that Fe^{3+} has a greater attraction for electrons than Sn^{4+} , and so Fe^{3+} should be able to take electrons from Sn^{2+} to give Fe^{2+} and Sn^{4+} . This suggests that the half-reaction for tin should be reversed to obtain the actual equation for the process, ie



The cell is therefore written as



$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = 0.77 - 0.15 = +0.62\text{V}$$

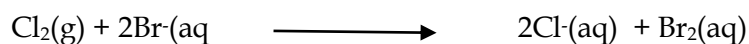
When two electrodes combine to form a cell the value of E^θ for the cell must be positive if the cell reaction is to happen spontaneously.

A redox reaction will go to almost to completion between two redox systems which differ by 0.3v or more in their electrode potentials.

Some reactions which are predicted to be feasible do not always occur this is because kinetic factors may make the reactions so slow that no change can be observed

2-It shows the order of reactivity of elements. The metals decrease in reactivity as the series descends, whilst the reverse is the case for non-metals.

3-It shows which elements can displace each other from solutions of their salts, e.g iron will displace copper from copper (ii) sulphate solution since it is higher up the series similarly; chlorine will displace bromide ions from their solutions:



4-It shows why zinc and aluminium may be used to protect the surface of iron- they are higher up in the series and so will dissolve first.

5-It can be used to predict the products discharged at the electrode during electrolysis but it should be remembered that other factors, such as the nature of the electrodes etc also affects.

b) State whether the reaction is feasible or not give a reason for your answer

Its is feasible because overall emf is positive and standard free energy change is positive

Some standard electrode potentials for metal/metal ion half-cells

Types of emf /voltaic/galvanic cells

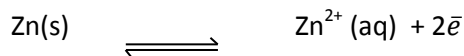
Primary cell

This is a voltaic cell in which the chemical reaction producing emf isn't satisfactory reversible and therefore cannot be recharged by application of a current e.g a Daniel cell, the lechlanche cell (dry cell, a fuel cell.

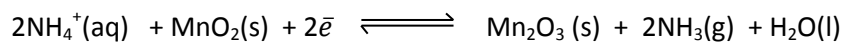
Lechlanche cell

Is made up of zinc container encasing the cell(anode),a graphite rod surrounded by a layer of manganese (iv) oxide(cathode) a mixture of pasted zinc chloride and ammonia chloride in water(electrolyte).

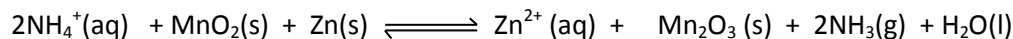
At the anode



At the cathode



Overall



Advantage of a dry cell

- Maintains a stable voltage over a long period of time
- Convenient and portable since its components are pastes which are tightly sealed from the environment.
- Its cheap

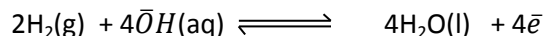
Disadvantage

- Cannot be recharged

Fuel cell

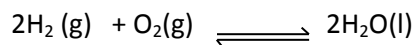
It's a primary cell in which the reactants are continuously replaced as the products are continuously removed the most common fuel cells generate electricity from hydrogen and oxygen using platinum electrodes and a solution in alkali

At the anode



At the cathode

Overall

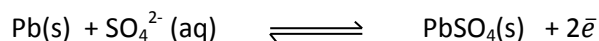


Secondary cells

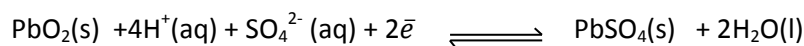
This is a cell that can be recharged by passing electricity through it from the external source

Atypical secondary cell is a lead storage battery or lead accumulator its made up of lead metal as the anode, a grid of lead packed with lead (iv) oxide (cathode) immersed in desirably dilute sulphuric acid as the electrolyte.

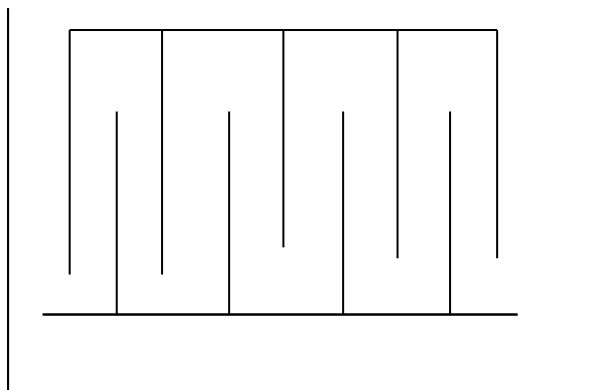
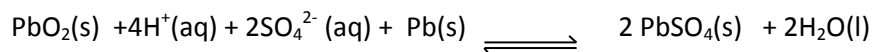
At the anode



At the cathode

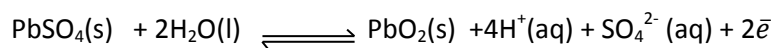
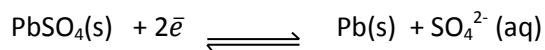


Over all



From the overall equation for the cell reaction if the cell continuously produces current the sulphuric acid gradually gets dilute as the H^+ and SO_4^{2-} ions are used up.

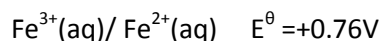
Recharging of the cell connected it to an external source of electricity triggers the reaction.



This produces more hydrogen and sulphate ions which combine to form sulphuric acid.

WORKED OUT QUESTIONS.

1. The standard electrode potential for some standard half cells are shown below

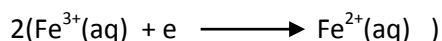


a) write the (i) cell convention for the combined cell



(ii) the equation for the over all reaction

Half equation



Over all equation



b) Calculate the emf of the cell

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = 0.76 - 0.54 = +0.22\text{V}$$

c) State what is observed at each electrode

i) at the anode the colourless solution turns brown

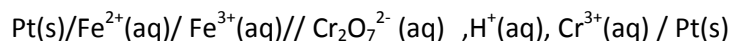
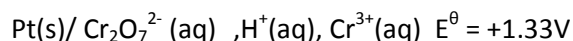
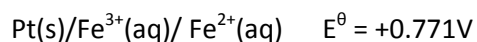
ii) at the cathode the brown solution turns green

2. The standard electrode potential for some standard half cells are shown below

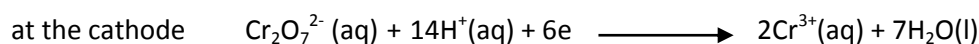
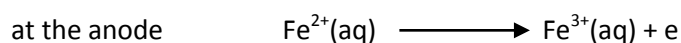
Half cell	E^{\ominus} (V)
$\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})/\text{Pt}(\text{s})$	-0.771
$\text{Cr}^{3+}(\text{aq}), \text{Cr}_2\text{O}_7^{2-}(\text{aq}), \text{H}^{+}(\text{aq})/\text{Pt}(\text{s})$	-1.33

a) write the cell notation for the cell formed when the two half-cells are connected

by convention half cells are written as reduction and more negative as LHS



b) write equation for the half reaction



overall equation

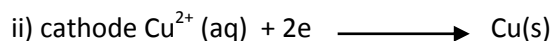
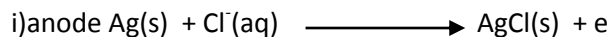


c) Calculate the emf of the cell

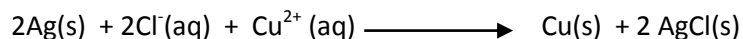
$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = 1.33 - 0.771 = +0.659\text{V}$$

3. The standard electrode potentials for the system $\text{Ag(s)}/\text{AgCl(s)}/\text{Cl}^-(\text{aq})/\text{CuCl}_2(\text{aq})/\text{Cu(s)}$ are +0.223 and +0.340 volts respectively.

a) write the equation for the half-cell reactions that take place at the



b) write the overall equation for the cell reaction



c) Calculate

i) the emf of the cell

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}} = 0.34 - 0.223 = +0.117\text{V}$$

ii) the standard free energy of the cell

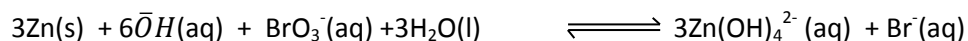
$$\Delta G^\ominus = -nFE^\ominus$$

$$= -2 \times 96500 \times 0.117 = -22.581 \text{ kJ mol}^{-1}$$

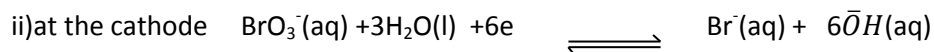
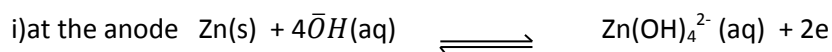
d) state whether the reaction is feasible or not give a reason for your answer

feasible because E_{cell} is positive or because ΔG is negative

4. The equation for some redox reactions are given below



a) write the half cell reaction taking place at each electrode



b) write the cell notation of the cell made by combining the electrode



The table below shows the electrode potentials for some group (i) metals

Electrode	Li^+/Li	Na^+/Na	K^+/K	Rb^+/Rb	Cs^+/Cs
E^\ominus volts	-3.09	-2.71	-2.92	-2.99	

State and explain the trend in variation of standard electrode potential of group (i)

Electrode potentials generally increase from sodium to rubidium

From sodium to rubidium, atomization energy, ionization energy and hydration energy decrease as full energy level is added from one element to the next and as ionic radius increases but both atomization energy and ionization energy decrease more rapidly than hydration energy thus making the electrode potential more negative.

However, the electrode potential of lithium is abnormally high. Lithium has higher sublimation and ionization energy due to its small ionic radius, but due to its high charge density it attracts a pool of water molecules and becomes heavily hydrated which results in abnormally high enthalpy of hydration, this offsets the large enthalpy of sublimation and ionization giving lithium an abnormally high negative value of electrode potential.

end