

PHYSICAL CHEMISTRY

Course outline;

1. Introduction

- Definition of physical chemistry
- Aim of studying chemistry at “A” level
- Nature of matter i.e atoms and molecules.
- Evidence for existence of particles.
- Kinetic theory and Brownian experiments.
- Diffusion of gases.
- Gas density measurements.
- Vector Meyer’s method
- Stiochiometry; empirical formula, molecular formula, using masses and percentage compositions.
- Calculating involving concentration in solutions
- Atomic structure
- Relative atomic mass of elements
- Relative molecular mass and methods of determining RMM
- Colligative properties e.g freezing, depression, evaluation of boiling points

2. Chemical bonding and structures of substances,

- Types of bonding, explanation on each and properties of structures formed by particular types of bonding.
- Types of material substances and their physical properties.

3. Chemical equilibrium

- Basic concepts.
- Homogenous systems of liquids and Calculations for K_c .
- Gaseous equilibrium and K_p .
- The heterogeneous system and K_p .
- Factors affecting equilibrium and lachetelier’s principle.

4. Ionic equilibrium.

4.1 Ionic equilibrium.

- Acidity and alkalinity as properties of a system K_a & P_{ka}
- PH and its calculation.
- PH scale.
- The relationship between K_b and PK_b ; K_w , PK_w and POH

4.2 Buffer solutions.

- Action of alkaline and acid buffer solutions.
- Calculations involved.
- Application of buffer solutions.

4.3 Acidic- base indicators.

- Definition of an indicator and K_{in}
- Action of how an indicator works.
- PH of an indicator.
- Neutrality of an indicator.

- Titration curves for;
- Strong acids - strong bases titration.
- Weak acid and strong base.
- Strong acid and weak base.
- Weak acid and weak base.

4.4 Solubility of salts

- Factors affecting solubility of a salts
- Sparing a soluble salts and solubility products.
- Solubility product, K_{SP}
- Uses of K_{SP} .
- An experiment to determine the solubility products.

4.5 Salt hydrolysis

- Definition of salt hydrolysis.
- K_H and its relationship with K_a & K_w

5. Phase equilibrium.

- Definition of terms e.g a phase, a component, phase diagram. types of component systems;

The 1 component system e.g water, sulphur, CO_2 (g)

The 2 component system e.g for miscible liquids, partly miscible and Immiscible liquids

- Raoult's law and its applications.
- Negative and positive deviations from Raoult's law.
- Steam distillation, definition, principles, experiment to demonstrate it and its calculations.

The 3 component system

(a) Liquid- liquid equilibrium

- Partition distribution
- Condition required for a law
- Its determination
- Application of the distribution law eg in
- Solvent extraction its definition, condition and calculation.
- Investigation of complex ions to determine the coordination number of ligands
- Identification of halides
- Ion exchange

(b) Solid-solid equilibrium

- Existence of solids and liquids in equilibrium
- Eutectic mixture i.e definition and the differences between them and compound.
- Diagram to illustrate Eutectic mixtures and description of the future of them.
- Cooling curves Eutectic mixtures
- Solidification of mixtures of two liquids with compound formation.

6. Chemical kinetics.

- Definitions of terms chemical
- Importance of studying chemical kinetics

- Factors affecting rate of reaction e.g temp. Pressure light, presence of a catalyst.
- Reaction paths for unimolecular and Bimolecular reactions.
- Classification of orders of reactions e.g Zero order, 1st order, 2nd order and 3rd order.
- Experiments to determine orders of reactions
- Methods of determining the rate of reactions e.g by recording time at intervals.
- By recording volume.
- Chemical analysis.
- Recording volume of gaseous product at a certain interval
- Recording a change in mass of gaseous mixture.
- Recording a change in coloured gaseous mixture.
- Recording a change in pressure at intervals during reaction.
- Calculations of chemical kinetics.

7. Thermo chemistry.

- Definition of term of thermo chemistry.
- Endothermic and exothermic reaction.
- Explanation in energy change that occur during chemical reaction.
- Factors affecting the heat evolved during chemical, enthalpy, definition, standard enthalpy and their notations
- Types of enthalpies of a reaction, formation, combustion, Neutralization, atomization, solution, displacement, Evaporation, fusion, hydration and sublimation.
- Experiment determining enthalpy of combustion of solid eg carbon, a liquid eg ethanol.
- Experiment to determine enthalpy of neutralization
- Experiment to determine enthalpy of solution
- Hess's law and born energy cycle
- Determination of standard enthalpy by cancellation method
- Estimate of enthalpy changes bond energy
- Direct determination of enthalpy changes in reaction from bond energy
- Stability of compounds
- Electron of affinity, atomization energy, ionization energy, lattice energy and their applications in born Haber cycle.
- Factors affecting lattice energy
- Energy diagram for the formation of ionic and calculations involved
- Standard enthalpy solution and hydration, definition and energy diagrams to illustrate them and calc. involved
- Calculation of energy changes using anhydrous and hydrated compound.
- Enthalpy of precipitation, definition experiment using silver nitrate and calculation involved.

8. Electro chemistry.

- Definitions of terms e.g non conductors, conductors, electrolytes, resistance, resistivity, electrolytic conduction
- Factors affecting conductivity of an electrolyte.

- Measurement of conductance.
- Molar conductivity.
- Effect of concentration on molar conductivity.
- Molar conductivity at infinite zero.
- Ionic mobility and Kohlrausch's law and calculations involved.
- De of a weak acid in term of conduct metric titrations and curves
- Electro chemical cells.
- Reduction and oxidation in terms of electronic transfer
- Electrode potential
- Absolute and relative electrode potential.
- An experiment to measure the standard electrode potential of an electrode.
- Cell diagram, notation and calculations for e.m.f
- Electrolysis of aqueous solutions e.g acidified water NaOH, CuSO₄, NaCl, PbBr₂, CuCl, NaCl, NaBr etc.
- Faraday's laws and calculations.
- Applications electrolysis e.g corrosion of iron, electro plating, extraction of metals, manufacture of sodium hydroxide solution.

Aims of the studying chemistry at "A" level.

- It helps students to appreciate the use and importance of chemistry in daily life.
- To teach students argue from the observed (qualitative aspects) and to adopt quantitative and approve to chemical problems.
- To help students develop the necessary intellectual and manipulative skills to solve practical chemistry problems
- To enable students to obtain and utilize the relevant chemical information necessary for understanding to world around them.
- Help students to appreciate applicability of chemistry to other disciplines.
- To help students develop an initiative for inventiveness.
- To help the students to develop interest in and careful environment.

MATTER

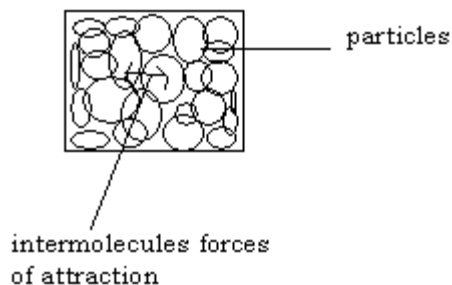
This is any material substance which occupies space and has mass. Matter exists in three states i.e solid, liquid and gaseous state. These 3 states of matter are interconvertible depending on the prevailing physical conditions i.e pressure and temperature.

Simple kinetic theory of matter.

Kinetic theory is the theory that was put forward to explain the behavior of particles in the 3 states of matter and the way this behavior of particles gives matter particular physical properties.

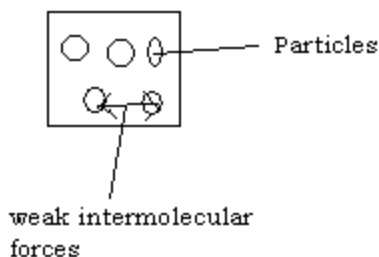
Behavior of particles in solids.

In solids particles are very closed packed together with strong inter molecular forces of attraction. These forces make particles stationary at fixed position within the bulk. The particles only oscillate about their main position when the temperature of the solid is raised. However if the temperature is increased to a higher level the intermolecular forces break up and a solid changes to liquid at its melting point.



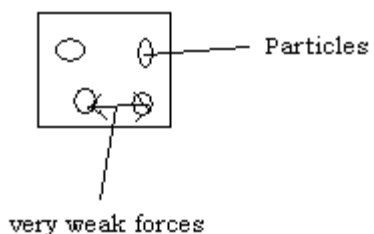
Behavior of particles in liquids.

In liquid, the particles are far apart with weak forces of attraction, they are therefore free to move from 1 point to another within the bulk of the liquid. When liquids temp increase they gain kinetic energy move faster with higher velocities. When the temperature the system is lowered, the liquid cooled down and the vapour condenses back to liquid in the process called condensation.



In Gases.

The particles are very far apart with very weak inter molecular forces between them. The gas particles move almost independent of one another and tend to move faster than those in liquid. When the temperature of a gas increased the particles move even faster but they tend to collide with one another.



Fundamental differences between all the three states of matter.

Solid	Liquid	Gas
High density	Moderate density	Low density

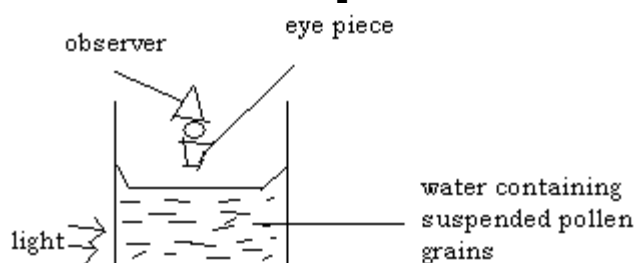
Definite shape	No definite shape	No definite shape
Definite volume	Takes up the volume of the container	No volume
Strong forces of attraction	Weak forces	Very weak forces

Evidence for existence of particles in matter

Matter is known to be made of particles hence the phrase particulate nature of matter. The particulation nature of matter is deduced from experiments such as random or Brownian motion, diffusion.

Brown motion experiments.

Random motion in liquids



Method

Pollen grains suspended in water and observed under a microscope

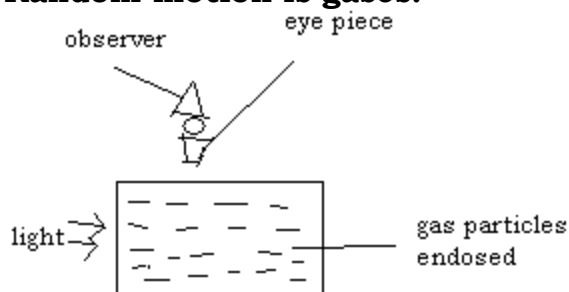
Observe.

Yellow particles are seen moving around randomly

Conclusion

Yellow particles move randomly because were colliding with water particles which were moving randomly because liquid particles show random motion.

Random motion in gases.



Method

White smoke from burning paper is enclosed in smoke cell and observed under a microscope.

Observation

The white specks are seen moving about randomly

Conclusion

Gases exhibit random motion.

What is observed when a smoke cell is cooled or its temperature is raised?

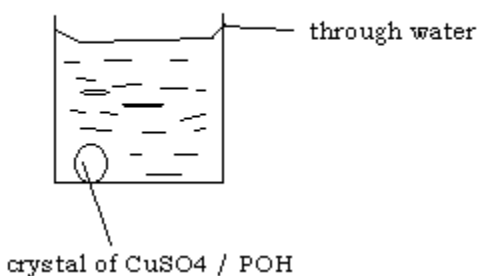
The speed at which the white specks move reduces due to loss of kinetic energy. On the other hand when the temperature of smoke cell is increased the speed with which the particles move increases because kinetic energy of particles would have increased.

Note; Brownian motion or random motion is disorganized motion exhibited by solid particles suspended in gases or liquid.

Diffusion

Is the movement of particles from where they are more concentrated to where they are less concentrated along a concentration gradient.

Diffusion in liquids



Method

A crystal of CuSO_4 is dropped in water in a trough

Observation

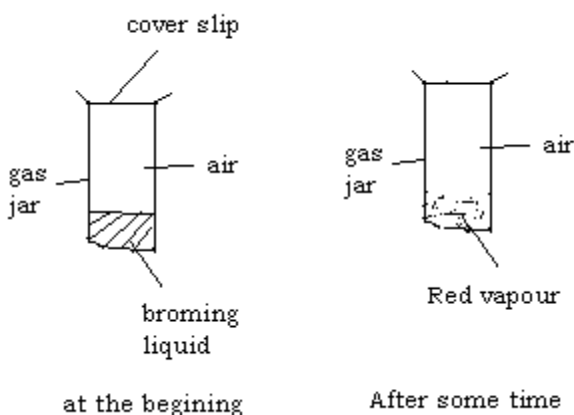
- The crystal sinks in the water in the trough.
- The crystal sinks and dissolves producing one solution at the base of the trough.
- The blue colour migrates upward in the trough and after some period of time, the entire mixture appears uniformly blue in colour.

Conclusion

- Water / liquid allow diffusion to occur
- CuSO_4 crystal dissolved in H_2O because the H_2O molecules were colliding with the crystals.
- Blue colour dispersed in the trough by diffusion because the blue coloured particles were in continuous collision with randomly moving water molecules hence diffusion results from collision between the particles.
- The mixture became uniformly blue in colour because the rate of downward diffusion of the same ion had reached equilibrium so even diffusion continues to occur the colour of the mixture will not change.

Diffusion in gases

Example



Method

Liquid bromine is poured in glass jar full of air covered with cover lip.

Observation

- Bromine vaporizes giving a red vapour
- The red vapour slowly but steadily disperses in a gas jar
- At the beginning the red vapour is concentrated at the bottom of a gas jar but after some time, the mixture inside the gas jar becomes uniformly red in colour.

Conclusion

Diffusion takes place in gases. Dispersal of the red vapour from the bottom to the top of gas jar resulted from random collision between air and bromine which consists of particles. The mixture inside the gas jar becomes uniformly red in colour when the rate of diffusion of bromine in all directions reached an equilibrium.

GAS LAWS

Kinetic theory of gases is the theory that was put forward to explain the behavior of molecules in gases.

Properties of gases.

- Gases are compressible
- The gas has low densities
- They diffuse rapidly
- They expand on heating and contract on cooling
- Most gases are colourless
- They show a large change in volume when change in pressure.

Assumptions made.

- Gases are made up of tiny particles called molecules.
- Molecules are in state of rapid and random motion.
- A molecule undergoes elastic collision with one another.
- Their kinetic energy is directly proportional to absolute temperature and independent on the nature of the gas.
- When the molecules collide with one another the pressure of the gas increases.

The gas laws include, pressure law, Boyle's law, Charles law, Avogadro's law, Dalton's law of partial pressure.

BOYLE'S LAW

It states that the volume of fixed mass of a gas is inversely proportional to its pressure at constant temperature mathematically, Boyle's law can be.

$$V \propto \frac{1}{P} \quad \text{(i)}$$

$$V = \frac{k}{P} \quad \text{(ii)}$$

$$PV = k \quad \text{(iii)}$$

If the gas of volume V_1 at pressure P_1 . If its pressure is changed to P_2 the volume also changed to V_2 and therefore

$$V_1P_1 = V_2P_2.$$

Examples.

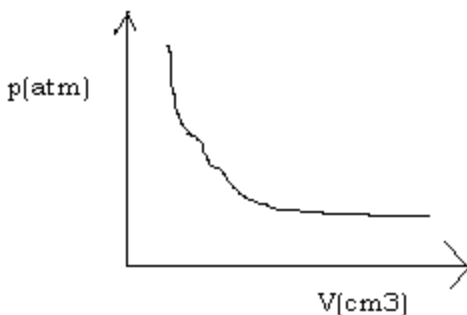
1. The volume of fixed mass of a gas of pressure of 4 atmospheres is 200cm^3 . Calculate volume at the pressure of 1.25 at 4 atm0sphere.

$$\text{From } V_1P_1 = V_2P_2$$

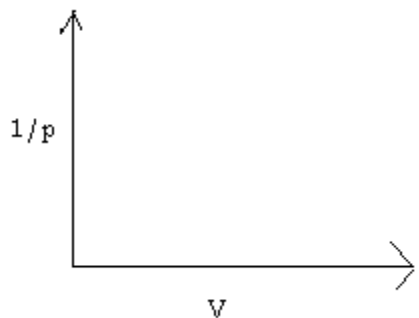
$$=$$

$$V_2 = 640\text{cm}^3$$

Graphical representation of Boyle's law



If $\frac{1}{P}$ is plotted against V a straight line graph is given out.



CHARLES LAW

It states that the volume of a fixed mass of a gas is directly proportional to its absolute temperature at constant pressure mathematically the law is pressed as follows.

$$V \propto T \quad \text{(i)}$$

$$V = KT \quad \text{(ii)}$$

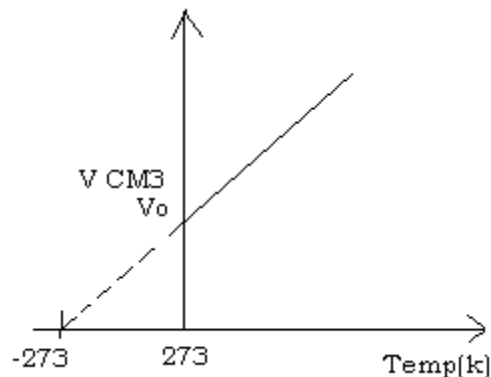
$$= K \quad \text{(iii)}$$

For the gas of volume V_1 and T_1 . If its temperature is changed to T_2 and the V_2 and the expression becomes.

$$V_1 T_1 = V_2 T_2$$

=

Graphically, Charles's law is expressed as follow



The dotted line is theoretical expressions of Charles's law since any temperature than 0°C cause the gas to undergo. The volume of a fixed mass of a gas at 25°C is 100cm^3 . Calculate its volume at 10°C .

From $V_1 T_1 = V_2 T_2$

$$100 \times 25 = V_2 \times 10$$

=

$$V_2 = 250\text{CM}^3$$

PRESSURE LAW (Gay lussac's)

It states that the pressure of a fixed mass of a gas is directly proportional to its temperature at a constant volume. Mathematically it is expressed as follows;

$$P \propto T \text{ -----(i)}$$

$$P = KT \text{ -----(ii)}$$

$$= K \text{ -----(iii)}$$

For a given gas of pressure P_1 at temperature T_1 if its temperature changes to T_2 even the pressure changes to P_2 . The expression therefore becomes.

=

The equation of state

When Charles' law and Boyle's law are combined the following equation of state is formed.

=

Ideal gas equation

An ideal gas is the gas whose qualities are borne is the kinetic theory of gases.

When the Charles's law, Boyle's and Gay are combined they give a simple equation representing the relationship between pressure, volume and absolute temperature o f a gas is given by;

= K therefore $PV = nRT$ where P = pressure of the gas, V - volume of a gas and R is the gas constant and T - absolute temperature n = number of moles of the gas. The value of R can be calculated as

$R =$

For 1 mole of a gas at STP, $P = 1.0132 \times 10^5 \text{ Nm}^3$, $V = 22.4 \times 10^{-3} \text{ m}^3$, $T = 273$, $n=1$

$R =$

$R =$

$R = 8.3145 \text{ K}^{-1} \text{ mole}^{-1} / \text{NM}^{-1} \text{K}^{-1} \text{ mole}$ **OR** $R = 0.082 \text{ litres Atm}^{-1} \text{K}^{-1} \text{ mole}$

ie if the pressure is given in Atm and the volume in litre.

Dalton's law of gases

It states the total pressure exerted by a mixture of non reactive gases is the sum of component gases at constant temperature. For a mixture of 2 gases A and B in an increased system there total pressure is given by the expression $P_T = P_A + P_B$ where;

P_T – is the total pressure

P_A – is the partial pressure of gas A

P_B – is the partial pressure of gas B

Partial pressure

Is the pressure that gas exerts when allowed to occupy the entire volume of the space of the ex.

Partial pressure for gas A is given by the expression; $P_A = X_A \cdot P$ where P_A is the partial pressure.

X_A is the mole fraction of gas A

P is the pressure exerted by pure gas A

The partial pressure for B is given by $P_B = X_B \cdot P$ where P_B is the partial pressure of B.

X_B – is the mole fraction of gas B

P – is the pressure exerted by the pure gas B.

Mole fraction.

Is the simple number of moles of a substance in the mixture divided by the total number of mole of all moles in the mixture.

X_A = also the mole fraction of B

X_B =

Avogadro's law

It states that as constant temperature and pressure equal volumes of gases contain the same number of particles.

Avogadro's number N_A is the number of 1 mole of particles and therefore it is given by; $N_A = 6.02 \times 10^{23}$

1. Calculate the pressure exerted by mixing 5 moles of hydrogen and 2 moles of neon ($P^\circ_{\text{Ne}} = 200 \text{ mmHg}$, $P^\circ_{\text{H}_2} = 100 \text{ mmHg}$).
2. A mixture was formed by cooling 43g of hexene C_6H_{14} and 10g Heptene (C_7H_{16}). The partial pressure exerted Hexene and Heptane respectively is 50KN and 45KM.
 - (a) Determine the vapour pressure of the above mixture
 - (b) Determine the composition of distillate formed if the vapour in (a) is condensed.
3. State the Gay Lussac's laws of combining volume. If 20 cm^3 of H_2 react with 10 cm^3 of O_2 to produce 20 cm^3 of steam. The deduce the formula of steam.

4. (a) 40cm^3 of a nitrogen hydride (N_xH_y). Deduce the molar mass of Nitrogen hydride.

(b) State the assumption made

5. 15cm^3 of H_2 a gaseous hydro carbon are burnt completely in O_2 to form 90cm^3 of carbondioxide and 105cm^3 of steam. Determine the molecular formular of a hydro carbon and the volume of O_2 used.

6. Prove that the fraction of the total pressure exerted by 1 gas mixtures is equal to the fraction of the total no of moles provided by the component.

7 4dm^3 of O_2 at a pressure of 200KPa and 1 dm^3 of N_2 at a pressure of 200KPa are introduced in a 2 dm^3 vessels. What is the total pressure in the vessel.

8. A mixture of gases at stp contains 65% N_2 , 15% CO_2 amd 20% O_2 . What is the partial pressure of each gas in Kpa (standard pressure = $1\text{ atm} = 101.325\text{ Kpa}$)

9. The partial pressures of a compound of a mixture of gases are 26.64 Kpa for O_2 , 34KPa for N_2 , 42.6 Kp of H_2 . Find the percentages of the Vol of O_2 in the mixture.

(b) What is the fraction of O_2

Solutions

$$1. P_T = P_H + P_{\text{Ne}}$$

$$P_H =$$

$$X_{\text{Ne}} =$$

$$P_H = x \cdot 100 =$$

$$P_{\text{Ne}} = x \cdot 200 =$$

$$P_T = + =$$

$$= 128.5\text{mmHg}$$

$$2. \text{C}_6\text{H}_{14} = (12 \times 6) + 14 = 86$$

86g of C_6H_{14} occupy 1 mole

43g of C_6H_{14} occupy = 0.5 moles

$$\text{C}_7\text{H}_{16} = (12 \times 7) + 16 = 100\text{g}$$

100g of C_7H_{16} occupy 1 mole

10g of C_7H_{16} occupy = 0.1 moles

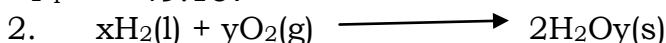
$$0.1 + 0.5 = 0.6 \text{ moles}$$

$$X_{\text{C}_6} = X_{\text{C}_7} =$$

$$P_{\text{C}_6} = x \cdot 50 = 41.667$$

$$P_{\text{C}_7} = x \cdot 45 = 7.5$$

$$P_T = = 49.167$$



$$20 : 10 \quad : \quad 20$$

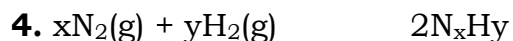
$$2 : 1 \quad : \quad 2$$

X moles of H_2 reactions with y of oxygen to produce 2 moles of steam

2 moles of H_2 reacts with 1 moles of O_2 to produce 1 mole of steam.

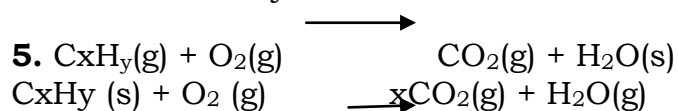
$$X = 2, y = 1$$

Therefore formula of steam = H_2O



$$40 \quad : \quad 40 \quad \longrightarrow \quad 40$$

$1 : 1 : 1$
 X moles of N_2 reacts with y moles of H_2O to produce 2 moles of N_xH_y
 1 mole of N_2 reacts with 1 mole of H_2 to produce
 1 mole of N_xH_y . $X = 1$ $y = 1$
 Molar mass of $NH = 14 + 1 = 15$
 N_2H_2
 Therefore $X = 2$ $y = 2$



Let the volume of O_2 be Zt

In terms of volume $15cm^3$: t : $90cm : 10 cm$

Reaction rate 1 6 7

From the equation 1 mole of C_xH_y reacts with $x + y$ of O_2 to give x moles of CO_2 and y moles of water. For volume 1 mole of C_xH_y reacts with moles of O_2 to give 6 moles of CO_2 and 7 moles of H_2O is $= y = 4$ $x = 6$.

Therefore molecular formula = C_6H_4

=

= 38

1 volume of C_xH_y react with $(x + y)$ volume of O_2

15 volume of C_xH_y reacts with $(x + y) \times 15$ O_2

$(x + y) \times 15$ cm^3 of O_2

7. $O_2 = 32$ $N = 14$

If 36 moles of O_2 contains 1 mole

Therefore 4 cm^3 of O_2 will contain () moles

If 14 moles of N_2 contains 1 mole

Therefore 1 dm^3 of N_2 will contain () moles

$XO_2 = 0.111$ $XN_2 = 0.71$

() = =

= 0.61

8. N_2 CO_2 O_2

6.8 1 1.8

$P_{N_2} = x \times 101.325$

$PCO_2 = x \times 101.325$

= 20.3Kpa

9(a) O_2	N_2	H_2
26.64	34	42.66
$\times 100$	$\times 100$	$\times 100$
25.8%	32.9	41.3

(b) O_2 N_2 H_2

1 1.28 1.60
=

Mole fraction of O_2 =

Ideal gases.

These are which obey the gas laws and ideal gas equation

Assumptions on ideal gases.

- Gas particles do not exert any inter molecular forces of attraction/repulsion between them.
- Particles execute perfectly elastic collision between them and with the walls of the container.
- Pressure entirely results from bombardment of the particles with the walls of the container
- Particles are main points and occupy a negligible volume of the container.

However, the ideal gases are rear in nature and most of the gases encountered are non ideal.

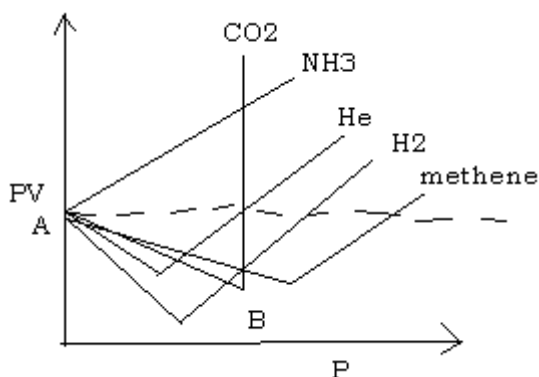
Non ideal gases/ real gases.

These are gases which don't obey the gas laws and equations expectedly.

Assumption made for non ideal gases.

- Gas particles exert any inter molecular forces of attraction/repulsion between them.
- Particles occupy a particular volume compared to total volume.
- Real gas may not execute elastic collision
- Pressure exerted by the real gas may not be accounted by the mean collision between them and walls of the container.

They show ideality or ideal condition as shown on the graph below.



For an ideal gas, plot of PV verse P gives a straight line graph parallel to axis but none of those gases give such behavior.

At low pressure, the gases tend to behave ideally and at such a low pressure the molecules are very far apart so that the intermolecular forces of attraction are not exerted in them.

The volume of the container is also very large such that the volume occupied by the gaseous molecules is negligible.

Hydrogen and Helium tend to approximate ideality because of their low molecules masses.

Ammonia and CO_2 show bigger deviation from ideal behavior because increased the magnitude of the van der waals forces. At first as pressure increases there is a fall in curve of both ammonia and CO_2 and later as pressure increase the curve raise. This is because at low pressure molecular attraction over weighs the molecular volume causing a reduction in pressure on the walls of container hence the value of p in the expression of Pv reduces causing a fall in curves of NH_3 and CO_2 .

At very high pressure the molecular volume over weighs the intermolecular force of attraction. At such high pressure the volume of the container is greatly reduced and the gas molecules tend to occupy the significant volume. Therefore and product of PV also increases. H_2 and He have low inter molecules is not significant but the only significant factor is not significant but the only significant factor is hence there is no fall in the value of p but there is a raise in the value of V in the PV as pressure increases causing a continuous raise in the curve of H_2 and He. The value PV is called compressibility factor and measure the deviation from ideal behavior.

Van der waals real gas equation.

A real gas occupies a significant volume in relation to the volume of a container. Consider a large vessel of volume, $V\text{cm}^3$. If the volume occupied by a particular molecular is 6 cm^3 the volume where other molecules can move or the compressible part is $(V-b)\text{ cm}^3$ if there is any number of molecule of the real gas in the container, then the volume becomes $(V- nb)\text{cm}^3$. Therefore from the expression

$$Pv = nRT$$

$$\text{But } V = (v-nb)$$

$$P(V-nb) = nRT.$$

A real gas has inter molecular forces of attraction causing the pressure reduction. Van der waal consider 2 molecules 1 in the interior of the container and the other around the wall. These molecules are by a sphere of other molecules surrounding them.

The pressure reduction is concentration of molecules the wall \times ie concentration of molecules in the interior of the container.

Pressure reduction -

The actual pressure would be;

$$P +$$

From the expression $PV = nRT$, it becomes $(P +) (v-nb) = nRT$.

It becomes $(P +) (V-nb) = nRT$

P - is the pressure

a -is a constant

n - is the volume of the container

b - is the actual volume of the real gas

$v-b$ - vol of free space in the container with one mole of gas molecular.

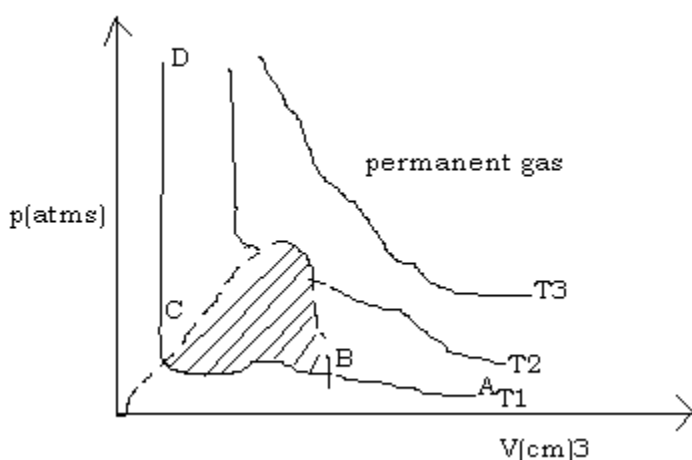
$v-nb$ = vol of free space with give number of moles

- a factor of collection of deviation in a vol exerted by the gas when attractive forces become significant.

LIQUEFACTION / CONDENSATION OF GASES.

At high temperature, CO_2 exists as gas because the molecules have very high kinetic energy which can overcome the intermolecular forces of attraction and the gas obeys Boyle's law exactly. At low temperature the kinetic energy reduces and the molecules of a gas move together and eventually liquefy. Therefore at low temperature the gas may no longer obey the Boyle's law.

The shaded region is significant in that CO_2 does not obey Boyle's law. The vapour remains in equilibrium with the liquid and this state happens when a certain temperature called **critical temperature** is applied.



Taking the curve ABCD, between A & B CO_2 is a gas. A decrease in volume causes an increase in pressure in accordance with Boyle's law. At point B CO_2 begins to liquefy, along BC there is a sharp decrease in vol. with no change in pressure showing that liquids do not exert pressure. At point C liquefaction is complete and all CO_2 will have change to a liquid. when the pressure is increased at constant volume the liquid carbondixde changes to solid cardixide i.e solidification occurs as shown along CD,. The shaded region shows that the liquid and vapour or gas phases are in equilibrium.

Methods used to liquefy gases.

1. Lowering the temperature to the value below critical temperature.
2. Increasing pressure forcing the molecules to come closer.
3. Simultaneous lowering of temperature and increasing the pressure.

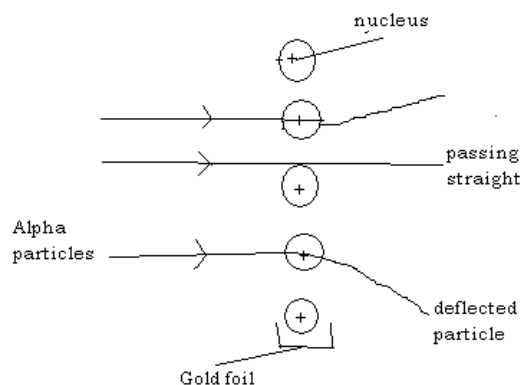
Atomic structure.

An atom is the smallest particle of matter that can take part in chemical reaction. Atoms consist of the fundamental particles and these include, protons, electrons and neutrons. The protons and neutrons are found in the nucleus of an atom while the electrons are found in energy levels.

Distribution of fundamental particles of an atom.

Protons

When alpha particles were subject to a gold foil most passed through unaffected but a few were deflected in various directions. Alpha particles were thought to be highly energetic with a high penetrating power and could penetrate several mm thick of a concrete. Their deflection led to a conc that since Alpha P. are truly charged they were coming close to the centre of the atom which is also truly charge. Since only the small fraction war deflected them the centre of the atoms is very small compared to the entire size of the atom. Since protons are positively charged, they should be in the centre or nucleus of an atom. Since most of the alpha p passed through then the space outside the nucleus is occupied by the negatively charged electrons rotating with in orbitals.



(b) Neutrons

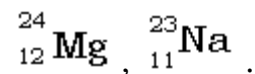
Mostly conducted series of experiments by weighing different atoms of different elements and found out that atomic masses are greater than the mass of protons and electron. To make up for exerted mass, the existence of masses was to prostituteate because since the proton mass that is concentrated in the nucleus and they have the same mass as protons with few variations. The nucleus was therefore found to contain protons and neutrons. The number of protons is called proton number/ neutron combine and make up the nucleon number or atomic mass / mass number.

Comparison in properties between protons, Neutrons and Electrons.

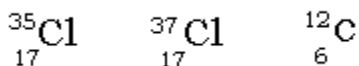
Properties	Protons	Electrons	Neutrons
Mass	1		1
Charge	Positive	Negative	No charge.
Deflection by Electric field.	by negative plate.	by positive plate.	No deflection.

Nuclides and isotopes.

A nuclide is any atom with a specific number of neutron and protons e.g



Isotopes there are different atoms of the same element with the same atomic number but if this mass number. Or are atoms of the same number of electrons and protons but of different electrons e.g



Since the chemical properties are determined by the number of electrons which are the same of in all isotopes. Therefore isotopes have got the same chemical properties. In order to evidence the existence of isotopes in atoms a mass spectrometer is used to detect the various isotopes on a mass spectrometer shown on a screen of recorder.

Radioactivity and nuclear structure.

Radioactivity is the spontaneous disintegration of unstable atoms of an element by giving new stable and fresh nuclides with emission of either alpha particles, Beta or Gamma rays. The element which disintegrates is said to be a radioactive element.

Properties of a radioactive elements

They are very unstable and disintegrate to give new nuclides. They emit rays or particles on disintegration such particles are alpha and Beta particles while the rays are Gamma. Radioactivity substances affect photographic materials due to them. When they disintegrate they release a lot of heat energy.

Results of radioactivity changes during radio.

Alpha particles

- These are Helium particles
- They are deflected by magnetic and electric field in direction showing that they are positively charged
- They are identified as He particles (${}^4_2\text{He}$) having a mass number of 4 and atomic no. 2
- They move with a very high velocity of about $\frac{1}{10}$ of light.

Beta particles

- These are negatively charged particles
- They can also be deflected by magnetic and electric field
- They are identified as fast moving electrons similar to cathode rays
- They have no mass number but have a charge of -1
- They penetrate more than Alpha particles and have the high velocity.
- They are presented as ${}^0_{-1}\text{e}$

Gamma rays

- These are neutral particles and are never deflected by either magnetic or electric field.
- They are electromagnetic radiation similar to x-rays
- They have no charge
- They do not have any mass
- They have a high penetrating power with greater velocity

Detection of radiation.

Use of photographic film

The radiation destroys them

- They cause surfaces for some substances to glow e.g if Beta particles which are fast moving part strike surfaces they cause it to glow.
- They also cause ionization of air molecules e.g when the fast moving electron of Beta collide with air molecule the knock off leaving charged ions.

Radioactive decay equation/reactions

(a) Alpha decay.

- An alpha particles is a Helium nucleus with a mass of 4 and atomic number 2.
- The loss of alpha particles results in reduction in mass number by 4 units and atomic no by 2 units. When an element undergoes alpha decay it produces a new element whose position is 2 places earlier.
- Most of the radioactive isotopes of element with atomic no. greater than 83 undergo alpha decay.

(b) Beta decay.

- Loss of beta particles results in increase of atomic number by one but the mass number remains the same.
- A Beta particle is a fast moving electron with no mass but a charge of -1.
- Beta decays also occurs in isotopes having atomic number over 83.
- The overall effect of Beta decay is to produce an element one place later in the periodic table.

(c) Emission of gamma rays.

- These are fast electromagnetic radiations.
- They have no mass when they are being emit there is no loss in mass or change in atomic number.

Complete the following Nuclear Reactions.

Difference radioactive reactions and ordinary

- Radioactivity reaction are affected by physical factors e.g pressure, temperature etc while chemical reactions are not affected by them.
- Radioactive reactions involve the nucleus which splits to give flesh nuclides while chemical reactions involve valence shell electrons.
- In nuclear reactions a lot of heat is given off while in chemical reactions give less heat.

Stability of the nucleus

This is a measure or an extent by which it remains dissociated and depends on neutron to proton ratio (n/p ratio) together with bonding energy. The nucleus contains protons and neutrons forming a nucleon. The protons are positively charged and continuously repelling each other with in the nucleus but they never split the nucleus and the nuclide remain stable. In forming the nucleus there is a loss in mass such that the sum of neutrons and protons mass is greater than the mass of the nucleus. The loss in mass is called mass defect which is converted into energy according to the following equation.

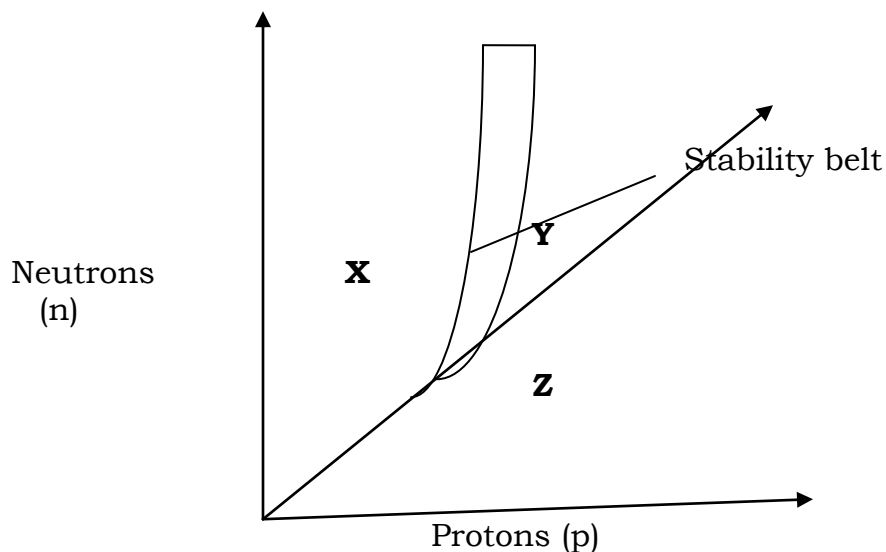
$E = mc^2$ where M is mass, C is velocity of light and E is energy. This energy is called binding energy and it keeps the protons and neutron together hence preventing the nucleus from splitting. The nucleus is said to be stable if it does not undergo radioactive and so does not emit radiation. The nucleus has a very long half time if it is to decay stable nuclei have low atomic numbers usually less than 20 and they have equal number of neutrons and protons such that the ratio $= 1$.

The nucleus is said to be unstable if it is radioactive and emits radiation and particles forming a stable nuclei. For unstable nucleus the half time is very short ranging from fractions, seconds or minutes to a few hours. They have a very high atomic number and the number of neutrons is not equal to the number of protons i.e

$$\neq 1$$

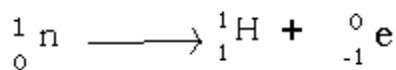
Heavy nuclei with atomic number between 21- 83 are unstable and undergo beta particle emission to form stable nuclei. Heavy nuclei with atomic number greater than 83 are equally unstable and they undergo alpha particle emission and to give stable nuclei.

A plot of neutron-proton number for stable and unstable nuclides.



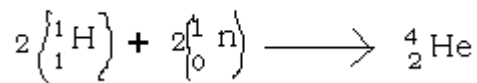
From the graph above all stable nuclides lie in the region which is shaded. Isotopes X, Y and Z are unstable and they can become stable by approaching the stability belt. X has no excess neutrons with few protons. To approach the stability belt it reduces on the number of neutrons and excess on the no of proton.

The neutron splits into an electron and a proton

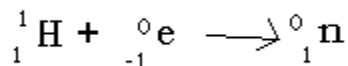


This reduces on the number of neutrons but increases the number of protons. The electron produced as a beta particle in a process called beta particle

emission. Nuclide Y has an excess of protons and neutrons which combine to form alpha particles



This reduces both protons and neutrons in alpha particles emitted. Z has an excess of neutrons and protons. To attain stability it reduces on the number of protons in its nucleus but increasing the number of neutrons. It does this through capturing an electron and liberating a neutron.



Laws of radioactivity.

1. Radioactive nuclides disintegrates spontaneously giving new and fresh element
2. The disintegration of an element is as a result of either emission of an alpha particle or Beta or Gamma rays.
3. The rate of disintegration of a nuclides not affected by physical factors e.g concentration, temperature, pressure etc
4. The rate of disintegration of an element depend on the initial amount it present at time (t).

Decay law

It states that the rate of decay is directly proportional to the number of un decayed atom or un decayed mass of a given sample of an element.

Ie Rate of decay un decayed atoms

$$Nt \text{ -----(1)}$$

$$Nt \text{ -----(2)}$$

Where x is decay constant

$$- = xdt$$

Integration

$$- = x$$

$$\ln Nt = \lambda t + c \text{ -----(3)}$$

$$\text{If } t = 0, \lambda t = N_0 = C$$

Substituting in equation (3) we get

$$\ln Nt = \lambda t - \ln N_0$$

$$\ln Nt + \ln N_0 = \lambda t$$

$$\text{Therefore } () = \lambda t \text{ -----(3)}$$

In term of logarithms to base ten

$$\text{From } \ln () = \lambda t$$

$$() = e$$

Taking log₁₀ on either sides

$$\log_{10} () = \log_{10} e^{\lambda t}$$

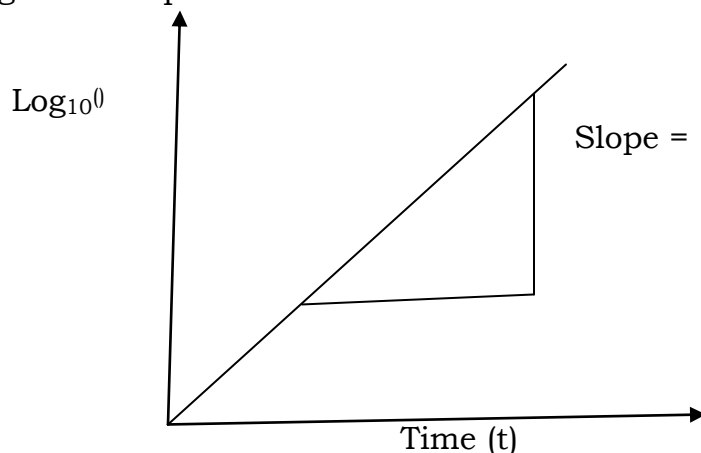
$$\log_{10} () = \lambda t \times$$

$$\log_{10} () =$$

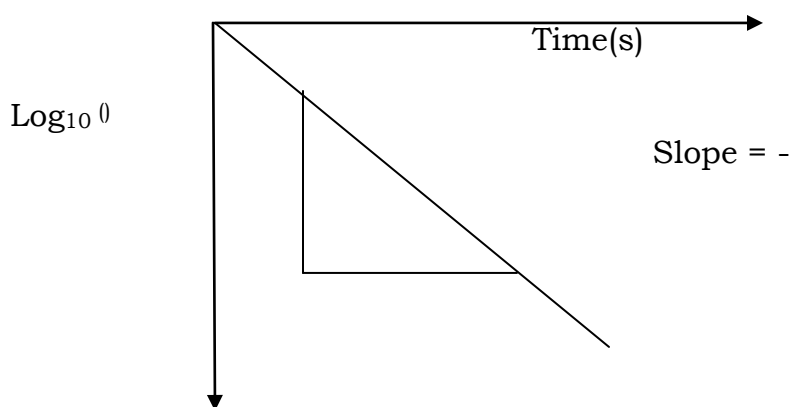
$$\log_{10} x \log_{10} () = \lambda t$$

$$2.303 \log_{10} () \lambda t$$

If a graph of $\log_{10} ()$ is plotted against time, a straight line from the origin is obtained with a positive gradient equal to λ as shown below.



However when a graph of $()$ is plotted against time, a straight line graph from the origin but with a negative gradient is obtained as shown below



Deriving an expression for half **life**.

Half life is the time taken for half of the initial amount of a substance to disintegrate to and remains constant regardless of the initial amount.

$$\ln () = \lambda t$$

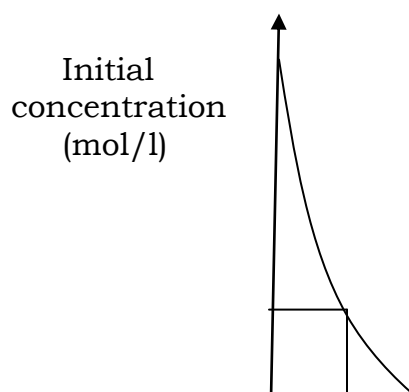
$$\text{If } t = t_{1/2}, N_0 = \frac{1}{2} N_0$$

$$\ln () = \lambda t_{1/2}$$

$$\ln () = \lambda t_{1/2}$$

$$\ln 2 = \lambda t_{1/2}, \quad t_{1/2} =$$

If a graph of initial mass/ concentration is plotted against time, a curve which does not pass through the origin is obtained and the half life of the given sample can be determined.



Time(s)

Examples.

1. A compound W was found to contain a radioactive X which emits alpha particles and has half life of 5720 years. Calculate the % of X that would remain w after 228800 years.

Solution.

$$t_{1/2} = 5720 \text{ years.}$$

$$t = 22880 \text{ years.}$$

$$N_0 = 100\%$$

$$N_t = ?$$

$$= 2$$

$$=$$

$$N_t = 6.25\%$$

2. (a) Define the term radio activity.

- *Radio activity refers to the spontaneous disintegration of an unstable nucleus to form a stable nucleus with emission of radiation like alpha, beta gamma rays.*

(b) Name three types of radiation emitted during radioactivity. State how they affected by nucleus of the radio isotope.

- Alpha particles
- **Effects;** when the nucleus emits an alpha particle, it loses 2 electrons and 4 neutrons hence decreases the atomic number by 2 units and the mass number by 4 units and it is converted to another element of a lower atomic number by 2 units.
- Beta particles.
- **Effects;** the atomic number increases by 1 unit but the mass number remains the same; the atom is converted to another with a higher atomic number by 1 unit.
- Gamma rays.
- **Effects;** the emission of gamma rays by the atom does not affect the atomic number and mass number but only energy is given out.

(c) The table below shows the mass of protactinium ${}^{234}_{91}\text{Pa}$ varies with time.

Mass of Pa	60.0	38.5	26.0	17.2	11.1
Time in	0	40	80	120	160

Sec					
-----	--	--	--	--	--

- (i) A graph of mass of Pa against time
- (ii) Use the graph to determine mass Pa
- (iii) Determine the time of 8g of Pa to decay up to 1 g

Solution.

from $\ln() = \lambda t$

$\ln() = 0.0108 t$

$\ln =$

$t = ()$

$t = 192.54s$

- (d) The data below shows the result of the disintegration of element y.

No	Nt	t(s)
0.01	0.01	0
0.00999	0.009	30
0.0985	0.008	60
0.0997	0.0073	90
0.01000	0.0066	120
0.00989	0.0053	180
0.01010	0.0044	240
0.0975	0.0028	360
0.01056	0.0020	480
0.0104	0.0013	600

- (i) Plot a graph of N_t against time (t).
- (ii) Use the graph to determine half life of the element.
- (iii) Decay constant of radioactive element Y
- (iv) Plot a graph of $\log_{10}()$ against t.
Use it to determine.
- (v) Decay constant of Y
- (vi) Half life of Y

Solution

No	Nt	()	$\log_{10}()$	()	$\log_{10}()$	t(sec)
0.01	0.01	1.000	0.000	1	0	0
0.00999	0.009	1.110	0.045	0.900	-0.046	30
0.0985	0.008	12.31	0.090	0.081	-1.092	60
0.0997	0.0073	1.377	0.137	0.073	-1.137	90
0.01000	0.0066	1.515	0.180	0.660	-0.180	120
0.00989	0.0053	1.867	0.271	0.536	-0.271	180
0.01010	0.0044	2.295	0.360	0.436	-0.361	240
0.0975	0.0028	34.821	1.542	0.029	-1.538	360
0.01056	0.0020	5.280	0.723	0.189	-0.724	480
0.0104	0.0013	8.000	0.903	0.125	-0.903	600

- (i) See on the graph.
- (ii) Half life = 64 years
- (iii) $t_{1/2} =$
 $t_{1/2} =$

$$=$$

$$=$$

$$\lambda = 0.0108$$

(iv) See on the graph.

(v) $t_{1/2} = 168$
 but $t_{1/2} =$
 $168 =$
 $=$
 $\lambda = 0.00413$

(vi) from $\ln() = \lambda t$
 $\ln() = 0.0413 t$
 $\ln =$
 $t = ()$
 $t = 192.54s.$

Exercise.

1. 1000g of a related was allowed to decay to 125g after 6 min. calculate the decay constant and hence the half life of radioactive element.

Solution.

- $N_0 = 1000g$, $N_t = 125g$, $t = 6\text{minutes.}$
 $\ln() = \lambda t.$
 $\ln() = 6\lambda.$
 $\lambda = \ln() = 0.3466\text{min}^{-1}$
 $t_{1/2} = , t_{1/2} = , t_{1/2} = 2\text{minutes.}$

2. If the decay constant of a radium is $1.356 \times 10^{-11}/\text{sec}$, calculate the time taken for 10% of the sample decay.

Solution.

- $\lambda = 1.356 \times 10^{-11} \text{ s}^{-1}$, 10% decayed and 90% remained.
 $\ln() = \lambda t$, $\ln() = 1.356 \times 10^{-11}$
 $t = \ln() \times , t = 7.7699 \times 10^9s.$

3. The half life of a radioactive element Y is 8days. Determine the time taken for 32g of Y to decay to 2g.

Solution

- $N_0 = 32g$, $N_t = 2g$, $t_{1/2} = 8\text{days}$
 $() = 2^0, = 2^()$
 $\log 16 = \log 2, t = , t = 32\text{days.}$

Uses of radioactivity;

- **Carbon dating**

The radioactivity of carbon 14 in archeological remains can be measured. The radio activity of a sample of a similar object can that is living can be determined. If the alf life of carbon 14 is known, then the values are used to calculate the age of the archeological.

$$3.303 \log_{10} () = \lambda t$$

where N – is the number of radiation emitted per min.

λ = is the decay constant

t = is the time in years since the death of the object

N.B: the radioactivity of the ^{14}C is measured by Geiger Muller which records the radiation of the sample in 1 min by making pulses or clicking on an electronic counter.

Examples.

1. Freshly killed piece of wood give 15 counts / min/ gram of carbon 14. An Egyptian mummy gives 9.5 counts/g/min of ^{14}C .How old is the mummy case if the half of ^{14}C if the half life of carbon -14 is 5600years.

$$\lambda = t^{-1/2} =$$

$$\lambda =$$

$$\lambda =$$

$$\lambda = 0.00012378\text{yr}^{-1}$$

$$2.303 \log_{10} \frac{N_0}{N} = \lambda t$$

$$t =$$

$$t =$$

$$t = 3690.75\text{years.}$$

2. A sample of wood from an Egyptian tomb give disintegration of $8.25\text{min}^{-1}\text{g}^{-1}$ if the sample of the living gives 15.3g/min/g of ^{14}C . Determine the age of Egyptian tomb.

Solution.

$$N_0 = 8.25\text{min}^{-1}\text{g}^{-1}, N = 15.3\text{min}^{-1}\text{g}$$

From $\lambda =$

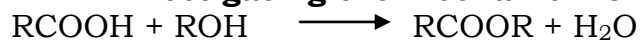
$$\lambda = 1.2378 \times 10^{-4}.$$

$$2.303 \log_{10} \frac{N_0}{N} = t.$$

$$t =$$

$$t = 2672\text{years.}$$

- **It is used to treat cancer.** Cancerous tissues are destroyed by radioactivity in preference for healthy carbon 60 which emits gamma rays of 5 yrs is used.
- **Sterilization of surgical instruments.** Surgical instruments are effectively sterilized by use of radioactivity by boiling.
- **Detecting faults in metal sheet.** The thickness of metal sheet is continuously checked by the radio activity which is detected through the metal sheets.
- **Detecting underground leakages in water and oil pipes.** The level of the radioactivity on the surface can be monitored by the radioactive substance with in water being moved within the pipe.
- **Detect engine wear;** they can also be detected by measuring the rate of radioactivity I the engine oil. Normally piston rings that are made up of radioactive are used.
- **Investigating the mechanism of the reaction** e.g in esterification i.e

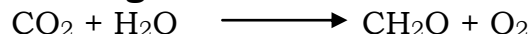


Acid alcohol Ester

In this reaction, the O_2 in H_2O comes from either an acid or an alcohol and to prove where O_2 come is labeled H_2O and the reaction is given time to produce.

On test of radioactivity of H₂O molecule given out it's found to be not radioactive. This can now lead to a conclusion that O₂ comes from acid.

Investigation of Bio chemical reaction e.g photosynthesis



The O₂ of CO₂ is labeled radioactive O₂-18 and supplied to plants to carry out photosynthesis. The O₂ then given is then tested by radioactivity and its to be non radioactive. This leads to a conclusion that the O₂ evolved during photosynthesis is comes from water.

NUCLEAR FUSION AND NUCLEAR FUSION.

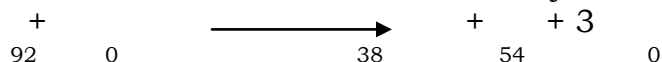
Nuclear fusion.

This is a process by which light nuclides combine at a very high temperature to form a heavy nuclide. This process is a companied by high amount of energy and some radiations are emitted e.g protons and neutrons.

The hydrogen bond is obtained by fusing 2 hydrogen nuclei at very high temperature of at about 10^{7k} and high amount of energy are release during fusion and this can cause explosion. The sun obtains its energy from hydrogen atoms and the sun's temperature is about 10,000,000°C which is enough H₂ atoms to fuse.

Nuclear fission.

This is a process by which unstable nuclide is bombarded with a nuclide to disintegrate and form stable nuclides and other particles being emitted. This process is accompanied by loss of large of amount of energy. For example Uranium – 238 undergoes nuclear fission when combined with a neutron. This process produces 3 more neutrons which can accelerate the reaction. The nuclear fission of Uranium -238 is shown by the following chain reaction.



Uses of uranium.

- Uranium – 238 is used in atomic bombs.
- It is also used in nuclear reaction to produce thermal electricity.

Atomic emission spectrum.

When atoms of elements are subjected to electrical discharge or heated, it is observed that the element emits electromagnetic radiation which can be ultra violet light or infra red or visible spectrum. This is caused by the atoms of the element absorbing some energy and then emitting it inform of electromagnetic radiation. When the radiation is passed through a spectrometer, it is observed that un like sun light which is composed continuous spread of colours, it forms definite lines on a screen with a black back ground. In the visible part of spectrum, coloured lines are observed and each colour has a definite wave length of radiation. The mere fact that it is a line spectrum and not a continuous spectrum, it indicates that the atoms contains energy levels to which electrons move when they are excited and therefore they should absorb certain amount of energy is called **quanta of energy**. When an electron absorbs a quantum of energy, it moves from its ground energy level to higher

energy level and on coming back it will emit the same amount of energy of specific frequency and wave length. the energy of radiation can be calculated using Planck's equation.

$DE = hv$ where DE is change in energy, h- is constant = $6.626 \times 10^{-34} \text{ ms}^{-1}$

$v = \frac{c}{\lambda}$ where C – speed of light and λ is wave length of radiation.

For most elements, the radiations are in invisible spectrum and each element produces a distinct colour of light and this enables us to identify a number of metal ions by their characteristic flame test colours e.g sodium imparts yellow colour when burnt in air, potassium gives purple/lilac, Calcium gives brick Red colour, Barium gives apple green colour.

The emission spectrum of atom elements provides evidence that electrons are distributed around the nucleus in various energy levels. Electrons occupying the same level are said to be in the same quantum shell because they absorb same quanta of energy to make them move from one level to another. The quantum shells are denoted by Principle quantum number which are 1, 2,3, 4and so on. If $n=1$, this means the 1st quantum shell near the nucleus. If $n = 2$, it means the 2nd shell etc. when we use spectrometers of high resolving power to analyze radiations, it is observed that the electron from the same quantum shell have slightly different energy and their positions in quantum shells are called sub shells/ sub energy levels/ orbitals. The orbitals are numbered using s, p, d and f. The s – orbital accommodates maximum of 2 electrons, p-orbital contains maximum of 6 electrons, d-orbital accommodates maximum of 10 electrons and f accommodates maximum of 14 electrons. Before the electrons occupy the orbitals, the following rules should be followed.

- **Paul's exclusion principle;** *it states that an orbital can take a maximum of two electrons on conditions that these electrons have opposite spins so that the magnetic effect is reinforced.*
- **Hundi's rule of maximum multiplicity;** *it states that when electrons are present in a number of degenerate orbitals (i.e orbital's of the same energy), they occupy all orbital's singly first with parallel spins pairing up in any one orbital occurs.*

An orbital is a region in which there is greater probability of finding a particular electron although they are not confined in those particular regions.

Hydrogen emission spectrum.

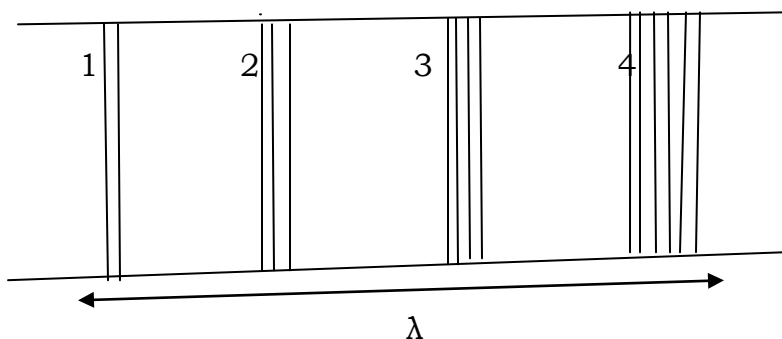
Emission spectrum of hydrogen atom has been explained by Bohr after careful observation he made. He suggested that despite hydrogen having one electron it has many energy levels in the space outside the nucleus. These energy levels have quantum numbers 1,2,3,4.....or letters K,L,M,N. He suggested a single electron of hydrogen rotates with in energy levels. These energy levels in which the electron rotates are called “**permissible energy levels**” in which the electron does not absorb or emit radiations.

Under normal circumstance the electron will occupy an orbital near the nucleus and it is said to be in the ground state. The electron does not emit energy because it is within the permissible energy levels. When the atom is given sufficient energy, the electron “jumps” from its ground state to higher

energy by absorbing energy. In this state the electron is said to be excited or promoted. In the excited state the atom is said to be unstable and would wish to get its electron back to the ground state in order to gain its stability.

The electron may return to the ground state at once and it may do so in the number of stages. In the process the electron emits energy of excitation which appears as radiation or coloured bands on the screen. When electron returns to the 1st quantum shell i.e $n=1$, regardless of energy level where it is coming from, it emits radiation as a line on the screen in the Lyman series. If it comes back to the 2nd quantum shell i.e $n = 2$, it forms Balmer series and if the electron comes to the 3rd shell i.e $n=3$, it forms Paschen's series and if it comes to the 4th quantum shell i.e $n=4$, it forms Brackett's series. This is shown on the diagram below;

The hydrogen spectrum can be represented as follows.



There are so many lines in the H_2 spectrum but the most important ones are from 1-4 which include lines in the Lyman, Balmer, Paschen and Brackett series. The lines get closer together as you move from the nucleus to decrease in the wave length of radiation emitted and eventually line emerge into a continuous spectrum. At this point the radiation emitted is in the invisible range and this one occurs at ionization when the electron is completely removed from an atom forming a gaseous ion. The emission spectrum of H_2 provides evidence for existence of energy levels within the H_2 atoms because of several lines each of which shows a particular radiation emitted. The energy levels have different wave lengths when an electron returns from them justifying the existence of different energy levels. The wave lengths of the radiation emitted is given by;

- $Rh \left(\frac{1}{n^1} - \frac{1}{n^2} \right)$ where Rh is Rydberg's constant, n^1 and n^2 are the energy levels.

In the Lyman series $n_1=1, n_2=2, 3, 4, \dots$ etc

In Balmer series $n_1 = 2, n_2 = 3, 4, 5, \dots$ etc

In Paschen $n_1 = 3, n_2 = 4, 5, 6, \dots$ etc

Examples.

1. Calculate the radiation emitted in Lyman's series if the electron turns from $n=4$, $R_h = 1.097373 \times 10^7 \text{ m}^{-1}$

Solution

$$\begin{aligned} &\text{From } n_1 = 1, n_2 = 4 \\ &= R_h \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= 1.097373 \times 10^7 \left(1 - \frac{1}{16} \right) \\ &= 1.097373 \times 10^7 \left(\frac{15}{16} \right) \\ &= 1.097373 \times 10^7 \times 0.9375 \\ &= 0.82302975 \times 10^7 \\ &\lambda = \frac{1}{\sigma} \times 10^9 = 121.5 \text{ nm} \end{aligned}$$

2. Calculate the radiation emitted in Balmer series if the electron turns from $n=3$ to n_2 , $R_h = 109678 \text{ m}^{-1}$

Solution.

$$\begin{aligned} &= R_h \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= 109678 \left(\frac{1}{4} - \frac{1}{9} \right) \\ &= 109678 \times 0.1388888888 \\ &= 15233.05556, \lambda = \frac{1}{\sigma} \times 10^9 = 65647 \text{ nm} \end{aligned}$$

Similarly the energy of the radiation emitted from the higher energy level to the lower energy can be calculated as;

$E = h\nu$. Where h = plank's constant, V – speed of light given by $V =$

$$\therefore E =$$

If an electron jumps from n_1 to n_4 and the energy in n_1 is E_1 and n_4 is E_4 then the energy of excitation is given by $(E_4 - E_1) =$.

Similarly the energy of radiation emitted when it jumps from n_4 to n_1 is given by $(E_4 - E_1) =$.

Examples.

1. The diagram below represents some energy levels of the hydrogen spectrum.

$E/\text{kJ/mol}^{-1}$



(a) If an electron is in the ground state, calculate the maximum amount of energy for its maximum ionization.

Solution.

$$E_1 = -1310 \text{ kJ mol}^{-1}, \quad E_\infty = 0 \text{ kJ mol}^{-1}$$

$$E = E_\infty - E_1$$

$$= 0 - (-1310)$$

$$= +1310 \text{ kJ mol}^{-1}.$$

(b) If the electron is in the 3rd quantum shell, $n = 3$, what is the frequency of radiation it can emit when coming back to the ground state $h = 3.99 \times 10^{-13} \text{ KJ s}^{-1}$.

Solution.

$$E_3 - E_1 = h\nu$$

$$(-145 - (-1310)) = 3.99 \times 10^{-13} \times \nu$$

$$\nu =$$

$$= 2.92 \times 10^{15} \text{ s}^{-1}$$

2.(a) Calculate the λ of light emitted in;

(i) Balmer series when the electron returns from $n = 5$

$$= R_h (-).$$

$$= 1.097373 \times 10^7 (-).$$

$$= 1.097373 \times 10^7 \times 0.96$$

$$\lambda = 9.492 \times 10^{-8}$$

(ii) Balmer series when the electron returns from $n = 5$

$$= R_h (-).$$

$$= 1.097373 \times 10^7 (-).$$

$$= 1.097373 \times 10^7 \times 0.21$$

$$\lambda = 4.34 \times 10^{-7}$$

(b) What is the energy of radiation emitted in (a) above in those series
velocity of light = $3 \times 10^8 \text{ m/s}$.

Solution.

(i) $E = h\nu$, $\nu =$, $E =$

$$E =$$

$$= 1261.33 \text{ kJ mol}^{-1}$$

(ii) $E = h\nu$, $\nu =$, $E =$

$$E =$$

$$= 275.81 \text{ kJ mol}^{-1}$$

RELATIVE ATOMIC MASS

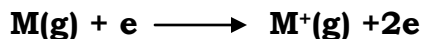
Is the number of times an atom of an element is heavier than the mass of carbon 12 (^{12}C). It can also be defined as a mass of 1 atom of an element divided by the mass of 1 atom of ^{12}C . Since it is a ratio, it has no units.

Determination of relative Atomic mass of an element.

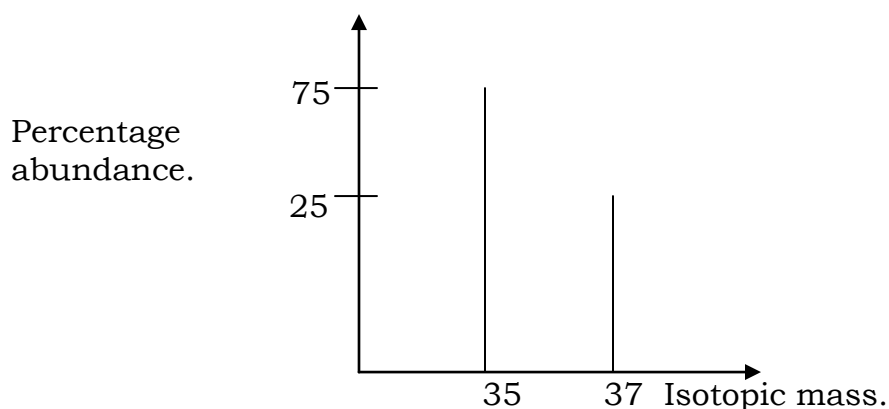
A mass spectrometer is an instrument used to determine the relative atomic mass of an element.

- A mass spectrometer is faster evacuated to be free from air molecules by connecting to a vacuum pump.
- A vaporized sample of an element is introduced in a spectrometer and then subjected to a beam of electron from electrically heated filaments

which act as an electron gun in ionization chamber. The gaseous atom collide with electrons to form 2 electrons



- The gaseous atoms are then accelerated by strong electric field at the same velocity. The ions then enter the magnetic field where various isotopes are separated and ions are deflected according to mass charge ratio (m/e) i.e lighter ions are deflected than the singly charge ions.
- The ions follow curved paths to the ion detect that is connected to the recorder. The recorder records series of lines or peaks giving a spectrometer.
- Each peaks represents an isotopes and its height represents the percentage or relative intensity eg Cl_2 has two isotopes and which are represented on the spectrum below;



Calculating R.A.M from isotopes.

R.A.M of elements can be obtained from the isotopes using the following expressions.

$$\text{R.A.M} = \sum ()$$

From the above spectrum of Cl the following information is obtained. The number of isotopes of element is 2.

- Isotopic masses of Cl are 35 and 37
- The most abundant isotope is chlorine 35 with the 75%
- the least peak is ^{37}Cl with 25%.

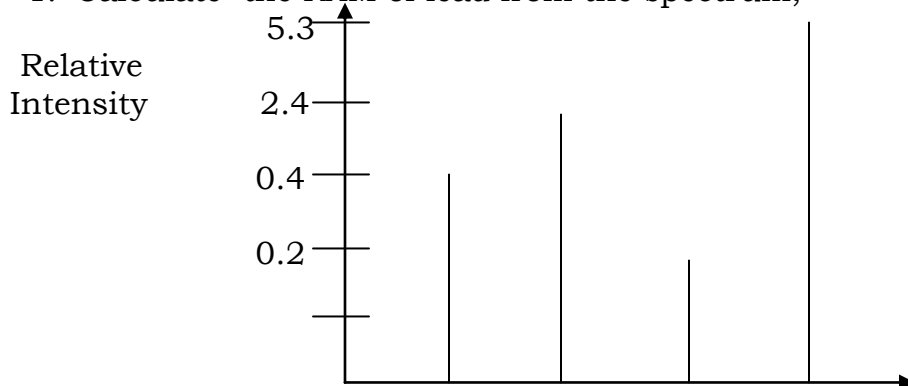
R.A.M of Cl can then be calculated as follows;

$$\text{From RAM} = \sum (), \text{RAM} = () + ()$$

$$\text{RAM} = 35.5$$

Examples.

1. Calculate the RAM of lead from the spectrum;



0.1

204 206 207 208 Isotopic mass

From $RAM = \sum ()$

$RAM () + () + () + ()$

$RAM = 9.831 + 59.566 + 4.988 + 132.892$

$RAM = 207$

2. A sample of Rubidium was introduced into a mass spectrometer and was found to give 2 isotopes whose masses are 84.9199 and 86.9092. It was found that there was in ratio of 5.4: 2.1 respectively. Calculate the RAM.

Solution

84.9199 : 86.9092

5.4 : 2.1

Total ratio = 7.5

$RAM = :$

$= 61.142 + 22.655 = 83.797$

3. Chlorine exists in 2 isotopes masses but its mass spectrum has 2 peaks at the mass charge ratio of 70: 72: 74 in the relative abundance of 9:6:1.

a) Calculate the RAM.

b) Deduce the RAM of Cl.

c) The two isotopic masses are 35 and 37. Calculate the relative abundance of each of masses using the

Solution

(a) $+ +$

$39.373 + 27 + 4.625 = 71$

(b) $RAM =$

Since Cl_2 is a diatomic $= = 35.5$

Let $^{35}Cl = x\%$, $^{37}Cl = (100-x)$

$35.5 = +$

$35.5 = +$

$35.5 =$

$=$

$^{35}Cl = 75\%$

$^{37}Cl = 25\%$

RELATIVE MOLECULAR MASS

Is the mass of one molecule or mole of an atom of an element or a compound divided by th of mass of 1 molecule or mole of carbon-12 (^{12}C). Since it is a ratio, it has no units.

Methods of determining relative molecular masses of compounds.

(i) Method of vapor density

The vapour density of a gas is expressed as a mass of a certain volume of a gas compared with mass of same of volume of hydrogen at a same temperature and pressure.

V.D =

V.D =

Since H₂ is a diatomic gas

V.D =

But mass of 1 molecule of a gas is its RMM

VD =

RMM = 2VD

Example.

1. Given the vapour density of a gas, its RMM can be calculated eg The mass of 257cm³ of a gas at 18°C and 100400Pa pressure is 0.162g. calculate the molar mass using its V.D.

From =

=

V₂ =

V₂ = = 248.2

Density =

= 6.53 x 10⁻⁴g/cm³

Density of H₂ =

RMM of Hydrogen = 2

=

= 8.93 x 10⁻⁵

V.D =

RMM = 2 x 7.334

= 14.67

(ii)Victor Meyer's method.

Procedure;

- In this method, a large container full of a certain gas is weighed; let its mass be *ag*.
- It is then evacuated and weighed a gain; let its mass be *b g*.
- The mass of a certain is then obtained as (a-b)g.
- The volume of Vcm³ of contain is noted and the temperature and pressure at which this is does are also noted from the ideal gas equation

Pv = nRT

n= = PV = RT

but mass of a gas = (a – b)

where PV = RT

∴ Mr =()RT

RFM of a gas can be calculated from the expression above.

Note: when using this method, the following conditions must be satisfied.

- The gas must be pure
- The container should be completely evacuated at the same temperature and pressure
- The weight should be done on the same temperature and pressure.

(iii) Determining the RFM of volatile liquids.

Procedure;

- A fixed mass of a volatile liquid whose RFM is to be obtained is injected into a syringe e.g a hypodermic syringe.
- Steam is passed into the steam jacket and is used to heat a volatile liquid to form a vapour whose volume is read on a scale of a calibrate syringe.
- The temperature of the steam jacket is donated using a thermometer and the pressure at which the experiment is done is also noted.

Diagram.

Results

Let the mass of the liquid be ag .
 Volume of vapor is $V\text{cm}^3$.
 Temperature of the jacket is TK .
 Pressure of the system is p atmosphere.
 From the ideal gas equation
 $Pv = nRT$
 $N =$
 $Pv = RT$
 $Mr = () RT$.

Examples.

1. When 0.16g volatile was injected into gas syringe at 72°C and 745mmHg, 61.5cm^3 of the vapour was produced. Calculate the molar mass of x. Given that $R = 8.314$

Molar gas volume at STP = 22.4l
 If 760 mm contain 101231NM^{-2}
 $\therefore 745\text{mm}$ contain $(x \ 745)$
 $= 99325.66\text{mm}$
 $\text{Volume} = 61.5 \times 10^{-6}\text{m}^3$

$Mr = 75$.

Method 2;

$= , = , V = 47.7\text{cm}^3$
 47.7cm^3 of gas contain 0.16g.
 22400cm^3 of a gas will be $()g$
 $Mr = 75$.

2. A gas syringe contains 20.6cm^3 of air at 45°C was injected with 0.24g of a volatile liquid . After vaporization the volume of was found to be 63.7cm^3 at pressure of $1.0 \times 10^5\text{pa}$. calculate the relative formula mass of volatile liquid.

Solution.

Volume of vapour of the liquid produced = $63.7 - 20.6\text{cm}^3$.
 $= 43.1\text{cm}^3$ or $43.1 \times 10^{-6}\text{m}^3$

From the equation, $pV = \frac{mRT}{M_r}$ where m = mass of liquid injected, M_r = molar mass of the liquid.

$P = 1.01 \times 10^5 \text{ Pa}$, $T = 273 + 48 = 321 \text{ K}$.

$M_r = \frac{mRT}{pV} = 150.8 \text{ g}$.

(iv) GRAHAM'S LAW OF DIFFUSION AND RMM OF GASEOUS SUBSTANCES.

It states the rate of diffusion of gas at constant temperature and pressure is inversely proportional to the square root of its density or relative formula/molecular mass. Mathematically Graham's law is written as follows;

$$R \propto \frac{1}{\sqrt{M_r}} \quad (1)$$

$$R \propto \frac{1}{\sqrt{M_r}} \quad (2)$$

$$R = \frac{k}{\sqrt{M_r}} \quad (3)$$

For the two gases 1 & 2 diffusing through the same porous partition with their molar masses. If the molar mass of one gas is known then the R formula mass of the other can be calculated as follows.

$$R_1 = \frac{k}{\sqrt{M_{r1}}} \quad (4)$$

$$R_2 = \frac{k}{\sqrt{M_{r2}}} \quad (5)$$

$$\frac{R_1}{R_2} = \frac{\sqrt{M_{r2}}}{\sqrt{M_{r1}}}$$

$$M_{r2} = \left(\frac{R_1}{R_2} \right)^2 M_{r1} \quad (6)$$

Examples.

1. It takes 2 minutes for 50 cm^3 of helium to diffuse through a porous partition. How long will it take for the same volume of ammonia to diffuse?

$M_r(\text{NH}_3) = 17$

$M_r(\text{He}) = 4$

$R_{\text{He}} = \frac{V}{t} = \frac{50 \text{ cm}^3}{2 \text{ min}}$, $R = \frac{V}{t} \text{ cm}^3 / \text{min}$, $M_r(\text{He}) = 4$, $M_r(\text{NH}_3) = 17$

From the equation, $\frac{R_1}{R_2} = \frac{\sqrt{M_{r2}}}{\sqrt{M_{r1}}}$, $\frac{25}{R} = \frac{\sqrt{17}}{\sqrt{4}}$

$$(25)^2 = R^2 \times \frac{17}{4}, \quad t^2 = \frac{4}{17} \times 25^2, \quad t = 4.123 \text{ minutes.}$$

2. A certain gas diffuses four times faster than O_2 through the same porous partition. Calculate the molar mass of the gas.

Solution

$R_{\text{O}_2} = y$, $R_g = 4y$, $\frac{R_g}{R_{\text{O}_2}} = \frac{\sqrt{M_{r\text{O}_2}}}{\sqrt{M_{rg}}}$, $\left(\frac{4y}{y}\right)^2 = \frac{32}{M_{rg}}$, $M_{rg} = 2$

3. 141.4 cm^3 of an inert gas diffuses through porous plug in the same time as it takes 50 cm^3 of O_2 to diffuse through the same plug under identical conditions. Calculate the molar mass of inert gas.

Solution

$\frac{R_1}{R_2} = \frac{\sqrt{M_{r2}}}{\sqrt{M_{r1}}}$, $\frac{141.4}{50} = \frac{\sqrt{M_{rn}}}{\sqrt{32}}$, $M_{rn} = 40$,

4. 6.3 cm^3 of X diffuses through a porous plug in 5 minutes. If 7.4 cm^3 of oxygen diffuses through the same plug and same time. Calculate the molar mass of X.

Solution.

$\frac{R_1}{R_2} = \frac{\sqrt{M_{r2}}}{\sqrt{M_{r1}}}$, $\frac{6.3}{7.4} = \frac{\sqrt{M_{rx}}}{\sqrt{32}}$, $M_{rx} = 44.2$

EMPIRICAL FORMULA AND MOLECULAR FORMULA

An empirical formula is a simplest formula that expresses its composition by mass. **A molecular formula** is a formula which expresses the exact number of atoms present in 1 molecule/ mole of a compound. A molecular formula can be calculated from an empirical formula if the molar mass of the compound is given.

The expression below can be used;

Molecular = (empirical formula)_n, Where n gives is the exert number of atom in the atom in each kind.

Examples;

1. When 20cm³ of gaseous hydrocarbon was exploded with 150cm³ of oxygen which was in excess, the residual gases occupied a volume of 110cm³. After shaking these gases with aqueous NaOH, the final volume was 30cm³. Calculate the molecular formula.

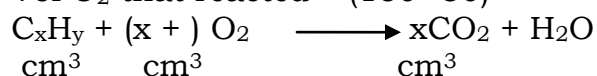
Vol of O₂ = 150cm

Vol of residue gas = 110cm³

Excess volume of O₂ = 30cm³

Vol of CO₂ = (110 – 30) = 80cm

Vol O₂ that reacted = (150 -30)



1 : 6:4

X = 4

4 + = 6

y =8

MF = C₄H₈

2. When a hydrocarbon (C_nH_m) was exploded with excess O₂, there was a contraction of 30cm³, when the mixture was cooled to room temperature. On heating with concentrated potassium hydroxide, there was further contraction to 20cm³. Determine value of n and m.



1 : 3 : 2

n=2, = 3

= + = 3, 8 + m = 12, M =4, MF C₂H₄

RELATIVE MOLECULAR MASSES IN SOLUTIONS.

When a solution is dissolved in a solvent to form a solution the properties of a solvent change. Such properties are called Colligative properties. Colligative property is a property of a solution which depends on the number of non volatile solute particles dissolved in a given amount of a solvent but independent on the decimal nature of the solute particles. There are 4 Colligative properties

- Lowering of vapour
- Elevation of a boiling point of
- Increase in osmotic pressure
- Depression of the freezing point

These Colligative properties can be used to determine RMM of a solute in solution.

Lowering of vapour pressure

When a non volatile solution is dissolved in a solvent to form a solution there is lowering of vapour pressure. The solute molecules are non volatile and show no tendency to escape into the vapour state at the same time, they exert small forces of attraction on to the fast moving solvent molecules that are about to escape because of the strong attractive forces between the molecules of the solute and solvent. Therefore fewer molecules of the solvent escape and the vapour pressure is lower than that would be expected in absence of a solute. This is shown on a graph of vapour pressure verses Time below.

A graph

If P^0 is the pressure of the solvent. P is the pressure of solution. Therefore Vapour pressure lowering is given by $(P^0 - P)$

Relative V.P = $\frac{P^0 - P}{P^0}$

Relative lowering of V.P is proportional to mole fraction. If n_a is the no. of moles of a solution and n_b is the number of moles of a solvent. Therefore relative V.P = $\frac{n_a}{n_b}$

For every dilute solution for equation above, this is Raoult's law of;

Raoult's law states relative lowering of V pressure of dilute solution is proportional to the mole fraction of a solute.

When the conc of the number of moles of the solution are much less than the no. of moles of solvent.

Since $n_a \ll n_b$

Thus $\frac{n_a}{n_b} = \frac{P^0 - P}{P^0}$

But $n_a = \frac{w_a}{M_a}$, $n_b = \frac{w_b}{M_b}$

$\frac{P^0 - P}{P^0} = \frac{w_a}{w_b} \times \frac{M_b}{M_a}$

$\frac{P^0 - P}{P^0} = \frac{w_a}{w_b} \times \frac{M_b}{M_a}$

$M_a =$

Conditions where Raoult's law applied;

1. The solution must be very dilute
2. The solution must be non volatile
3. The solution should not react with the solvent
4. The solute should not associate with solvent
5. The solute should not dissociate with solution

Examples;

1. The VP of a pure water is 3167 Pa. the V.P of a solution contain 4 g of sugar in 100g of water at the same temperature is 3154 ps. What is RMM of sugar

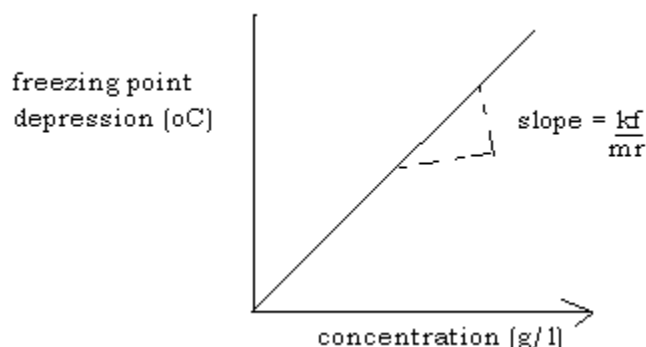
From

$M_r = 1.5143$

2. The lowering of V.P of 1% aqueous solution for sucrose at 371k is 50.08. the V.P of pure water at 371k is $9.42 \times 10^4 \text{ NK}^{-2}$, calculate the vapour pressure of the solution.

Depression of freezing point.

Freezing point is a temperature at which a pure substance. Eg the freezing point H_2O is 0°C and that of Ethanol is -120°C , Ethanoic acid is 17°C . When a non volatile solute is added to a solvent to form a solution, the freezing point of a solvent is lowered eg when sugar is added to water, the freezing point of water is less than 0°C . The difference between the boiling point of solvent and it is also called Cryoscopic method. Freezing point depression increases with increase in mole fraction of the solute. Therefore the Fp depression is directly proportion to mass dissolved in of the solute. Dissolved in the given volume of a solvent and shown below graphically.



$\Delta T = K_f \cdot m$

The depression of F.P is also proportional to RMM of a non volatile solute dissolved in a solvent.

$\Delta T = K_f \cdot m$

Where ΔT - is the depression of freezing pt

K_f - is the cryoscopic constant

m - is the mass of solute dissolved

M_r - Molecular mass of the solute

A cryoscopic constant is the depression of the freezing pt solvent caused by 1 mole of a non volatile solute dissolved in 1000g of a pure solvents are given below

Solvent	$K_f \text{ } ^\circ\text{Ckg}^{-1}\text{mole}^{-1}$
Water	1.86
Benzene	5.5
Ethanoic acid	3.9
Camphor	40.0

A summing that 10g of the solvent dissolve a g of a solute 1000g of a solvent will dissolve (x 1000)g of a solute. Therefore from the expression

$$\Delta t^{\circ}\text{C} = K_f$$

$$M = \text{repts (x 1000)}$$

$$\Delta t^{\circ}\text{C} =)$$

An experiment to determine R. Molecular mass of a non – volatile solute by depression of freezing pt (Beckman's method)

Procedure

- A known mass of a solvent is put in an inner tube fitted with a stirrer and Beckman's thermometer
- The tube is placed in air jacket which is in turn placed in a freezing mixture
- The temperature of a pure solvent is noted until when it just begins to freezing.
- The constant temperature at which freezing occurs is also noted. This is the freezing pt of the pure solvent
- The inner tube is then removed and warm on a flame to melt the frozen solvent. It is then replaced in the jacket and a known of a non – volatile solute molecular mass is to be determined is introduced into the inner tube through the side arm.
- The solution/mixtures is stirred continuously to dissolve the solute. The temperature of the solute is note until a constant temperature at which the solution begins to freeze, is noted. This will be the freezing pt of the solution

Diagram.

Treatment of results

Let a be of solute

b be the mass of solvent

$t_1^{\circ}\text{C}$ be the freezing pt of a solvent

$t_2^{\circ}\text{C}$ be the freezing pt of a solution

let the RMM of solute be m_r .

bg osf solvent dissolve ag of solute

1000g of solvent will dissolve (x 1000)g of solute

But depression of freezing pt = $(T_1 - T_2)^{\circ}\text{C}$ D + $^{\circ}\text{C}$

D + $^{\circ}\text{C}$ in the D.F. Pt caused by (x 1000) $^{\circ}\text{C}$

$K_f^{\circ}\text{C}$ is D. freezing caused by (x 1000 x)

Rasts method of determining molecular Mass of non volatile eg camphor and Naphthalene

Procedure

- The mass of a pure Naphthalene is measured e gag and placed in a tube
- A thermometer is inserted and a test tube is heated together with its contents in a beak of boiling water
- Using a thermometer, the melting Naphthalene is stirred until when it all melt to form a liquid
- The melted Naphthalene is allowed to cool while stirring and noting down the temp on a thermometer until when the crystals first appears.
- The freezing point of Naphthalene of a steady state is noted as t_1 °C.
- A known mass eg b g of camphor is added to liquid Naphthalene and the mixture is stirred gently stirred.
- The temperature of solution noted until the first crystals appeared

Graphs of temperature against time use plotted

If the freezing point depression of Naphthalene is known F.pt of camphor can be determined

Treatment of results

- Mass of pure solute be ag.
- Mass of pure solvent be bg.
- Freezing temperature of pure solvent is t_1 °C
- Freezing pt of solution is T_2 °C
- Cryoscopic constant is k_f
- a g of Naphthalene will be (x 1000 x)
- k_f is the d.f.pt caused by (x 1000 x)

Limitations of depression freezing method.

1. The solution must be dilute
2. It is only the solvent which freezes out
3. The solute should not react with the solvent
4. The solute should not dissociate or associate with solvent
5. The solute must be non volatile

Effects of dissociation or association of depression of freezing point. when solute dissociate with a solvent the number of molecules increases

The depression of freezing point also increases since

Δt °C

The RFM of the solute lowers since for it inversely proportional of f.pt

If the number of particles in the solution doubles, the relative M.Mass will become half. If there is association, the number of particles reduces and this reduces the depression of F. pt. the molecular mass of the solute will increase at a higher value than expected.

Examples;

1. 0.55g of nitrobenzene were dissolved in 22g of ethanoic acid. The d.f.p caused was 0.78°C . Calculate the RFM of Benzene given that K_f for ethanoic acid is 3.9°Ckg

Solution.

- 22 g of ethanoic acid dissolve 0.055g of nitro benzene.
- 1000g of Nitrobenzene will be $(\times 0.55) = 2.5\text{g}$
- 0.78°C is the depression of point caused by 25g.
- 3.9°C is the depression of freezing point caused by $(\text{g}) = 125$
RFM of nitrobenzene = 125

2. When 1.5 g of x was dissolved in 30g of water, the solution formed had the freezing point of -1.04°C at atmospheric pressure. Calculate the relative formular mass of X, k_f of $\text{H}_2\text{O} = 1.86^{\circ}\text{C kg/mol}$.

Solution.

- 30g of water dissolved 1.5g of x .
- 1000g of water dissolved by $(\times 1000) = 50\text{g}$.
- 1.04°C is the depression of freezing point caused by 50g.
- 1.86°C is the depression caused by $(= 89.4$
RFM of X is 89.4

3. A solution containing 1.54g of Nephthalene in $(\text{C}_{10}\text{H}_8)$ in 18g of camphor froze at 148.3°C . the freezing point of camphor is 175°C . Calculate cryoscopic constant (k_f) of camphor.

Solution.

- Freezing point depression = $(175 - 148.3) = 26.7^{\circ}\text{C}$.
- 18g of camphor dissolve 1.54g of naphthalene.
- 1000g of camphor dissolve $(\text{g}) = 85.56\text{g}$.
- RFM of $\text{C}_{10}\text{H}_8 = 128$
- 85.5g of naphthalene cause a freezing point depression of 26.7°C .
- 128g of naphthalene cause a freezing point depression of $(\text{g}) = 39.9^{\circ}\text{C}$.
- K_f of camphor is 39.9°C .

4. A solution was prepared by dissolving 7.5g of propan 1,2,3 triol ($\text{C}_3\text{H}_8\text{O}_3$) IN 200g at 25°C . calculate the freezing point of the solution at atmospheric pressure. (K_f of water = $1.86^{\circ}\text{Ckg}^{-1}\text{mol}^{-1}$).

Solution.

- RFM of $\text{C}_3\text{H}_8\text{O}_3 = 92$
- 200g of water dissolve 7.5g of propan 1,2,3 triol.
- 1000g of water dissolve (g) .
- 92g of propan 1,2,3 triol cause a freezing point depression of water of 1.86°C .
- 37.5g of propan 1,2,3 triol causes a freezing point depression of (g)

$$= 0.748^{\circ}\text{C}.$$

- The freezing point of the solution $= (0 - 0.758) = -0.758^{\circ}\text{C}$

Elevation of boiling point (Ebullioscopic method)

Boiling pt of a liquid is a constant temp of which a liquid's V. pressure is equal to the external atmospheric pressure eg at 760mmHg the boiling of H_2O is 100°C and that Ethanol is 78°C .

When a non-volatile liquid of a solvent the solution boils at a higher temperature than that of a pure solvent. This causes an elevation in boiling pt. the elevation in boiling pt is denoted by (Δt)

The Δt is proportional to a mass of a non-volatile solution dissolved in the solute.

$$\Delta t \propto M \text{ -----(i)}$$

Elevation of Boiling pt is also inversely proportional to the molar mass of a non volatile solute.

$$\Delta t \propto \frac{1}{M} \text{(ii)}$$

Combining the two equations and introducing a constant

$$\Delta t \propto \frac{1}{M} = K_b \text{ -----(iii)}$$

Where Δt – is the elevation of

K_b – Ebullioscopic constant

M – Mass of the solute dissolved in a solution

M_r – molar mass of E

Ebullioscopic is the elevation of boiling point caused by 1 mole of a non-volatile solution dissolved in 1000g of a pure solvent.

If a g is the mass of the solution

b g is the mass of the solvent

a g of solvent dissolves b g of solute

1000g of a solvent dissolves ($\times 1000$) of solution

Δt $^{\circ}\text{C}$ is the Elevation of boiling point caused by ($(\times 1000)$ g

K_b is the elevation of boiling pt caused by ($\times 1000 \times$)

TMF of a solute = ($\times 1000 \times$)

Since the boiling point of the solute is higher than that of a pure solvent. The particles of a non – volatile solvent occupy the surface of the solution to prevent escape of solvent molecules into vapour phase. The V. pressure of the solution is also lowered. More heat is required to raise the vapour pressure of the solution to be equal to external ATM pressure so that the solution boils.

The graphs of variation of VP against temp. for both a pure solvent and solution are plotted as below

Since solution two is more solution, it contains more solute particles than solution 1. The vapour pressure of a solvent and solution, increases with increase in temperature because at high temperature the solvent molecules gain more kinetic energy and tend to escape into vapour phase at a higher rate compared to that lower temperature.

The rate escape of molecules of pure solvent is higher than that from solutions because the non volatile solute particles occupy the surface of the solution and tend to prevent the escaping molecules of the solution into the vapour phase.

From the graph above to- is the boiling point.

A- Is the vapour pressure of its boiling point

T_1 = is the B.p of solution and point C is V.P of its V.P

T_2 – is the B.p of solution 2

The difference between A and B is the lowering o V.P of solution 2. The difference between T_0 and T_1 elevation is B.P of solution 1. As the concentration increases, the elevation of B.P also increases.

According to Repults law R. lowering of V.P = mole fraction

=

Where A –V.P of solvent

B-V.P of solution

n_0 - no of moles of the solute

n_1 - no of mole of solution

considering triangles ABC and CBE, AC:CE = AB:CB

therefore =

Where AB – lowering of V.P of solution, AC = Elevating of B.pc

AC = Dt also AB = BC = Dt

Dt =

But $n_1 =$ -

$n_0 =$

Dt = A () ÷ (+)

Since the solution is very dilute; $n_1 + n_0 = n_0$

Dt = A (+)

Dt = A(x)

For expression above, the elevation of B.P is directly proportional to solvent and inversely proportional of RMM of solute measuring that Mr_1 is very high.

The boiling point elevation constant for some solvents are given below

Solvent	B. Point can not
Water	0.53
Ethanoic	3.08
Benzene	2.60
Ethan	1.11
Ethoxyethane	2.16

COTTRELL'S METHOD;

- A known mass of a pure solvent, ag, is placed in the boiling tube in the side arm fitted with a Cottrell's pump and a thermometer.
- The solvent is heated electrically using a platinum wire until it begins to boil.
- The boiling point of the solvent is recorded and noted as T_0 °C

- A known mass, bg of a non volatile solute, whose RFM is to be determined, is added to the solvent through the side arm.
- The mixture is shaken to dissolve solute completely.
- The solution formed is also heated electrically until it boils
- The boiling point of the solution is also noted and recorded as T_2 °C

Treatment of results

Let the boiling point elevation of constant be k_b

Elevation of B.pt is $(T_i - T_0)$ °C

A g of the solvent dissolves b g of solute

1000g of the solvent will dissolve ($\times 1000$)

$(T_1 - T_0)$ is the elevation of B.p caused by ($\times 1000 \times$)

RFM of a solvent is []

Procedure;

- A known of a pure solvent is placed in a graduated tube fitted with a thermometer.
- The pure solvent is heated using the vapour from a conical flask until when it boils.
- The boiling point of a pure solvent is recorded at a steady state temperature.
- The pure solvent is then allowed to cooled and a known mass of the non volume whose Molar Mass sis to be determined is introduced into the solvent.
- The solution is heated using the vapour from the conical flask until when it boils.
- The B.P of the solution is noted at a steady state. The volume of the solution is read off from the scale of the graduated tube

Limitations of this method

- i. Super heating, ie temperature of the solvent or solution may raise abnormally above the normal B.p without boiling taking place. This is minimized boiling using vapour and other using direct heating or boiling of solution. This ensures boiling is slow or gentle.
- ii. Variation in atmospheric pressure affects the B. points hence giving inaccurate results
- iii. The elevations in boiling points are usually very small therefore a thermometer.

NOTE: for accuracy in reading off the thermometer boiling curves are plotted against time.

Qn. a solution of 2.8g of cadmium (ii) iodide in 20g of water boiled at 100.2°C. calculate the molar mass of cadmium (ii) iodide given that K_b for water is $0.52\text{mol}^{-1} \text{kg}^{-1}$

Solution;

20g of water dissolves 2.8g of cadmium (ii) iodide.

1000g of water will dissolve $\frac{2.8 \times 1000}{20}$

0.2°C is the elevation of boiling point caused by 140g of cadmium(ii) iodide.

0.52°C is the elevation of boiling point caused by $\frac{140 \times 0.52}{0.2}$

FRM of $\text{CdI}_2 = 364$

OSMOTIC PRESSURE

Osmosis is the movement molecules from a region of their high concentration (dilute solution) to a region of low concentration (concentrated solution) until an equal equilibrium is attained.

Osmotic pressure; this is the pressure that must be applied to a solution to prevent movement of solvent molecules from a region of their high concentration to a region of their low concentration (I.e from a solvent to a solution) through a semi permeable membrane. Osmotic pressure can be measured using osmometer.

Measuring osmotic pressure

Procedure

- A solvent is allowed to enter the solvent tube until it reaches point x
- The solution of a known conc. Is placed outer tube which is connected to the pressure gauge and piston
- Osmosis is allowed to take place i.e solvent molecules are allowed to move the side of solvent to the solution through a semi permeable membrane of a porous pot
- The level of the solvent in the capillary tube is seen of having dropped
- Pressure is applied on the solution to force the solvent molecule move back into the solution until the when the level of the solvent reaches x again in capillary tube.
- The pressure is noted on the pressure gauge and this is the osmotic pressure applied to the solution to prevent the solvent molecules to move to the solution.

Diagram.

Effect of concentration and temperature on osmotic pressure

Osmotic pressure is directly proportional to the conc of the solution and absolute temperature. This is because when the conc of the solution is high, the movement of solvent molecules from the side of solvent to solution through a semi permeable membrane, increases. Therefore more osmotic pressure is required to force back the solvent molecule into the solution.

The increase in Temperature increases kinetic energy of the solvent molecules and therefore molecules move faster from the solvent to the solution. This therefore requires a high osmotic pressure to force the solvent molecules move back into the solvent.

Deriving an expression for Osmotic pressure.

C

T

$$C \text{-----}(1)$$

$$T \text{.....}(2)$$

CT

$$= KCT \text{.....}(3)$$

For 1 mole of volatile solute dissolved in a given volume of solvent or solution

V dm³ of solution contains 1 mole of solution

1 dm³ of will be ()

C =

From equation -----(3)

$$= k T$$

=

$$TV = KT \text{-----}(4)$$

Since the solution behaves like an ideal gas, for 1 mole of the solute becomes

$$r = RT$$

Where R=gas constant

If V is in M³, in NM⁻²

T :n Kelvins

$$R = 8.314 \text{JK}^{-1} \text{mol}^{-1}.$$

But if V is in dm⁻³(litres)

is in atmosphere, T is in Kelvin

$$R = 0.8314 \text{ atm litres}$$

$$r = RT \text{ atm stp}$$

Limitations

- The solute must be non – volatile
- There should not association or dissociation
- The temperature must no be or too low
- The solute must have high molecular mass.

Examples.

1. At 25°C, 19.15g sugar was dissolved in 1 dm² of solution. Determine the relative molecular mass of the polymer.

solution

$$T = 25 + 273 = 298\text{K}$$

$$\text{RFM of sucrose } C_{12}H_{22}O_{11} = 144 + 22 + 176 = 342$$

Number of moles of sucrose = ()

$$= 0.056 \text{ moles}$$

From V = nRT

=

=

$$= 138744.032 \text{NM}^{-2}$$

To apply the first principle method on the Osmotic pressure we need to use standard

1 mole of a solute in 22.4dm^{-3} at 273K causes an osmotic pressure of 101325NM^{-2} (1 atm or 760mmHg)

The increase in conc. Increases the osmotic pressure and when decrease.

2. At 25°C the osmotic pressure of a protein contains 1.35g was found to be 1216 pa. Calculate the molecular formula of a protein.

solution

1216pa is the osmotic pressure of 100cm^3 of solution caused by 1.35g of protein.

1216 pa is the osmotic pressure of the 22400cm^3 of solution at 298 caused by (x 22400)g

Therefore 101321 is the osmotic pressure of 22400cm^3 at 25°C caused by x x)

RFM = 27505.43

NB: Osmotic pressure method is very useful in determining RFM of polymers. Polymers have high RM masses and a very small amount of a polymer causes osmosis and an approachable or significance figure develops.

CHEMICAL KINETICS (RATES OF CHEMICAL REACTIONS).

Chemical kinetics is the study of rates of the chemical reactions and how these reactions depend on the factors affecting them.

It deals with measurement of reactional velocities or speeds and determination of mechanisms taken by the chemical reactions.

Importance of studying chemical kinetics

- (i) It helps to adjust the reaction conditions for better results.
- (ii) It helps to know the mechanism by which a reaction occurs.

Definitions of terms used;

a. Mechanism of a reaction

This is the path way by which a reactant is converted to the product. It can also be defined as the path taken by a chemical reaction to produce the products.

b. Rate of a chemical reaction

This is the speed at which the concentration of one of the reactants decreases or the speed at which one of the products increases.

Thus: R

= R =

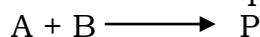
Where R = rate

Dc= change in concentration

Dt = change in time

K = rate constant

Consider the equation of the reaction



(reactants) (product)

Therefore the rate of reaction for the above equation of reaction may be defined as

$$R = R = \frac{-dA}{Dt} \quad (1)$$

$$\text{Or } R = R = \frac{Dp}{Dt} \quad (2)$$

Where R= rate

-dA = Decrease in concentration of A

Dp= Increase in concentration or product

Dt= change in time

K= rate constant

But the rate of the reaction depends on concentration of the reactants

Thus Rate =

But [A]

Rate [A]

Introducing a constant

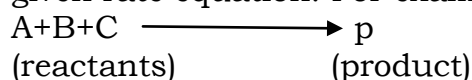
$$\text{Rate} = K[A]^x \quad (3)$$

Where K= rate constant

[A] = concentration of A

Order of reaction

This is the sum of the powers raised to the concentrations of the reactants in a given rate equation. For example in the equation



The rate equation is rate = $K[A]^x[B]^y[C]^z$

Therefore the order of the reaction = $x+y+z$

Where the reaction is of the order X with respect of A, y with respect to B and Z with respect to C.

NOTE: The order of the reaction is not related to the stoichiometry of the reaction and the values of x, y, and z are often whole numbers (ie 1 or 2 and rarely 0,3) or fractions eg $\frac{1}{2}$.

Rate constant/velocity constant or specific reaction rate

This is a constant applied in the place of the proportionality sign. It can also be defined as the value of rate of reaction for the unit concentration of each of the reactant. For example in the rate equation.

$$\text{Rate} = K[A]^0 [B]^p [C]^q$$

Therefore K has a definite value for a given reaction at a given temperature.

K =

Units for rate constant

Rate of reaction is measured in moles per cubic decimeter per second. ($\text{mol dm}^{-3} \text{ s}^{-1}$) or in moles per litre per second ($\text{mol l}^{-1} \text{ s}^{-1}$)

Concentration of each of the reactants is measured in moles per cubic decimeter (mol dm^{-3}) or moles per litre

Therefore the units for rate

Constant =

$$= \text{mol dm}^{-3} \text{ (3x3) S}^{-1}$$

$$\text{Mol}^{-2}\text{dm}^{-6}\text{S}^{-1}$$

Or =

Molecularity of the reaction

This is the number of particles (ie atoms, molecules or ions) that form the activated complex from which the products are formed.

It can also be defined as the total number of particles (ie atoms, molecules or ions) that take part in the rate determining step.

Differences between order of the reaction and molecularity of the reaction

1. The order of the reaction is the sum of the exponents to which the concentration of the reactants must be raised while molecularity of the reaction is the number of particles (atoms, molecules, ions or radicals) in that step required to form the activation complex from which the products are formed.
2. The order of the reaction can be a whole number, zero or a fraction while the molecularity of reaction is always a whole number.

Activation energy. This is the minimum energy required for the reaction to proceed. It can also be defined as the minimum energy required for the formation of activated complex from which the products are formed.

Activated state/transition state: This is a state in which the old bonds of the reactants are broken up leading to the formation of new bonds in the products. This always takes place the peak of energy barrier when the reactant molecules acquire activation energy and change into products.

Activated complex: This is an unstable species with the maximum or highest potential energy on the energy system. The old bonds in it are partially broken and the new bonds are partially formed eg $[\text{Ho} \cdots \text{R} \cdots \text{X}]$. it can decompose either back words into reactants or forward into products.

Characteristics of activated complex

- i. It has maximum potential energy.
- ii. It is an intermediate species which is unstable
- iii. The old bonds in it are partially broken up
- iv. The new bonds are partially formed
- v. It can decompose either backwards into reactants or forward into products.

Rate equation: This is the equation which shows the relationship between the rate of formation of products or rate of disappearance of reactants with the concentration of reactants.

$$\text{Thus Rate} = [\text{A}]^x [\text{B}]^y$$

Factors affecting the rate of a reaction.

Most of the factors that affect the rate of a chemical reaction can be explained in terms of collision theory of reaction. *This theory states that before two or more substances can react together, their particles must collide. This theory is only applied to solution of liquids and gases whose particles collide and the collisions between the two substances result in a chemical change.* This means that chemical bonds in the reactant particles break up while new bonds are made to produce the products. These colliding particles before the chemical

bonds are broken up and new bonds form broken up and new bonds form. Therefore a chemical reaction will only take place when the particles of the reacting substances come into close contact and hence collide more frequently.

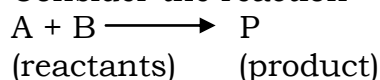
Note: a chemical reaction cannot take place between solid substances. This is because the particles of these solid substances tend to vibrate but don't move from one point to the other. These factors include;

1. Concentration
2. Temperature
3. Pressure
4. Surface area
5. Catalyst
6. Light

Effect of concentration on the rate of the reaction

For most reactions, the reactional rate always depends on the concentration of the reactants. When the concentration of one of the reactants is high, the rate of the reaction is also high and the decrease in the concentration of the reactant lowers the rate of the reaction.

Consider the reaction

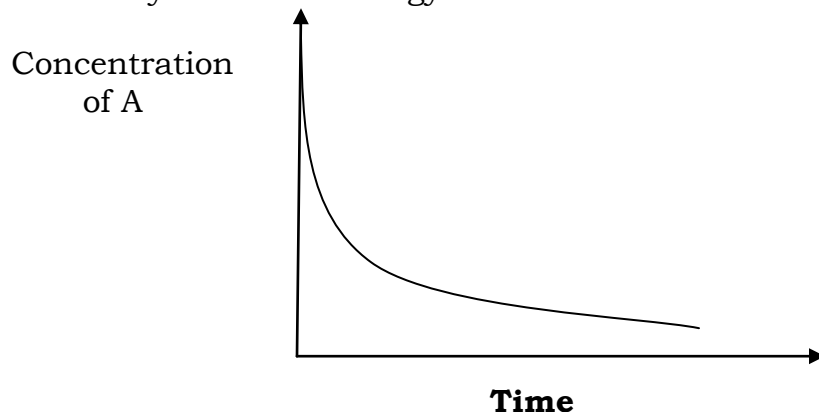


For such a reaction the rate of the reaction is affected by the concentration of one of the reactants in that the number of molecules with necessary activation energy required for reaction to take place is a fixed fraction of the total number of molecules. Therefore an increase or a decrease in the number of molecules in a given volume of a reactant.

For any reaction to take place the particles involved must collide and they always collide with the right or necessary activation energy.

An increase in the concentration of one of the reactants, increases the number of molecules in a given volume. This in turn increases the chances particles colliding the particles colliding with the necessary activation energy and hence the rate of the reaction.

Conversely, a decrease in the concentration increases the number of molecules in a given space. This then decreases the chances of particles colliding with the necessary activation energy and therefore decreasing the rate of the reaction.



Effect of temperature on the rate of a reaction

Temperature mainly influences the rate of the reaction and the rate at which the reaction reaches an equilibrium or completion. The effect of temperature on the rate of reaction is based on two assumptions which include;

- (i) The reacting molecules or particles must collide before they react.
- (ii) The molecules must have acquired minimum or activation energy before they collide to react.

When the temperature of the reaction is raised, the rate of reaction also increases. This is because increase in temperature increases the average molecular velocity which in turn results in greater number of collisions per second. This in turn results in the increase in the number of molecules required to react with the necessary activation energy hence the faster the rate of the reaction. However, when the temperature of the reaction is lowered, the average molecular velocity of the reacting particles reduces and this then decreases the number of collisions per second.

This also decreases the number of molecules required to react with the necessary activation energy hence the rate of the reaction reduces.

Reaction profiles/ path ways for exothermic reactions.

An exothermic reaction is the one which takes place with evolution of heat energy.

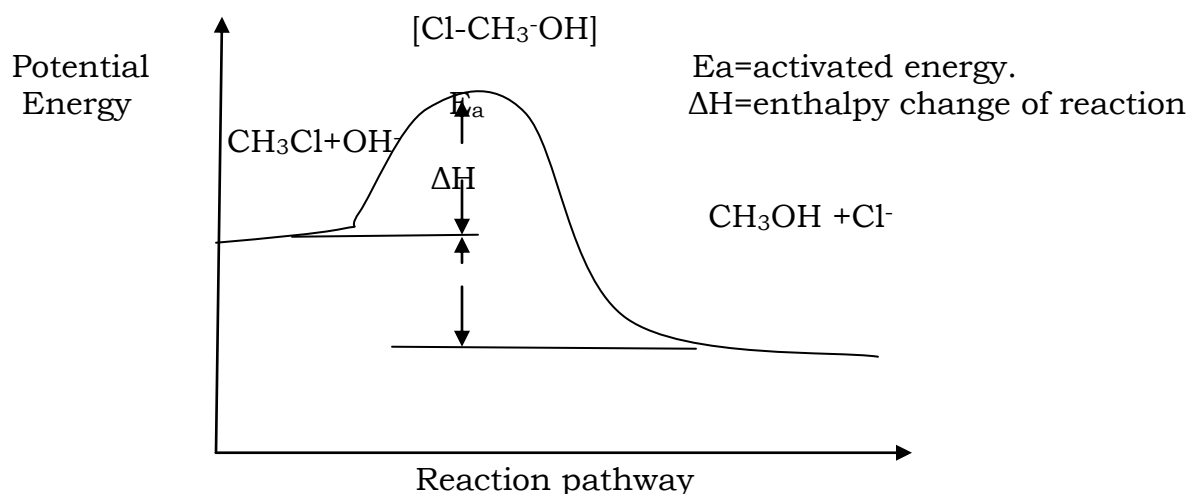
(a) Single step or bimolecular reaction

Consider a reaction



This reaction takes place in a single step mechanism and this referred to as bimolecular reaction. Thus $\text{CH}_3\text{-Cl} + \text{OH}^- \longrightarrow \text{CH}_3\text{-OH} + \text{Cl}^-$

It involves the formation of a single activated complex from which the products are formed. This can be represented on the energy profile as follow



From the energy diagram above, the C-Cl bond is partially broken up in the activated complex as the C-OH bond is partially formed. The final products formed are CH_3OH and Cl^-

Note: Bimolecular reactions are common among primary alkyl halides

A bimolecular reaction is a type of reaction which involves two molecules in the rate determining step or activated complex.

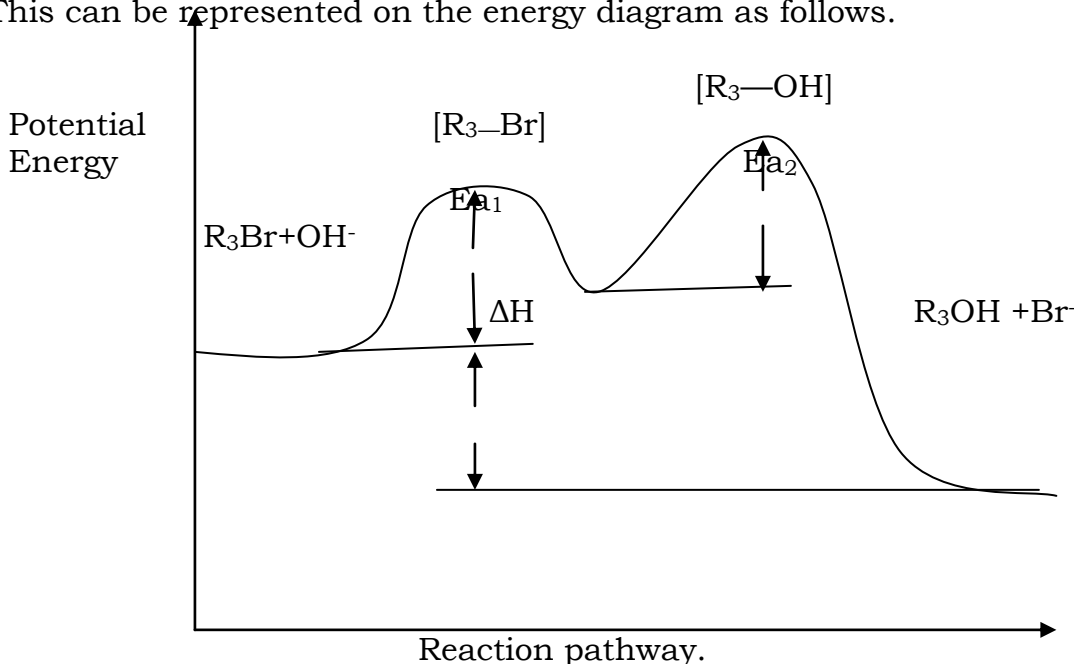
(b) Double step (unimolecular reaction)

All molecular reaction is the type of reaction which involves only one molecule in the rate determining step.

This reaction always takes place in double step mechanism in which the first activated complex (i) is formed in the first step and the second activated complex (ii) is also formed in the second step. Thus: $R_3Br \longrightarrow R_3^+ + Br^-$

Then; $R_3^+ + OH^- \longrightarrow R_3-OH$

It is the second activated complex from which the final products are formed. This can be represented on the energy diagram as follows.

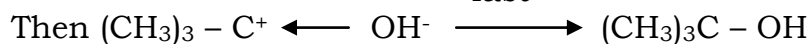
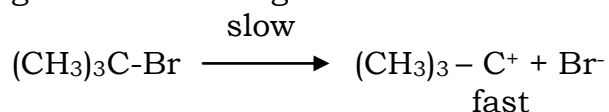


Where ΔH = Enthalpy change of the reaction

E_{a1} = First activation energy

E_{a2} = Second activation energy

Note: unimolecular reaction is common among tertiary alkyl halides especially when they undergo hydrolysis e.g 2bromo 2methyl propane $[(CH_3)_3C-Br]$ under goes the following mechanism.



From the energy diagram above up in the first activated complex while C-OH bond is partially formed in the second activated complex. The final products formed are R_3OH and Br^- .

Reaction profiles/ path ways for endothermic reactions

An endothermic reaction is a type of reaction which occurs with absorption of heat energy.

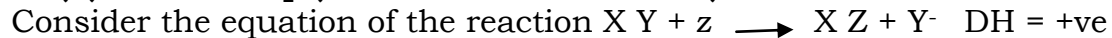
(a) Single step or bimolecular reaction

Consider a reaction



Suppose the reaction takes place in a single step mechanism, then it is also referred to as a bimolecular reaction since it involves one molecule in the rate determining step. It also involves the formation of a single activated complex from which the final products are formed. This is represented on the following energy diagram. From the energy of the reaction diagram above, the A-B bond is partially broken up in the activated complex as the A-X bond is partially formed. The final products are A-X and B⁻

(b) Double step (unimolecular reactions)



Suppose the reaction occurs in a double step mechanism, then it is referred to as a unimolecular reaction since it involves two molecules in the rate determining step. It also involves the formation of two activated complexes, one formed in the first step and the other of the second step. This can be represented on the energy diagram as follows. From the energy diagram, the X-Y bond is partially broken up in the first activated complex while X-Z bond is partially formed in the second activated complex. The final products formed are XZ and Y⁻

Note: In bimolecular reaction the rate of reaction depends on both reactants that are involved in the rate determining state; thus Rate = K(CH₃Cl)⁻ (OH)

Therefore the overall order of reaction is 2 hence bimolecular reaction.

2. In unimolecular reaction the rate of reaction depends on only one of the reactants which involves in the rate determining state.

Thus Rate = K(R₃-Br)

Therefore all order of reaction is 1 hence unimolecular reaction.

Effect of pressure on the rate of reaction

Pressure mainly affects gaseous systems since it has negligible effect on the volumes of solids and liquids as they are almost incompressible. Pressure affects the rate of reaction of the gaseous system by increasing or decreasing the rate of collisions of molecules per second. An increase in the pressure of the gaseous system reduces the volume of the gases in the container. This in turn increases the rate of collision per second occurring between the molecules since they are very close to one another. The molecules then collide more rapidly with the necessary activation energy hence increasing the rate of reaction and amount of the products formed. However when the pressure of the system is reduced, the volume increases and the reacting particles collide less frequently since they are far apart. The increased volume reduces the chances of collision of molecules with the necessary activation energy hence lowering the rate the reaction.

Effect of a catalyst on the rate of the reaction.

A catalyst is an agent or a substance which alters the rate of a chemical reaction and left unchanged in mass and chemical nature at the end of the reaction.

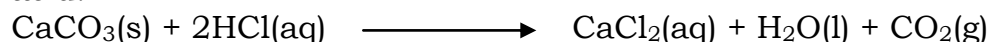
Catalysis is a change in the rate of a chemical reaction brought by an agent (catalyst) which is left unchanged at the end of reaction. A catalyst increases the rate of the reaction by providing an alternative path way in which the

activated complex requires a smaller amount of activation energy. This enables a larger proportion of the molecules to achieve the state of transition where the activated complex occurs. The path of reaction and the accompanying energy changes may be represented on the energy diagram shown below. However catalysts are usually used as solids and should be finely divided like in form of powders, pellets, fibres or gauze to increase the surface area for their catalytic action to occur. This process is called adsorption. Some catalysts work by forming a short-lived intermediate compound with reactants. The compound then breaks up to give the catalyst and products. A particular catalyst alters rate of a certain reaction but not rates of all reactions.

Effect of surface area on the rate of the reaction.

Surface area only affects the rate of reaction for solids whose reacting particles have different sizes unlike liquids and gases whose particles have uniform sizes. When solid substances are ground, the sizes of the particles are reduced. This increases the surface area of the particles thus increasing the area of contact between reacting particles. The greater the surface area of contact between reacting particles, the higher the rate of the reaction. Conversely, when the surface area of contact between reacting particles is reduced (ie by having large sized particles), the rate of the reaction also reduces.

For example, in a reaction between calcium carbonate and dilute hydrochloric acid.



When powdered calcium carbonate is used, the reaction takes place more vigorously and reaches completion earlier than that of the unground calcium carbonate. Smaller particles with large surface area also collide more frequently with the necessary energy hence react more quickly than the large lumps.

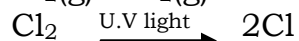
Effect of light on the rate of some reaction.

Light is a form of energy. It can influence the rate of some chemical reactions by energizing some of the particles involved.

Examples of such reactions which are accelerated by light include the following

- i. Decomposition of hydrogen peroxide
- ii. The combination of hydrogen and chlorine
- iii. Chlorination of methane
- iv. Photosynthesis

These reactions are represented by the following equations.



Light increases the number of effective collisions per unit time thus increasing the rate of reaction.

However, in absence of light the number of effective collisions per unit time is reduced hence decreasing the rate of the reaction.

NOTE: photographic plates are normally coated with silver bromide. Therefore processing of films is done in a dark room to avoid decomposition of the silver bromide.

CLASSIFICATION OF ORDERS OF REACTION.

Orders of reactions can be classified as follows;

Zero order reaction.

This is the one in which the rate of the reaction does not depend on the concentration of the reactants. E.g iodination of propanone is zero order.

Consider the reaction $X + Y \longrightarrow P$

The rate of decrease in the concentration of the reactant, X is given by $-\frac{d[X]}{dt}$.

Introducing a constant,

$$-\frac{d[X]}{dt} = k_0 \quad \text{.....1}$$

Where k_0 = rate constant.

$$\text{Thus } -\frac{d[X]}{dt} = k_0$$

By integrating,

Introducing natural log.

$$\ln [X] = -k_0 t + C \quad \text{.....2}$$

Converting to log base 10.

$$2.303 \log_{10} [X] = -k_0 t + C \quad \text{.....3}$$

When $t=0$, $x=[X_0]$, substituting in the equation 3

$$2.303 \log_{10} [X_0] = -k_0 \cdot 0 + C.$$

$$\therefore C = 2.303 \log_{10} [X_0] \quad \text{.....4}$$

Substituting equation 4 in equation 3 and when $t = t_{1/2}$, $[X] = \frac{1}{2}[X_0]$.

$$2.303 \log_{10} \frac{1}{2}[X_0] = -k_0 t_{1/2} + 2.303 \log_{10} [X_0].$$

$$2.303 \log_{10} \frac{1}{2}[X_0] - 2.303 \log_{10} [X_0] = -k_0 t_{1/2}.$$

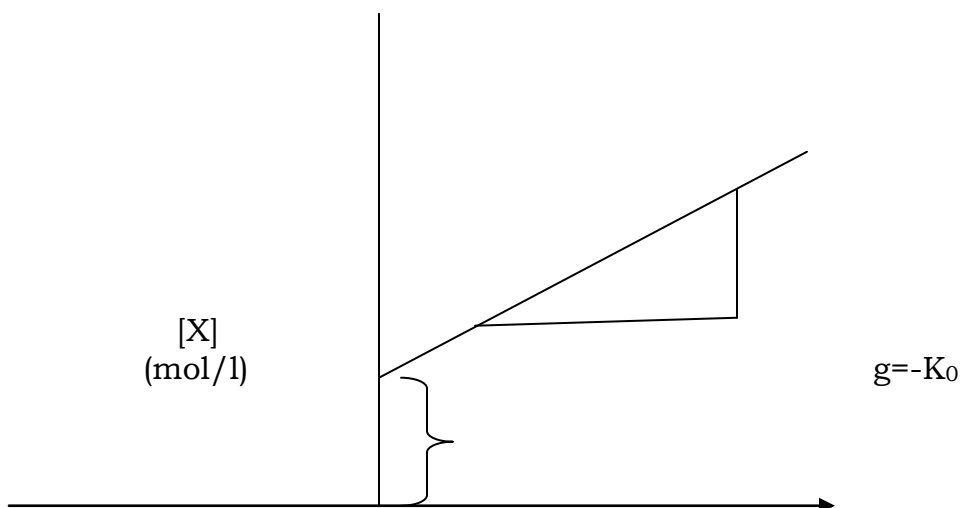
$$2.303 \log_{10} \frac{1}{2} = -k_0 t_{1/2}.$$

$$2.303 \log_{10} \frac{1}{2} = -k_0 t_{1/2} \quad \text{.....5}$$

$$k_0 = \frac{2.303 \log_{10} 2}{t_{1/2}} \quad \text{.....6}$$

$$t_{1/2} = \frac{2.303 \log_{10} 2}{k_0} \quad \text{.....7}$$

If the graph of $[X]$ against t is plotted, a straight line graph is which does not pass through the origin is obtained as shown below;



[X₀]

Time (seconds).

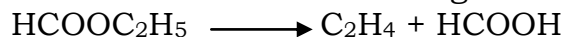
If a graph of $\frac{[X_0]}{\text{Time}}$ against concentration is plotted, a straight line also obtained as follows;



From the last graph above, the rate of the reaction does not depend on the concentration of the reactants.

First order reaction.

This is the one in which the rate of increase in the concentration of one of the products depends on the concentration of a single reactant. This means that the concentration of one of the products is directly proportional to the first power of the concentration of a single reactant. For example in the reaction



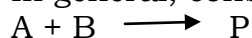
The rate of increase in concentration of ethane is proportional to the concentration of ester

$$\text{Thus: } \text{rate} = K_1 [\text{HCOOC}_2\text{H}_5]$$

$$\text{But rate} = \frac{d[\text{C}_2\text{H}_4]}{dt} \therefore \text{rate} = K_1 [\text{HCOOC}_2\text{H}_5]$$

This is a first order reaction since the rate of increase in the concentration of ethane is directly proportional to the concentration of the ester.

In general, consider the reaction;



If C = change in concentration of A then the rate equation is given by;

$$\text{Rate} = K$$

$$\text{But } \text{rate} = K C \text{-----(1)}$$

Let a be the initial concentration of A and X be the decrease in concentration of A in time (t)

$$\text{The concentration of A at time (t) } = (a-x)$$

$$\text{Therefore } C = (a-x)$$

Substituting (a-x) for C in equation (1)

$$\text{Then } \text{rate} = K_1(a-x) \text{-----(2)}$$

$$\text{Then } \text{rate} = K_1 (a-X)$$

To separate variables x and t are arranged on different sides of the equation

$$\text{-----(3)}$$

By integration

$$= K_1$$

$$dx = k_1$$

Introducing natural log

$$\ln(a-x) = K_1 t + C$$

Since $-\ln x = 2.303 \log_{10} x$

Introducing log to base 10

$$\therefore 2.303 \log_{10} (a-x) = K_1 t + C \dots\dots\dots(4)$$

When $t = 0, x = 0$

$$\therefore C = 2.303 \log_{10} a = K_1 t$$

Substituting in equation 4

$$2.303 \log_{10} (a-x) = K_1 t + 2.303 \log_{10} a$$

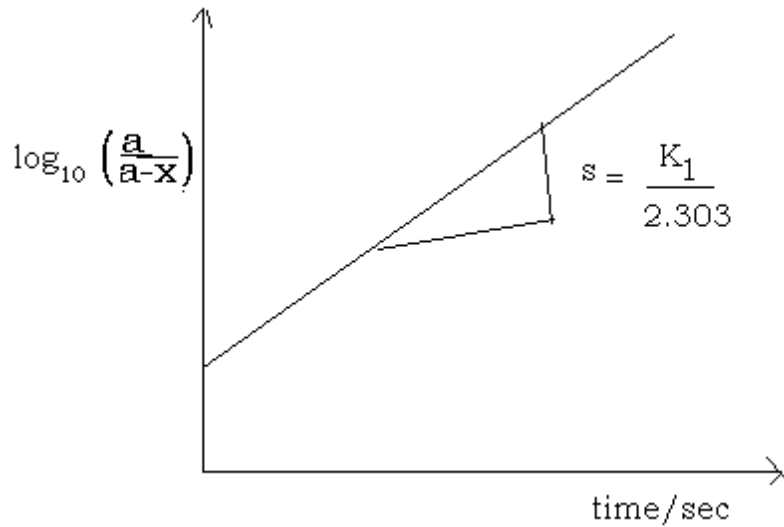
$$2.303 \log_{10} (a-x) - 2.303 \log_{10} a = K_1 t$$

$$=$$

$$\log_{10} \frac{a}{a-x} = \dots\dots\dots (5)$$

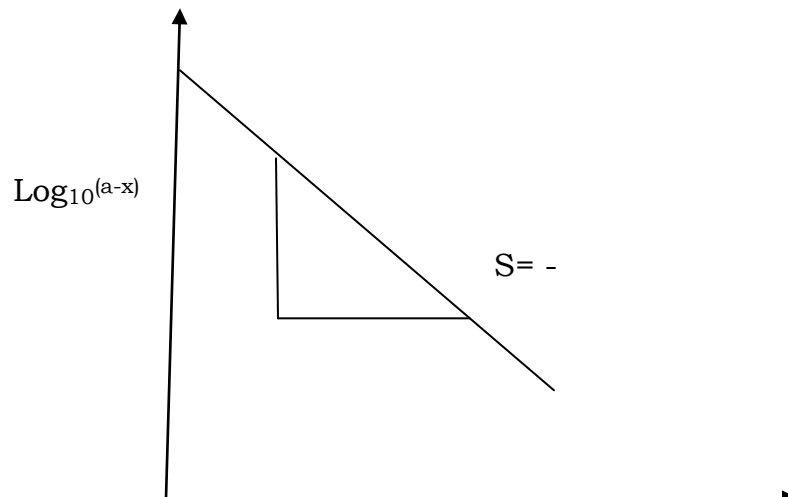
$$\therefore \log_{10} \frac{a}{a-x} = \frac{K_1}{2.303} t$$

If a graph of $\log_{10} \left(\frac{a}{a-x} \right)$ is plotted against time a straight line is obtained as follows;

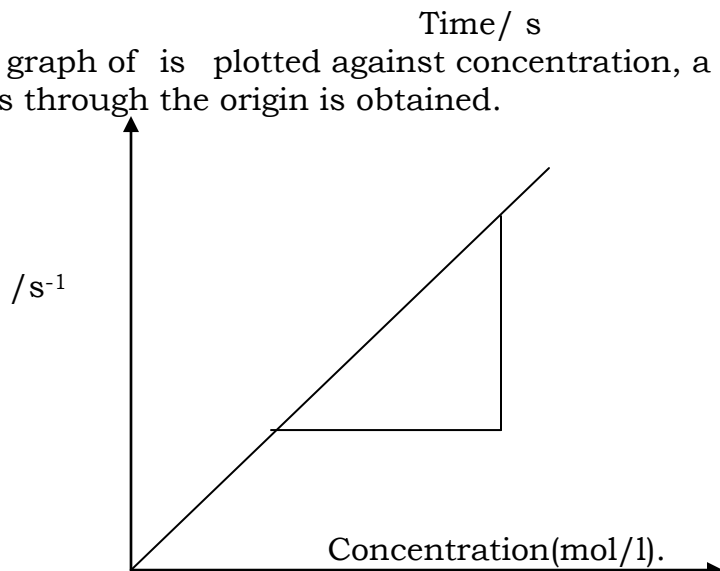


From equation (5), $\log_{10} a - \log_{10} (a-x) = \dots, \therefore \log_{10} (a-x) = -\dots + \log_{10} a$, where $\log_{10} a = \text{constant}$.

If a graph of $\log_{10} (a-x)$ is plotted against time, a straight line is also obtained as follows;



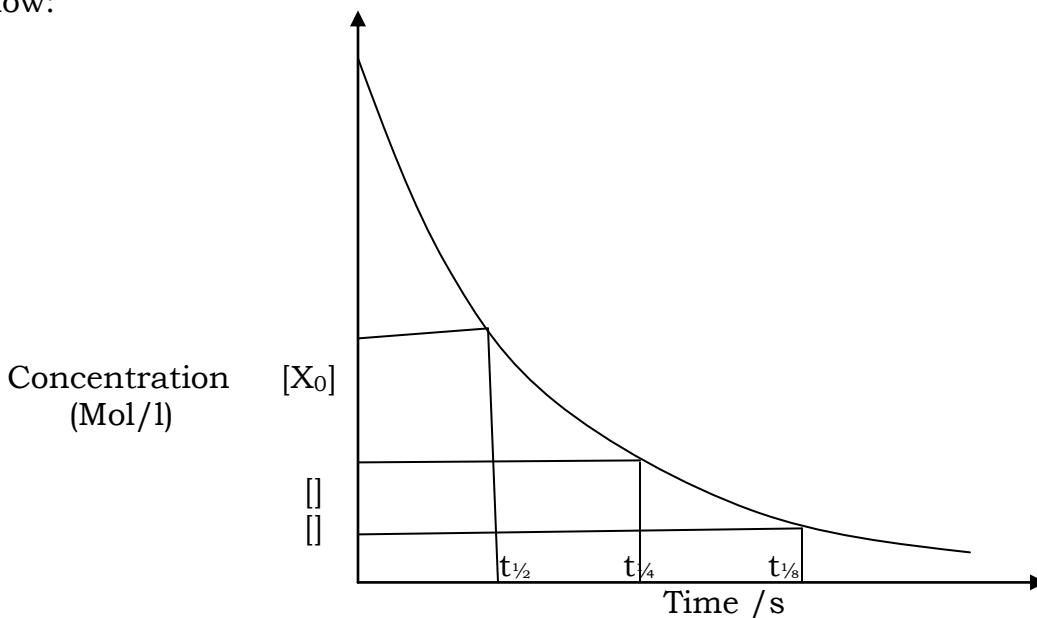
However if a graph of $\frac{1}{[X]}$ is plotted against concentration, a straight line graph which passes through the origin is obtained.



The straight line graphs obtained above are characteristic of first order reaction in which the rates are directly proportion to the first power of the concentration of the single of the single reactant.

Half life method for first order reaction.

If a graph of concentration is plotted against time a curve is obtained as shown below:



If the half life is constant that is $t_{1/2} = t_{1/4} = t_{1/8}$ etc, the order of the reaction is first order since the rate of the reaction is directly proportional to the concentration of the a single reactant.

Then rate $[X]$,

\therefore Rate $K[X]$.

$t_{1/2} = \frac{1}{K}$ where $t_{1/2}$ is the half life, K is a constant.

The equation above can be used to calculate for half life in the rate equation;

Deriving the expression for half life;

$$\text{Rate} = -\frac{d[X]}{dt} = -K[X_0] \dots\dots\dots 1$$

Separating the variables and integrating, we get;

$$\int \frac{1}{[X]} d[X] = -K \int dt \dots\dots\dots 2$$

Introducing natural log

$$\ln[X] = \ln[X_0] - Kt \dots\dots\dots 3$$

Converting to log e, it gives;

$$\log e = \log e^{-Kt}$$

Dividing through by log e, gives, $-Kt = \log e^{-Kt}$

$$X = X_0 e^{-Kt} \dots\dots\dots 4$$

$$t = t_{1/2}, X = \frac{X_0}{2} = e^{-Kt}$$

$$\frac{1}{2} = e^{-Kt} \dots\dots\dots 5$$

$$\therefore 2 = e^{Kt}$$

Reintroducing natural log.

$$\ln 2 = \ln e^{Kt} \dots\dots\dots 6$$

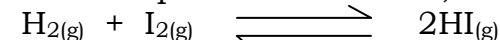
But $\ln e = 1$, $\ln 2 = Kt$, also $\ln 2 = 0.69$.

$$K = \frac{0.69}{t_{1/2}} \dots\dots\dots 7$$

Second order reaction.

This is the one in which the rate of change in concentration of a product is proportional to the product of concentrations of two reactants or to the square of the concentration of a single reactant.

For example in the reaction,

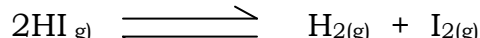


The increase in the concentration of the hydrogen iodide at any time is given by;

$$= K_2 [H_2] [I_2].$$

The forward reaction is first order with respect to hydrogen and first order with respect to iodine. The overall reaction is a second order.

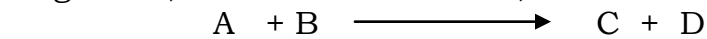
Similarly when the reaction is reversed, the dissociation of hydrogen iodide is a second order reaction.



$$= K_2 [HI]^2.$$

$$\text{Also } = K_2 [HI]^2.$$

In general, consider the reaction;



$$\text{Initially; } \begin{matrix} a & a & & 0 & 0 \end{matrix}$$

$$\text{At a time, } t \begin{matrix} (a-x) & (a-x) & & x & x \end{matrix}$$

If a is the initial number of moles of either A or B, then x is number of moles of either C or D formed. The rate of increase in the concentration of C or D is proportional to the product of the concentration of A and B.

$$\text{Thus; } (a-x)^2 = k(a-x)^2 \dots\dots\dots 1$$

$$\text{Separating variables; } = K_2 dt \dots\dots\dots 2$$

$$\text{Integrating, } = K_2, (a-x)^{-1} = K_2 t + C \dots\dots\dots 3$$

$$\text{Introducing log to base 10, } 2.303 \log \frac{1}{a-x} = K_2 t + C \dots\dots\dots 4$$

$$\text{When } t=0, x=0, (a-x)=a \therefore C = 2.303 \log \frac{1}{a} \dots\dots\dots 5$$

Substituting equation 5 in equation 4, we get;

$$2.303 \log_{10} \left(\frac{[x]_0}{[x]} \right) = K_2 t + 2.303 \log_{10} [x]_0 \quad \dots\dots\dots 6$$

$$2.303 \log_{10} \left(\frac{[x]_0}{[x]} \right) - 2.303 \log_{10} [x]_0 = K_2 t$$

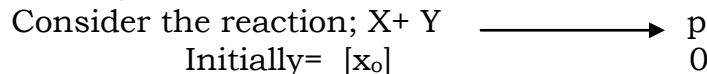
$$2.303 \log_{10} \left(\frac{[x]_0}{[x]} \right) = K_2 t, \quad 2.303 \log_{10} \left[\frac{[x]_0}{[x]} \right] = K_2 t$$

$$\therefore \log_{10} \left[\frac{[x]_0}{[x]} \right] = \dots\dots\dots 7$$

$$\text{Hence, } \log_{10} \left[\frac{[x]_0}{[x]} \right] t, \quad K_2 = 2.303 \log_{10} \left[\frac{[x]_0}{[x]} \right] \text{ or } K_2 = \left[\frac{2.303 \log_{10} \left[\frac{[x]_0}{[x]} \right]}{t} \right]$$

The values of K_2 are characteristic of the second order reaction.

Alternatively, the expression for second order reaction can also be derived as follows;



The rate of the reaction depends on the decrease in the concentration of the reactant (x) at agiven time.

$$\text{Thus; } -\frac{d[x]}{dt} = K_2 [x]^2 \quad \dots\dots\dots 1$$

$$\text{Separating variables; } -\frac{d[x]}{[x]^2} = K_2 dt \quad \dots\dots\dots 2$$

$$\text{Integrating, } \int \frac{d[x]}{[x]^2} = -K_2 \int dt \quad \dots\dots\dots 3$$

$$\text{Introducing natural log, in} = K_2 t + C \quad \dots\dots\dots 4$$

$$\text{Converting to log base 10, } 2.303 \log_{10} [x] = K_2 t + C \quad \dots\dots\dots 5$$

$$\text{When } t=0, [x]=[x_0], \therefore c=2.303 \log_{10} [x_0] \quad \dots\dots\dots 6$$

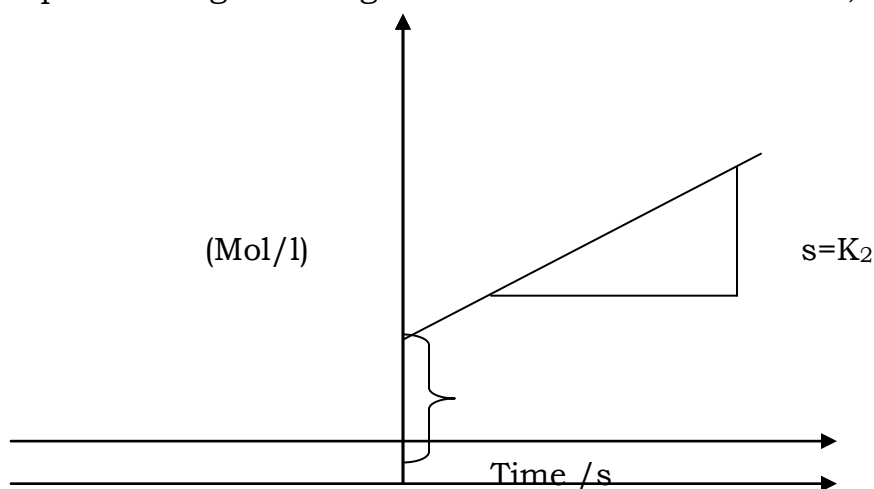
Substituting equation 6 in equation in 5 gives;

$$2.303 \log_{10} [x] = K_2 t + 2.303 \log_{10} [x_0] \quad \dots\dots\dots 7$$

$$2.303 \log_{10} [x] - 2.303 \log_{10} [x_0] = K_2 t.$$

$$2.303 \log_{10} \left[\frac{[x]}{[x_0]} \right] = K_2 t, \quad K_2 = 2.303 \log_{10} \left[\frac{[x_0]}{[x]} \right] \text{ OR } K_2 = \left[\frac{2.303 \log_{10} \left[\frac{[x_0]}{[x]} \right]}{t} \right] \quad \dots\dots\dots 8$$

When agraph of $\log_{10} \left[\frac{[x_0]}{[x]} \right]$ against t from equation is plotted, a straight line which does not pass through the origin is obtained as shown below;



HALF LIFE METHOD FOR SECOND ORDER REACTION.

In the second order reactions, the time, t taken for the reaction to reach half of the original concentration of the reactant, depends on the original concentration of the reactant.

$$\text{if } [x] = \frac{[x]_0}{2}, \text{ then } t = t_{1/2}, \quad [x] = \frac{[x]_0}{2}$$

$$\text{From } K_2 = \frac{2.303 \log_{10} \left[\frac{[x]_0}{[x]} \right]}{t} \quad \dots\dots\dots 1$$

$$\text{Substituting in equation 1; } K_2 = \frac{2.303 \log_{10} \left[\frac{[x]_0}{[x]_0/2} \right]}{t_{1/2}}, \quad K_2 = \frac{2.303 \log_{10} 2}{t_{1/2}}$$

$$= K_2 t_{1/2}$$

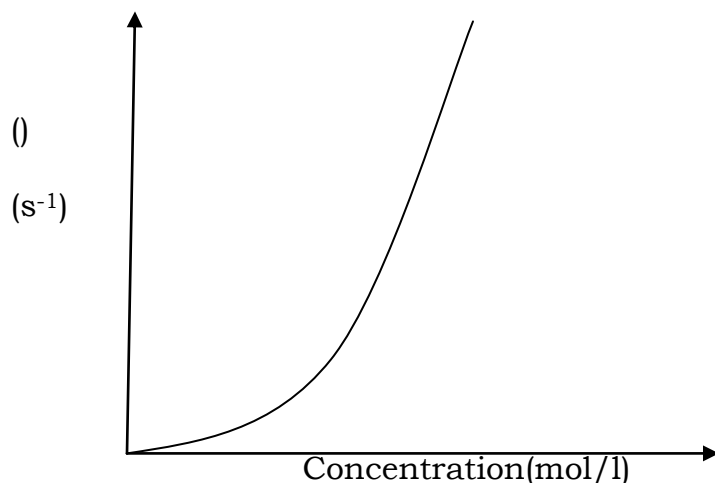
$$= K_2 t_{1/2}, = K_2 t_{1/2} \dots \dots \dots 2$$

$$t_{1/2} = \dots \dots \dots 3$$

$$\text{OR } K_2 = \dots \dots \dots 4$$

Equation 3 above shows that the half life ($t_{1/2}$) of the second order reaction depends on the initial concentration of the reactants.

If a graph of $t_{1/2}$ is plotted against concentration, a curve is obtained as shown below;

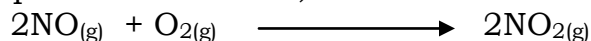


From the graph above, the rate of the reaction increases exponentially with increase in the concentration of the reactant.

Third order reaction.

Is the one in which the rate of reaction is proportional to the third power of the concentration of a single reactant or to the product of concentration of some three reactants.

For example in the reaction;



Initially a a 0
At time (t) (a-x) (a-x) x

Let a be the initial number of moles of NO or O_2 and x be the decrease in their concentration. The rate of a reaction increase in concentration of NO_2 is given by;

$$= K_3 [\text{NO}]^2 [\text{O}_2]$$

The above reaction is second order with respect to NO and first order with respect to O_2 . The overall order of the reaction is 3 i.e third order reaction.

$$\text{But since } (a-x)^3, = K_3 (a-x)^3 \text{ or } = dt \dots \dots \dots 1$$

$$\text{Integrating; } = K_3, \quad dx = K_3 t + C$$

Introducing natural log.

$$\ln = K_3 t + C \dots \dots \dots 2$$

Converting to base 10.

$$2.303 \log 10(= K_3 + C \dots \dots \dots 3$$

$$\text{When } t=0, x=0, \text{ then } (a-x)^2 = (a-0)^2 = a^2.$$

$$C = 2.303 \log 10() \dots \dots \dots 4$$

$$\therefore 2.303 \log 10() = K_3 t + 2.303 \log ()$$

$$2.303 \log 10 () - 2.303 \log () = K_3 t.$$

$$2.303 \log 10 (-) = K_3 t$$

$$2.303 \log 10 () = K_3 t.$$

$$K_3 = 2.303 \log 10 () \dots\dots\dots 5$$

Note: the time, t required for the reaction to reach half of the original concentration of the reactant is given by;

$$t = \dots\dots\dots 6$$

thus t, is inversely proportional to the square of the initial concentration or $a^2 t$ is a constant.

Methods of determining the rate of chemical reaction

There are various methods used to measure the rate of chemical reaction. These are mainly experimental methods and they divided into three categories namely.

(a) Recording the time for a reaction to reach a certain stage.

Examples of experiments where this method is applied include.

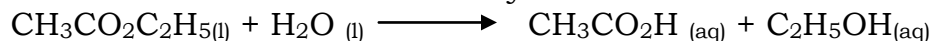
- (i) An experiment to determine iodine and starch, the time taken for iodine-starch colour to appear is recorded.
- (ii) An experiment to determine the rate of reaction between sodium thiosulphate and hydrochloric acid, the time taken for the sulphur precipitate to reach certain density is recorded.

(b) The progress of a reaction may be followed by chemical analysis.

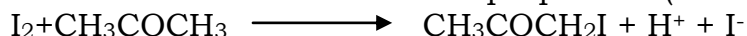
Here known volumes are got from the reaction mixture at regular intervals of time and each sample is quickly run into an excess of a reagent which stops the reaction or the reaction may be stopped by rapid cooling.

The sample is then analyzed usually by titration to determine the concentration of either a reactant or a product. Examples of reactions where this technique is applied are;

- (i) Acid catalyzed hydrolysis of an ester such as a reaction between ethyl ethanoate ($\text{CH}_3\text{COOC}_2\text{H}_5$) and water. The concentration of the ethanoic can be determined by titration with a standard base since a mineral acid is added as a catalyst.



- (ii) Reactions between iodine and propanone (Acetone)

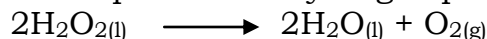


In this reaction, samples are got and after neutralizing the H^+ ions, each sample can be titrated with standard sodium thiosulphate solution order to estimate the iodine left.

(c) The progress of reactions may also be followed by physical methods.

Examples of physical methods include

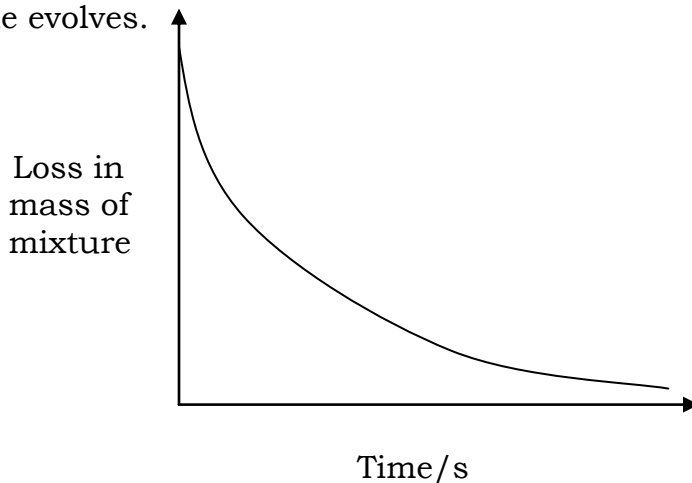
- (i) The volume of the gaseous product is continuously recorded by collecting the gas in a graduated. For example the rate of decomposition of hydrogen peroxide can investigated by this method



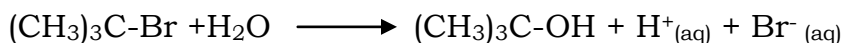
- (iii) The loss in mass of reaction mixture due to the loss of a gaseous product. For example in the reaction.



In this reaction, the mass of reaction mixture decreases as carbon dioxide evolves.



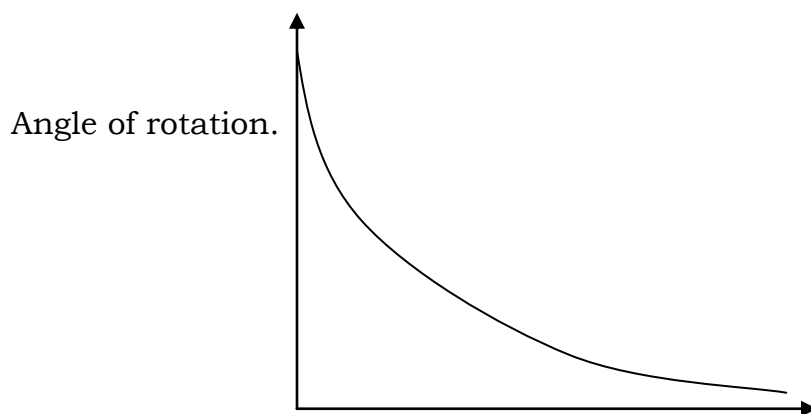
- (iv) The rate of change in concentration of a coloured reactant can be followed by colorimeter. This translates the intensity of light transmitted by a coloured solution into an electrical measurement, by means of a light sensitive cell. Examples of reactions where this method is applied include the reaction between iodine and propanone. The reaction between permanganate and oxalate ions.
- (v) The change in conductivity of a liquid, due to the change in the number of ions present may also be used to follow a reaction. For example, in the hydrolysis of a halogeno alkane the conductance of the reaction mixture will increase.



(d)Optical rotation/activities.

The ability of a certain substance to rotate the plane of light is a useful parameter in kinetic studies. A light ray consists of vibrations in all directions perpendicular to its path. To follow the reaction where optical activity changes the reaction mixture changes the reaction mixture is replaced in the polarimeter tube and optical rotation is measured at definite time intervals.

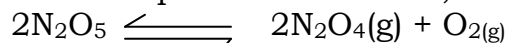
If the angle of rotation is plotted against time the following curve is obtained.



Time/s

(e)The change in gas pressure

For example in the reaction;



In the above reaction, if the volume is kept constant the increase in pressure can be followed and used as a parameter for determining the rate of decomposition of nitrogen pent oxide.

(f) The change in the absorption spectrum by the use spectro-photometer.

This measures absorption of light of various wave lengths.

Calculations in chemical kinetics.

1. The rate of a reaction between propene and bromine is given by relationship
Rate = K (CH₃CH = CH₂) (Br₂) where k=30 mol⁻¹s⁻¹

(a)(i) What is the overall order of the reaction?

(b) Calculate the rate of the reaction when the concentration ions of both propene and bromine are 0.02 mol l⁻¹ and 0.02 mol l⁻¹ respectively.

Solution

(a)(i) The overall order of reaction = 1+1 = 2

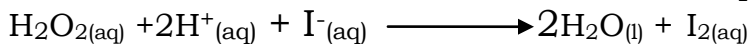
(b)From rate = [CH₃CH =CH₂] [Br₂]
= 30.(0.02)²
= 0.012 mol l⁻³S⁻¹

2. (a) Explain what is meant by the following terms;

(i)Rate constant

(ii)Order of reaction

(b)In experiments to determine the rates of reaction represented by the equation;



The following experimental data were recorded

Experiment	Concentration			
	[H ₂ O ₂] (mol dm ³)	[I ⁻] (mol dm ³)	[H ⁺] (mol/dm ³)	Rate (mol/dm ³ S ⁻¹)
1	0.010	0.010	0.10	1.75 x 10 ⁻⁶
2	0.030	0.010	0.10	5.25 x 10 ⁻⁶
3	0.030	0.020	0.10	10.5 x 10 ⁻⁶
4	0.030	0.20	0.20	10.5 x 10 ⁻⁶

(i)Derive the rate equation for the reaction.

(ii)Determine the rate constant (K) for the reaction giving its units.

(iii)Calculate the order of the reaction.

Solution

(a)(i) and (ii) see notes

(b)(i) Rate = K (H₂O₂) (I⁻), Since H⁺ is a catalyst

(ii) K =

Considering experiment [5]

$$K = 75 \times 10^{-2} \text{ mol}^{-1}\text{dm}^{-3}\text{S}^{-1}$$

$$K = \text{mol}^{-1}\text{dm}^{-3}\text{S}^{-1}$$

(iii) Order of reaction with respect to H_2O_2

From experiment (1) and (2)

$$X \log () = \log ()$$

$$X \log () = \log ()$$

$$X \log 3 = \log 3$$

$$\log_3 x = \log_3$$

$$X = 1$$

The order of reaction with respect to H_2O_2 is 1. The order of reaction with respect to (I-)

From experiments (2) and (3)

$$y \log () = \log ()$$

$$y \log () = \log ()$$

$$y \log 2 = \log 2$$

$$y = 1$$

The overall order of the reaction on is $1+1 = 2$

3. At 329K and the concentration of 0.2 mol l^{-1} , the rate of decomposition of hydrogen iodide is $6.04 \times 10^{-5} \text{ mol l}^{-1}\text{S}^{-1}$.

(a) Write down the rate equation.

(b) Calculate

(i) The rate constant

(ii) Its units

Solution

(a) Rate = $K(\text{HI})^2$

(b) Rate constant = = = $1.51 \times 10^{-3} \text{ mol l}^{-1}\text{S}^{-1}$

4. The table below shows the rates of reaction between A and B at different concentrations.

Experiment	Concentration (mol dm^{-3})		Rate ($\text{mol/dm}^3\text{S}^{-1}$)
	A	B	
1	0.50	0.50	2.0×10^{-2}
2	1.00	0.50	8.0×10^{-2}
3	1.00	1.00	16.0×10^{-2}

(a) Determine

(i) The order of reaction with respect to A & B.

(ii) The overall order of the reaction.

(b)(i) Write an expression for the rate of the reaction.

(ii) Calculate the rate constant for the reaction and state its Units.

Solution

(a)(i) let the rate equation be

$$\text{Rate} = K[\text{A}]^x [\text{B}]^y$$

From experiments (i) and (2)

The order of reaction with respect to A

$$\begin{aligned}
 X \log () &= \log () \\
 X \log 2 &= \log 4 \\
 \therefore X \log 2 &= 2 \log 2 \\
 X &= 2
 \end{aligned}$$

\therefore The order of reaction with respect to A is 2

From experiments (2) and (3)

$$\begin{aligned}
 Y \log () &= \log () \\
 Y \log 2 &= \log 2 \\
 Y &= 1
 \end{aligned}$$

\therefore The Order of reaction with respect to B is 1

(ii) The overall order of reaction = 2 + 1 = 3

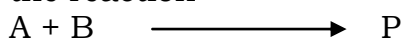
(b)(i) Rate = $K[A]^2[B]$

Rate constant =

From experiment (1)

$$\begin{aligned}
 K &= \\
 &= 0.16 \text{ mol}^{-2}\text{dm}^{-6}\text{S}^{-1}
 \end{aligned}$$

5. The table below shows the data obtained from an experiment on the rate of the reaction



Experiment	[A] mol / l $\times 10^{-3}$	[B] mol / l $\times 10^{-3}$	Rate $\times 10^{-3}$ Mol / l S ⁻¹
1	1.2	4.4	12.1
2	2.4	4.4	24.3
3	1.2	1.1	3.0

(a) Deduce an expression for the rate law

(b) Calculate the rate constant

(c) Determine the over order of the reaction

Solution

(a) Let the rate equation be

$$\text{Rate} = K[A]^x [B]^y$$

Taking experiment (1) and (2) where the concentration of B is kept constant.

The order of reaction with respect A is given by

$$\begin{aligned}
 X \log () &= \log () \\
 X \log 2 &= \log 2 \\
 X &= 1
 \end{aligned}$$

The order of reaction with respect to a is 1

Taking experiments (1) and (3) where the concentration is A is constant.

(b) $K = 2.273 \times 10^3 \text{ mol/dm}^3\text{s}^{-1}$

(c) The overall order of reaction = 1 + 1 = 2

6. Propanone reacts with iodine in presence of an acid catalyst according to the equation; $\text{CH}_3\text{COCH}_3 + \text{I}_2 \longrightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$

The reaction is first order with respect to propanone and independent of the concentration of iodine.

(a) Write the expression for the rate law of the reaction.

- (b) State what would happen to the rate of the reaction when.
- The concentration of propanone is doubled but the concentration of iodine is kept constant
 - The concentration of propanone and iodine are doubled
 - The concentration of propanone is kept constant and that of iodine is doubled.
 - The concentration of propane halved and that of iodine is kept constant

Solution

(a) Rate = $K [\text{CH}_3\text{COCH}_3] [\text{I}_2]^0$

(b) (i) The rate of reaction also doubles

(ii) The rate of reaction also doubles.

(iii) The rate of reaction also remains constant.

(iv) The rate of reaction also halves.

(b)(i) Rate = $K [\text{CH}_3\text{COCH}_3] [\text{I}_2]^0$

Assuming $K = 1$

$$\text{Rate} = [2]^1 [1]^0 = 2$$

(ii) Rate = $K [\text{CH}_3\text{COCH}_3] [\text{I}_2]^0$

$$= [2] [1]^0 = (2 \times 1) = 2$$

If $K = 1$

(iii) Rate = $K [\text{CH}_3\text{COCH}_3] [\text{I}_2]^0$

$$= [2] [1]^0$$

$$= 1$$

(iv) Rate = $K [\text{CH}_3\text{COCH}_3] [\text{I}_2]^0$

If $K = 1$

$$\text{Rate} = () (1)^0$$

$$\text{Rate} = \frac{1}{2}$$

$$= \frac{1}{2}$$

7.(a) Explain the following terms;

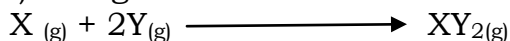
(i) order of the reaction.

(ii) rate constant.

(iii) activation energy.

(iv) Activated complex.

(b) Two gases X and Y react according to the reaction.



Experiments were performed at 400K in order to determine the order of this reaction and the following results were obtained.

Experiment	Concentration of X [mol/l]	Concentration of Y [mol/l]	Rate [mol/dm ³ s ⁻¹]
1	0.10	0.10	1.0x10 ⁻⁴
2	0.10	0.20	4.0x10 ⁻⁴
3	0.20	0.10	2.0x10 ⁻⁴

(i) What is the order of the reaction with respect to X and Y.

(ii) Write down the rate equation for the reaction.

(iii) Using the rate equation, predict a possible mechanism for the reaction.

(iv) calculate the value of the rate constant, K and state its units.

Solution.

(a) (i) –(iii) see notes.

(b) (i) the order of reaction with respect to X is given by ;

Taking experiment (1) and (3)

$$X \log() = \log(), \quad x \log 2 = \log 2, \quad x = 1.$$

The order of the reaction with respect to X is 1.

The order of the reaction with respect to Y is given by;

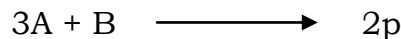
From experiments (1) and (2)

$$Y \log() = \log(), \quad Y \log 2 = \log 4, \quad Y \log 2 = 2 \log 2, \quad Y = 2$$

$$\text{Rate} = K[X][Y]^2$$

$$(iii) \text{Rate} = [X][Y]^2$$

8. The data below shows some kinetic study of the following reaction



Exp't No.	[A] (mol dm ⁻³)	[B] (mol dm ⁻³)	Initial rate (mol dm ⁻³)
1	0.20	0.20	1.2 x 10 ⁻⁸
2	0.20	0.60	1.2 x 10 ⁻⁸
3	0.40	0.60	4.8 x 10 ⁻⁸

(a) Determining the order of reaction with respect to;

(i) A

(ii) B

(b) Determine the over all order of reaction.

(c) Write the rate equation for the reaction.

(d) Calculate the rate constant and state its units.

Solution.

(a) (i) Second order reaction with A, because when the concentration of A is doubled the initial rate is multiplied by 4.

$$\text{i.e. } 2^x = 4, \quad 2^x = 2^2, \quad x = 2.$$

Proof;

$$\text{Expt 2; } 1.2 \times 10^{-8} = K [0.2]^x [0.6]^y$$

$$\text{Expt 3; } 4.8 \times 10^{-8} = K [0.4]^x [0.6]^y$$

Dividing 3 by 2.

$$\log[] = \log[]$$

$$\log 4 = x \log 2, \quad 2^2 = 2^x, \quad x = 2.$$

(ii) Zero order with B, because when the concentration of B is trippled the initial rate remained constant (multiplied by 1)

$$3^y = 1, \quad 3^y = 3^0, \quad y = 0$$

Proof;

$$\text{Expt 1; } 1.2 \times 10^{-8} = K(0.2)^x(0.2)^y$$

$$\text{Expt2; } 1.2 \times 10^{-8} = K (0.2)^x (0.6)^y$$

Dividing 2 by 1,

$$\log[] = \log[]$$

$$1 = 3^y, 3^0 = 3^y, Y=0$$

(b) Over all order = $2+0 = 2$.

$$(c) \text{ Rate} = K [A]^x [B]^y$$

$$\text{Rate} = K[A]^2[B]^0$$

$$\text{Rate} = K [A]^2$$

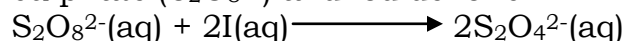
(d) Rate constant

$$1.2 \times 10^{-8} = K(0.2)^2$$

$$K = [] []$$

$$K = 3 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3$$

9. The following results were obtained in a study of a reaction between peroxide sulphate ($\text{S}_2\text{O}_8^{2-}$) and iodide ions



Expt No	$[\text{S}_2\text{O}_8^{2-}]$ (mol dm^{-3})	$[\text{I}^-]$ (mol dm^{-3})	Initial rate ($\text{mol dm}^{-3} \text{ s}^{-1}$)
1	0.024	0.12	9.6×10^{-6}
2	0.048	0.12	1.92×10^{-5}
3	0.048	0.06	9.6×10^{-6}

(a) Determine the order of reaction with respect to

(i) $\text{S}_2\text{O}_8^{2-}$ ions

(ii) I^- ions

(b) Determine the overall order of reaction

(c) Write the rate equation for the reaction

(d) Calculate the rate constant for the reaction and state its units.

Solutions.

$$(a) (i) \text{ Rate} = K(\text{S}_2\text{O}_8^{2-})^x (\text{I}^-)^y$$

$$\text{Consider; Expt1; } 9.6 \times 10^{-6} = K(0.024)^x (0.12)^y.$$

$$\text{Expt2; } 1.92 \times 10^{-5} = K(0.048)^x (0.12)^y.$$

Dividing 2 by 1,

$$\log[] = \log[]$$

$$2 = 2^x, 2 = 2^x, X = 1$$

The reaction is of first order with respect with $\text{S}_2\text{O}_8^{2-}$ ion

$$(ii) \text{ Rate} = K(\text{S}_2\text{O}_8^{2-})^x (\text{I}^-)^y$$

$$\text{Expt2; } 1.92 \times 10^{-5} = K(0.48)^x (0.12)^y$$

$$\text{Expt3; } 9.6 \times 10^{-6} = K(0.48)^x (0.06)^y$$

Dividing 3 by 2,

$$\log[] = \log[]$$

$$(\frac{1}{2}) = (\frac{1}{2})^y, Y = 1$$

The order of reaction with respect to I^- ions is one.

(b) Over all order = $1 + 1 = 2$

(c) Rate equation;

$$\text{Rate} = K[\text{S}_2\text{O}_8^{2-}]^1 [\text{I}^-]^1$$

$$\text{Rate} = K[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

(d) Rate constant;

$$\text{For expt 9.6} \times 10^{-6} = K(0.024)(0.12)$$

$$K = \quad, K = 3.33 \times 10^{-3} \text{ mol}^{-1}\text{dm}^3\text{S}^{-1}$$

10. The rate equation of the reaction between substances A, B and C is of the form $\text{rate} = K[A]^x[B]^y[C]^z$ where $x+y+z = 4$

Expt	[A] (mol dm^{-3})	[B] (mol dm^{-2})	[C] (mol dm^{-3})	Initial rate ($\text{mol dm}^{-3}\text{S}^{-1}$)
1	0.10	0.20	0.20	8.0×10^{-5}
2	0.10	0.05	0.20	2.0×10^{-5}
3	0.05	0.10	0.20	2.0×10^{-5}
4	0.10	0.10	0.10	A

(a) Use the data to determine the order of reaction with respect to it and with respect to B and hence deduce the order of reaction with respect C.

(b) Calculate the value of A.

(c) Determine the value of the rate constant and state its units.

(d) How does the value of K change when the temperature of the reaction is increased?

solutions

(a) Expt1; $8.0 \times 10^{-5} = K(0.1)^x(0.20)^y(0.20)^z$

Expt2; $2.0 \times 10^{-5} = K(0.1)^x(0.05)^y(0.20)^z$

Dividing 1 by 2

$$\text{Log } [] = \log ()^x ()^y ()^z$$

$$\text{Log } 4 = y \log 4, y = 1.$$

The order of the reaction with respect to B is 1.

Consider;

Expts1; $8.0 \times 10^{-5} = K(0.1)^x(0.2)^y(0.2)^z$

Expt2; $2.0 \times 10^{-5} = K(0.1)^x(0.05)^y(0.20)^z$

$$\text{Log } [] = \log ()^x ()^y ()^z$$

$$1 = 2^{(x-y)}, 0 = x - y \text{ but } y = 1, X = 1$$

The Order of reaction with respect to A is one.

$$\text{From, } X + y + z = 4, 1 + 1 + z = 4, \therefore Z = 2$$

The Order of reaction with respect to C is two.

(b) Consider;

$$\text{Expt3; } 2.0 \times 10^{-5} = K(0.05)^x(0.10)^y(0.20)^z$$

$$\text{Expt4; } A = K(0.10)^x(0.10)^y(0.10)^z$$

$$\log [] = \log ()^x ()^y ()^z$$

$$[] = 2^{-x} 2^z, \text{ but } x = 1 \text{ and } z = 2, [] = 2^{-1} \cdot 2^2$$

$$= 2.0 \times 10^{-5} = 2a, a = 1.0 \times 10^{-5}$$

$$(c) 8.0 \times 10^{-5} = K(0.10)^1(0.20)^1(0.20)^2$$

$$K =$$

$$K = 0.1 \text{ mol}^3\text{dm}^9\text{S}^{-1}$$

(d) When the temperature is increased, the rate of reaction between A, B and C increases while the concentration of A, B and C reduces. This results into an increase in K. Thus K increases with increase in temperature.

11. In an experiment where the initial conc of ethanol was steadily increased, the following results for the initial rate of the reaction were obtained.

[CH ₃ CHO] (mol/dm ³)	[CH ₃ CH ₂] ²	Initial rate (mol dm ⁻³ S ⁻¹)
0.10	0.01	3.74 x 10 ⁻⁴
0.20	0.04	1.50 x 10 ⁻³
0.30	0.09	3.37 x 10 ⁻³
0.40	0.16	5.98 x 10 ⁻³
0.50	0.25	9.35 x 10 ⁻³

(a) Plot a suitable graph of initial rate against [CH₃CHO] and use it to determine the order of the reaction.

(b) Write the rate equation.

(c) Calculate the rate constant and state its units.

Solution.

(a) See on the graph paper,

The order of reaction is 2nd order since it gives an exponential curve showing that the initial increases exponentially with increases in concentration of CH₃CHO.

$$\text{Slope} = K, K = \text{Slope} = () \times 10^{-4} = 0.0259 \text{ S}^{-1}$$

(b) Rate equation; Rate = K[CH₃CHO]²

(c) $1.5 \times 10^{-3} = K(0.20)^2$, $K =$, $K= 0.0375 \text{ mol}^{-1}\text{dm}^3\text{S}^{-1}$

12. The kinetic data for the reaction $\text{P} \longrightarrow \text{products}$

Time (min)	0	5	10	20	30
[P] (mol dm^{-3})	0.020	0.0133	0.010	0.0069	0.0051

(a) Plot a graph [P] against time.

(b) Deduce the order of reaction using the method of half life.

(c) Deduce the order of reaction by the method of determining rates at a particular concentration.

Solution.

(a) See graph on the graph paper.

Since $2^{\text{nd}} t_{1/2} = 2 \times 1^{\text{st}} t_{1/2}$, it is a 2^{nd} order reaction.

$$\text{Rate} = K(P)^x$$

$$\text{At } t = 5$$

$$\text{Rate} = 0.5 \text{ at } t=20 \text{ rate } 0.05$$

$$\text{Expt 1 } 0.2 = k(0.0133)^x \text{-----R}_1$$

$$\text{Expt 2 } 0.05 = K (0.069)^x \text{-----R}_2$$

$$= =$$

$$\text{b. } 1^{\text{st}} t_{1/2} = 10$$

$$2^{\text{nd}} t_{1/2} = 31$$

$$2^{\text{nd}} t_{1/2} - 1^{\text{st}} t_{1/2} = 31-10 = 21$$

Since $2^{\text{nd}} t_{1/2} = 2 \times 1^{\text{st}} t_{1/2}$ it is second order reaction

C. Rate at [P] = 0.0069

$$=$$

$$=$$

$$= 1.882 \times 10^{-4}$$

$$\text{Rate at [P] = 0.014}$$

$$=$$

$$=$$

$$= 1.882 \times 10^{-4}$$

$$\text{Expt1 } 1.882 \times 10^{-4} = K(0.00069)^x$$

$$\text{Expt2 } 2.1 \times 10^{-3} = K(0.014)^x$$

$$= =)^x$$

$$11.1111 \quad 2.02899^x$$

$$\text{Log } 11.1111 = x \log 2.02899$$

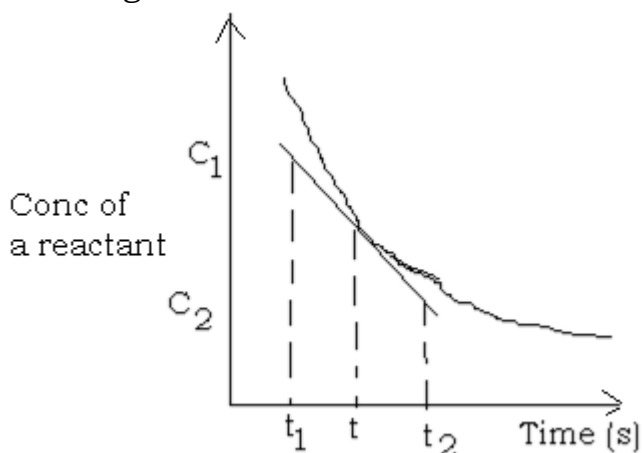
$$X =$$

$$X = 3$$

Chemical kinetics

Chemical kinetics is the study of rates of chemical reactions and factors that affect them. Rate of reaction can be defined as the change in the concentration (amount) of a reactant or product in a unit time.

Rate of reaction can be obtained from the graph of concentration against time by drawing a tangent on the curve at a particular point and determining its gradient eg.



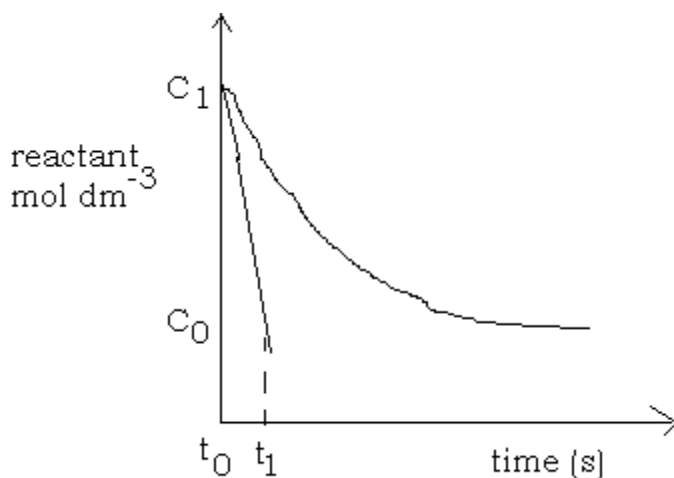
Gradient = Rate at time t

$T =$

$=$

Initial rate of reaction

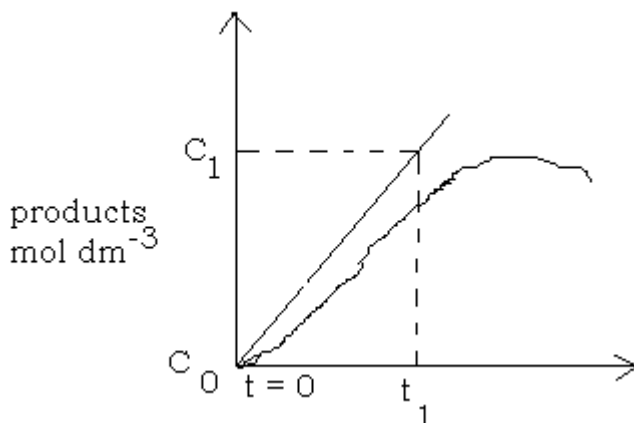
Initial rate of reaction is the rate at the start of the reaction when an infinitesimally small amount of the reactant have been used up in the reaction. It is always obtained from the graph by drawing a tangent at $t=0$ and finding its gradient.



Gradient = initial rate

=

In this case the gradient has a negative value because the reactants are decreasing with time.



Gradient = initial rate

=

The initial rate is very useful in determining the order of reaction because it is always the highest as it is obtained from the steepest part of the tangent.

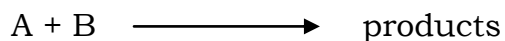
The initial rate is always high because the reactants are still in very high concentration.

Order of reaction and rate equation

Order of reaction is the sum of the powers to which the concentration terms of the reactants are raised in the rate equation.

The rate equation is an expression showing the relationship between the rates of reaction and the concentrations of reactants raised to appropriate powers which are the orders of reaction with respect to the reactants.

Consider the reaction



Rate of reaction $[A]^m[B]^n$

$$\text{Rate of reaction} = K [A]^m[B]^n$$

Where K is the rate constant which is the constant of proportionality in the rate equation.

M and n are orders of reaction with respect to A and B respectively

[A] and [B] are molar concentration of A & B respectively

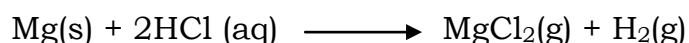
Therefore order of reaction = m + n

Determining the order of reaction

- Order of reaction with a particular reactant is experimentally determined.
- The concentration of a reactant in a reaction is monitored which is seen to change with time.
- A graph of conc against time is plotted and the initial rate determined from the graph.
- For example 1M HCl is reacted with excess Mg ribbon and the volumes at hydrogen gas are recorded at intervals at time is plotted and the initial rate determined.
- The experiment is repeated using a 2M HCl and the initial rate also determined.
- The two initial rates are compared

$$[\text{HCl}] = 1 \quad R_1$$

$$[\text{HCl}] = 2 \quad R_2$$



If $R_2 = R_1$ then the order of reaction with HCl is zero. Rate = $K[\text{HCl}]^0$

If $R_2 = 2R_1$ then the order of reaction is one (1st order) with HCl.

$$\text{Rate} = K [\text{HCl}]^1$$

If $R_2 = 4R_1$ then the order of reaction is two (2nd order) with to the conc of HCl

$$\text{Rate} = K[\text{HCl}]^2.$$

$$\text{If } R_1 = R_2$$

$$R_1 = K[1]^x$$

$$R_2 = K[2]^x$$

$$= , 1 = 2^x, 2^0 = 2^x, X = 0$$

If $R_2 = 2R_1$, $= , = 2x, 2 = 2x, X=1$, Order of reaction is 1.

If $R_2 = 4R_1$, $= , = , 2^2 = 2^x, X=2$ order of reaction is 2.

When two reactants are used the concentration of one is kept constant while the other is varied and corresponding initial rate determined. And the order wrf such a reactant can be deduced using two experiments. If the orders of the

reaction are known, then the conc of both reactants can be changed or varied
eg $\text{Rate} = k [\text{A}]^2 [\text{B}]^1$

What will happen to the rate if the concentration of both reactants is doubled.

Expt 1 = $R = K(x)^2 \times y^1$

$$R_2 = K(2x)^2 = (2y)$$

$$R_1 = Kxy$$

$$R_2 = K4x^2 2y; 8Kx^2 2y; =$$

$$= 8; R_2 = 8R$$

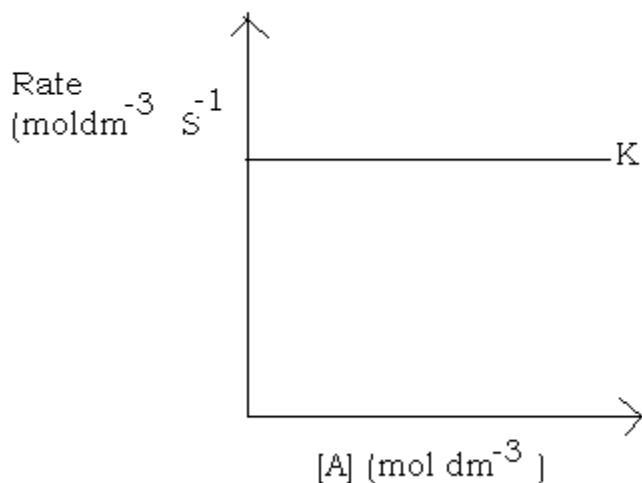
Therefore the rate increases by 8 times

There are two ways of determining the order of reaction from the given data

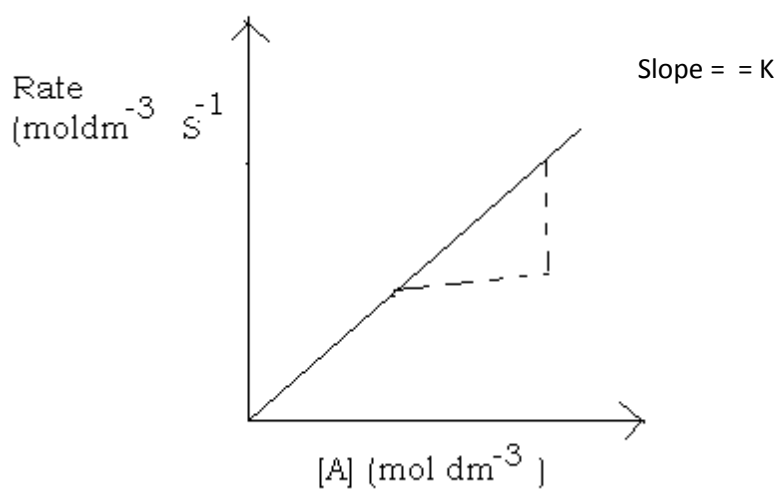
- By Calculation
- By Inspection

Graphic representation of data

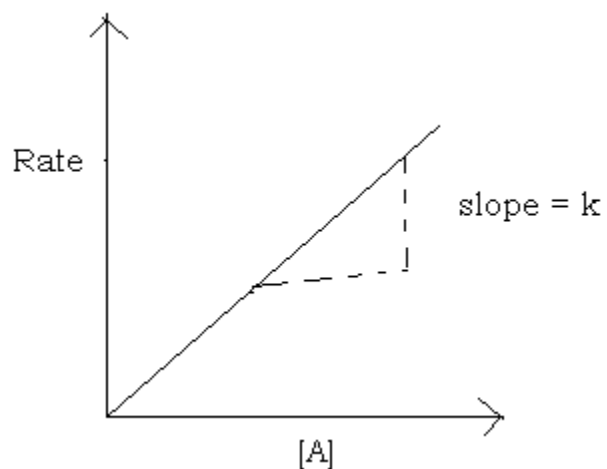
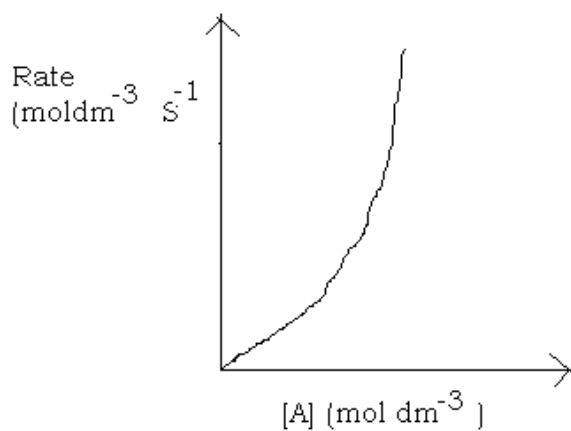
When a graph of rate of reaction is plotted against the conc of a reactant a straight line graph or a curve is obtained depending on the order of reaction wrt that reactant eg $\text{Rate} = K(\text{A})^0$ (Zero order reaction)



$\text{Rate} = K(\text{A})$ (1st order reaction)



Rate = $k[A]^2$ (2nd order reaction)



Half life of first order reaction

Half life is the time taken for the conc of a reactant to decrease to half its original value

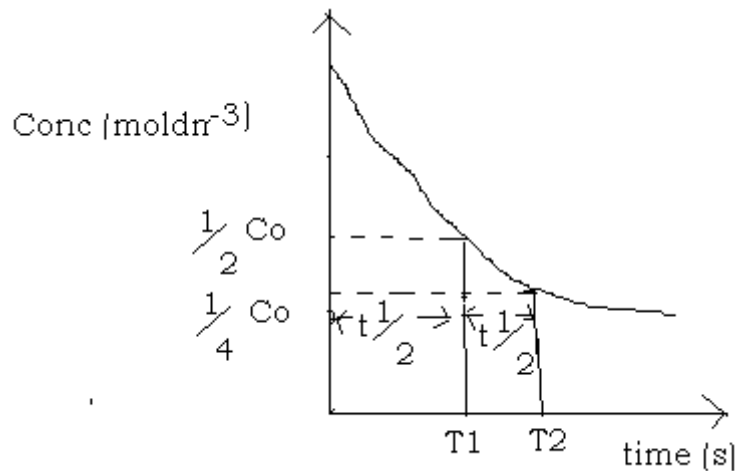
If $[A] = C_0$ and $[A]_t = C_t$

At $t = t_{1/2}$, $C_{t_{1/2}} = \frac{1}{2} C_0$

Determining half life from the graph

When a graph of conc is plotted against time for 1st order reaction or 2nd order reaction an exponential curve is obtained.

For a 1st order reaction



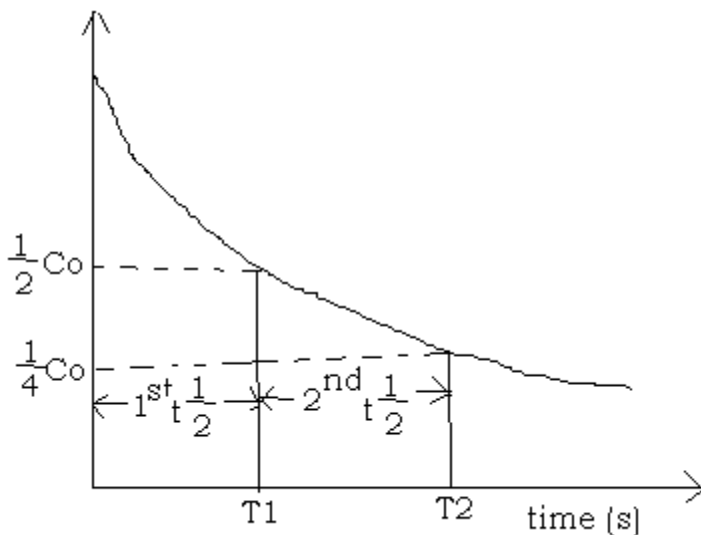
1st $t_{1/2} = T$

2nd $t_{1/2} = (T_2 - T_1)$

1st order reaction

1st $t_{1/2} = 2^{\text{nd}} t_{1/2}$

For 2nd order reaction



$$1^{\text{st}} t_{1/2} = T_1$$

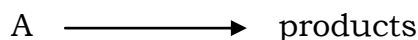
$$2^{\text{nd}} t_{1/2} = T_2 - T_1$$

For 2nd order reaction

The tangent of the curve at any point gives us that rate of reaction at that time. When the rates at different points are compared with their corresponding conc, the order of reaction can be determined.

Integrated rate equation for first order reaction

Given the reaction



$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

If $[A]_{t=0} = a_0 \text{ moldm}^{-3}$ and at time t , $x \text{ moldm}^{-3}$ of A has reacted, therefore amount of A remaining in the reaction mixture at time t .

$$[A]_t = a_0 - x$$

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]_t$$

$$= k(a_0 - x)$$

$$= kdt$$

Taking integrals on both sides

$$= K$$

$$- \ln(a_0 - x) = kt + e$$

Initially at $t = 0$, $x = 0$

$$- \ln(a_0 - x) = K(0) + C$$

$$- \ln Cl_0 = C$$

$$- \ln(a_0 - x) = kt - \ln Cl_0$$

Collecting like terms

$$-\ln(a_0 - x) + \ln Cl_0 = Kt$$

$$\ln = kt$$

Or

$$-kt = \ln(a_0 - x) - \ln a_0$$

$$-kt = \ln$$

$$\ln = -kt$$

Interms of logarithm to base ten

$$\ln = \log_e$$

$$\log_e = kt$$

$$= e^{kt}$$

$$\log_{10} = kt$$

$$\log_{10} =$$

$$x \log_{10} = kt$$

$$2.303 \log_{10} = kt$$

$$\text{Or } 2.303 \log = -kt$$

Deriving an expression for the half life

At half life $(t_{1/2})^x = \frac{1}{2} a_v$

$$2.303 \log_{10} = kt$$

$$2.303 \log 10 = kt$$

$$2.303 \log 10 =$$

$$2.303 =$$

$$2.303 \times 0.3010 =$$

$$= 0.693$$

=

- Derive the expression for the half life for a first order reaction. $2.303 \log(= kt$, where a_v is the initial concentration of the reactant and $(a_0 - x)$ is the concentration at time t .
- The half life of a first order reaction is 100g
- Calculate the rate constant
- Determine the percentage of the reactant that reacted after 250s

$$\mathbf{a.} \quad 2.303 \log_{10} = kt$$

$$\text{at } t = t_{1/2}$$

$$x = \frac{1}{2} a_0$$

$$2.303 \log_{10} =$$

$$2.303 \log 10 =$$

$$2.303 =$$

$$0.6931 = , =$$

$$\mathbf{b.} \quad = 100s$$

$$\mathbf{(i)} \quad = 0.0931$$

$$K =$$

$$K =$$

$$K = 6.931 \times 10^{-3} \text{S}^{-1}$$

$$\mathbf{(ii)} \quad t = 250s$$

$$2.303 \log_{10} = kt$$

$$2.303 \log_{10} \quad 6.931 \times 10^{-3} \times 250$$

$$\text{Log} =$$

$$\text{Log} = \log$$

$$= 5.6544$$

$$565.44 - 5.6544x = 100$$

$$465.44 = 5.6544x$$

$$X = 82.3\%$$

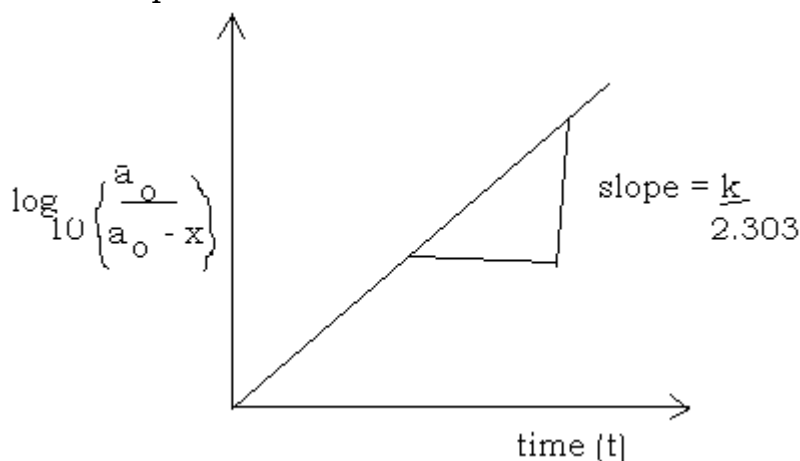
The percentage that reacted is 82.3%

Graphic representation integrated rate equation for first order reaction

From $2.303 \log_{10} = kt$

Or $2.303 \log = -kt$

A plot of $2.303 \log$ (against t gives a straight line with a positive gradient (slope) which is equal to



The table below shows the results for the reaction $A \longrightarrow \text{Products}$

Time (min)	0	9	18	27	40	54	72	105
$[A]_t$ (mol dm ⁻³)	0.106	0.096	0.086	0.077	0.065	0.054	0.043	0.030

- Plot a graph of $\log_{10}[A]_t$ against time
- Use your graph to determine the order of reaction with respect to A
- The rate constant for the reaction and state its units

Time (min)	0	9	18	27	40	54	72	105
$[A]_t$ (mol dm ⁻³)	0.106	0.096	0.086	0.077	0.065	0.054	0.043	0.030
$\log_{10}(A)_6$	-0.9747	-1.0178	-1.0655	-1.1135	-1.1871	-1.2677	-1.3665	-1.5229

2. The data in the table below was obtained for the reaction $2A \longrightarrow \text{products}$

The data in the table below was obtained for the reaction $A \longrightarrow \text{Products}$

Time (hrs)	0	1.3	2.0	4.0	5.3
$\log_{10}[A]$	-0.07	-0.24	-0.33	-0.57	-0.74

- Plot a graph of $\log_{10}(A)$ against time
- From graph determine the order of reaction
- Calculate
 - The rate constant for the reaction
 - The half life of the reaction

1st order reaction

Slope =

= - 1.2586 = -0.1259

Slope =

-0.1259 x 2.303

K = 0.2899hr⁻¹

=

=

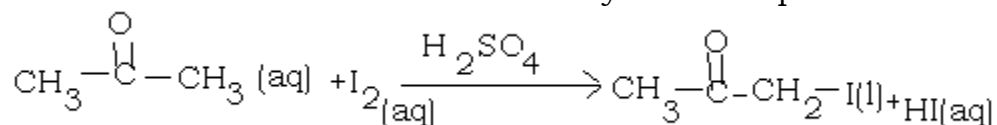
=2.3905hrs

Experiments to determine orders of reactions

Zero order

Experiment to show that iodination of propanone is zero order with respect iodine

Iodination of propanone is a reaction between propanone and aqueous solution of iodine and the reaction is catalysed by dilute sulphuric acid.



Known concentration of propanone, iodine in potassium iodide and dilute sulphuric acid are prepared and brought to a required temperature in other most at bath.

The conc of propanone is higher than that of iodine.

Known volumes of propanone and iodines are mixed in a beaker or conical flask.

A known volume of dilute sulphuric acid is added to the mixture and at the same time a stop watch / clock is started.

The reaction mixture is stirred occasionally

At regular time intervals, a known volume of the mixture is pipette and run into a cornical flask containing sodium hydrogen carbonate solution which neutralizes the acid and stops the reaction

The conc of iodine in this mixture is determined by titrating it with a standard solution of sodium thiosulphate.

Iodine reacts with sodium thiosulphate according to the following equation.

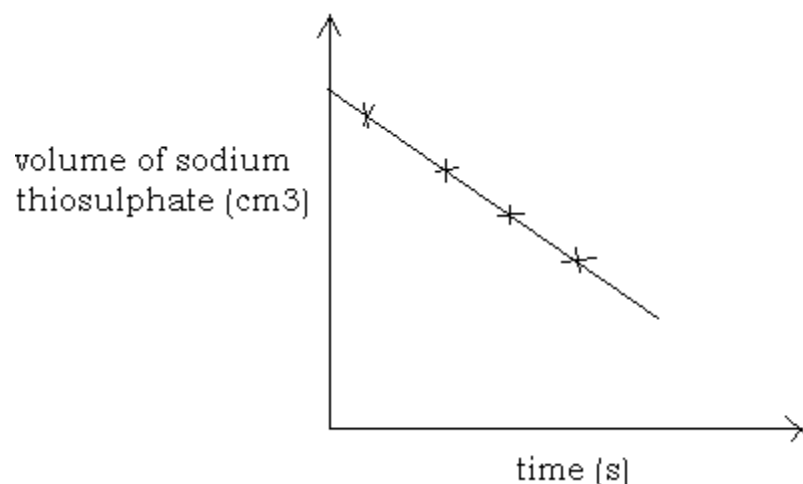


The experiment is repeated with out stopping the stop clock at half minute intervals for 5 mins.

The volume of sodium throsulphate required to reach the end point is directly proportional to the amount of iodine remaining in the reaction mixture.

A graph of volume of sodium thiosulphate against time is plotted.

A straight line graph with negative gradient is obtained



This shows that the conc of iodine is decreasing at a constant rate and therefore the order of reaction with respect iodine is Zero

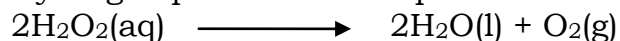
$$\text{Rate} = k[\text{I}_2]^0$$

The slope of the graph gives the rate constant

2. First order reaction

Experiment to show that catalytic decomposition of hydrogen peroxide is first order.

Hydrogen peroxide decomposes according to the following equation



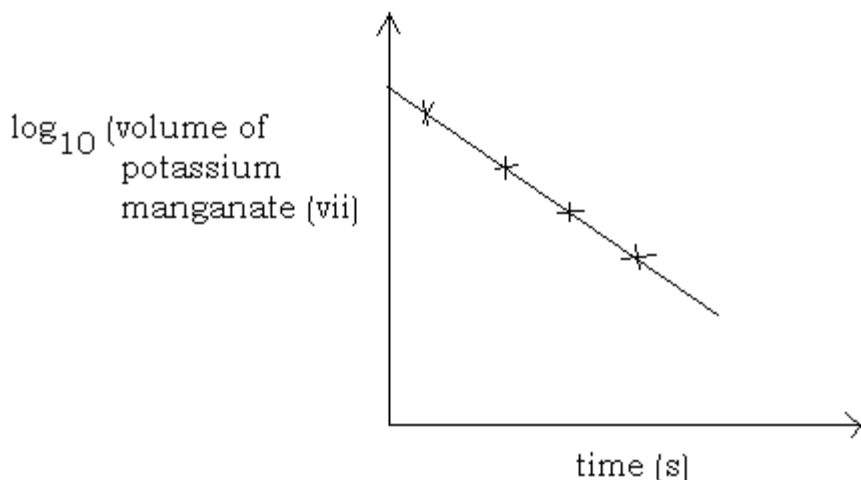
- A known volume of standard hydrogen peroxide solution is transferred into a conical flask.
- A fixed volume of iron (iii) chloride solution is added which is followed by an equivalent volume of sodium hydroxide solution and the stop clock is simultaneously started.
- The mixture is allowed to stand at the room temperature (iii) catalyzes the mixture and the sodium hydroxide neutralizes the acid in the solution which inhibits the decomposition of hydrogen peroxide.
- After specific time intervals, a known volume of the reaction mixture is pipette into a flask containing dilute sulphuric acid and stops the reaction by neutralizing the alkali.
- The reaction mixture is titrated against a standard solution of potassium permanganate and the volume of potassium permanganate is noted.

The procedure is repeated at several time intervals

A graph of volume of potassium manganate (vii) against time is plotted.

The graph is an exponential curve with constant half lives implying that the reaction is first order.

A graph of \log_{10} volume of potassium manganate (vii) against a straight line graph of negative gradient is obtained showing that the reaction is first order.



Experiment to show that the order of reaction between sodium thiosulphate and hydrochloric acid is the with thiosulphate ions.

The reaction between sodium thiosulphate solution and dilute hydrochloric acid produces a yellow ppt of sulphur according to the equation.



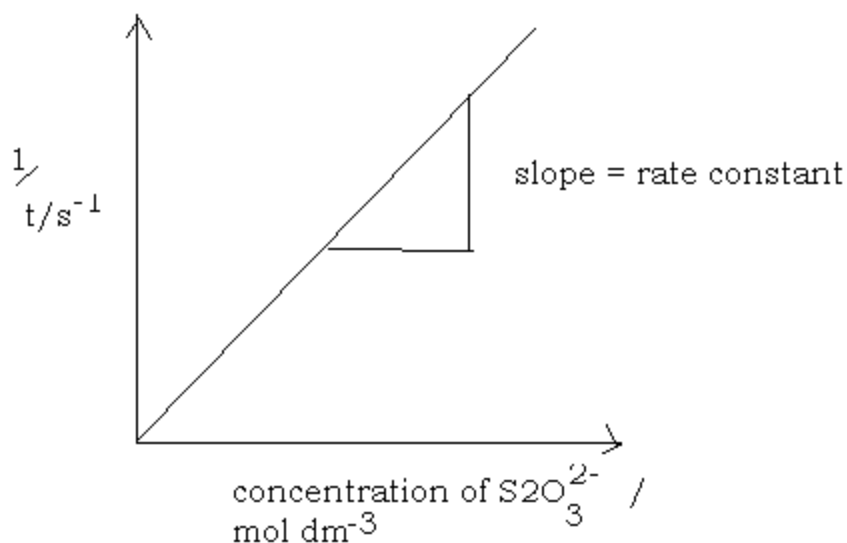
- A known volume of sodium thiosulphate solution of a known concentration is placed in a beaker which is sitting on a white piece of paper containing a big cross or dot.
- A known volume dilute hydrochloric acid of known concentration is added to sodium thiosulphate solution and at the same time, a stop clock started.
- The mixture is shaken occasionally
- The time taken for the ppt of sulphur to block from view to cross or dot is noted
- Concentration of hydrochloric acid is kept constant but higher than that of sodium thiosulphate.
- The experiment is repeated by changing the conc of sodium thiosulphate by diluting the solution with water

The time for the ppt of sulphur to block / obscure from view a big cross/dot noted at each new conc.

A graph of \log_{10} against conc of sodium thiosulphate is plotted.

A straight line graph through the origin is obtained showing that the rate of reaction is directly proportional to the conc of sodium thiosulphate an indication that the reaction is first order with respect to sodium thiosulphate.

Note: = rate of reaction



$$\text{Rate } K = k[\text{S}_2\text{O}_3^{2-}]$$

$$\text{Slope} = K$$

50 cm³ of 0.15 M sodium thiosulphate solution and 5 cm³ of 2.0 M HCl are mixed in a flask over a paper marked with a cross

The cross is viewed from and time for it to vanish is noted.

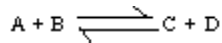
The experiment is repeated with other concentrations of sodium thiosulphate which are obtained by dilution. The table below shows the results of the experiment.

Volume of 0.15M Na ₂ S ₂ O ₃ (cm ³)	Volume of water (cm ³)	Conc of Na ₂ S ₂ O ₃ (mol dm ⁻³)	Time taken for the cross to be obscured (s)	Rate of reaction
50	0	0.15	43	0.0233
40	10	0.12	55	0.0182
30	20	0.09	66	0.0152
20	30	0.06	105	0.0095
10	40	0.03	143	0.0070

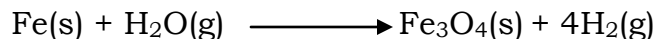
- Complete the table above
- Plot the graph of rate against concentration of sodium thiosulphate
- Use the graph to determine
 - The order of reaction with respect to sodium thiosulphate
 - The rate constant and state its units

CHEMICAL EQUILIBRIUM.

This topic deals with reversible chemical reactions in which the conc of reactants and products are not changing with time because the system is in thermodynamic equilibrium. *Reversible reactions are those reactions which go in both directions, the forward direction and the backward direction.* At one stage reactants combine to form products and in another stage the product combine to form reactants.



At equilibrium the rate of formation of C and D (rate of formation of products) is equal to the rate of formation of reactant ie A and B. The rate of reaction can be defined as the decrease in the conc of the reactants per unit time or the increase in the conc of the products per unit time. Eg when steam is passed over heated iron hydrogen gas and tri iron tetraoxide over heated iron, hydrogen gas and tri iron tetraoxide are formed as products. If however hydrogen gas is passed over treated tri iron tetra oxide steam and iron are formed as the products. The reversible reaction is as shown below.

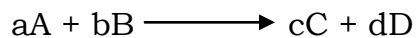


The direction of the reaction depends on the conditions available. If hydrogen gas is removed as soon as it is formed, then the reaction will proceed in the forward direction. But if steam is constantly removed from the reaction mixture, the reaction will proceed in the backward direction and with the time the metal oxides will be converted into iron.

The equation is a balanced reaction is a dynamic one and not a static one because the reactants are still reacting to form products and also some products are reacting to form back the reactants, but the velocities (rates) of the forward and the backward reactions have become equal.

Equilibrium law

It states that if a reversible reaction is allowed to reach equilibrium, then the product of the concentration of the products raised to appropriate powers divided by the products on the concentration of the reactants raised to appropriate powers has a constant value at constant temperature. The constant ratio is called the equilibrium constant, K_c or K_p . K_c is equilibrium constant for a reversible reaction in terms of molar concentrations. K_p is equilibrium constant for the reversible reaction in terms of partial pressure



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$K_p =$$

K_p is for only those reactions involving gases

K_c is for reactions both in gaseous state and liquid state

It is noted that the conc of the solid is taken as unity

$$\text{I.e } [\text{Fe}] = [\text{Fe}_3\text{O}_4] = 1$$

$$P_{\text{Fe}} = P_{\text{Fe}_2\text{O}_4} = 1$$

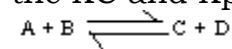
Write the expression for K_c or K_p for the following reactions



$K_c = K_p$ units

Calculations of K_c and K_p

In a reaction of the type $A + B \rightleftharpoons C + D$ if a mole of A and b moles of B were initially present in a volume of $V \text{ dm}^3$. At equilibrium and at a given temperature x mole of A and x moles of B have reacted to form x mole of C and x moles of D. the K_c and K_p can be calculated as follows.



Initial moles

a b 0:0

Reacting

Moles

x x x: x

Equilibrium

moles

a-x b-x x :x

Equilibrium

concentrations

$K_c =$ =

$K_c =$:

-

$K_p =$

Partial pressure = mole fraction x total pressure

Total number of moles of equation

$a - x + (b - x) + x + x$

Let P_T be the total pressure of the gaseous mixture

$P_A = \left(\frac{a-x}{a+b-x+x} \right) P_T$

$P_B = \left(\frac{b-x}{a+b-x+x} \right) P_T$

$P_C = \left(\frac{x}{a+b-x+x} \right) P_T$

$P_D = \left(\frac{x}{a+b-x+x} \right) P_T$

Therefore $K_P = \left(\frac{x}{a+b-x+x} \right)^2 P_T$

$\left(\frac{x}{a+b-x+x} \right)^2 P_T$

Phosphorus (V) Chloride dissociates at higher temperature and pressure according to the equation



84.3 of PCl_5 were placed in a vessels of volume 9.23dm at equilibrium and a certain temperature 11.1g of a chloride are produced at a total pressure of 250.

Calculate

K_c for the equation [$P=31$, $Cl = 355$]

$$\text{R.F.M of } \text{PCl}_5 = 31 + 35.5 \times 5 = 208.5$$

$$\text{R.F.M of } \text{PCl}_3 = 31 + 3 \times 5 = 131.5$$

$$\text{R.F.M of } \text{PCl}_2 = 35.5 \times 2 = 71$$

$$\text{No. of moles of } \text{PCl}_5 = = 0.4$$

$$\text{No. of moles of } \text{PCl}_2 = = 0.156$$

$\text{PCl}_5 (\text{s})$	$\text{PCl}_3 (\text{g})$	$\text{Cl}_2 (\text{g})$	
Initially	0.4	0	0
Reacting moles	x	x	x
Equation moles	0.4-x	x	x
But x=0.156			
Equation moles	0.244	0.156	0.156
Equation conc			

$$K_c =$$

$$= [$$

$$= 0.0108 \text{ mol dm}^{-3}$$

Partial pressures

$$\text{Total moles} = 0.244 + 0.156 + 0.156 = 0.556$$

$$\text{PCl}_2 = x \cdot 280 = 70.14$$

$$\text{PpCl}_3 = x \cdot 280 = 70.14$$

$$\text{PpCl}_5 = x \cdot 230 = 109.71$$

$$K_p = =$$

$$= \mathbf{44.84dm}$$

When 60g ethanoic acid were heated with 46g of ethanol until equation was attained, 12 g of water and 58.7g of ethyl ethanoate were formed.

- Calculate the equation constant K_c for the reaction at the temperature
- Calculate the mass of ethyl ethanoate that would be formed when 90g of ethanoic acid were heated with 93g of ethanol at that tempe.

$$\text{R.F.M of } \text{CH}_3\text{CH}_2\text{CH} = 2 \times 12 + 16 + 6 = 40$$

$$\text{R.F.M of } \text{CH}_3\text{COOH} = 2 \times 12 + 4 + 16 + 2 = 60$$

$$\text{R.F.M of } \text{H}_2\text{O} = 18$$



Initially	: 1	: 1	0	0
Reacting moles	x	x	x	x

Equation moles	1-x	1-x	x	x
But x = 6.67	1-0.67	1-0.67	0.67	0.67
	0.33	0.33	0.67	0.67

Equation conc

K_c =

K_c =

K_c = 4.1221

Nitrogen and hydrogen are mixed in a molar ratio 1:3. At equilibrium at 600°C and 10 atm, the percentage of ammonia in the mixture of gases is 15%. Calculate the value of the equilibrium constant K_p for the reaction at 600°C

	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$		
Initial amounts	1	3	0
Reacting moles	a	3a	2a
Eqn moles	1-a	3-3a	2a
Total no. of moles =	1-a + 3-3a + 2a		
	4-2a		

Percentage of ammonia = $\frac{2a}{4-2a} \times 100 = 15$

a = 0.26

Mole fraction

Partial pressure of N₂, P_{N₂} = $\frac{P_T}{4-2a}$

= $\frac{10}{4-2(0.26)}$

=

Partial pressure of H₂, P_{H₂} = $\frac{3(1-a)}{4-2a} \times 10$ =

Partial pressure of NH₃, P_{NH₃} = $\frac{2a}{4-2a} \times 10$

=

K_p =

= 0.1646 atm⁻²

3. A mixture of 3 moles of hydrogen and 1 mole of Nitrogen is allowed to reach equilibrium at a pressure of 5 × 10⁶ NM⁻². The composition of the gaseous mixture is then 8% NH₃, 23% N₂, 69% H₂ by Volume calculate K_p.

4. A mixture contained 1.00 mole of ethanoic acid and 5.00 moles of ethanol. After the system has come to equilibrium, a portion of the mixture was titrated against 0.2M sodium hydroxide solution. The titration showed that the whole of the equilibrium mixture would require 289 cm³ of the standard alkali for neutralization. Find the value of K_c for the esterification reaction.

5. The equilibrium mixture formed by heating 1 mole of nitrogen and 3 moles of hydrogen at 50 atm were found to contain 0.8 moles of ammonia. Determine the value of the K_p under these conditions.

6. hydrogen and iodine react to form hydrogen iodide according to the following equation.



(i) Write the expression for the equilibrium constant K_c for the reaction

(ii) 1 mole of hydrogen and 1 mole of Iodine were heated together at 450°C until equilibrium was attained. Calculate the number of moles of hydrogen iodide present in the equilibrium mixture at 450°C [The equilibrium constant K_c for the reaction between H₂ and I₂ is 50].

(b) Briefly explain how the conc of I_2 in the equilibrium mixture can be determined.

Experiment to determine the equilibrium constant for the esterification reaction [reaction between ethanoic acid and ethanol] known weights of acetic acid (a mole) and ethyl alcohol (b mole) are sealed in a glass tube at a definite temp ie 50°C . After some hrs at this temperature the acid and the alcohol will have reacted to form the equilibrium mixture. The tube is then cooled and the amount of acid it contains is found by titration with standard alkali.

If there are x moles of acid present at equilibrium it follows that (a-x) moles of acid have been converted into ester and water. Since 1 mole of ester and 1 mole of water were formed from 1 mole of acid, there must be (a-x) moles of ester and of water present in the equilibrium mixture (a-x) moles of alcohol must have been used up so that the amount of alcohol present at equilibrium will be [b-(a-x)] moles.

For a sealed tube of volume V litres equilibrium concentration in mole per litre would be as follows.

Acid Ester

Alcohol water

The equilibrium constant will be given by

$K_c =$

Factors affecting equilibrium reactions

The concentration – catalyst

Temperature

Pressure

Concentration

The effect of conc of the equilibrium of reaction was predicted by Le Chatelier's principle which states that if one of the external factors affecting the system in equilibrium is altered, then the system tends to react in such a way as to minimize any changes resulting from the alteration of external factors.

Effect of conc does not change the equilibrium constant but it affects the equilibrium position ie the reaction may tend to go to the forward or may take the backward reaction

eg $A + B \rightleftharpoons C + D$

$K_c =$

If the concentration of A is increased by adding more A to the reaction mixture at equilibrium, the system has to adjust to reduce on the conc of A and the reaction will move to the right ie forward reaction is favoured.

The excess A will react with B to produce more C and D therefore the conc of B decreases while that of C and D will increase.

This is done to keep K_c constant provided other conditions such as temp. and pressure are kept constant.

If the conc of C is increased by adding it from outside the reaction mixture at equilibrium the equilibrium position will shift to the left.

This is done to minimize the effect of conc at C. the excess C will react with D to form A and B.

The conc of the reactants will increase while that of D will decrease. This is done to keep K_c constant.

Similarly, if the conc D_c is reduced by constantly removing it from the reaction mixture the position of equation will shift to the right i.e. the forward reaction will be favoured i.e. more A and B will react to replace C. This is done to keep K_c constant.

In the contact process where SO_2 and O_2 react to form SO_3 .



Excess air is used for maximum yield of SO_3 . Almost all the SO_2 will react with excess air to form SO_3 .

Temperature

In all reactions an increase in temperature causes an increase in the rate at which the reaction takes place. The rate of reaction approximately doubles or triples for every 10°C rise in temperature. This is because the reactant molecules gain enough K_e and collide more frequently and this results into a faster rate of reaction. At higher temperatures the equation position is altered more rapidly increase in temperature can promote the forward reaction or backward reaction depending on the type of reaction. Temperature also has an effect on the value in the equation constant.

$\log k$ (Exothermic reaction)

\log (Endothermic reaction)

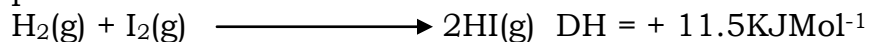
Where K = equation constant

ΔH = Enthalpy of reaction

T = absolute temperature (K)

For exothermic reactions where ΔH is negative, increase in temperature decreases the K_c value and the equation position will shift to the left the conc of the reactants increases while the conc of the products decreases.

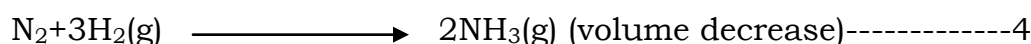
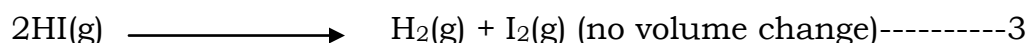
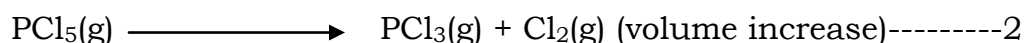
For endothermic reactions increase in temperature increases the forward reaction and the equation constant increases because the concentration of the products increases while the conc of the reactants decreases.



The above reaction is an endothermic reaction. When the temperature increases, more H_2 and I_2 will combine to form HI and therefore K_c or K_p will increase. But when the temperature is lowered, the equation position will shift to the left HI will dissociate to form H_2 gas and I_2 molecules and K_c will decrease.

Effect of pressure on equilibrium reactions.

Pressure only affects those reactions which involve gases but it has little or no effect on reactions involving liquids or solids. When the pressure is increased in gaseous reaction of molecules of the reactants, will come closer and this speeds up the rate of chemical reaction. Pressure only affects equilibrium position but does not affect equilibrium constant. Increase or decrease in pressure will shift the equilibrium position to the right or to the left depending on the type of reaction. A reaction proceeds with volume decrease, increase or no change in volume.



In reaction 1 the forward reaction proceeds with decrease in volume. The gaseous reactants occupy 3 volumes and the products occupy 2 volumes.

When the pressure is increased, the system will adjust to reduce on the applied pressure and the reaction will take the direction whose there is less volume (forward ran) therefore increase in pressure favours the forward reaction and equation will shift to the right. More SO_3 will form while the reactants will reduce and this is done to keep the equation constant the same.

For reaction (2) increase in pressure will favour the back ward reaction and the equation position will shift to the left. The conc of the reactants will increase while the conc of the products will decrease. This is done to keep K_p or K_c constant.

Reaction (3) proceeds with no volume change and therefore increase or decrease in pressure will not change the equation position.

Effect of catalyst on the equation reactions

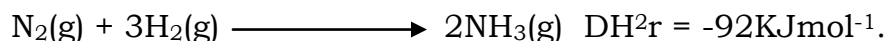
A catalyst is a substance that alter, the rate of chemical reaction with and itself being consumed at the end of the reaction although it may lake part in the reaction.

In the hydrolysis of esters the reaction is catalysed by dilute sulphuric acid which is acting as a catalyst. In equation of reaction both forward and reverse reactions are equally affected when the catalyst is used. A catalyst can speed up the rate of a farword reaction in the same way as a back ward reaction. A catalyst does not affect the position of equation but it increases the rate of attainment of equation.

Application of equilibrium reactions of industrial processes.

1. Haber process.

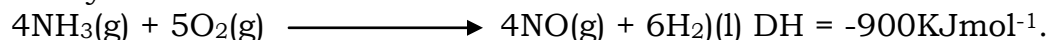
This is the process of producing ammonia on a larve scale from nitrogen and hydrogen. The reaction is exothermic and a companied by decrease in volume.



The forward reaction proceeds with decrease in volume therefore high pressure favour the forward reaction. Maintaining high pressure is quite expensive. A rational pressure of 500 atm can be used for optimum yield at ammonia. Also the reaction proceeds with evolution of heat on exothermic reaction. Therefore temperature will favour the forward reaction because decrease in temperature will shift the equation position to the right. The reactants will combine to produce more heat. Low temperature will lead to low attainment of equilibrium and therefore a compromise temperature of 500°C is used for optimum yield of ammonia. But the rate is still low because of the triple bond in the nitrogen molecules therefore iron catalyst is used.

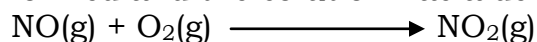
2. Ostwald process.

This is the process of producing nitric acid on large scale which involves catalytic oxidation of ammonia.



In this reaction, there is a small increase in volume. It would be expected that low pressure will be used. Therefore 9 atm are used for the optimum yield of NO. Temp between 600-900°C are used for the reaction with platinum rhodium as a catalyst.

Nitrogen monoxide is cooled and is allowed to react with more oxygen / air to form nitrogen dioxide which when reacted with water 10% w/w nitric acid is formed and the solution has a density of 1.4 gcm⁻³.



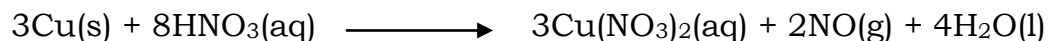
- Nitric acid is used in the manufacture of
 - Dyes
 - Explosives
 - Fertilizers

Nitric acid can react with copper in two ways.

When concentrated



When dilute



It can react with sulphur to form sulphuric acid



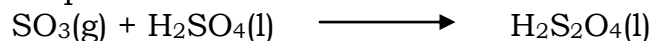
3. Contact process

In contact process SO₂ react with O₂ to form SO₃. The reaction proceed with decrease in volume and heat is evolved.

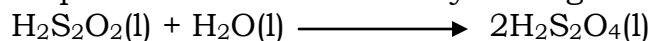


High pressure and low temperatures increase the yield of sulphur trioxide but the optimum yield of SO_3 is obtained at 450, 2 atm and vanadium penta oxide catalyst.

Sulphure trioxide is dissolved in conc sulphuric acid to form oleum.



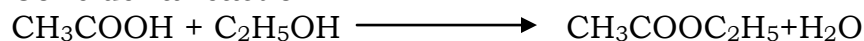
Oleum is diluted with a particular amount of water to obtain 98% w/w sulphuric acid with a density of 1.8gcm^{-3} .



Sulphuric acid is used in the manufacturer of superphosphates which are fertilizers.

Liquid system (homogeneous)

Consider a reaction



Suppose that a mole of ethanoic and are mixed with b mole of ethanol and total volume of the mixture is V/m^3 .

1 mole of the acid alcohol and if at equilibrium x moles of each have reacted the concentration in mole M^{-3} of acid alcohol and the ester plus water are given below.

	$\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$		$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$	
Initially	a	b	0	0
At eq m	(a-x)	(b-x)	x	x
	((((

By the law of mass action the equilibrium constant K_c is given by
 $K_c =$

$$K_c =$$

$$=$$

$$K_c =$$

Example

1. When 8.28g of ethanol were heated with 60g of ethanoic acid, 49.74g of the acid remained at equilibrium. Calculate the value of K_c

Solution

RMM of Ethanol = 46g

RMM of ethanoic acid = 60g

No of moles of $\text{C}_2\text{H}_5\text{OH} = = 0.18$

No of moles of $\text{CH}_3\text{COOH} = = 1$

Remaining moles = = 0.829

Moles that reacted = (1-0.829)

X = 0.171

From $K_c =$

$K_c =$

GASEOUS EQUILIBRIUM (HOMOGENEOUS)

Consider a reaction



Suppose we start with a mole of hydrogen iodide and at equilibrium x mole have dissociated.

Since 1 mole of HI on dissociation finishes $\frac{1}{2}$ mole of hydrogen and $\frac{1}{2}$ mole of iodine vapour, there we have



Total number of moles

$$= a - x + \quad +$$

$$+ \quad + \quad =$$

$$= \quad / \quad / \quad /$$

$$= a \text{ moles}$$

Partial pressure = mole fraction \times total pressure

$$\text{I.e. } P^0 = X^0 P$$

$$P^0(\text{HI}) = () p$$

$$P^0(\text{H}_2) = () p$$

$$= () p$$

Therefore $K_p =$

$$= =$$

$$= = \div$$

$$\times$$

$$(=$$

$$K_p =$$

From an opposite direction by heating hydrogen and iodine together



If we start with a mole of iodine and b moles of hydrogen in the total volume of V (mm^3) and if at equilibrium x moles of hydrogen n and iodine have disappeared the concentrations of the substance present atabove since the volume remains constant.

Then by law of mass action

$$K_c =$$

$$=$$

$$K_c =$$

K_p calculation of K_p

At eq m (a-x) mole of I_2 and (b-x) of H_2 together 2x of HI

$$\begin{aligned}\text{Total number of moles} &= (a-x) + (b-x) + 2x \\ &= a-x + b-x + 2x \\ &= (a+b)\end{aligned}$$

$$H_2 = () P$$

$$I_2 = () P$$

$$= () P$$

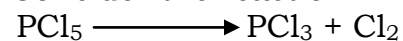
$$K_p = =$$

$$= =$$

$$K_p =$$

K_c in terms of degree of dissociation.

Consider the reaction



Initially 1 0 0

- Degree of dissociation

V- Volume at eq m (1-)

Considering a certain volume V

() () ()

From the law of mass action

$$K_c =$$

$$K_c =$$

$$=$$

$$K_c =$$

In moles per metre

For K_p in terms of degree of dissociation and total pressure, P at eqm is as follows;

$$\text{Total number of moles} = (1-x) + +$$

$$= 1- + 2$$

$$= 1 +$$

Therefore

$$(PCl_5) = ()P$$

$$(Cl_3) P^0(Cl_2) \text{ and given as below}$$

$$=()P$$

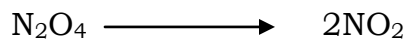
$$K_p = =$$

$$K_p =$$

$$K_p =$$

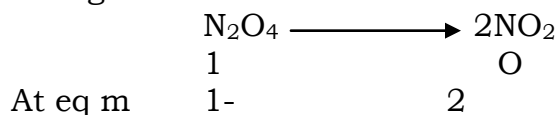
$$K_p =$$

6. Dissociation of Dinitrogen tetraoxide



Initially there is 1 mole of N_2O_4

= degree of dissociation



Consider a given volume, V we get

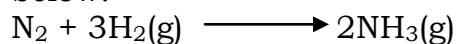
$$K_c =$$

$$= =$$

$$K_c =$$

7. Combination of Nitrogen and hydrogen.

1 mole of nitrogen combines with 3 moles of hydrogen as shown the equation below.



eq m 3()

From the law of mass action

$$K_c =$$

$$K_c =$$

$$K_c =$$

$$K_c =$$

$$K_c =$$

$$K_c =$$

$$\text{But since } (3-x)^2 = (3-3x)^2 \cdot (3-3x)$$

$$= 3(1-x)^2 \cdot 3(1-x)$$

$$= 3^2(1-x)^2(1-x)$$

$$\text{For } K_p; \text{ total number of moles} = 1-x + 3-3x + 2x = 4-2x$$

$$P^0(\text{NH}_3) = ()P$$

$$P^0\text{N}_2 = ()P$$

$$P^0H_2 = ()P$$

$$K_p =$$

$$K_p =$$

CHEMICAL EQUILIBRIUM

The reversible process is a closed system at constant temperature will eventually react to attain a state of dynamic equilibrium. This is the state at which the rate of the non is in a direction is equal to the rate of the non in the reverse direction. At the state of equilibrium the conc of the reactants and product remain constant provided temperature remains constant produced temperature remains constant.

Consider a gaseous reversible non



rate of forward non $R_f [A]^a [B]^b$

rate of backward non $R_b [C]^c [D]^d$

$$R_f = K_1 [A]^a [B]^b \quad R_b = K_2 [C]^c [D]^d$$

At eqb m $R_f = R_b$

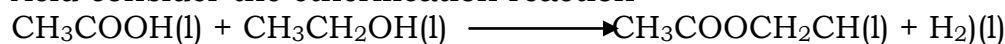
$$K_1 [A]^a [B]^b = K_2 [C]^c [D]^d$$

$$K_1 = K_2$$

The ratio gives the equilibrium constant K_c at constant temperature remains constant and it is defined as the ratio of the concentration of the reactants to the conc of the reactants raised to the appropriate powers as derived from the stoichiometric equation at constant temps.

$K_c =$ are powers to which the reactants and the products are raised in the stoichiometry of the equation.

Acid consider the etherification reaction

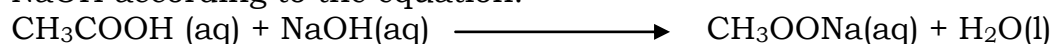


$$K_c =$$

Experimental determination of K_c .

The value of K_c for the above equation system can be experimentally determined. In this investigation known moles of ethanol and ethanoic acid or mixed in a closed container and the container is left to stand in a mainbafor maintained at a constant temperature for ample time in order for equation to be established.

After the equation has been attained a known volume of the non mixture is pipette and tritated to stimatard solution of NaOH using phenolphthalein indicator. The volume of NaOH needed to reach point is noted and the conc of ethanoic acid present at equation can be determined. Ethanoic and reacts NaOH according to the equation.



The concentration of ethanoic acid that has reacted can be computed and since 1 mole of ethanoic acid of Ethanol acid reacts with 1 mole Alcoholl (Ethanol) then the moles of ethanol reacted can be determined. Again 1 mole of ethamoic

acid reacts to give 1 mole of the ester and 1 mole of water then the conc of the products formed can be determined

Treatment of results

Let initial moles of ethanoic acid can be a moles

Initial moles of ethanol be b moles

Volume of container be V dm³

Moles of ethanoic acid reacted be X moles

	CH ₃ COOH(l) + CH ₃ CH ₂ OH(l)		CH ₃ COOCH ₂ CH(l) + H ₂ (l)	
Initial	a moles	b moles	0	0
Let x moles Of the acid React	-x moles	-x moles	+x moles	+x moles
Moles at Eqbm	(a-x) moles	(b-x) moles	x moles	x moles
Conc (mol dm ⁻³)	()	()	()	()
K _c =				

K_c =

=

Examples.

1. Stoichiometric moles of ethanoic acid and ethanol were introduced in a 1L vessel and cooked at 298 K. the reaction was allowed to attain eqbm. At eqbm 0.2 moles of the ester were formed. Calculate the value of K_c at this temperature.

	CH ₃ COOH(l) + CH ₃ CH ₂ OH(l)		CH ₃ COOCH ₂ CH(l) + H ₂ (l)	
Initial	1 moles	1 moles	0	0
if x moles reacted at Eqbm	-x	-x	+x	+x
Conc (mol dm ⁻³)	()	()	()	()
K _c =				
K _c =				
=				
= 0.0625				

2. 0.4 moles of ethanoic acid were mixed with 0.6 moles of ethanol in a 1 L vessel at incubated at 298K the reaction was allowed to attain eqbm. the vessel was found to contain 0.2 moles of ethanoic acid (a) Calc the value of K_c at this temp (b) if stoichiometric moles of acid and Alcohol were used instead at the same temperature and the reaction allowed to attain eqbm. Calculate the eqbm moles of all the participating species.

	CH ₃ COOH(l) + CH ₃ CH ₂ OH(l)		CH ₃ COOCH ₂ CH(l) + H ₂ (l)	
Initial	0.4 moles	0.6 moles	0	0
if x moles reacted at	-x	-x	+x	+x

Eqbm

Conc (mol dm⁻³) () () () ()

But at Eqbm moles of ethanoic acid are 0.2 moles

Therefore (0.4-x) = 0.2

X = 0.2

K_c =

=

=

= 0.5

(b) CH₃COOH(l) + CH₃CH₂OH(l) CH₃COOCH₂CH(l) + H₂ (l)

Initial 1 moles 1 moles 0 0

if x moles -x -x +x +x

reacted

at Eqbm (1-x) (1-x) x x

Conc (mol dm⁻³) () () () ()

K_c =

=

0.5 =

X² = 0.5[(1-x) (1-x)]

X² = 0.5 (1-2x + x²)

X² = 0.5 - x + 0.5x²

0.5x² = 0.5 - x

ax² + bx + C = 0

0.5x² + x - 0.5 = 0

X =

X = 0.1414

= 0.414

X -2.4

Eqbm moles

i. CH₃COOH = (1-0.414) = 0.586moles

ii. CH₃CH₂OH = (1-0.414) = 0.586moles

iii. CH₃COOCH₂CH₃ = 0.414 = 0.414moles

iv. H₂O = 0.414 = 0.414 moles

When 1 mole of Ethanoic acid is maintained at 25°C which 1 mole of ethanol in a 1 L vessel and the reaction allowed to attain eqbm, of ethanoic acid remained when eqbm is attained. How much would have remained if of ethanol had been used instead of 1 mole of the same temperature.

CH₃COOH(l) + CH₃CH₂OH(l) CH₃COOCH₂CH(l) + H₂ (l)

Initial 1 moles 1 moles 0 0

if x moles -x -x +x +x

reacted

at Eqbm (1-x) (1-x) x x

Conc (mol dm⁻³) () () () ()

But at eqbm of ethanoic acid remained

(1-x) = x =

K_c = =

= =

= 4.0

If of Ethanol had been used instead

	CH ₃ COOH(l) + CH ₃ CH ₂ OH(l)		CH ₃ COOCH ₂ CH(l) + H ₂ (l)	
Initial	1 moles	1 moles	0	0
if x moles reacted	-x	-x	+x	+x
at Eqbm	(1-x)	(-x)	x	x
Conc (moldm ⁻³)	()	()	()	()
Kc = 4 =				

$$X^2 = 4(-x - x + x^2)$$

$$X^2 = 4(-x + vx^2)$$

$$X^2 = 3-7x + 4x^2$$

$$-3x^2 + 7x + 3 = 0$$

$$3x^2-7x + 3 = 0$$

$$Ax^2 + bx + c = 0$$

$$X = 0.57$$

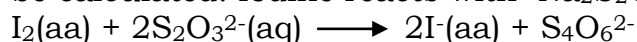
The amount of Ethanoic acid that remained was (1-0.57)

= 0.43

Consider the eqbm



Involving the dissociation of HI. The conc expression for eqbm constant Kc = . The value of the eqbm constant Kc can be determined experimentally. Known moles of HI are put in a sealed bulb known volume with is introduced into an incubator 400K. the non is given ample time to reach and one eqbm is attained the bulb is ...cooled to room temperature and broken KI(aq) solution. The Iodine liberated iswhich standard solution of Na₂S₂O₃ (sodium sulphate) using starch indicator at the ... and the moles of iodine formed at between can be calculated. Iodine reacts with Na₂S₂O₃



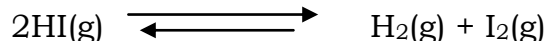
Treatment of results

Let moles of hydrogen iodide used be a moles

Moles of iodide formed be X moles

Moles of HI reacted will be 2 x (according to the equaton)

Volume of the vessel = vdm³



1.54g of HI when heated in a 600cm³ were heated in a 600cm³ bulb at 530°C. when equilibrium was attained the bulb was rapidly cooled to room

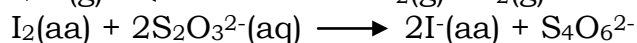
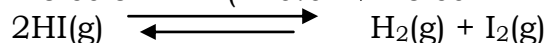
temperature and broken under KI solution. The iodine formed from the decomposition required 67cm³ of 0.1 sodium tetrathiosulphate for complete reaction. Calculate the no. of moles of HI present initially

(H= 1, I= 127)

iii) The value of K_c at this temperature

Molar mass of HI = (1+127) = 128g

Moles of HI = (= 0.012 moles



Moles of S₄O₆²⁻ used = (x 67) moles

2 moles of S₄O₆²⁻ react with 1 mole of I₂ (aq) 6.7 x 10⁻¹ moles of S₄O₆²⁻(aq) will react with

= (3.35 x 10⁻³)

Moles of I₂ present at eqbm = 3.35 x 10⁻³ moles

	2HI(aq)	H ₂ (g) + I ₂ (aq)
Initial	0.012 moles	O O
Of x reaction	-2x	+x +x
At eqbm	(0.012-2x)	x x

But at equilibrium moles of I₂ = 3.35 x 10⁻³

X = 3.35 x 10⁻³ moles

Equilibrium moles of HI = 0.012 - (2x3.35 x 10⁻³)

= 5.3 x 10⁻³ moles

Molar conc of HI at equilibrium ()

Molarity = 8.83 x 10⁻³M

Molar concentration of I₂ at equilibrium = ()

= 5.583 x 10⁻³M

Molar conc of H₂ at equilibrium ()

= 5.583 x 10⁻³M

(i) K_c =

=

0.4

Consider an industrial important reaction

	N ₂ (g) + 3H ₂ (g)	2NH ₃ (g)
Initially	1mole 3 moles	0
At eqbm	-x -3x	+2x
Concn. In mol/L	(((

K_c =

=

Stoichiometric moles of H₂ and N₂ were reacted at 400K in a 1L vessel at equilibrium a vessel was found to contain 0.8 moles of Ammonia.

Calculate

(i) Equilibrium moles of N₂ and H₂

(ii) The value of K_c at this temperature and state its units

Solution

	N ₂ (g) + 3H ₂ (g)	2NH ₃ (g)
Initially	1mole 3 moles	0

$$\text{NO}_2 = 2 \times 1.125 = 2.25 \text{ moles}$$

Kc =

- iv) If the temperature is raised to 600K, the vessel was found to contain 30% of the initial oxygen. Calculate the value of Kc at the temperature.

The vessel contains $x \times 1.5 = 0.45$ moles

$$(1.5 - x) = 0.45$$

$$x = 1.05 \text{ moles}$$

$$\text{New equilibrium of NO}_2 = 2x = 2 \times 1.05 = 2.1$$

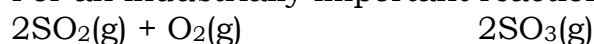
$$\text{O}_2 = (1.5 - 1.05) = 0.45$$

$$\text{NO} = (3 - 2 \times 1.05) = 0.9$$

$$K_c = \frac{0.9^2}{2.1^2 \times 0.45} =$$

$$K_c = 12.10 \text{ mol}^{-1}$$

For an industrially important reaction



If stoichiometric moles were used and the reaction gives time to attain equilibrium then

	$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$		$2\text{SO}_3(\text{g})$
Initially	2 moles	1 mole	0
If reacted	-2x	-x	+2x
At eqbm	(2-2x)	(1-x)	2x
Concn. In mol dm^{-3}	()	()	()

Ex3. 3 moles of SO_2 were mixed with 2 moles of O_2 in a one litre vessel which was tightly corked and the mixture allowed to attain equilibrium at 400K. When 20% of the initial sulphur dioxide. Calc the values of Kc at this temperature.

	$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$		$2\text{SO}_3(\text{g})$
Initially	3 moles	2 moles	0
If reacted	-2x	-x	+2x
At eqbm	(3-2x)	(2-x)	2x

$$\text{By 20\% change} = x \times 3 = 0.6 \text{ moles}$$

$$\text{SO}_2 \quad 3 - 2x = 0.6$$

$$x = 0.7 \text{ moles} \quad 1.2 = x$$

$$\text{SO}_3 \quad 2x = 2 \times 1.2 \quad x = 2.4 \text{ moles}$$

$$\text{O}_2 \quad (2 - 0.7) = 0.3$$

$$K_c =$$

$$\frac{2.4^2}{0.6^2 \times 0.3} =$$

$$18.15 \text{ mol}^{-1} \text{ dm}^3$$

1 mol of SO_3 was introduced in a 1 dm^3 vessel. The vessel was heated to 100K until equilibrium was attained. At equilibrium, 0.35 moles of SO_3 was present.

- Write an equilibrium for the decomposition of SO_3
- An expression for the equilibrium constant Kc. Calculate the value of Kc and state the units. 0.2 moles of SO_2 , 0.1 moles of $\text{O}_2(\text{g})$ and 0.7 moles of SO_3^{2-} . Were introduced into the vessel in an at look. Calc the value of Kc.

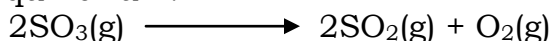
$$K_c =$$

Initially	1 moles	0	0
-----------	---------	---	---

If reacted	-2x	+2x	+x
At eqbm	(1-2x)	(2x)	x
Concn. In moldm ⁻³ (((
1-2x = 0.35			
X = 0.325 moles			
Concn. Of SO ₂ = 2 x 0.325 = 0.65 moles			
O ₂ = x			
Kc =			
= 1.12 moldm ⁻³			

Equilibrium moles and mole fractions

Equilibrium moles is the actual number of moles of a particular component in the mixture when a particular component in the mixture when the system has attained equilibrium. It may or may not be expressed in % eg for the equilibrium.



If the vessel of equilibrium contains 20% of SO₃ then the equilibrium moles of SO₃ which is 0.2.

Mole fraction refers to the number of moles of a compared divided by the total number of moles of the system. It is usually expressed as a percentage. For the above equilibrium system. If the vessel contains 20% SO₂ at equilibrium then this is its mole fraction.

If stoichiometric moles of SO₃ are allowed to dissociate in a closed container at a fixed temperature and that at equilibrium moles of other compounds can be determined.

	2SO ₃ (g)	2SO ₂ (g)	+	O ₂ (g)
Initially	1mole	0		0
If reacted	-2x	+2x		+x
At eqbm	(2-2x)	(2x)		x

But at equilibrium, the vessel contains mole fraction 20% of SO₃

=

$$0.2 = ($$

$$0.4 + 0.2x = 2-2x$$

=

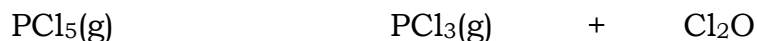
$$X = 0.75$$

$$X = 0.73$$

Qn : Phosphorous pentachloride dissociates according to the equation



1 tonne of PCl₅ when heated in a 2 dm³ vessel at 100k. at equilibrium the vessel was found to chlorine. Chlorine 25% Calculate the value of V at their temperature.



Initially	1 mole	0	0
If reacted	-x	+x	+x
At eqbm	1-x	x	x

$$\text{Total equilibrium moles} = \frac{(1-x + x+x)}{(1+x)}$$

At equilibrium =

$$X = 0.25 + 0.25x$$

$$0.75x = 0.25$$

$$X = 0.33 \text{ moles}$$

$$K_c =$$

$$K_c =$$

Equilibrium containing

$$\text{PCl}_5 = (= 0.335 \quad K_c = 0.0825$$

$$\text{PCl}_3 = (= 0.165 \quad K_c = 0.08$$

$$\text{Cl}_2 = (= 0.165$$

Question 5. Nitrogen was reacted with hydrogen in a 2dm³ vessel at 500k where equilibrium was attained, the vessel was found to contain 80% of ammonia. Calculate the value K_c of this temperature.

	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	$2\text{NH}_3(\text{g})$
Initially x	1 mole 3 moles	0
Equilibrium	1-x (3-3x)	2x
Total number of moles =	$(1-x) + (3-3x) + (2x) = (4-2x)$	

$$=$$

$$0.3 (4-2x) = 2x$$

$$X = 0.888$$

$$\text{Conc of N}_2 \text{ is } = 0.05 \text{ moles}$$

$$\text{Mol dm}^{-3}$$

$$\text{H}_2 \text{ is } = 0.168 \text{ moles}$$

$$\text{NH}_3 \text{ is } 2 \times 0.888 = 1.776 \text{ moles}$$

$$K_c =$$

$$K_c =$$

$$K_c = 1995.6$$

$$K_c = 13303.4$$

Note: This value of K_c may have or not have units. If the change in stoichiometric number of moles on the product and reactant side is Zero then K_c has no units eg



K_c = hence has no units

If the change in stoichiometric number of moles is greater or less than zero, then K_c has units eg



$$K_c =$$

(ii) The equilibrium rule only applies to system which have attained equilibrium

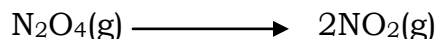
(iii) The K_c value remains constant provided temperature remains constant

(iv) The value of K_c shows the extent of chemical reaction. A high value of K_c indicates a high proportion of products to reactants and a small value of K_c shares a small proportion of products compared to reactants.

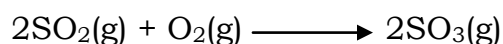
EQUILIBRIUM CONSTANT (K_p) AND PARTIAL PRESSURES.

The equilibrium constant K_p is only applicable to gaseous systems of equilibrium and is expressed in terms of partial pressures

Consider a reaction



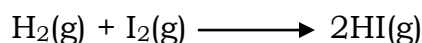
K_p where P is partial pressure of the gas similarly



K_p

Relationship between K_p and K_c

Consider a reaction



$K_p =$

From ideal gas equation $PV = nRT$

Or $P = \frac{n}{V}RT$

But $\frac{n}{V}$ is concn of the gas if V is in dm^3 therefore $p = [\text{gas}] RT$ in a closed container of volume volm^3 , the value of P is equal to the partial pressure of a particular gas ie

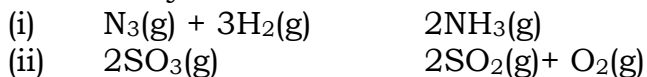
$P_{\text{gas}} = [\text{gas}] RT$

Partial pressure of $\text{HI} = [\text{HI}] RT$

Partial pressure $\text{I}_2 = [\text{I}_2] RT$

Partial pressure of $\text{H}_2 = [\text{H}_2] RT$

Example: show the relationship between K_p and K_c for the following equilibrium system



Solution

$K_p =$

But $P_{\text{NH}_3} = [\text{NH}_3]RT$

$P_{\text{N}_2} = [\text{N}_2]RT$

$P_{\text{H}_2} = [\text{H}_2] RT$

$$K_p =$$

=

$$K_p = K_c(RT)^{-2}$$

$$K_p =$$

$$\text{But } P_{SO_2} = [SO_2] RT$$

$$P_{O_2} = [O_2] RT$$

$$P_{SO_3} = [SO_3] RT$$

$$K_p =$$

$$K_p =$$

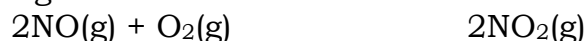
$$K_p = K_c RT$$

In general

$$K_p = K_c(RT)^n$$

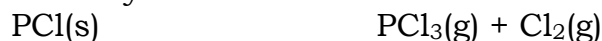
Where n = (stoichiometric moles on product side) - (stoichiometric moles on reactant side)

Eg for the reaction



$$K_p = K_c(RT)^{-1}$$

Similar for the reaction



$$K_p = K_c(RT)^{-1}$$

Example

At 700K, the equilibrium constant for the reaction



Calculate the value of K_c at the same temperature and comment on extent of the forward reaction.

Solution

$$K_p = K_c(RT)^{-1}$$

$$K_c =$$

$$= 3.093 \times 10^{-4} \text{ mol dm}^{-3} \times 10^{-3}$$

$$= 3.093 \times 10^{-7} \text{ mol dm}^{-3}$$

From $PV = nRT$

$$R =$$

$$= \text{Nm mol}^{-1}$$

The value of K_c is very small showing that the reaction lies more on the left i.e. there are more reactants than products.

Partial pressures and mole fractions

Partial pressure of a gas is the pressure a gas exerts if it is alone in the gaseous container. Gaseous container where there are 3 gases for example the total pressure of the system is the sum of the partial pressures i.e. $P_T = P_1 + P_2 + P_3$

At constant temperature the total pressure of the system remains constant and is related to the partial pressures of the individual gases by their mole fraction i.e.

Partial pressure = mole fraction of the gas \times total pressure

Or $P_i = X_i \cdot P_T$

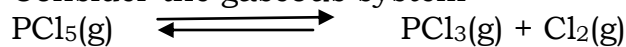
Where P_i = partial pressure of gas i

X_i = mole fraction of gas i

P_T = total pressure of the system

If the moles of the gases are n_1, n_2 and n_3 then mole fraction of gas 1 =

Consider the gaseous system



Initially 1 0 0

X -x +x +x

Eqbm (1-x) x x

Total eqbm moles = (1-x) + x + x

= (1+x) moles

$P_{\text{PCl}_5} = X_{\text{PCl}_5} P_T$

= () P_T

$P_{\text{Cl}_2} = X_{\text{Cl}_2} \cdot P_T$

=) P_T

$K_p =$

Stoichiometric moles of N_2 and H_2 were reacted at 50 atm in a closed vessel. When equilibrium was attained 0.5 moles of NH_3 were formed.

a)(i) write an equation for the reaction that took place

(ii) Write the expression for the equilibrium constant

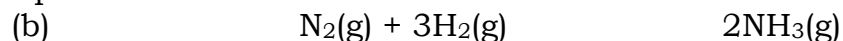
b. Calculate (i) The number of moles of N_2 and H_2

(ii) The value of the equilibrium constant and state its units

Solution



$K_p =$



Initially 1 mole 3 moles 0

If x react -x -3x +2x

Eqbm (1-x) (3-3x) (2x)

But at equilibrium 0.8 moles of ammonia were formed

$2x = 0.8$, $x = 0.4$ moles

Equilibrium moles of (i) $N_2 = (1-x) = 1.0.4$
 $= 0.6$ moles

$H_2 = (3-3x) = (3-3 \times 0.4)$
 $= 0.8$

Total equilibrium moles $= (0.8 + 0.6 + 1.8)$
 $= 3.2$ moles

Using $P_2 = X_1 P_T$

$P_{NH_3} = (x/50) = 12.5$

$P_{NH_3} = (x/50) = 9.38$ atms

$P_{H_2} = (x/50) = 28.13$ atms

$K_p =$

$7.484 \times 10^{-4} \text{ atm}^{-2}$

3.4 moles of SO_3 were decomposed at 600K in a 50 dm^3 vessel at a pressure of 120 atms when the equilibrium was attained the vessel was found to contain 0.06 moles of SO_2 . Calculate the value of K_p at this temperature and use it to deduce the value of K_c .

Soln.

	$2SO_3(g)$	$2SO_2(g)$	+	O_2
Initially	3.4 moles	0		0
If x	-2x	+2x		+x
At eqbm	$(3.4 - 2x)$	2x		x

Total equilibrium moles $= (3.4 - 2x + 2x + x)$
 $= (3.4 + x)$

But at equilibrium $2x = 0.06$

$x = 0.03$ moles

Equilibrium concentration

(i) $SO_3 = 0.0668 \text{ m}$

(ii) $SO_2 = 1.2 \times 10^{-3} \text{ m}$

(iii) $O_2 = 6 \times 10^{-4} \text{ m}$

Total equilibrium concentration $= () = 0.0686 \text{ m}$

$K_p =$

$=$

$= 3.39 \times 10^{-4} \text{ atms}$

$K_p = K_c(RT)^1$

$K_c =$

$= 6.89 \times 10^{-6} \text{ mol dm}^{-3}$

Qn. Stoichiometric moles of SO_2 and O_2 were allowed to reach equilibrium at 80 per and 400K m^{-1} a closed vessel.

a(i) Write an equation for the equilibrium system above

(ii) Write an expression for the equilibrium constant

(b) At equilibrium the vessel above was found to contain 20% sulphur trioxide (SO_3)

Calculate (I the equilibrium moles of SO_2 and O_2

(i) The value of the equilibrium constant and state its units

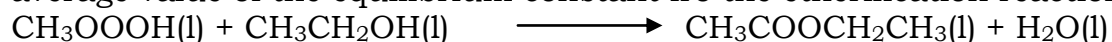
Question 2: The reaction

$N_2(g) + H_2(g) \rightleftharpoons 2NH_2(g)$

(i) Calculate the % of NH_3 in equilibrium mixture formed at 400k and 3.0×10^7 Pa pressure. When gaseous H_2 and N_2 are mixed in the ratio 3:1 and 61% of N_2 has been converted to ammonia at equilibrium.

(ii) Write an expression for the equilibrium constant in terms of the partial pressure and state its units.

Question 1: 1 mole of Ethanoic Acid was allowed to react with (a) 0.5 moles, (b) 0.2 0 and (d) 4.0 moles of ethanol. At equilibrium the amount of the gas remaining was in a) 0.58, 0.33, 0.15, 0.07 moles respectively. Calculate the average value of the equilibrium constant from the etherification reaction.



Question 2: calculate the amount of ethylethanoate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$) formed when 1 mole of ethanoic acid and 3 moles of ethanol are allowed to come to equilibrium. The value of the equilibrium constant is 4.

Question 3: A mixture of iron and steam is allowed to come to equilibrium at 600°C . The equilibrium pressures of hydrogen and steam are 3.2 Kpa and 2.4 Kpa. Calculate the equilibrium constant K_p for the reaction.



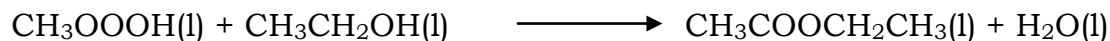
Question 3: The equilibrium constant for the reaction



If 1 mole of carbonmonoxide and 1 mole of water are allowed to come to equilibrium. What fraction of CO will remain? What fraction would remain. If 2 moles of CO were used instead of 1 mole.

Solution

(i) The equation



1mole 0.5 moles 0 moles 0 moles

-x -x +x +x

(1-x) (0.5-x) x x

But 0.58 = 1-x Equilibrium of moles

0.58 = -x Acid = 0.58 moles]

-0.42 = -x Ethanol = 0.5 - 0.42

X = 0.42 moles = 0.08 moles

Ester = 0.42

Water = 0.42moles

$K_c =$

=

$K_c = 38$

b) At equilibrium

The acid = (1-x)

Ethanol = (1-x)

Ester = x

Water = x

But 0.33 = (1-x)

0.33-1 = -x

$$-0.67 = -x$$

$$X = 0.67$$

$$\text{Equilibrium moles of Acid} = (1-x) = 1-0.067 = 0.33 \text{ moles}$$

$$\text{Ethanol} (1-x) = 1-0.67 = 0.33 \text{ moles}$$

$$\text{Ester} = x = 0.67 \text{ moles}$$

$$\text{Water} = x = 0.67 \text{ moles}$$

$$K_c =$$

$$K_c = 4.12$$

(c) At equilibrium

$$\text{The Acid} = (1-x)$$

$$\text{Ethanol} = (2-x)$$

$$\text{Ester} = x$$

$$\text{Water} = x$$

$$\text{But } 0.15 = 1-x$$

$$0.15-1 = -1$$

$$-0.85 = -x$$

$$X = 0.85$$

$$\text{Equilibrium moles of}$$

$$\text{Acid} = (1-x) = 1-0.93 = 0.07 \text{ moles}$$

$$\text{Ethanol} = (4-x) = 4-0.93 = 3.07 \text{ moles}$$

$$\text{Ester} = x = 0.93 \text{ moles}$$

$$\text{Water} = x = 0.93 \text{ moles}$$

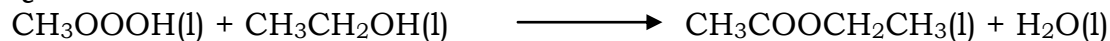
$$K_c =$$

$$K_c = 4.02$$

$$\text{Average value of } K_c =$$

$$\text{Average } K_c = 4.032$$

Question. 2



$$K_c =$$

1mole	3moles	0 moles	0 moles
-x moles	-x moles	+x moles	+x moles
(1-x)	(3-x)moles	x	x

$$\text{But } K_c = 4$$

$$4 =$$

$$4 =$$

$$X^2 = 4(3-4x+x^2)$$

$$X^2 = 12-16x + 4x^2$$

$$0 = 12-16x + 4x^2-x^2$$

$$0 = 12-16x + 3x^2$$

$$3x^2 - 16x + 12 = 0$$

$$X = 4.43 \text{ or } x = 0.9$$

$$X = 0.9$$

The amount of Ethyl ethanoate formed is 0.9 moles

Question. Stoichiometric moles of sulphur dioxide and oxygen were heated in a 1L vessel at 400K and 2 atm. When equilibrium was attained the vessel was found to contain 20% SO_3 . Calculate

- The equilibrium moles of the participating species
- The value of equilibrium constant at the same temperature.

Solution

	$2\text{SO}_2(\text{g})$	+	O_2	$2\text{SO}_3(\text{g})$
Initially	2 moles		1 mole	0
If x	-2x		-x	+2x
Eqbm moles	2-2x		1-x	2x moles

Total equilibrium moles $(2-2x) + (1-x) + 2x = (3-x)$

At equilibrium =

=

$$3-x = 10x$$

=

$$X =$$

Equilibrium moles of $\text{SO}_2 = (2-2x)$

$$= 2-2() = \text{moles}$$

Equilibrium moles of $\text{O}_2 = 1-x = 1-$

$$= \text{moles}$$

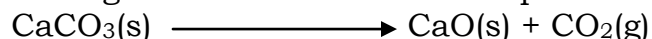
Equilibrium of $\text{SO}_3 = 2x = \text{moles}$

(ii) $K_p =$

Total equilibrium moles $= 3-x = 3- =$

HETEROGENEOUS EQUILIBRIUM

These are equilibrium systems where the participating species are not in the same physical state at equilibrium. Some may be solids, others liquids and some gases. Consider the decomposition of CaCO_3 .



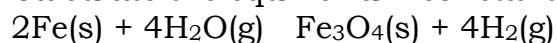
The expression for K_p is expected to be

Solids don't exert partial pressure and at equilibrium they affect on the magnitude of K_p isn't significant.

Therefore it's only CO_2 that affects the value of K_p so the expression of K_p is written as

$$K_p = P_{\text{CO}_2(\text{g})}$$

Eg A mixture of iron and steam is allowed to come to equilibrium at 600°C . the equilibrium pressures of Hydrogen and steam are 3.2 Kpa and 2.4 Kpa. Calculate the equilibrium constant K_p for the reaction.



$$K_p = = = 3.16$$

For the equilibrium reaction



write an expression for K_p and K_c if

- i. All A, B, C and D are gases
K_p =
 - ii. All are liquids
K_c =
- If A, C, D are solid but B is a gas
K_p =

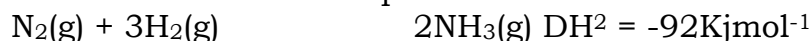
FACTORS AFFECTING EQUILIBRIUM SYSTEM

The factors affecting equilibrium or the value of the equilibrium constant. These factors include

1. Temperature of the system
2. Concentration/potential pressure
3. Volume of the system
4. Pressure of the system
5. Catalyst

Effect of temperature

This depends on whether the reaction is exothermic in the forward direction. Consider a highly exothermic reaction leading to formation of ammonia in the Haber process.



Since the forward reaction is exothermic it is favoured by low temps. Lowering the temperature of the above system increases the eqm position from the left to the right more of H₂ combines with N₂ forming ammonia.

An increase in the conc of Ammonia at eqm causes an increase in the magnitude of the eqm constant (K_p/K_c).

An increase in temp of the above system shifts the equilibrium position from right to left increasing the equilibrium yield of ammonia but increasing the eqm concs of N₂ and H₂. The effect of this is a lowered value of the equilibrium constant

For a highly endothermic reaction



The forward reaction is favoured by high temperature since it is endothermic therefore an increase in forming HI. This increases the equilibrium yield of hydrogen iodide and shifts the equilibrium position magnitude of the value of the equilibrium constant.

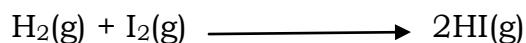
Increase in temperature for the above shifts the equilibrium position from right to left since the back reaction is exothermic and is favoured by low temps. This increases the equilibrium conc of HI and hence the magnitude of the equilibrium constant increases. (K_c/K_p).

The effect of temperature on any equilibrium system has been explained by Le Chatelier's principle which states that for any system that has attained equilibrium when subjected to a change in equilibrium, the system adjusts itself to a new equilibrium stage so as to oppose the change.

The effect of pressure

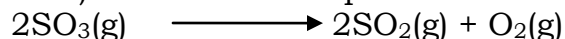
The effect of pressure depends on the stoichiometry of the reaction i.e.

- a) Reactions where there is no change on the stoichiometric moles on the left and right e.g.



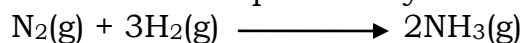
The 2 volumes on the left react to give 2 volumes on the right so pressure has no effect on both the equilibrium position and the value of the equilibrium constant.

b) Reactions that proceed with increase in no. of volumes



An increase in pressure shifts the equilibrium position from right to left because the backward reaction proceeds by increase in number of molecules. This has been explained in terms of Le Chatelier's principle i.e. for a system at equilibrium when subjected to a change in pressure it tends to oppose the change by adjusting to a new equilibrium stage. Increase in pressure makes the many volumes get over crowded and to overcome the overcrowding they react to form the few. There is no effect on the value of the equilibrium constant.

Reactions which proceed by increase in no. of molecules.



4 volumes

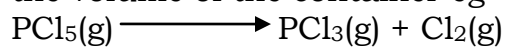
2 volumes

An increase in pressure shifts the equilibrium position from left to right since there are more molecules on the left compared to the right. More of N_2 and H_2 combine to form ammonia according to Le Chatelier's principle but there is no effect on the value of K_c . An increase in pressure shifts the equilibrium position from right to left because the backward reaction proceeds by increase in volume and is favoured by pressures.

Effect of volume of the system

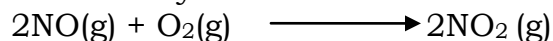
The effect of volume depends on the stoichiometry of the reactions which proceed. None change in the number of stoichiometric moles or number of volumes are not affected by changes in the volume of the container.

Reactions which proceed by increase in no. of volumes are favoured by increase in the volume of the container e.g.



Since the forward reaction proceeds by increase in no. of volume. Increase in volume of the container shifts the equilibrium position from the left to the right.

Reactions which proceed by increase in the number of molecules or volumes are favoured by increase in the volume of the container e.g.

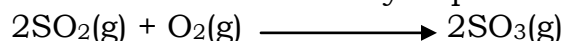


Since the forward reaction proceeds by increase in no. of molecules/volumes. It is favoured by increase in the volume of the container which causes the equilibrium position to shift from left to right without change in the magnitude of the equilibrium constant.

Effect of conc/partial pressure of the component.

Or a system that has attained equilibrium at a particular temperature when subjected to a change in concentration of a particular component or partial pressure by either removing some of the component or introducing more of it, the system opposes that change and adjusts to a new equilibrium stage.

Consider the industrially important reaction



Withdrawal of some of the SO_3 from the above equilibrium disturbs the equilibrium and to restore the equilibrium of O_2 and SO_2 .

The presence and absence of a catalyst has of the equilibrium yield but its presence does it in a shorter time combine forming SO_3 . This shifts the equilibrium position from left to right without change in the value of the equilibrium constant (K_c).

Introducing excess to the above system disturbs the equilibrium and to restore the equilibrium the excess O_2 reacts with SO_2 forming SO_3 shifting the equilibrium from left to right.

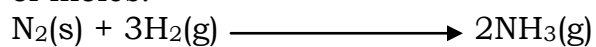
Removing sulphur dioxide from the above system disturbs the equilibrium and to restore the equilibrium SO_3 dissociates to replace the removed SO_2 . Shifting the equilibrium position from right to left without change in the value of the equilibrium constant.

Effect of a catalyst

A catalyst speeds up the rate of attainment of equilibrium by speeding up both the forward and backward reactions such that the equilibrium is attained in a shorter time than in its absence. A catalyst does not appear in the expression of K_c or K_p so has no net effect on the equilibrium position and the magnitude of the equilibrium constant. A catalyst has no effect on the equilibrium yield but the same yield is attained as in its absence only in a longer time.

Effect of an inert gas

Eg Neon, Argon, Neon. This depends on the need stoichiometric moles on the reactant and products side where there is no change in number of moles. The inert gas has no effect on both position of equilibrium and the value of the equilibrium constant. For reactions where there is... And the value of the equilibrium constant. If reaction where there is change in stoichiometric number of moles.



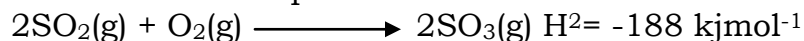
The effect of the inert gas depends on pressure and of the system. At constant pressure, when an inert gas such as He, Ne, Argon is introduced into the system. The inert gas reduces the partial pressure of which individual gases in order to be accommodated at a constant pressure.

This causes a dilution effect shifting the equilibrium position in the direction leading to a reduction of more volumes. Therefore in the Haber process introducing helium at a constant pressure the ammonia dissociates to form N_2 and H_2 shifting the equilibrium position from right to left. No effect on the value of the equilibrium constant K_c or K_p .

Adding the inert gas at constant volume, has no effect on both position of equilibrium and the value of the equilibrium constant. Since the inert gas does not appear in the expression for K_c or K_p .

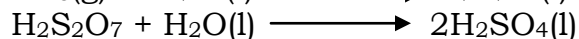
Application of equilibrium system in industrial processes.

1. In the contact process for the manufacture of H_2SO_4 .



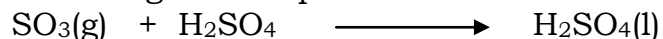
Equilibrium yield of SO_3 is increased by low temperatures since the forward reaction is exothermic and is favoured by low temperatures according to Le Chatelier's principle. However, although low temperatures make the reaction thermodynamically stable in the forward direction, the reaction becomes kinetically very slow. So a temperature of 450°C is used to speed up the rate of attainment of equilibrium.

- Increasing the concentration of SO_2 or O_2 but excess O_2 is preferred since it is readily available from air.
- Increasing the concentration of SO_3 by constantly removing it as soon as it is made. This shifts the equilibrium from left to right.
- High pressure/low volume since the forward reaction proceeds by a decrease in the number of molecules or volume. It is favoured by high pressure.
- Using a catalyst (vanadium pentoxide V_2O_5) has no effect on the equilibrium, but a lot of SO_3 is made in a shorter time than in the absence of the catalyst.
- The above equilibrium is important in the industrial manufacture of sulphuric acid (H_2SO_4).



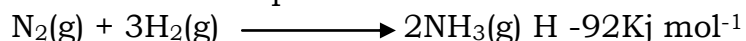
The SO_3 formed is dissolved in concentrated sulphuric acid forming Oleum which is later hydrolyzed which is about 98% acid.

It is possible to make sulphuric acid by directly dissolving SO_3 in water according to the equation.



But the reaction is highly exothermic and occurs violently so it cannot be controlled.

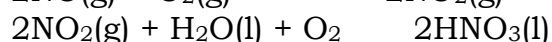
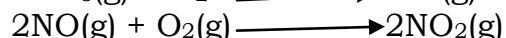
2. In the Haber process for the manufacture of ammonia



The equilibrium yield of ammonia is increased by using low temperatures, high pressure, employing a catalyst, adding excess nitrogen and hydrogen and continuously removing ammonia as soon as it is made. Like in the contact process, low temperature makes the reaction kinetically very slow, so to increase the rate of the reaction a temperature of about 550° is used.

High pressure is required and usually a pressure of 2-5 atmospheres is used by which they may break the pipes involved in the plant. The catalyst used is finely divided iron which speeds up the rate of attainment of equilibrium.

The ammonia released from the Haber process is used in the catalytic manufacture of nitric acid.



The reactions involve an initial catalytic oxidation of ammonia using a heated platinum catalyst to form nitrogen monoxide which is oxidized by air to NO_2 , NO_2 is dissolved in water in the presence of O_2 to form nitric acid which is about 70% acid.

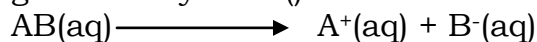
IONIC EQUILIBRIUM

This is an equilibrium established between the ions and the undissolved molecules of either a weak electrolyte or a solid of a sparingly soluble salt.

Consider a weak electrolyte AB which weakly ionizes in solution according to the equation.



The extent to which AB has ionized is called the degree of ionization and is given the symbol α



Initially 1 0 0

After ionization 1- α α α

Concn at equbm $c(1-\alpha)$ C C

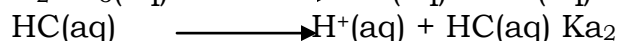
By law of Mass action

$K_{eqbm} =$

$K_{equilibrium} =$

Maximum ionization for a weak electrolyte occurs at 0 concn (zero) or infinite dilution. α is maximum and for a weak electrolyte even at infinite dilution the value of α is small such that $1-\alpha \approx 1$. This is called the Ostwald's dilution law which states that At infinite dilution weak electrolytes give the max ionization and the extent of ionization is low even at infinite dilution. From Ostwald's dilution law
 $K_{equilibrium} = C\alpha^2$

The above expression is applicable to weak acids that ionize in a single step. For acids that ionize stepwise such as carbonic acid. The expression takes a different form i.e.



Overall $H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq) \quad K_a$

Initially 1 0 0

After ionization 1- α 2α

Concn at equbm $c(1-\alpha)$ $2C$ C

By law of mass action

$K_a =$

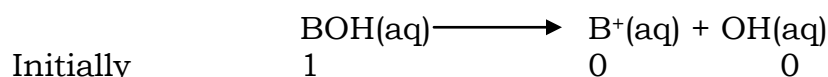
But $1-\alpha \approx 1$

$K_a = 4C\alpha^3$

$\alpha =$

Note: The value of K_{a1} is greater than K_{a2} because it is easier to remove a proton from a molecular acid than removing it from the ionized acid HCO_3^- because after removal of the 1st proton the negative charge attained strongly attracts the remaining proton. Therefore the increased electrostatic attraction between negative charge and the proton reduced the ionization of the acid lowering the value of K_{a2} .

Consider a weak base that only slightly ionizes



Initially

1

0

0

At eqbm

1-

Concn at eqbm

c(1-

C

C

By law of mass action

$K_c =$

, $K_c =$, But 1- 1, $K_c = C^2$, =

But for weak bases the constant is given as K_b .

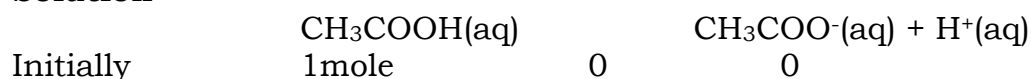
=

Where K_b is the base ionization constant

Examples

1. Calculate the degree of ionization of a 0.1 m solution of ethanoic acid $K_a = 1.8 \times 10^{-3}$

Solution



Initially

1mole

0

0

At eqbm

(1-)

Concn at eqbm

c(1-

C

C

$K_a =$

=

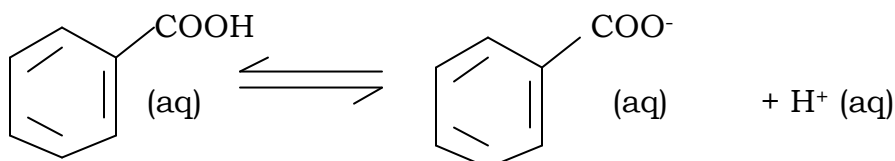
But 1- 1

$K_a = C^2$

=



2. Benzoic Acid is 0.2% ionized at 25°C calculate the acid ionization constant for a 0.1 m solution of Benzoic acid at this temperature.



Initially

1mole

0

0

At eqbm

(1-)

Concn at eqbm

c(1-

C

C

By law of mass action

=

But =

= 0.002

$K_a =$

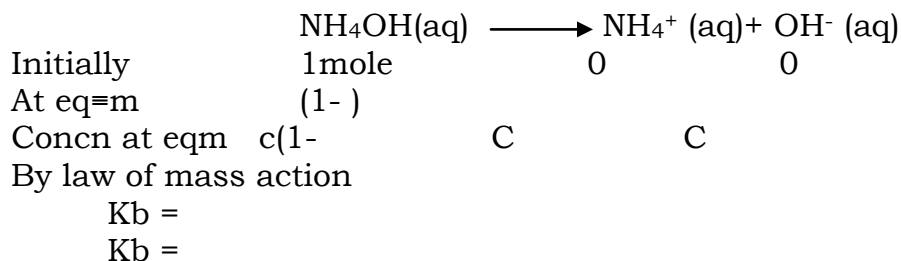
$K_a = 4 \times 10^{-7}$

4.008×10^{-7}

3. (a) Calculate the degree of ionization of a 1M solution of ammonia at 25°C (K_b for ammonia = $1.75 \times 10^{-5} \text{ mol dm}^{-3}$)

(b) Determine the molar concentration of the hydrogen ions in the solution of ammonia in (a) above

Solution



$$K_b = C^2$$

When 1- 1

$$= =$$

$$= 4.18 \times 10^{-3}$$

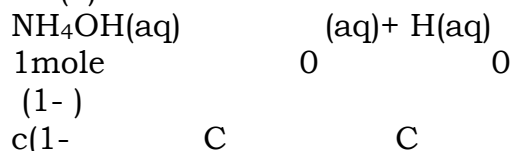
$$(b) [H] = C$$

$$= 1 \times 4.183 \times 10^{-3}$$

$$= 4.183 \times 10^{-3} \text{mol dm}^{-3}$$

Question: A 0.1m solution of ammonia is 4% ionized at 25°C. calculate

- (i) The base dissociation constant at this temperature
- (ii) The molar concentration of hydroxide ions in solution



$$K_b =$$

$$K_b =$$

$$K_b = C^2$$

When 1- 1

$$\text{But } = = 0.04$$

$$K_b = 0.04^2 \times 0.1$$

$$K_b = 1.6 \times 10^{-4}$$

$$[\text{OH}] = C$$

$$= 0.1 \times 0.04$$

$$= 4 \times 10^{-3} \text{mol dm}^{-3}$$

ACIDS AND BASES

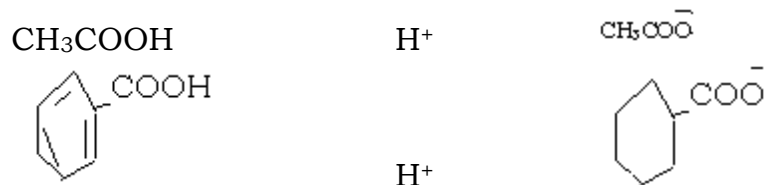
An acid is a proton donor while a base is a proton acceptor. According to Bronsted and Lasry because the product formed after loosing a proton can readily accept the proton to form back the acid.

Therefore the experiment that donates a proton is called a conjugate acid and the product that can accept a proton is called a conjugate base.

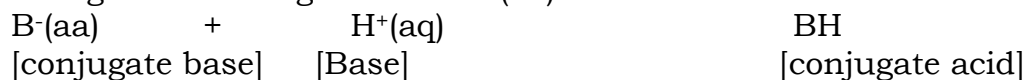
Consider the acid HA $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$

Other examples

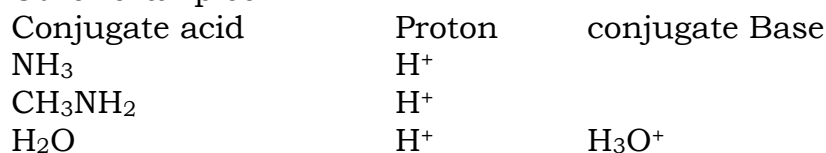
Conjugate acid	Protton	conjugate Base
HCl	H^+	Cl^-
HNO_3	H^+	NO_3^-



A base which it gains the proton from a minute and is therefore called conjugate base eg the base B (aa)

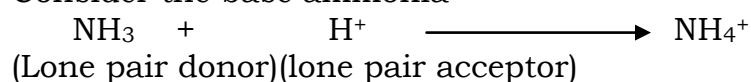


Other examples



Acids and Bases are therefore conjugate pairs and a conjugate pair differs by a proton. Lewis defines an acid as a lone pair of electrons acceptor while a base as a lone pair donor.

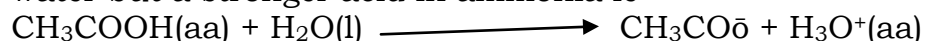
Consider the base ammonia



Strength of an acid

A strong acid is one which completely ionizes and dissociates in solution e.g. all mineral acids. A weak acid is one which only slightly ionizes in solution releasing few hydrogen ions in solution e.g. all organic acids. These differences apply to a weak and strong base only that the base releases hydroxide ions in solution. According to Bronsted and Lowry, the strength of an acid is measured so the ease with which it donates a proton. The strength of an acid or base depends on:

Nature of the solvent used. The more basic the solvent the stronger is the acid and the less basic the weaker is the acid e.g. Ethanoic acid is a weaker acid in water but a stronger acid in ammonia i.e.



Bond strength between the hydrogen and acid (H-acid bond), the stronger the bond the weaker the acid. This depends on the length of the bond which is determined by the atomic radius e.g. HCl is a weaker acid than HBr and hydroiodic acid. Down the group the atomic radius of the halogens increases this makes the bond weaker and the halogen can easily release a proton in solution therefore HI hydroiodic acid is the strongest acid followed by HBr and HCl is the weakest.

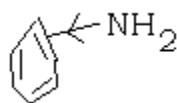
Nature of the attached group of the acid e.g.

If the group is electron withdrawing the strength of the acid is high but if the group is electron donating the strength of acid reduces. The methyl group in ethanoic acid is electron donating. Bond making it difficult to release a proton. The

phenyl $\left[\text{C}_6\text{H}_5\text{CH}_2\text{C}(=\text{O})\text{OH} \right]$ and chloride gaps $\left[\text{ClCH}_2\text{C}(=\text{O})\text{OH} \right]$ are electron withdrawing reducing the electron density around the acid and weak using the oxygen. Hydrogen bond so the proton is easily released. Similarly ammonia (NH_3) is a weaker base than methyl amine (CH_3NH_2)

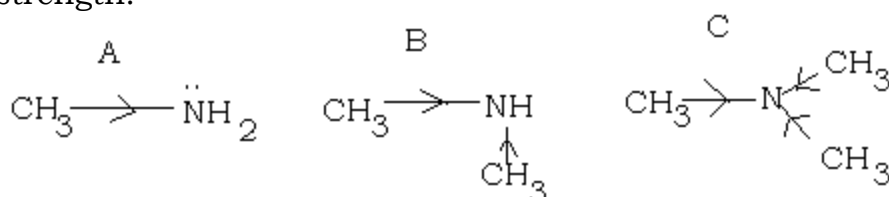
$\text{H} - \text{NH}_2$
 $\text{CH}_3 \longrightarrow \text{NH}_2$

 Increased electron density



The benzene ring is electron withdrawing reducing the electron density on the amine group electron the lone pair of electrons unavailable for accepting a proton.

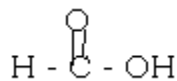
Note: An increase in the number of electron donating groups increases the basic strength.



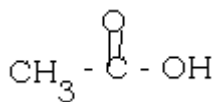
Molecule C is expected to be the strongest base but it is the weakest followed by A and B is the strongest base. In C the many methyl groups increase the electron density around the Nitrogen atom but they mask the lone pair of electrons. This is called steric hindrance.

The strength of an acid or base is determined from the value of the dissociation or ionization constant, K_b or K_a . The greater the value the stronger the acid or base.

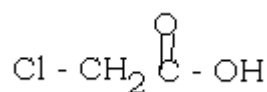
Acid $K_a/\text{mol dm}^{-3}$



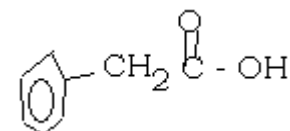
2.0×10^{-4}



1.8×10^{-5}



1.6×10^{-3}

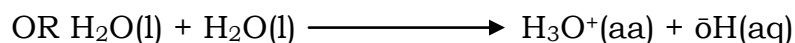
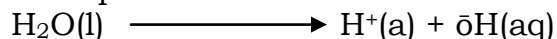


1.8×10^{-3}

Chloro ethanoic acid and phenyl ethanol acid are the strongest acids because of the negative inductive effect of the attached group. Ethanoic acid is the weakest acid because of the positive inductive effect of the methyl group.

Amino benzene is the weakest base and has the lowest value of K_b because of the phenyl group is electron withdrawing. Amino methane (or methylamine) is the strongest base with the highest value of K_b because the methyl group is electron bonding.

Ionic product of water



K_{eq} equilibrium = or K_{eq} equilibrium

$$K_{\text{eq}} [\text{H}_2\text{O}] = [\text{H}^+] \cdot [\text{OH}^-] = K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

$$\text{In pure water at } 25^\circ\text{C} \quad [\text{H}^+] = 1.0 \times 10^{-7}$$

$$[\text{OH}^-] = 1.0 \times 10^{-7}$$

$$K_w = 1.0 \times 10^{-7} \times 1.0 \times 10^{-7}$$

$$K_w = 1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$$

Water is a weak electrolyte and weakly ionizes as above. The ionic product of water is defined as the product of the concentration of hydrogen ions or hydroxonium ions and hydroxide ions in pure water at 25°C .

Note: K_w remains constant at constant temperature and is assigned a value of $1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$ at 25°C favours the backward reaction reducing the concentration of hydrogen and hydroxide ions hence lowering the value of K_w .

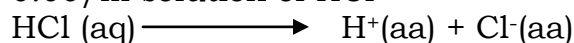
Temp/ $^\circ\text{C}$	18	25	40	70
$K_w/\text{mol}^2\text{dm}^{-6}$	0.01×10^{-14}	1.0×10^{-14}	2.92×10^{-14}	16.9×10^{-14}

The hydrogen ion index (pH)

This gives a measure of hydrogen ion concentration in solution. *It is defined as the molar concentration of hydrogen ions expressed as a logarithm to base ten. It is the negative logarithm to base 10 of molar hydrogen ion concentration.*

$$\text{pH} = -\log_{10}[\text{H}^+]$$

This eliminates very small fraction of hydrogen ions in solution. For pure water, the hydrogen ions has a concentration of 1.0×10^{-7} and therefore the P.H of pure water $\text{pH} = -\log (1.0 \times 10^{-7})$. For acidic solutions the pH is less than 7 eg 0.001m solution of HCl



$$1.01 \quad \quad \quad 0.001$$

$$\begin{aligned} \text{pH} &= -\log_{10}[\text{H}^+] \\ &= -\log_{10} [0.001] \\ &= 3.0 \end{aligned}$$

For alkaline solutions, the P.H is greater than seven for example for a solution containing 0.01m NaOH $[\text{OH}^-] = 0.01$

$$\text{But from } K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

$$\begin{aligned} [\text{H}^+] &= \\ &= 1.0 \times 10^{-12} \end{aligned}$$

$$\text{p.H} = -\log [\text{H}^+]$$

$$= \log (1.0 \times 10^{-12})$$

$$= 12$$

Relationship between pH and poH

poH is the negative to base ten of molar hydrogen ion concentration

$$\text{poH} = -\log_{10}[\text{OH}^-]$$

for pure water the hydroxide concentration is 1.0×10^{-7}

$$\text{poH} = -\log (1.0 \times 10^{-7})$$

$$= 7.0$$

pH and poH are related by the ionic product of water ie

$$K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

Introducing $-\log_{10}$

$$-\log_{10} K_w = -\log_{10}[\text{H}^+] + -\log_{10}[\text{OH}^-]$$

$$\log_{10}(1.0 \times 10^{-14}) = -\log_{10}(1.0 \times 10^{-7}) + -\log_{10}(1.0 \times 10^{-7})$$

$$14 = 7+7$$

$$14 = 14$$

And therefore

$$\text{p}K_w = \text{pH} + \text{poH}$$

$$14 = \text{pH} + \text{poH}$$

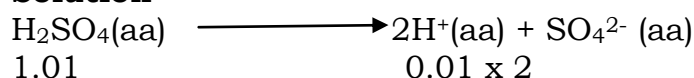
For pure water, the sum of pH and poH equals 14.

Calculating, pH of a strong electrolyte

a) Strong acid

b) Calculate the pH of a 0.01m solution of H_2SO_4

Solution



$$1.01 \qquad \qquad \qquad 0.01 \times 2$$

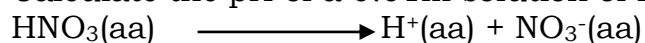
$$[\text{H}^+] = 0.02\text{m}$$

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$= -\log_{10}(0.02)$$

$$= 1.7$$

Calculate the pH of a 0.01m solution of nitric acid solution



$$1.01 \qquad \qquad \qquad 0.01$$

$$[\text{H}^+] = 0.01\text{m}$$

$$\text{pH} = -\log [0.01]$$

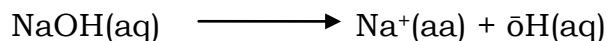
$$= -\log [0.01]$$

$$= 2.0$$

b) Strong bases

Solution

Calculate the P.H of a 0.1m solution of NaOH



But we know that $K_w = [\text{H}^+] \cdot [\text{OH}^-]$

$$[\text{H}^+] =$$

$$[\text{H}^+] = 1.0 \times 10^{-13}$$

$$\text{pH} = -\log_{10}(1.0 \times 10^{-13})$$

$$= 13$$

Alternatively

Since $[\text{OH}] = 0.1$

$$\text{pOH} = -\log_{10}[\text{OH}]$$

$$= -\log_{10}$$

$$= 1$$

$$\text{But } \text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - 1$$

$$= 13$$

Calculate the pH of a solution made by mixing 20cm^3 of a 0.1 M NaOH with 15cm^3 of 0.1M HCl. What is in excess will determine the P.H of the solution.

$$\text{Moles of HCl} = (= 1.5 \times 10^{-3}$$

$$\text{Moles of NaOH} = = 2.0 \times 10^{-3}$$

$$\text{Moles of excess NaOH} = (2.0 \times 10^{-3} - 1.5 \times 10^{-3})$$

$$= 0.5 \times 10^{-3}$$

$$\text{Total volume} = 20 + 15 = 35\text{cm}^3$$

$$35\text{cm}^3 \text{ contain } 0.5 \times 10^{-3} \text{ moles of NaOH}$$

$$1000\text{cm}^3 \text{ of solution contain (moles of NaOH}$$

$$= 0.014\text{M}$$



$$0.014 \qquad \qquad \qquad 0.014$$

$$[\text{H}^+] = =$$

$$= 7.143 \times 10^{-13}$$

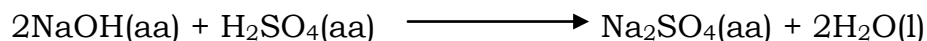
$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$= -\log [7.143 \times 10^{-13}]$$

$$= 12.1$$

Calculate the pH of a solution made by minimizing 80cm^3 of 0.1M H_2SO_4 with 20cm^3 of 0.1M NaOH.

Solution



$$\text{Moles of sodium used} = (\times 20) \text{ moles}$$

$$2 \text{ moles of NaOH react with 1 mole of } \text{H}_2\text{SO}_4$$

$$\text{Moles of NaOH reacted} = \frac{1}{2} ()$$

$$1.0 \times 10^{-3} \text{ moles}$$

$$\text{Initial moles of } \text{H}_2\text{SO}_4 = (\times 80)$$

$$= 8.0 \times 10^{-3} \text{ moles (moles supplied)}$$

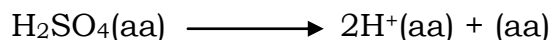
$$\text{Excess moles of } \text{H}_2\text{SO}_4 = 8.0 \times 10^{-3}$$

$$= 7.0 \times 10^{-3} \text{ moles}$$

$$\text{Initial vol} = 20 + 80 = 100\text{cm}^3$$

$$\text{Molar concentration of excess } \text{H}_2\text{SO}_4 = (7.0 \times 10 = 3 \times)$$

$$= 0.07\text{M}$$



$$0.07 \qquad \qquad \qquad 0.07 \times 2$$

$$[\text{H}^+] = 0.14\text{M}$$

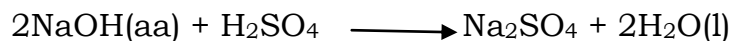
$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$= -\log_{10} (0.14)$$

$$= 0.8539$$

Calculate the pH of a solution by mixing 25cm³ of 0.2m NaOH with 10cm³ of 0.1 m H₂SO₄

Solution



Moles of sulphuric acid

Used = (x 10)

= 1 x 10⁻³ moles

But

1 mole of H₂SO₄ reacts with 2 moles of NaOH (1 x 10⁻³) moles of H₂SO₄ react with 1 x 10⁻³ x 2

1x 10⁻³ moles

Initial moles = (x 25) moles = 5 x10⁻³ moles

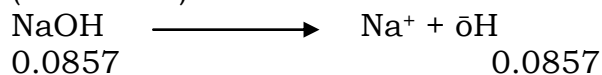
Excess moles of base

= (5 x 10⁻³ – 2 x10⁻³) moles

= 3 x 10⁻³ moles

Concentration of the base

(3 x 10⁻³ x)m = 0.0857m



[H⁺] =

[H⁺] =

= 1.6686 x 10⁻¹³

pH = -log [H⁺]

= 11.2

= 12.93

3. Calculate the concentration of moldm⁻³ of Mg ions in a solution of magnesium hydroxide whose pH is 9.60 (K_w = 1.0 x 10⁻¹⁴)

Solution

pH = -log₁₀[H⁺]

9.6 = -log[H⁺]

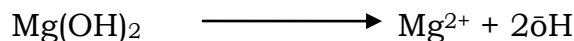
[H⁺] = 2.5 x 10⁻¹⁰

[H⁺] = 10 x 10⁻¹⁴

[H⁺] =

[̄OH] =

̄OH = 4 x10⁻⁵moles



2moles of hydroxide ions are released for 1 mole of Mg²⁺.

4 x 10⁻⁵ moles of (̄OH) ions react with

= 2.0 x 10⁻⁵M

Calculating pH of a weak electrolyte

Weak electrolytes partially ionizes in solution and their pH is derived from the dissociation constant/ionization constant at equilibrium.

Consider a weak acid CH₃COOH. This partially ionizes according to the equation



By law of mass action

$$K_a =$$

Assumptions

$$\text{At eqbm } [\text{CH}_3\text{COO}^-] = [\text{H}^+]$$

$$K_a =$$

$$=$$

$$[\text{H}^+] =$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = -\log_{10}$$

Ex 1.

Calculate the pH of a 0.1 mole ethanoic acid at 25°C (K_a for CH_3COOH at 25°C is $1.8 \times 10^{-5} \text{ mol dm}^{-3}$)

Solution



$$K_a =$$

Assumptions

$$\text{At eqbm } [\text{CH}_3\text{COO}^-] = [\text{H}^+]$$

$$K_a =$$

$$[\text{H}^+] =$$

$$=$$

$$= 1.34 \times 10^{-3}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$= -\log_{10} (1.34 \times 10^{-3})$$

$$= 2.872$$

Question. 0.1m solution of methanoic acid has a P.H of 2.4 at 25°C. calculate the value of the ionization constant at this temperature.

Solution



$$K_a =$$

$$\text{At equilibrium } [\text{HCOO}^-] = [\text{H}^+]$$

$K_a =$

But from $-\log_{10} [H^+] = 2.4$

$\log_{10}[H^+]^{-1} = 2.4$

$10^{2.4} =$

$[H^+] = 3.0 \times 10^{-3} M$

$K_a =$

$= 1.58 \times 10^{-4} \text{ mol dm}^{-3}$

A 0.01M solution of chloromethanoic Acid is 18% ionized. Calculate

- The ionization constant of the acid at the same temperature
- The pH of the acid

Solution

$\text{ClCOOH}(\text{aa}) \qquad \qquad \text{ClCOO}^-(\text{aa}) + \text{H}^+(\text{aa})$

Initially $\qquad \qquad 1 \qquad \qquad 0 \qquad \qquad 0$

At equilibrium $\qquad (1-x)$

$K_a =$

$K_a = 3.95 \times 10^{-4}$

pH from $K_a =$

at equilibrium $[\text{ClCOO}^-] = [H^+]$

$K_a =$

$[H^+] =$

$=$

$= 1.987 \times 10^{-3}$

But

$\text{pH} = -\log_{10}[H^+]$

$= -\log_{10} (1.987 \times 10^{-3})$

$= 2.7$

For weak bases eg Ammonia, they ionizes as follows

$\text{NH}_3(\text{aa}) + \text{H}_2\text{O}(\text{l}) \qquad \qquad \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aa})$

By law of mass action

$K_b =$

Note: water is in large excess so its concentration remains constant

At equilibrium $=$

$[\text{OH}^-] =$

$[H^+] =$

$=$

Calculate the pH of a 0.1M solution of Ammonia at 25°C ($K_b(\text{NH}_3) = 1.75 \times 10^{-5} \text{ mol dm}^{-3}$ at 23°C).

Solution

$\text{NH}_3(\text{aa}) + \text{H}_2\text{O}(\text{aa}) \qquad \qquad (\text{aa}) + \text{OH}^-$

$K_b =$

At equilibrium $] = [\text{OH}^-]$

$K_b =$

$[\text{OH}^-] =$

$$= 1.75 \times 0.1 = 1.32 \times 10^{-3} \text{M}$$

$$\text{From } K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

$$[\text{H}^+] = \frac{1.32 \times 10^{-3}}{1.75} = 7.58 \times 10^{-12}$$

$$\text{pH} = -\log_{10} [\text{H}^+]$$

$$= -\log_{10}(7.58 \times 10^{-12})$$

$$= 11.12$$

Exercise

Qn 1: The pH of a 0.1M propanoic Acid is 3.8 at 25°C

Calculate

- i. The ionization constant for the Acid
- ii. The PKa of the acid
- iii. The degree of ionization of the acid at the same temperature

Qn2. A 0.01M solution of dimethylamine has a pH of 10.2 at 25°C. calculation

- i. The base dissociation constant (Kb)
- ii. The degree of ionization of the base at the same temperature (Kw at 25°C = 1.0×10^{-14})

Qn 3. Calculate the pH of a solution made by mixing 35cm³ of 0.1M H₂SO₄ with 15cm³ of 0.1M KOH

Qn 4: 25cm³ of a 0.1M solution NaOH was titrated with a 0.1 M hydrochloric acid. Calculate

- (i) The pH of the solution at half neutralization
- (ii) The pH of the solution at complete neutralization

SALT HYDROLYSIS

Salts derived from strong acids and weak bases such as ammonium chloride, methyl ammonium Nitrate (CH₃NH₃NO₃) as well as those derived from weak acids and strong bases such as sodium ethanoate undergo hydrolysis in solution to give either an acid or alkaline solution.

- (1) Salts derived from strong bases and weak acids eg sodium ethanoate. This salt is derived from a weak acid ethanoic acid and a strong base sodium hydroxide.

The salts formed is a strong salt with fully dissociates

The ethanoate conc liberated undergo hydrolysis by abstracting a proton from water because of the removal of H⁺ from the water equilibrium it becomes disturbed and to restore the equilibrium more water molecules ionize to liberate more hydroxide ions which remain in excess making the resultant solution alkaline with a pH greater than 7. The overall hydrolysis reaction is written as

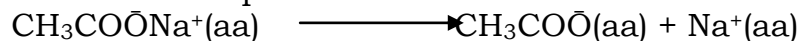


Since it is the anion that undergoes hydrolysis. This is called anionic hydrolysis. From the above equation an expression for the hydrolysis K_l can be written

KL =

The following assumptions are made when writing the above expression

- Water is taken to be in large excess and its concn remains constant at equilibrium so it does n't appear in the expression for KL.
- Sodium ethanoate is a strong salt and fully dissociates according to the equation.



Since 1 mole of $\text{CH}_3\text{COO}^-\text{Na}^+$ releases 1 mole of ethanoate ions, then

$$[\text{CH}_3\text{COO}^-\text{Na}^+] = [\text{CH}_3\text{COO}^-]$$

At equilibrium assumed that

$$[\text{CH}_3\text{COOH}] = [\text{OH}^-]$$

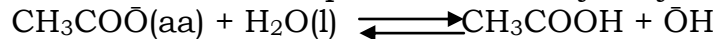
So the expression for KL can be written as

KL =

Example

Sodium ethanoate undergoes hydrolysis when dissolved in water

- Write an equation for the hydrolysis reaction



- Write an expression for the hydrolysis constant

KL =

- Calculate the pH of the solution made by dissolving 8.4g of the salt in 1 L of water ($K_w = 1.0 \times 10^{-14}$, $K_L = 5.5 \times 10^{-10}$)

Qn. Sodium propanoate ($\text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+$) undergoes hydrolysis.

- Write equations for the hydrolysis reactions of constant of sodium propanoate.
- Write the expression for the hydrolysis constant of sodium propanoate
- The P.H of a 0.1M solution of sodium propanate is 8.9. calculate the hydrolysis constant for the salt ($K_w = 1.0 \times 10^{-14} \text{mol}^2 \text{dm}^{-6}$)

Solution



(ii) KL =

At equilibrium $[\text{CH}_3\text{CH}_2\text{COOH}] = [\text{OH}^-]$

KL =

From $\text{pH} = -\log [\text{H}^+]$

$$8.9 = -\log_{10}[\text{H}^+]$$

$$10^{8.9} =$$

$$[\text{OH}^-] =$$

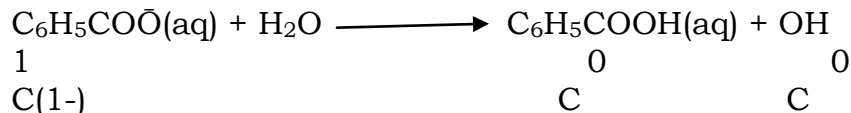
KL =

$$= 6.299 \times 10^{-14} \text{M}$$

Degree of salt hydrolysis

Since water is a weak electrolyte it only slightly ionizes releasing very few H^+ ions which can be abstracted. Therefore much of the salt remains unhydrolyzed. The

extent of hydrolysis can be calculate. Consider the hydrolysis of sodium Benzoate



KL = =

Since the extent of hydrolysis is very small

1- 1

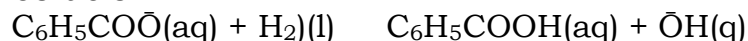
KL = C²

=

Example a 0.01m solution of sodium benzoate undergoes hydrolysis

- Calculate the degree of hydrolysis
- Calculate the pH of the resultant solution (K_l = 5.0 x 10⁻¹⁰)

Solution

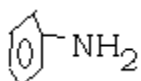


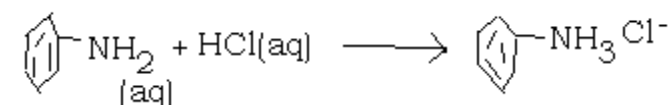
The degree of hydrolysis is

K_l = C²

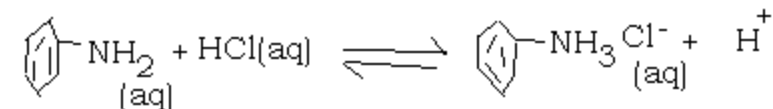
= =

= 2.24 x 10⁻⁴

Phenyl amine 



The salt formed is phenyl amine hydrochloride. The salt undergoes hydrolysis



H₂O(l)

H⁺(aq) + OH⁻(aq)

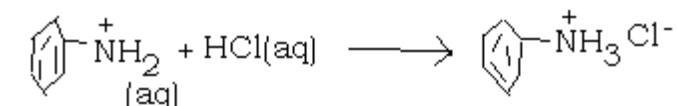
Phenyl ammonium removes OH from the water equilibrium which becomes disturbed and to restore the ionic equilibrium of water more water molecules ionise leaving an excess of hydrogen ions in solution making the resultant solution acidic.

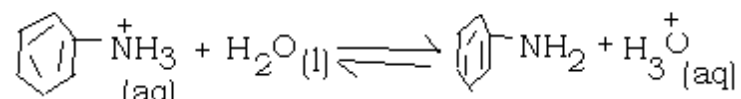
Note: during cationic hydrolysis the cation donates a proton to water, so water behaves as a base by abstracting a proton and the hydrolysis reaction is written as



Calculate the mass of phenyl amine HCl that should be added to 1 litre of H₂O to form a solution of pH 5.2 (K_l = 6.0 x 10⁻⁵M).

The solution formed undergoes hydrolysis.





$$K_L = \frac{[\text{C}_6\text{H}_5\text{NH}_2] \cdot [\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

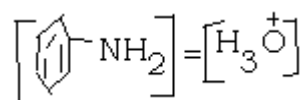
$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

$$5.2 = \log_{10} [\text{H}_3\text{O}^+]$$

$$10^{5.2} =$$

$$\text{H}_3\text{O}^+ = 6.3 \times 10^{-6} \text{ M}$$

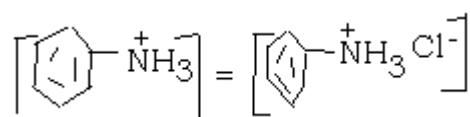
Assumption at equilibrium



$$K_L = \frac{[\text{H}_3\text{O}^+]^2}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

$$6 \times 10^{-5} = \frac{(6.3 \times 10^{-6})^2}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

$$[\text{C}_6\text{H}_5\text{NH}_3^+] = 6.6 \times 10^{-7}$$



Molar mass of $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}^-$

$$= 0.0631$$

(iii) New pH of solution

$$= 3.212 = 5$$

$$10^{5.2} =$$

$$[\text{H}_3\text{O}^+] = 6.31 \times 10^{-6}\text{M}$$

$$K_L =$$

$$[\text{C}_6\text{H}_5\text{N}^+\text{H}_3] = 1.0 \times 10^{-6}\text{M}$$

$$[\text{C}_6\text{H}_5\text{N}^+\text{H}_3] = [\text{C}_6\text{H}_5\text{N}^+\text{H}_3 \text{NO}_3^-]$$

Molar mass of $\text{C}_6\text{H}_5\text{N}^+\text{H}_3\text{NO}_3^-$

$$= (12 \times 6) + (1 \times 8) + (14 \times 2) + (16 \times 3)$$

$$= 156 \times 156$$

$$\text{Mas of salt} = 1.0 \times 10^{-6} \times 156$$

$$1.56 \times 10^{-4}\text{g/l}$$

Relationship between K_a , K_w and K_L

Consider the ionization of weak ethanoic acid



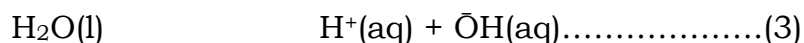
$$K_a = \dots\dots\dots(1)$$

Consider also the hydrolysis of sodium ethanoate ($\text{CH}_3\text{COO}^-\text{Na}^+$)



$$K_h = \dots\dots\dots(2)$$

Consider also the ionization of water



$$K_w = [\text{H}^+][\text{OH}^-]$$

Dividing 3 by 1

$$= =$$

$$=$$

$$= K_h$$

Relationship between K_h , K_w and K_b

Consider the ionization of a weak base e.g ammonia



$$K_b =$$

Consider also the hydrolysis of ammonium chloride



$$K_h =$$

Consider the self ionization of water

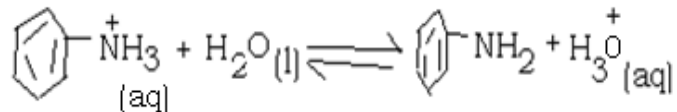


$$=$$

$$= K_h$$

Qn: Phenyl ammonium chloride undergoes hydrolysis. Calculate the pH of a 0.1 M solution of phenyl ammonium chloride (K_b for phenyl amine is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$)

Solution



$$K_L = \frac{[\text{C}_6\text{H}_5\text{NH}_2] \cdot [\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

At equilibrium

$$[\text{C}_6\text{H}_5\text{NH}_2] = [\text{H}_3\text{O}^+]$$

$$K_L = \frac{[\text{H}_3\text{O}^+]^2}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

But $K_L =$

$$5.88 \times 10^{-10} =$$

$$[H_2O^+] =$$

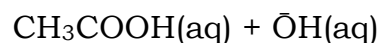
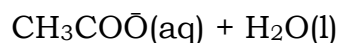
$$= 7.67 \times 10^{-6}$$

$$pH = -\log(7.67 \times 10^{-6})$$

$$= 5.12$$

Qn: Calculate the mass of sodium ethanoate that should be added to 1 litre of water to make a solution of pH 8.9 (K_a for ethanoic acid is 1.8×10^{-5})

Solution



$$K_h =$$

$$\text{At equilibrium. } (CH_3COOH) = [OH^-]$$

$$K_L =$$

$$\text{But } pH + pOH = 14$$

$$pOH = 14 - pH$$

$$(14 - 8.9) = 5.1$$

$$pOH = \log_{10}[OH^-]$$

$$5.1 = -\log_{10}[OH^-]$$

$$[OH^-] = 7.94 \times 10^{-6} M$$

Substituting in the expression

$$5.56 \times 10^{10} =$$

$$[CH_3COO^-] = 0.11 M$$

$$[CH_3COO^-] = [CH_3COONa^+]$$

RFM of CH_3COONa^+

$$= (12 \times 2) + (3) + (16 \times 2) + (23) = 82$$

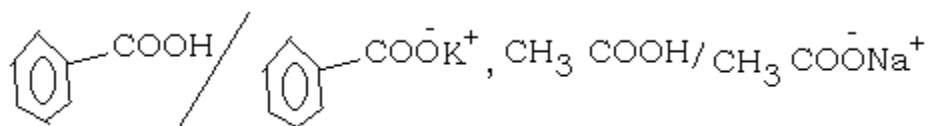
Mass of CH_3COONa^+

$$= 82 \times 0.11$$

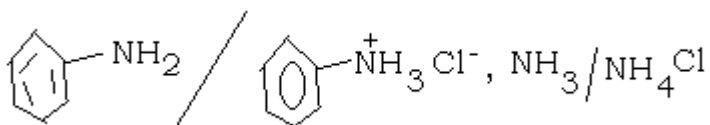
$$= 9.02 \text{ g l}^{-1}$$

Buffer solutions

A buffer solution is defined as a conjugate base acid pair that is resistant to changes in pH when a small amount of acid or base is added. There are two types of buffer solutions ie basic buffers and Acidic Buffers an acidic buffer is obtained from a weak acid and its salt derived from a strong base. Eg



A basic buffer is made up of a weak base and its salt derived from a strong acid eg



Action of a buffer solution

A buffer works by maintaining the pH constant when a small amount of acid or base is added to its solution

a) Acidic buffer

Consider the $\text{CH}_3\text{COO}^-\text{Na}^+ / \text{CH}_3\text{COOH}$ buffer solution. The acid is weakly ionized.



The salt is fully dissociated



(Excess)

The buffer contains a large excess of an ionized molecules of the acid (CH_3COOH) and a large excess of ethanoate ions. On addition of a small amount of the acid in form of hydrogen ions. The hydrogen ions are removed by ethanoate ions forming molecules of Ethanoic acid. Therefore the pH does not change.



On addition of a small amount of the base in form of hydroxide ions (OH^-) they have removed by reacting with molecules of ethanoic acid



Therefore the pH of the buffer solution remains constant.

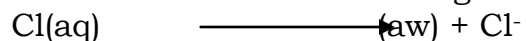
NB: The effectiveness of an acidic buffer depends on the presence of a large supply of ethanoate ions to buffer the hydrogen ions and a large supply of ethanoic / acid molecules to buffer the hydroxide ion introduced.

b) Basic buffer

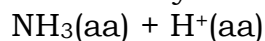
Consider a buffer $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer ammonia is a weak base and only slightly ionized.



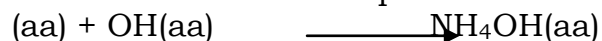
Ammonia chloride is a strong salt and fully dissociated.



Therefore the solution contains a large excess of ammonium molecules and ammonium ions addition of a small amount of the acid in form of (H^+) , they are removed by the common molecules (NH_3) and the pH doesn't change.

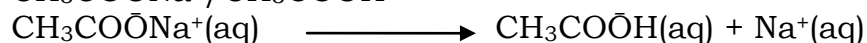
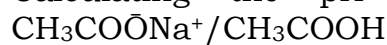


Addition of a small amount of the base in form of (OH^-) they are removed by ammonium ions so the pH doesn't change.

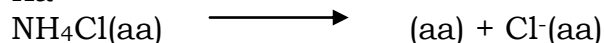


The effectiveness of a basic buffer therefore depends on the presence of a large number of ammonium ions to buffer the hydroxide ions.

Calculating the pH of buffer solution consider the acidic buffer



$K_a =$



$K_b =$

$$[\text{OH}^-] = K_b$$

Assumptions

$$[\text{NH}_4^+] = [\text{salt}]$$

$$[\text{NH}_3] = [\text{base}]$$

Question. Calculate the pH of a solution made by mixing 0.5M of (CH_3COOH) with 0.5M of sodium Ethanoate.

$$K_a = (\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$$

Solution



$K_a =$

$$[\text{H}^+] = K_a$$

$$= K_a$$

$$1.8 \times 10^{-5}$$

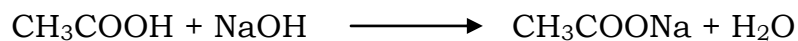
$$\text{pH} = -\log(1.8 \times 10^{-5})$$

$$\text{pH} = 4.74$$

question 1: Calculate the pH of a solution made by mixing 25cm³ of 0.1M ethanoic acid with 10cm³ of 0.1M sodium hydroxide

$$K_a = (\text{CH}_3\text{COOH}) = (1.8 \times 10^{-5})$$

Question 2. Calculate the pH of a solution made by mixing 6g l⁻¹ of $\text{CH}_3\text{COOH} = 8.2\text{g l}^{-1}$ of CH_3COO^- ($K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$)



Vol of excess acid = (25 – 10)

$$= 15\text{cm}^3$$

1000cm of excess acid contain 0.1 mole

15cm³ of excess acid contain (

35cm³ of mixture contain (moles

1000cm³ of mixture contain ()

$$= 0.0429\text{M}$$

1 mole of NaOH = 1mole of CH₃COONa

Moles of NaOH = () moles

35cm² of mixture contain ()

1000cm² of mixture contain ()

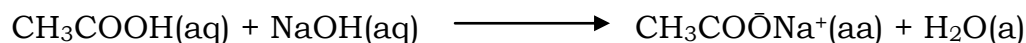
$$= 0.0286\text{M}$$

$$\text{pH} = \text{Pka} + \text{Log}_{10}$$

$$= 4.74 + \log_{10} () = 4.57$$

Calculate the pH of a solution made by mixing 50cm³ of 0.1M ethanoic acid with 0.1 mole of 50cm of sodium ethanoate. (K_a CH₃COOH = 1.8 x 10⁻⁵)

Question. Calculate the pH of a solution made by mixing 100cm³ of 0.1M ethanoic acid with 20cm³ of 0.1 M NaOH solution. (CH₃COOH) = 1.0 x 10⁻⁵)



The salt formed and the excess acid constitute a buffer solution

Moles of NaOH used = (x 20) moles

Moles of CH₃COOH used = x 20) moles

Moles of excess acid

$$= () - (x 20)$$

$$= 0.01 - 0.002$$

$$= 0.008 \text{ moles}$$

1 mole of NaOH reacts with 1 mole of ethanoic acid to form 1 mole of $\text{CH}_3\text{COO}^-\text{Na}^+$

Moles of $\text{CH}_3\text{COO}^-\text{Na}^+$

Formed = $\times 20$)

= 0.002 moles

Total volumes of solution

= $100 + 20 = 120 \text{ cm}^3$

Molar concn of salt

= 0.002 +

= 0.0167M

Molar concn of excess acid

= 0.008 x

= 0.067M

Question: Calculate the pH of a solution by mixing 50cm^3 of 0.1M hydrochloric acid with 50cm^3 of 0.2M aqueous ammonia $K_b(\text{NH}_3) = 1.75 \times 10^{-5} \text{mol dm}^{-3}$

Solution



The salt formed and the excess ammonia constitute a buffer solution

Moles of HCl used Moles of NH_3 used

= $\times 50$ (

Excess moles of NH_3

= $-(\times 50)$

= $(\times 50)$

1mole of HCl reacts with the ammonia to give

1 mole of the salt

Moles of salt formed = $\times 50$

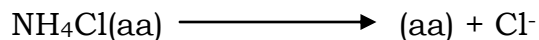
Total number = $50 + 50 = 100\text{cm}^3$

Molar concentration of excess

$$\text{NH}_3 = x \text{ } 50 \text{ } x$$

Molar concentration of salt formed

$$= x \text{ } 50 \text{ } x$$



$$K_b =$$

$$[\bar{\text{O}}\text{H}] = K_b$$

$$1.75 \times 10^{-5} \text{ } x$$

$$[\bar{\text{O}}\text{H}] = 1.75 \times 10^{-5}$$

$$\text{pOH} = -\log_{10} [\bar{\text{O}}\text{H}]$$

$$= -\log_{10}[1.75 \times 10^{-5}]$$

$$\text{pOH} = 4.757$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = 14 - 4.57$$

$$= 9.24$$

Question a 0.1m solution of ethanoic acid was titrated with a 0.1M NaOH solution. Calculate the pH of the solution when;

- i. The titration has not been started.
- ii. When the acid is half neutralized in the acid is completely neutralized.
- iii. Twice as much sodium has been added compared to that needed for neutralization

$$(\text{K}_a(\text{CH}_3\text{COOH} = 1.8 \times 10^{-5})$$

Solution

Before the titration, pH is determined by 0.1M CH_3COOH



$$K_a =$$

$$\text{At equilibrium} = [\text{CH}_3\text{CO}\bar{\text{O}}] = [\text{H}^+]$$

$$K_a =$$

$$[\text{H}^+] =$$

=

$$[H^+] = 1.34 \times 10^{-3}$$

$$pH = -\log_{10}[H]$$

$$= -\log_{10}[1.3 \times 10^{-3}]$$

$$= 2.873$$

At half neutralization



At half neutralization

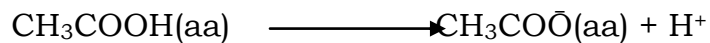
$\frac{1}{2}$ [Acid] has reacted to form the salt

$$[Acid] = \frac{1}{2} (0.1) = 0.05$$

$$[Salt] = \frac{1}{2} (0.1) = 0.05$$

Therefore at half neutralization

$$[Acid] = [Base]$$



$$K_a =$$

$$[H^+] = K_a$$

$$[H^+] = K_a$$

$$[H^+] = 1.8 \times 10^{-5}$$

$$pH = -\log_{10}[H^+]$$

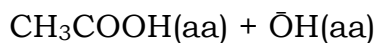
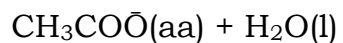
$$= -\log_{10}(1.8 \times 10^{-5})$$

$$pH = 4.7$$

At neutralization, the solution contains only the salt formed and the mixture water. All the acid has reacted to form 1 mole of the salt.

$$[salt] = 0.1M$$

The salt formed hydrolyses



But $K_L =$

At eqbm $[\text{CH}_3\text{COOH}] = [\text{OH}^-]$

$K_m =$

$$5.56 \times 10^{-10} =$$

$[\text{OH}^-] =$

$$\text{pOH} = -\log_{10} 7.4565 \times 10^{-6}$$

5.13

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = 8.87$$

$$\text{excess NaOH} = (0.2 - 0.1) = 0.1\text{M}$$

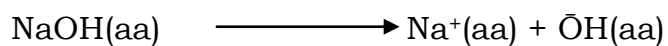
$[\text{NaOH}]$ for neutralization 0.1M

$$\text{Twice as much} = 0.1 \times 2 = 0.2 \text{ m}$$

$$\text{Excess (NaOH) in solution} = (0.1 \times 0.1)$$

$$= 0.1\text{M}$$

0.1M NaOH is responsible for the pH



0.1

0.1

$$[\text{OH}^-] = 0.1\text{M}$$

$$\text{pOH} = -\log(0.1)$$

$$= 1.0$$

$$\text{pH} = 14 - 1$$

$$= 13$$

25cm³ of a 0.1M HCl were titrated with 0.1m ammonia calculate the pH of the solution when

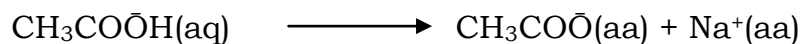
- i. The acid is half neutralized
- ii. The acid is completely neutralized

- iii. Twice as much ammonia has been added compared to that needed for neutralization.

$$(K_b(\text{NH}_3) = 1.75 \times 10^{-5}).$$

Qn. Calculate the mass of sodium ethanoate that should be added to 1 litre of a 0.1 methanoic acid to give a solution of pH 5.56 ($K_a = (\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$)

Solution



$$K_a = K_a =$$

$$[\text{H}^+] =$$

$$[\text{H}^+] = K_a$$

$$\text{But pH} = -\log_{10}[\text{H}^+] = 5.56$$

$$[\text{H}^+] = 2.75 \times 10^{-6}\text{M}$$

$$2.75 \times 10^{-6} =$$

$$[\text{salt}] = 0.65\text{M}$$

$$\text{RFM of CH}_3\text{COO}^-\text{Na}^+$$

$$=(12 \times 2) + (3) + (16 \times 2) + 23 = 82$$

$$\text{Mass of salt} = 0.65 \times 82 = 53.3\text{g/l}$$

Effect of adding a small amount of acid or base on to the PH of a buffer.

Consider a buffer made up of CH_3COOH and $\text{CH}_3\text{COO}^-\text{Na}^+$.



(a) Addition of a small amount of acid (H^+ ion]. The H^+ ions react with the ethanoate ions forming ethanoic molecules.



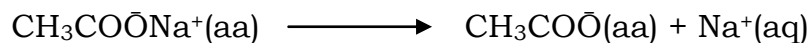
This increases the [Salt] but increases [acid] by the same amount.

Question: A solution is made by mixing 0.5M ethanoic acid with 0.5 M sodium ethanoate.

Calculate

- (i) The pH of the solution
- (ii) The change in pH when a small amount of 0.01M HCl is added to a litre of the solution.

Solution



$$K_a = K_a =$$

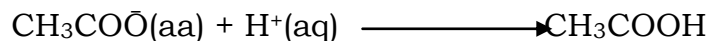
$$[\text{H}^+] = K_a$$

$$[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.74$$

So pH changes by 0.01 moles (very effective buffer)

Addition of a small amount of 0.01M HCl. The H^+ ions are buffered by the CH_3COO^- ions



This increases the $[\text{CH}_3\text{COOH}]$ by 0.01M

A new $[\text{CH}_3\text{COO}^-]$

$$= 0.5 + 0.01$$

$$= 0.51 \text{ M}$$

It decreases the $[\text{CH}_3\text{COO}^-]$ by 0.01M

$$\text{A new } [\text{salt}] = 0.5 - 0.01$$

$$= 0.49$$

$$[\text{H}^+] = K_a$$

$$[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$$

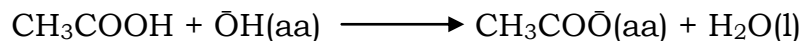
$$\text{pH} = 4.73$$

$$\text{change in pH} = 4.74 - 4.73$$

$$= 0.01$$

So pH changes by 0.01 moles (very effective buffer)

Addition of a small amount of a base. The added OH^- ions react with the molecules of ethanoic acid.



This decreases the $[\text{CH}_3\text{COOH}]$ but increases the $[\text{CH}_3\text{COO}^-]$ by the same amount. Small amount of 0.001M NaOH is added to the buffer.

Indicators

An acid – base indicator is a substance which changes colour according to the $[\text{H}^+]$ of the solution in which it is the ionized molecules of the indicator in a different color from the un ionized molecules. Common examples include phenolphthalein, methyl orange, methyl red, litmus etc

Action of an indicator

Consider the ionization of phenolphthalein



The un-ionized molecules of the indicator are colourless while the ionized are red (pink) in acidic solution the concn of $[\text{H}^+]$ is high and the ionized molecule shifting the equilibrium from right to left and the indicator appears colourless.

In Alkaline medium, the $[\text{OH}^-]$ is high which reacts with the hydrogen ions forming water disturbing the equilibrium to restore the equilibrium, more the removed hydrogen ions and the indicator appears pink in alkaline reaction.

Consider the ionization of methyl orange which is considered to be a weak base



Molecules Me are yellow but when they ionize by abstracting a proton they appear orange. In acidic medium the high concn of $[\text{H}^+]$ combine with methyl orange molecules, forming the ionized indicator shifting the equilibrium from left to right and the indicator appears orange in acidic medium.

In alkaline medium, the high $[\text{OH}^-]$ reacts with the H^+ shifting the equilibrium from right to the left and the indicator appears yellow in alkaline medium

Indicator constant (K_{in})

Consider the indicator which is a weak acid



$K_{\text{in}} =$

Or $[H^+] =$

The intermediate colour between the acidic and alkaline colour exists when

$$[HIn] = [In]$$

$$[H^+] = K_{in}$$

Indicator has its K_{in} eg for phenolphthalein it is 7.0×10^{-10}

$$[H^+] = K_{in} = 7.0 \times 10^{-10}$$

$$\text{And } pH = -\log_{10}[H^+]$$

$$= -\log_{10}(7.0 \times 10^{-10})$$

$$= 9.15$$

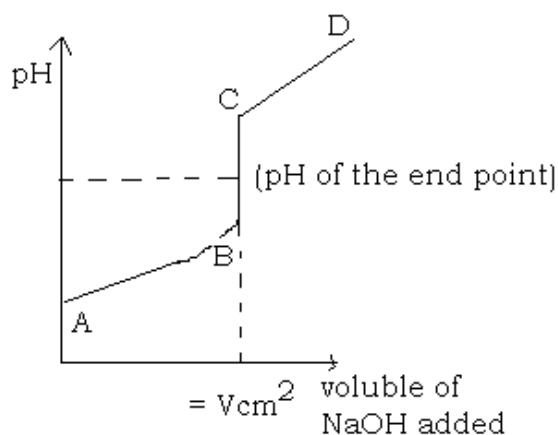
For methyl orange has a pH of 3.7 as it's acid base color. The end point of the reaction occurs at the pH of the intermediate acid-base colour. But they can't detect this end point. So a range of $pH = \pm 2$ is required either to have a full acid colour or alkaline color.

An acid – Base indicator suitable for a titration is one whose pH range fits in the pH of the resultant solution at the end point of the titration eg for a titration of a strong acid with a strong base, the pH range for the solution is between 5.0 to 10.0. therefore phenolphthalein indicator is suitable while for a titration between a weak acid and a strong base the pH range of the phenolphthalein indicator is suitable for a strong acid weak base titration the pH range of the resultant solution is 3.0 – 6.5 and methyl orange is suitable.

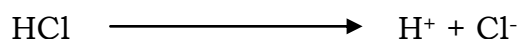
Titration curves

Titration is a strong acid against a strong base.

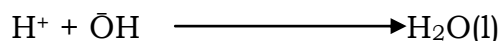
Titration of a strong acid against a strong base



The initial pH is too at point A base HCl is a strong acid and is fully ionized in solution releasing many hydrogen ions which are responsible for the low pH along AB the pH increases gradually because the hydrogen ions are still in excess and any added OH^- are immediately neutralized forming water.



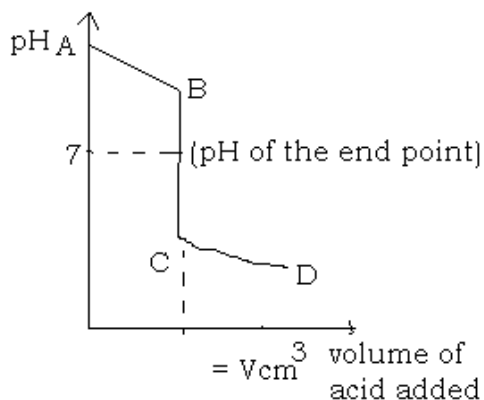
H^+ in excess



At point B all the H^+ are neutralized and this gives the end point of the titration and the volume of the base required is $V\text{cm}^3$ because all the H^+ has been neutralized any slight addition of the base causes a sharp increase in PH along BC the pH of the resultant solution is neutral ($\text{pH} = 7$) because the salt formed (NaClO does not undergo hydrolysis, the gradual increase in pH along CD is because of excess base added.

The pH at the end point can be detected by any indicator is changes colour at the pH range between B & C but preferably the midpoint is taken as the pH of the resultant solution.

2. Strong base against weak acid eg ($\text{NaOH} / \text{CH}_3\text{COOH}$)

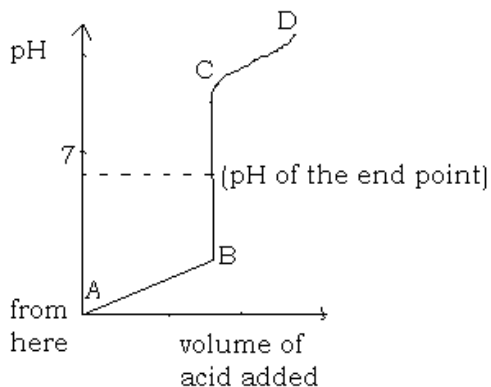


Initially the pH is high because NaOH is a strong base and fully dissociates in solution releasing many (OH^-) which are responsible for the high pH along AB the pH decreases gradually because the OH^- are still in excess, so any added H^+ from the acid are neutralized immediately at point B all the OH^- at point B there is a sharp decrease in pH along BC with slight addition of the acid, the pH at the end point is greater than 7 because the salt formed undergoes hydrolysis.



This releases OH^- in solution giving a pH greater than 7. The gradual decrease in pH along CD is because of the excess acid added and the buffering action of the thanoic acid and sodium ethanoate.

3. Strong acid against weak base eg (HCl / NH_3OH)

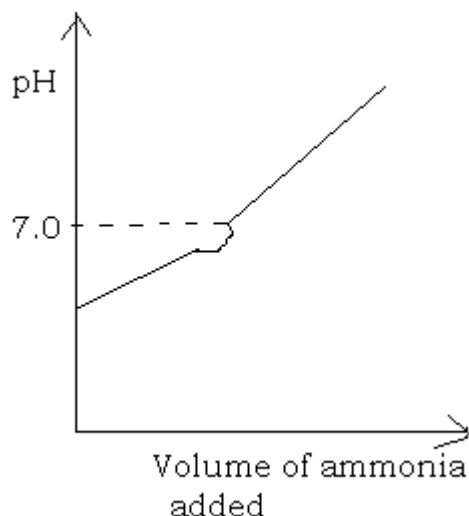


Initially the pH is low because the acid is fully ionized releasing many hydrogen ions in solution, the gradual increase in pH along AB is because the H^+ are still in excess and any added (OH^-) from ammonia are immediately neutralized. At point B all the H^+ have been neutralized and this is the end point of the titration. So any slight addition of the base causes a sharp rise in pH along BC the pH at the end point is less than 7 because the salt formed ammonia chloride undergoes hydrolysis releasing



The gradual increase in pH along CD is because of the excess base added and the buffering action of the (NH₄Cl/ Ammonium buffer).

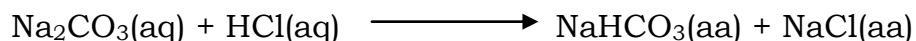
4. Weak acid against weak base titration eg (Ammonia & Ethanoic acid)



In titration of a weak acid against a weak base there is no observed sharp rise in pH hence it can't be followed using an acid base indicator.

Titration of Na₂CO₃ with HCl

But Na₂CO₃(aq) undergoes stepwise neutralization



Sodium carbonate undergoes step wise neutralization 1st it is half neutralized to NaHCO₃ and then neutralized to NaCl.

The gradual increase in pH along AB is because of the half neutralization of Na₂CO₃. Neutralisation of Na₂CO₃ is exactly half neutralized and the volume of the acid required for half neutralization is ½ cm³. The pH at half neutralization is greater than 7 the undergo hydrolysis releasing hydroxide ions in solution



The gradual decrease in pH along XC is due to neutralization of sodium hydrogen carbonate and at point C it is neutralized. The vol of the acid required for complete neutralization is V cm³. The pH of the resultant solution is neutral (7) because the salt formed (NaCl) doesnot undergo hydrolysis. The gradual decline in pH along DE is because of excess acid added.

The 1st end point is marked by using phenolphthalein indicator with changes from pink to colourless with the 2nd end point is marked by using methyl orange indicator with changes from yellow to orange. (The bi-carbonate ions undergo hydrolysis)

The following kinetics data was obtained for the reactants $A + B \longrightarrow C$

Experiment No.	Concn of mol dm^{-3}		Initial rate $\text{mol dm}^{-3} \text{s}^{-1}$
	A	B	
1	1.0×10^{-4}	2.0×10^{-4}	1.8×10^{-5}
2	2.0×10^{-4}	2.0×10^{-4}	1.8×10^{-5}
3	3.0×10^{-4}	8.0×10^{-4}	7.2×10^{-5}

a) Determine the order of reaction

i. A

ii. B

b) Calculate the rate constant and state its units

c) Calculate the initial rate of reaction of $[A] = 0.1 \text{ M}$

$$[B] = 0.2 \text{ M}$$

A Using experiments 1&2

$$() = ()$$

$$= 4y \quad = 4^1 \quad y = 1$$

(b) & C done

Question: Calculate the relative molecular mass of a solution of 2% glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) (but solution 100.12°C). boiling point constant for water is $0.52^\circ\text{C mol}^{-1}\text{kg}^{-1}$

Moles of solvent = 98g

Mass of solute = 2g

98g of water dissolved 2g of glucose

100g of water dissolved

$$\Delta t = (100.12 - 100) = 0.12^\circ\text{C}$$

0.12 is elevation caused by 20.4g

0.52 is elevated caused by

Question: Silver oxalate is a sparingly soluble salt

i. What an equation for the solubility of silver oxalate

ii. Write an expression for the solubility constant of the salt. Calculate the solubility of silver oxalate at 75°C (K_{sp} is 1.10×10^{-10})

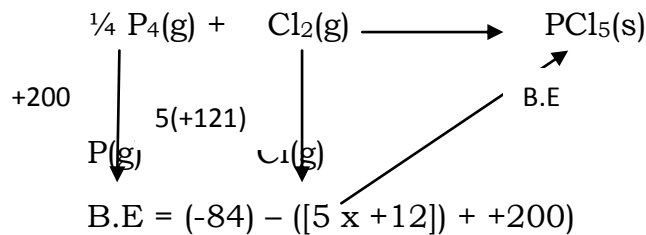


$$K_{sp} = [Ag^+]^2 [C_2O_4]^{-2}$$

Question: Determine the phosphorous chloride bond energy in phosphorus penta chloride given the thermochemical data

- Enthalpy of formation of phosphorus penta chloride is -84 KJmol^{-1}
- Atomization energy of Chlorine atoms $+121 \text{ KJmol}^{-1}$
- atomization energy of phosphorous atoms $+200 \text{ kJmol}^{-1}$

Solution



$$= -84$$

$$B.E = -84 - 805$$

$$= -889 \text{ KJmol}^{-1}$$

$$= 177.8$$

Name one reagent which can be used to distinguish between the following pairs of ions. In a case state what would be observed if the reagent is separately treated with the

- i. Ba^{2+} and Ca^{2+}
- ii. and
- iii. and
- iv. I^- and Cl^-
- v. $C_2O_4^{2-}$ and
- vi. Cr^{3+} and Cr^{6+}
- vii. Mg^{2+} and Ca^{2+}
- viii. and HCO_3^-
- ix. $C_2O_4^{2-}$ and CH_3COO^-
- x. and $C_2O_4^{2-}$

- (i) Potassium chromate solution and ethanoic acid with Ba^{2+} yellow ppt insoluble in ethanoic acid with Ca^{2+} pale yellow ppt soluble in ethanoic as.
- (ii) Acidified potassium dichromate solution and heat with turns from orange to green solution with no visible change (even (iii))
- (iii) Lead nitrate solution with I^- yellow ppt with Cl^- white ppt
- (iv) Acidified $KMnO_4$ with $C_2O_4^{2-}$ with CO_3^{2-} purple color from purple to colourless persists.

Revision

Ionic equilibria

Ionization of weak electrolytes and work out

- i. Degree of ionization
- ii. pH
- iii. ionization constant
- a. a weak acid eg ethanoic acid

	$\text{CH}_3\text{COOH(aq)}$	$\text{CH}_3\text{COO}^-(\text{aq})$	$+\text{H}^+$
Initially	1mole	0	0
If is degree	-	+	+
Of ionization			
At eqbm	(1-)		
Conc	c(1-)		

$$K_a =$$

Assumption

Calculate pH of 0.1M of ethanoic acid (K_a of acid = $10 \times 10^{-5}\text{M}$)



$$K_a =$$

Assumption at equilibrium $[\text{CH}_3\text{COO}^-] = [\text{H}^+]$

$$K_a =$$

$$[\text{H}^+]^2 = K_a(\text{CH}_3\text{COOH})$$

$$=$$

$$[\text{H}^+] = 1.0 \times 10^{-6}\text{M}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$= -\log 1.0 \times 10^{-6}$$

$$= 6$$

$$\text{pH} = 6$$

2. A solution of 0.05M propanoic acid has a pH of 4, calculate

- i. its degree of dissociation
- ii. Value of the acid dissociation constant

Solution



Assumption at equilibrium $[\text{CH}_3\text{COO}^-] = [\text{H}^+]$

$$K_a =$$

$$\text{From pH} = -\log[\text{H}^+]$$

$$[\text{H}^+] = 1 \times 10^{-4}$$

$$K_a =$$

$$2.0 \times 10^{-7}$$

$$= \text{From } K_a = c$$

$$= 2.0 \times 10^{-3}$$

$$K_a = K_a =$$

$$2.0 \times 10^{-7}$$

2. 0.01 solution of dimethyl amine is 2% ionized. Calculate

i. the base dissociation constant

ii. the pH of the solution



$$\begin{array}{ccc} 1 & 0 & 0 \\ \text{C(1-)} & \text{c(} & \text{c(} \end{array}$$

$$K_b = \quad \text{but } = 0.02$$

$$=$$

$$K_b = 4.08 \times 10^{-6} \text{ mol dm}^{-3}$$

$$K_b =$$

$$\text{At equilibrium } [(\text{CH}_3)_2\text{NH}] = [\text{OH}^-]$$

$$K_b =$$

$$[\text{OH}^-] =$$

$$=$$

$$= 2.0 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{But } [\text{H}^+] =$$

$$=$$

$$= 5.0 \times 10^{-11} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$= -\log 5.0 \times 10^{-11}$$

$$= 10.30$$

$$\text{pH} = 10.30$$

calculate the pH of a solution made by mixing 20cm³ of 0.1M HCl with 30cm³ of 0.2M NaOH.

Solution

Acid

100cm³ of solution contain 0.1 moles of HCl

20cm³ of solution will contain (x 20)

$$= 2.0 \times 10^{-3} \text{ moles of HCl}$$

Base

100cm³ of solution contain 0.2 moles of NaOH

30cm³ of solution will contain (x 30)

$$= 6.0 \times 10^{-3} \text{ moles of NaOH}$$

$$\text{Excess moles of NaOH} = (6.0 \times 10^{-3} - 2.0 \times 10^{-3})$$

$$4 \times 10^{-3} \text{ moles of NaOH}$$

50cm³ of solution contain 4 x 10⁻³ moles of NaOH

1000cm³ of solution will contain x 100

$$= 0.08 \text{ M NaOH}$$

$$\text{pH} = \text{p}^{K_w} - \text{p}^k[\text{OH}^-]$$

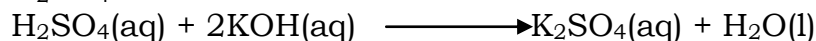
$$= 14 - \log 0.08$$

$$14 + \log 0.8$$

$$12.9$$

$$\text{pH} = 12.9$$

calculate the pH of a solution made by mixing 20cm³ of 0.1M KOH with 50cm³ H₂SO₄



$$[\text{KOH}] \text{ reacted} = [x \ 20 \ x]$$

2moles of KOH react with 1mole of H₂SO₄

0.029 moles of KOH will react with (x 69)M

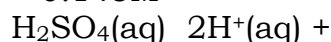
$$= 0.0145\text{M of H}_2\text{SO}_4$$

$$[\text{H}_2\text{SO}_4] \text{ used} = x \ 50 \ x$$

$$= 0.143\text{M}$$

$$\text{Excess } [\text{H}_2\text{SO}_4] = 0.143 - 0.0145$$

$$= 0.143\text{M}$$



$$0.1285 \quad (0.1285 \times 2)$$

$$0.251$$

$$\text{pH} = -\log[\text{H}^+]$$

$$= -\log 0.257$$

$$= 0.59$$

$$= 0.6$$

0.1M CH₃COOH was titrated with NaOH using phenolphthaleine indicator. Calculate

(i) The pH of the solution at half neutralization

(ii) The pH of the solution before the titration

(iii) The pH of the solution at complete neutralization (K_a CH₃COOH = 1.0x10⁻³M)

Solution

(i) From the equation



$$K_a =$$

$$\text{at equilibrium } [\text{CH}_3\text{COO}^-] = [\text{H}^+]$$

$$K_a =$$

$$[\text{H}^+]^2 =$$

$$=$$

$$[\text{H}^+] = 1.0 \times 10^{-3}\text{M}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$= -\log(1 \times 10^{-3})$$

$$\text{pH} = 3$$

(ii) At half neutralization ; [CH₃COO⁻] = [CH₃COOH]

Then from, K_a =

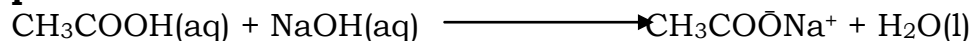
$$K_a = [\text{H}^+]$$

$$[H^+] = 1.0 \times 10^{-5}$$

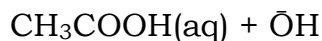
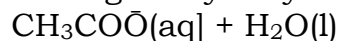
$$pH = -\log[H^+]$$

$$= -\log 1 \times 10^{-5}$$

$$pH = 5$$



At the end point, the contains the salt formed from a neutralization which undergoes hydrolysis.



$$K_l =$$

$$\text{At eqbm } [CH_3COOH] = [OH^-]$$

1 mole of the acid reacts to give 1 mole of the salt

$$\text{Conc of salt} = 0.1M$$

Again

$$K_L =$$

$$=$$

$$1.0 \times 10^{-9}M$$

$$1.0 \times 10^{-9} =$$

$$[OH^-] =$$

$$= 1.0 \times 10^{-5}M$$

$$pH = pK_w - pK[OH^-]$$

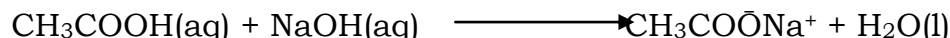
$$= 14 - \log 1.0 \times 10^{-5}$$

$$= 9$$

$$pH = 9$$

calculate the pH of a solution made by mixing 80cm³ of 0.1M ethanoic with 20cm³ of 0.1M NaOH ($K_a(CH_3COOH) = 1.0 \times 10^{-5}$)

solution



The excess CH_3COOH and the salt constitutes a buffer solution

$$[NaOH] = \frac{0.1 \times 20}{100}$$

$$0.02M$$

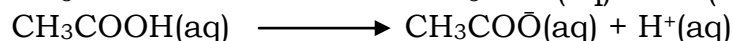
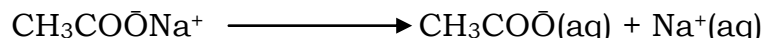
But 1 mole of NaOH is completely neutralized to form 1 mole of $CH_3COO^-Na^+$

$$[CH_3COO^-Na^+] = 0.02M$$

$$[CH_3COOH] \text{ used} = \left(\frac{0.1 \times 80}{100} \right)$$

$$\text{Excess } [CH_3COOH] = 0.08 - 0.02$$

$$= 0.06M$$



$$K_a =$$

Assumption: all CH_3COO^- are derived from the salt

$$[H^+] =$$

$$3.0 \times 10^{-5}$$

$$[H^+] = 3.0 \times 10^{-5}$$

$$pH = -\log[H^+]$$

$$= -\log 3.0 \times 10^{-5}$$

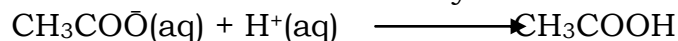
$$= 4.52$$

$$pH = 4.52$$

Calculate the change in pH that occurs when 2cm³ of 0.1M HCl were added to the above mixture.

Solution

Added H⁺ ions are buffered by the ethanoate ions



This increase [CH₃COOH] but decreases [CH₃COO⁻]

Total vol of solution = 102cm³

[H⁺] added = $\frac{2}{100} \times 0.1$

= 1.96 x 10⁻³ M

New [CH₃COOH] = (0.06 + 1.96 x 10⁻³) M

= 6.2 x 10⁻² M

New [CH₃COO⁻] = 0.02 - 1.96 x 10⁻³

= 1.80 x 10⁻² M

[H⁺] =

=

[H⁺] = 3.44 x 10⁻⁵

pH = 4.46

change in pH

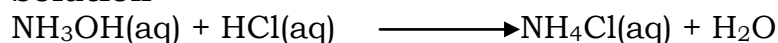
= 4.52 - 4.46

= 6.0 x 10⁻²

0.06

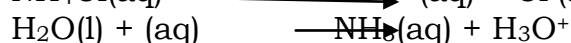
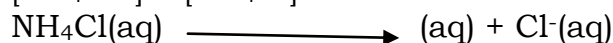
30cm³ of 0.1M Solution of ammonia was titrated with hydrochloric acid. At the end point, 5cm³ of acid had been added. Calculate the pH of the resultant solution (K_a for NH₃ is 1.5 x 10⁻⁵ moldm⁻²)

Solution



1mole of NH₃ reacts with 1 mole of HCl

[NH₃] = [NH₄Cl]



K_L =

[NH₃] = [O]

K_L = but K_L =

[O] =

pH = -log (

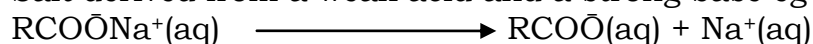
= -log

pH = 5.16

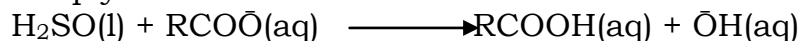
Salt hydrolysis

This is a reaction of salt with water in which the ions equilibrium of water is disturbed resulting into an acid or alkaline solution

Salt derived from a weak acid and a strong base eg RCOONa⁺

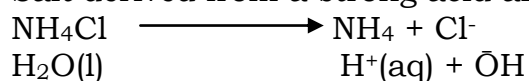


Simply

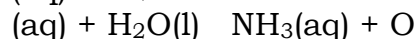


This is called ionic hydrolysis

Salt derived from a strong acid and a weak base eg RNH_3Cl^-



Or simply



This is called cationic hydrolysis

Example

Calculate the pH of a solution ethanoate made by dissolving 8.4g of the salt in 1 litre of water (for sodium ethanoate = $5.5 \times 10^{-10}\text{M}$)

Solution

$$\text{RFM of } \text{CH}_3\text{COO}^-\text{Na}^+ = (12 \times 2) + (16 \times 2) + (1 \times 3) + (23 \times 1)$$

$$= 82$$

$$\text{Conc of } \text{CH}_3\text{COO}^-\text{Na}^+ = 0.102\text{M}$$



$$K_L =$$

At equilibrium

$$[\text{CH}_3\text{COOH}] = [\text{OH}^-]$$

$$K_L =$$

$$K_L =$$

$$[\text{OH}^-] =$$

$$=$$

$$[\text{OH}^-] = 7.48999 \times 10^{-5}$$

$$[\text{H}^+] =$$

$$=$$

$$[\text{H}^+] = 1.335 \times 10^{-9}\text{M}$$

Example 2

Sodium propanoate hydrolyses in water

- i. Write equation for the hydrolysis
- ii. Give expression for hydrolysis constant K_L
- iii. If a pH of 0.1M aqueous solution of sodium propanoate is 8.9. calculate the value of K_L



$$K_h =$$

$$\text{pH} = 8.9$$

$$8.9 = \log[\text{H}^+]$$

$$\text{Log}[\text{H}^+]^{-1} = 8.9$$

$$[\text{H}^+]^{-1} =$$

$$1.26 \times 10^{-9}$$

At equilibrium $[\text{CH}_3\text{CH}_2\text{COOH}] = [\bar{\text{O}}\text{H}]$

$$K_h =$$

$$[\bar{\text{O}}\text{H}] =$$

$$=$$

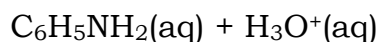
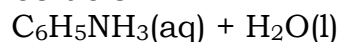
$$7.9365 \times 10^{-6}$$

$$K_h =$$

Example 3

Calculate the mass of phenyl amyl hydrogenchloride that should be added to 1 litre of water to form a solution of pH 5.2 ($K_h = 6.0 \times 10^{-5} \text{ mol dm}^{-3}$)

Solution



$$K_h =$$

$$K_h =$$

$$6.0 \times 10^{-5} =$$

$$= 6.6 \times 10^{-7} \text{ M}$$

From 1 mole of reacts with 1 mole of -

$$= 6.6 \times 10^{-1} \text{ M}$$

$$\text{RFM of } = (12 \times 6) + (1 \times 6) + (14 \times 1) + (35.5 \times 1)$$

$$= 127.5$$

$$\text{Mass} = \text{RFM} \times$$

$$= 127.5 \times 6.6 \times 10^{-7}$$

$$= 7.65 \times 10^{-5}$$

Degree of hydrolysis of a salt

Eg (aq)



Before hydrolysis 1mole 0 0

If has hydrolysed 1-

$$K_h =$$

A 0.01 M solution of sodium benzoate undergoes hydrolysis

Calculate

i. The degree of hydrolysis of the salt

ii. The pH of the solution ($K_h = 5.0 \times 10^{-10}$)

A solution of 0.01M sodium ethanoate is 2% hydrolysed. Calculate

i. The hydrolysis constant

ii. The pH of the solution

Solution

$$K_l = \text{but } 1 - 1$$

$$2 = 2.236 \times 10^{-4}$$

Calculate the pH of 0.01M solution of ammonium chloride ($K_h = 6.84 \times 10^{-8}$)

$$[\bar{\text{O}}\text{H}] =$$

$$=$$

$$= 7.96 \times 10^5$$

$$[\text{H}^+] =$$

=

$$= 1.2559 \times 10^{-10}$$

$$\text{pH} = -\log(1.2559 \times 10^{-10})$$

$$= 9.9$$

Examples of salts that hydrolyse



Solution

No.1

$$[\text{OH}^-] = 2.236 \times 10^{-6}$$

$$[\text{H}^+] =$$

= (

$$[\text{H}^+] = 4.472 \times 10^{-9}$$

$$\text{pH} = -\log [4.472 \times 10^{-9}]$$

$$= 8.35$$

(ii) pH

$$[\text{OH}^-] =$$

$$= 2.02 \times 10^{-4}$$

$$[\text{H}^+] =$$

= (

$$= 4.949 \times 10^{-11}$$

$$\text{pH} = -\log [4.9498 \times 10^{-11}]$$

$$= 10.31$$

SOLUBILITY PRODUCT CONCEPT

Applicable to sparingly soluble salts i.e. a salt that slightly dissolves in water forming ions which remain in equilibrium with undissolved solid at a constant temperature.

Solubility product

Product of the ionic concentration is a saturated solution of a product of a sparingly soluble salt raised to appropriate powers from the stoichiometric equation at a constant temperature.

Example calculate the solubility of BaSO_4 in

i. Water

ii. 0.1M sodium sulphate ($K_{\text{sp}} \text{BaSO}_4$ at $25^\circ\text{C} = 1.0 \times 10^{-10}$)

Calculate the amount of the BaSO_4 which was precipitated as a result of dissolving barium sulphate in 0.1M sodium sulphate



Let solubility of BaSO_4 be $s \text{ mol dm}^{-3}$

$$[\text{Ba}^{2+}] = s$$

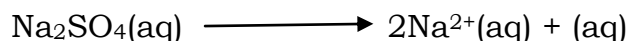
$$[\text{SO}_4^{2-}] = 0.1 + s$$

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$1.0 \times 10^{-10} = s(0.1 + s)$$

$$s =$$

$$= 1 \times 10^{-5} \text{M}$$



Let the new solubility be $s^1 \text{mol dm}^{-3}$

$$[] = [0.1 + S^1] \text{mol dm}^{-3}$$

$$[\text{Ba}^{2+}] = S^1$$

But $0.1 \gg S^1$ such that $0.1 + S^1 = 0.1$

$$1.0 \times \dots\dots\dots$$

$$S^1 = 1 \times 10^{-1} \text{M}$$

Moles precipitated $[1.0 \times 10^{-5} - 1.0 \times 10^{-9}]$

Mass precipitated

$$\text{Ba} - \text{RFM} = 233$$

$$(1.0 \times 10^{-5} - 1.0 \times 10^{-9}) 233$$

$$2.33 \times 10^{-12}$$

Calculate the solubility of calcium chloride in

- i. Water
- ii. 0.01 M solution of sodium fluoride
- iii. 1.0M solution of hydrogen fluoride (K_{sp} for $\text{CaF}_2 = 4.0 \times 10^{-11}$, K_a for $\text{Hf} = 5.6 \times 10^{-4} \text{M}$)

Solution



Let the solubility in water be $s \text{mol dm}^{-3}$

$$[\text{Ca}^{2+}] = s \quad [\text{F}^-] = 2s$$

$$K_{sp} = [\text{Ca}^{2+}] [\text{F}^-]^2$$

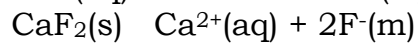
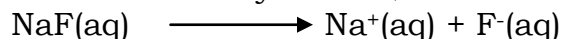
$$4.0 \times 10^{-11} = s(2s)^2$$

$$S^3 =$$

$$S =$$

$$= 2.15 \times 10^{-4} \text{M}$$

Let the solubility of CaF_2 in 0.01m NaF be a mol dm^{-3}



$$[\text{Ca}^{2+}] = a \text{mol dm}^{-3}$$

$$[\text{F}^-] = 22 (a + 0.01 \text{mol dm}^{-3})$$

But $0.01 \gg a$

$$[\text{F}^-] = 0.01 \times 2$$

$$4.0 \times 10^{-11} = 0.0001 a$$

$$= 4.0 \times 10^{-7} \text{M}$$



$$K_a =$$

$$[\text{H}^+] = [\text{F}^-]$$

$$K_a 5.6 \times 10^{-4} =$$

$$[\text{F}^-] =$$

$$= 1.4833 \times 10^{-3}$$

Let new solubility be y



$$2y + 7.4833 \times 10^{-3} \quad 7.4833 \times 10^{-3}$$

$$K_{sp} = [\text{Ca}^{2+}] [\text{F}^-]$$

$$4 \times 10^{-11} \text{ a } 7.4833 \times 10^{-3}$$

A =

$$5.345 \times 10^{-9} \text{M}$$

write the expression for the solubility product of iron (ii) hydroxide and give the units.

$$K_{sp} = [\text{Fe}^{2+}] [\text{OH}]^2$$

If the K_{sp} of $\text{Fe}(\text{OH})_2$ at 25°C is 6.6×10^{-15} , calculate the solubility in mol dm^{-3} of $\text{Fe}(\text{OH})_2$ first in pure water then in 1.0M ammonia (K_b Ammonia = $1.8 \times 10^{-5} \text{M}$)

In water let the solubility be $s \text{ mol dm}^{-3}$



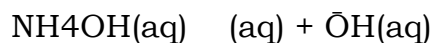
$$K_{sp} = [\text{Fe}^{2+}] \cdot [\text{OH}]^2$$

$$6.6 \times 10^{-15} = s(2s)^2$$

S =

$$1.1817 \times 10^{-5} \text{ mol dm}^{-3}$$

Ammonia ionizes in solution according to the equation



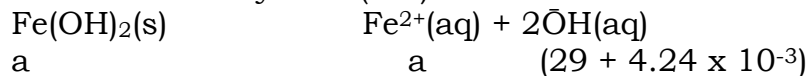
K_b = at equilibrium

$$1.8 \times 10^{-5} =$$

$$[\text{OH}] =$$

$$= 4.24 \times 10^{-3} \text{ M}$$

Let the solubility of $\text{Fe}(\text{OH})_2$ in 1M NH_3 be $a \text{ mol dm}^{-3}$



but $2a \ll 4.24 \times 10^{-3}$

such that $2a + 4.24 \times 10^{-3} \approx 4.24 \times 10^{-3} \text{ M}$

$$K_{sp} = [\text{Fe}^{2+}] [\text{OH}]^2$$

$$6.6 \times 10^{-15} = a.(4 \times 4.24 \times 10^{-3})$$

a =

$$= 3.67 \times 10^{-10} \text{M}$$

b) The K_{sp} of barium sulphate and strontium sulphate are 1.1×10^{-10} and $2.8 \times 10^{-7} \text{ mol}^2 \text{dm}^{-6}$ at 298K. sodium sulphate is gradually added to a solution containing 0.01M Barium chloride and 0.01M strontium chloride.

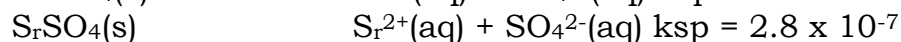
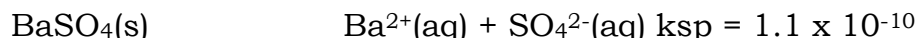
(i) Which cation will precipitate first give a reason.

Solution

Barium ions precipitate out first leaving strontium ions in solution because barium sulphate has a lower solubility product hence a low solubility and its K_{sp} is easily exceeded.

Calculate the concentration of BaSO_4 in a solution which is saturated with both barium sulphate and strontium sulphate.

Solution



Assumption

In a saturated solution of the two salts, the common ion comes from only the more soluble salt, so the sulphate are from SrSO_4



0.01

0.01

$K_{sp} = [Sr^{2+}] [$

$] =$

$=$

$= 2.8 \times 10^{-5}$

Barium sulphate

$K_{sp} = [Ba^{2+}] [$

$1.10 \times 10^{-10} = [Ba^{2+}] = 2.5 \times 10^{-5} M$

$[Ba^{2+}] =$

$[Ba^{2+}] = 3.93 \times 10^{-6} M$

Since 1 mole of $BaSO_4$ releases 1 mole of Ba^{2+}

Concentration of $BaSO_4 = [Ba^{2+}]$

$= 3.93 \times 10^{-6} M$

Experimental determination of the solubility product of calcium hydroxide

An excess of calcium hydroxide is added to a given volume of water and the mixture shaken such that no more solid can dissolve to obtain a saturated solution. The mixture is filtered to obtain a saturated solution.

Known volume of this solution are pipette and titrated using phenolphthalein indicator.

The volume of the acid need to reach end point is noted.

Treatment of results

Let concn of acid be $x \text{ moldm}^{-2}$

Volume of acid to reach end point is noted

Treatment of results

Let concentration of acid be $x \text{ moldm}^3$

Volume of acid needed to reach end be $V_1 \text{ cm}^3$

Volume of saturated solution pipette be $V_2 \text{ cm}^3$

Moles of acid used = $(x \times V_1)$

From the equation

$\bar{O}H(aq) + HCl(aq) \longrightarrow \bar{C}l(aq) + H_2O(aq)$

Moles of $\bar{O}H$ that reacted = $(x \times V_1)$ moles

$V_2 \text{ cm}^3$ of solution contain $()$ moles of $\bar{O}H$ ions

1000 cm^3 of solution (x) moles of $\bar{O}H$ ions.

From the equation

$Ca(OH)_2 \quad 2\bar{O}H(aq) + Ca^{2+}(aq)$

1 mole of $Ca(OH)_2$ releases 2 moles of $(\bar{O}H)$ ions

$[\bar{O}H] = (x) \times 2$

For every of $\bar{O}H$ released 1 mole of Ca^{2+} is released

$[Ca^{2+}] = \frac{1}{2} [\bar{O}H]$

$= (x) \times 2 \times$

$= (x)$

What is meant by the term common ion effect?

This is the precipitation of a sparingly soluble salt from its saturated solution by introducing a soluble salt containing one of the of the saturated sparingly soluble salt.

Calcium iodate, $Ca(IO_3)_2$ is sparingly soluble in water

Write

The equation for the solubility of calcium iodate in water.



An expression for the solubility product, K_{sp} of calcium iodate

$$K_{sp} = [\text{Ca}^{2+}] \cdot [$$

If the solubility product of calcium iodate at 25°C is 1.95×10^{-3} . Calculate the solubility in moles per litre at 25°C of calcium iodate in.

Water

$$K_{sp} = 1.95 \times 10^{-4} \text{mol dm}^{-3}$$

Let the solubility of $\text{Ca}(\text{IO}_3)_2$ in water be

$$K_{sp} = () (2)^2$$

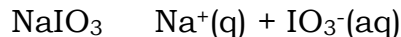
$$1.95 \times 10^{-4} \text{ M} = 4^3$$

$$=$$

$$= 3.653 \times 10^{-2} \text{M}$$

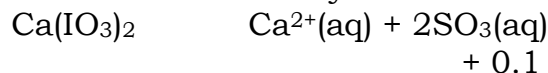
The solubility is $3.633 \times 10^2 \text{ M}$

A 0.01 M solution of sodium iodate



$$0.1 \qquad \qquad 0.1$$

Let the new solubility be



But $25 \lll 0.1$

$$2 + 0.1 = 0.1$$

$$K_{sp} = (0.1)^2$$

$$=$$

$$V = 1.95 \times 10^{-2}$$

Convert on your answer in (C) above

Addition of calcium iodate solution to a 0.1M solution of sodium iodate reduced the solubility of the sparingly soluble salt.

A solution containing $0.001 \text{ mol dm}^{-3}$ of methanoic acid is 1% ionized.

Calculate

The pH of methanoic and solution

Let the degree of ionization be x



$$1 \qquad \qquad 0 \qquad 0$$

$$1 -$$

$$\text{C}(1-) \qquad \qquad \text{C} \quad \text{C}$$

$$K_a =$$

$$K_a =$$

But $1 -$

$$K_a = 2\text{C} \quad \text{but} \quad = 0.01$$

$$(1 -) = 1 - 0.01$$

$$= 0.99$$

$$K_a = (0.01)^2 / 0.001$$

$$K_a = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

$$K_a = \text{but } [\text{HCOO}^-] = [\text{H}^+]$$

$$[H^+] =$$

$$[H^+] =$$

$$= 1 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log [H^+]$$

$$= -\log(1 \times 10^{-5})$$

$$= 5$$

$$\text{pH} = 5$$

(ii) The acid dissociation constant K_a for methanoic acid

$$K_a = 2 \times 10^{-4}$$

$$K_a = (0.01)^2 \times 0.001$$

$$1 \times 10^{-1} \text{ mol dm}^{-3}$$

Calcium fluoride is a sparingly soluble salt in water

(a) Write an equation for the solubility of calcium fluoride



(b) Expression for the solubility product K_{sp} of calcium include. Let the solubility be s

$$K_{sp} = [\text{Ca}^{2+}] [\text{F}^{-}]^2$$

Calculate the solubility for calcium fluoride in a solution containing 0.35 mol l^{-1} of fluoride ions at 25°C . ($K_{sp} = 1 \times 10^{-10}$ at 25°C)

Let the solubility be y



$$\text{But } 2y + 0.35 = 0.35$$

$$\text{Because } 2y \ll 0.35$$

$$K_{sp} = y \times (0.35)^2$$

$$1.7 \times 10^{-10} = y \times (0.35)^2$$

$$y =$$

$$= 1.3878 \times 10^{-9} \text{ M}$$

The solubility of calcium fluoride = 1.3878×10^{-9}

State one application of solubility product

- It is used in extraction of some salts

Write an equation for the ionization of methylamine in water



An expression for the base dissociation constant K_b for methyl amine

Let it be the degree of ionization



$$\text{Initially: } c(1-x)$$

$$K_b =$$

$$K_b =$$

$$K_b = Cx^2$$

(b) The hydrogen ion concentration of a 1 M methylamine solution is $2.5 \times 10^{-13} \text{ mol l}^{-1}$. Calculate K_b for methylamine.

$$[\text{CH}_3\text{NH}_2] = 1.0 \text{ M}$$

$$[\text{H}^+] = 2.5 \times 10^{-13} \text{ M}$$

$$K_b = \text{but } [\text{CH}_3\text{NH}_3] = [\bar{\text{O}}\text{H}]$$

$$K_b =$$

$$\text{But } K_w = [\bar{\text{O}}\text{H}] [\text{H}^+]$$

$$[\bar{\text{O}}\text{H}] =$$

$$=$$

$$[\text{OH}] = 4.0 \times 10^{-2} \text{ M}$$

$$K_b =$$

$$K_b = 1.6 \times 10^{-3} \text{ mol}^2\text{l}^{-2}$$

5. The solubility products of lead (ii) chloride is $1.6 \times 10^{-31-3}$ at 25°C

(a) Write an expression for the solubility products of lead(ii) chloride

$$K_{sp} = [\text{Pb}^{2+}] \cdot [\text{Cl}^-]^2$$

(b)(i) The concentration of the chloride ion in mol l^{-1} in a saturated solution of lead (ii) chloride at 25°C

Let the solubility be x

$$K_{sp} = [x] \cdot [2x]^2$$

$$1.6 \times 10^{-5} = 4x^3$$

$$x =$$

$$1.5874 \times 10^2 \text{ mol l}^{-1}$$

The concentration of chloride ions = $1.5874 \times 10^2 \text{ mol l}^{-1}$

The solubility lead (ii) chloride in grams per litre at 25°C ions litre contains 1.5874×10^2 moles

RFM of PbCl_2

$$207 + (35.5 \times 2)$$

$$278$$

$$\text{One litre contains } 1.5874 \times 10^{-2} \times 278$$

$$= 4.413 \text{ g l}^{-1}$$

(c)(i) State what would be observed if a saturated solution of lead (ii) ethanoate was added to a solution of lead (ii) chloride.

The solubility of lead (ii) chloride decreases

(ii) Give a reason for your answer in C(i)

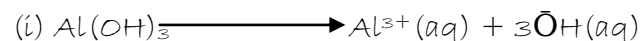
This is concentration of Pb^{2+} ions, according to Le Chatelier's principle the lead (ii) chloride equilibrium will shift to the left in order to reduce the concentration of the lead (ii) ions.

6. A solution containing $2.3 \times 10^{-6} \text{ mol dm}^{-3}$ of aluminium hydroxide completely ionizes in water ($K_w = 1 \times 10^{-14}$)

(i) Write equation for the reaction of aluminium hydroxide

(ii) Calculate the pH of the resultant solution.

Solution.



$$K_w = [\text{H}^+] [\bar{\text{O}}\text{H}]$$

$$[\text{H}^+] =$$

$$= 4.3 \times 10^{-9}$$

$$\begin{aligned} \text{pH} &= -\log(4.35 \times 10^{-9}) \\ &= 8.36 \end{aligned}$$

PHASE EQUILIBRIA

A pure substance can exist as a solid, liquid or gas/vapour depending on the prevailing temperature and pressure. It is again possible to find appropriate values of temperature and pressure at which two or three of the above phase can co exist without one phase tending to disappear or another tending to dominate such a situation is given the name phase equilibrium.

In phase equilibrium two terms are commonly used.

i) A phase

This is a physically distinct part of the phase system separated from other parts of the system by definite boundary called phase boundaries.

A phase system may be a two phase system such as liquid-

Vapour equilibrium or it may be a three phase system involving a solid, liquid and vapour in equilibrium with each other.

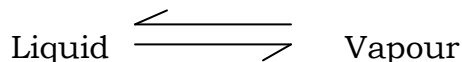
ii) A component

This is defined as the number of chemical species needed to define a phase system. It can be one component, a two component and a three component system.

One component systems;

There are phase systems made of one chemical species eg Water system which can be.

iii) The phase system eg liquid vapour equilibrium



GRAPH

Curve AB is called a phased boundary separating the liquid phase from the vapour phase any temperature and pressure a long this curve, liquid water remains in equilibrium with water vapour, Any temperature and pressure below the curve the vapour phase dominates because an increase in temperature at a constant pressure causes an increase in vaporization of water ie many molecules of water escape into the vapour phase compered to those that are condensing to form a liquid

When the temperature reaches curve AB, The number of molecules of liquid water that number one escaping into the vapour phase becomes equal to the number of molecules of water vapour that are condensing to form back the liquid. Another temperature and pressure and equilibrium is established. Beyond this temperature and pressure above the curve AB the liquid phase dominates andvapour phase tends to disappear ie more molecules of the vapour condensing to form back the liquid.

The three phase system of water

Point O is called triple point of water ie the temperature and pressure at which

On the three phase solid liquid and vapour can coexist in equilibrium with each other curve AO is the vapour pressure curve of ice or the sublimate curve of water. Any temperature and pressure along..... ice and water vapour remain in equilibrium without one contaminating or another disappearing.

Curve OB is the vapour pressure curve of liquid water or the vapoursation curve of liquid water. Any temperature and pressure a long this curve liquid water remains in equilibrium with water vapour. The curve shows the variations in boiling point of water with pressure. An increase in pressure causes an increase in Boiling point. Any temperature and pressure a long this curve being occurs and any particular temperature along this curve gives the boiling point of liquid water at that pressure.

Boiling point is defined as 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. Any temperature and pressure along this curve ice remains in equilibrium with liquid water. (The curve slopes towards the pressure axis toward the left) indicating that melting point of ice is lowered by an increase in pressure.

Point B is called the critical point of water i.e. the temperature beyond which the vapour can not be condensed by just applying pressure.

Which the system at any one phase e.g. is subjected to change in temperature or pressure or both, that phase will disappear and another phase will dominate.

When the pressure of the phase at point M 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 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 compresses the remaining vapour causing a further decrease in volume until all is liquid as phase O

When phase O is subjected to a decrease in temperature at constant pressure the liquid continues to cool but with out change 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 P

2) The phase diagram of carbon dioxide (CO₂)

Diagram;

Point A is the triple point of CO_2 i.e. the temperature and pressure at which all the three phases co-exist in equilibrium with each other.

Point C is the critical point of CO_2 i.e. the temperature beyond which CO_2 can not be liquefied no matter the applied pressure.

Curve AO represents the solid-vapour equilibrium or vapour pressure curve of CO_2 .

Curve AB represents the solid-liquid equilibrium or the melting point curve of CO_2 . The curve slopes towards the right showing that an increase in pressure cause a corresponding increase in mp of solid i.e.,

(i) Changes in phase can occur as a result of increasing the temperature of the phase at constant pressure eg if the solid phase is heated at a constant pressure, the solid expands causing an increase in the volume without a change in phase. However further heating of the solid makes it liquefy at its melting point when a long curve AB occurs. At this point the solid remains in equilibrium with the liquid.

Further heating of the solid turns everything into a liquid when the liquid is heated continuously it begins to vapourise until curve AC at what temperature the vapour remains in equilibrium with the liquid at the boiling point.

Decreasing the pressure at constant temperature. The solid for example 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.

3. Three phase diagram of sulphur.

Diagram;

Sulphur has two allotropes Rhombic and monoclinic sulphur which are stable over different temperatures. The transition temperature of 96°C determines which allotrop is stable at what temperature Rhombic is stable at temperature less than 96°C but monoclinic is stable at temperature greater than 96°C . Point C is called the triple point of sulphur where all the three phases can exist.

Point D is called the critical point of sulphur. When any of the phase is subjected to change in temperature or pressure it will disappear and another dominates.

When Rhombic Sulphur is heated no change in phase occurs but expands causing an increase in volume. This continues until curve EF is reached. When rhombic sulphur starts liquefying at its mp. The solid remains ineither 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 a change in phase but an increase in volume until when it vaporizes along curve CP where the liquid remains in equilibrium with the vapour. Further decreasing in pressure beyond curve CD, all the liquid turns into 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 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.

Examples.

1. The phase diagram for a certain substance is shown.

Label the following on the diagram

- i. The axis
- ii. The phase regions
- iii. The critical component
- iv. The triple point
- v. Define the terms
- vi. Critical point
- vii. Triple point

Explain what would happen when the substance in point x changes to point B

b) Solution

i) The temperature and pressure beyond which the vapour can not be liquefied no matter the applied pressure.

ii) Triple point

It is the temperature and pressure where all the three phase co-exist in equilibrium with each other.

Graph

When the phase at point x has its pressure reduced with high 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 (96°C). Further decrease in pressure with slight increase in temperature all rhombic sulphur turns into monoclinic sulphur is reduced its tendency to expand with no change in phase due to an increase in volume until when curve ED is reached at which point monoclinic sulphur turns into a vapour and the solid remains in equilibrium with the vapour at a given temperature and pressure.

Further decrease in pressure with slight increase in temperature all solid monoclinic turns into sulphur vapour.

TWO COMPONENTS SYSTEM

(Solidification of solutions)

When solutions containing different compositions of two components are cooled, one of the components solidifies out leaving the other in the liquid mixture. The component that solidifies out will depend on its composition eg

A 10% solution of sodium chloride when cooled, pure crystals of ice will be formed but at a temperature lower than 0°C because the presence of NaCl in

the solution depresses the freezing point of water. Similarly when a merely saturated solution of sodium chloride is cooled, crystals of sodium chloride form at a temperature lower than the true freezing point of NaCl because H_2O is acting as a solute which depresses the freezing point of sodium chloride. There is only one particular composition in the liquid mixture that if cooled, will give a solid made up of both sodium chloride and water.

This solid is called the Eutectic mixture.

The phase diagram for sodium chloride solution

When dilute solution of NaCl is cooled from room temperature, no change in phase until when the temperature has fallen below $0^{\circ}C$ that ice crystals begin forming. This is because the freezing point water is lowered by the presence of the solute.

Consider for example if a 10% solution of NaCl is cooled from temperature, no visible change occurs until point P a long curve AB is reached when crystal of ice begin forming leaving the salt in the solution.

Further decrease in temperature, more ice is formed along curve PB. When point B is reached both ice and solid. Sodium chloride solidify out together as an eutectic.

If a liquid mixture of composition 25% sodium chloride is cooled in room temperature no change in phase occurs until when point B is reached where both ice and solid sodium chloride solidification continue until all is a solid this gives an eutectic mixture.

Eutectic Mixture

Is defined as a liquid mixture which at constant pressure solidifies at a constant temperature to give a homogeneous solid of the same composition. The temperature at which an eutectic mixture solidifies is called an eutectic temperature. It is defined as then constant temperature is one which a liquid mixture solidifies at constant temperature to give a heterogeneous solid of the same composition. The point at which this occurs is called eutectic point.

Eutectic point

This is the temperature and pressure at which a liquid mixture solidifies to give a homogeneous solid of the same composition. Eutectic mixture behave as compounds but they are not compounds because;

- i. The composition varies with pressure yet they have a fixed composition despite fluctuations in atmosphere pressure.
- ii. They can be separated by physical means yetcan not be separated by physical means.

- iii. When observed under the microscope, the solid eutectic appears heterogenous yet compounds are homogenous.

Curve A represents the freezing point curve of water containing various compositions of NaCl. There is a decrease in freezing point of water along AB point of water. Along this curve the freezing is established between the liquid mixture and ice.

If a nearly saturated solution of NaCl of composition about 55% sodium chloride is cooled from a temperature above 30°C , no visible change until point t is reached when solid anhydrous sodium chloride begins to separate out by forming crystals and it continues doing so until the temperature is lowered upto point C where all the anhydrous sodium chloride has solidified out further lowering of temperature beyond C, the hydrated sodium chloride solidifies out and it continues along curve CB until point B where both solid NaCl and ice solidifies together as an eutectic until when all is converted into a solid.

Phase diagram for Benzene – Napthalene mixture.

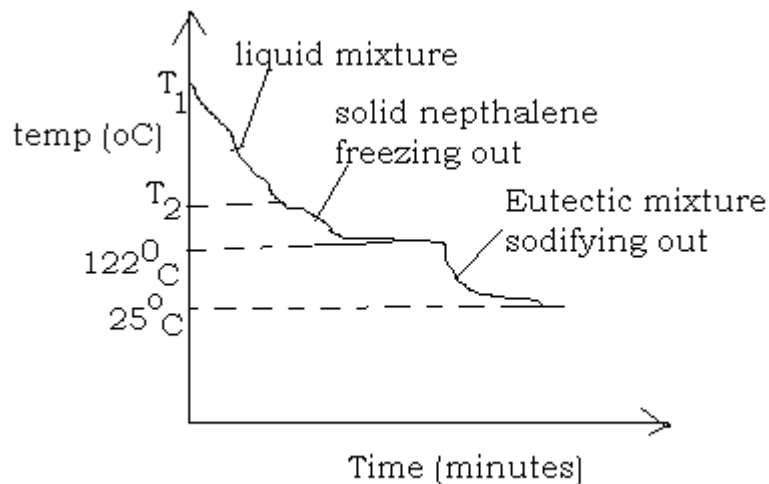
Curve AE and BE show the freezing point curves of pure benzene and naphthane respectively at various temperature.

Point A is the freezing point of pure liquid benzene or the melting point of pure solid benzene.

Point B is the freezing point of pure naphthane or the melting point of pure Napthalene.

Point E is called the eutectic point and the mixture is called the eutectic mixture. Consider a liquid of composition B if cooled no change in phase but there is a decrease in volume until a point along curve BE is reached when solid naphthalene starts to freeze out leaving the mixture richer in benzene. Freezing continues with further decrease in temperature until point E is reached where both decrease in temperature until point E is reached where both naphthane and Benzene solidifies out as constant temperature forming an eutectic mixture and this continues until all is converted into a solid. The eutectic is left to cool to room temperature.

The above change can be represented on a cooling curve



Qn: Explain what is meant by the term Eutectic mixture

Two components A and B form an eutectic mixture of temperature 0.75A. the melting points of pure A, B and Eutectic are 320, 260 and 140°C respectively using the above information sketch labeled phase diagram for the mixture A and B.

Explain what happens if a liquid mixture of 40% of 400°C is cooled to room temperature.

(c) If the mixture of 400°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 B and A solidify out together as an eutectic and they do do at a constant temperature until when all is converted into a solid which is left to cool to room temperature.

Question: The melting point of pure condenium and pure bismuth are 32°C and 271°C respectively. The table below shows the melting points of the various composition of the two metals.

% of cd	20	35	50	65	80	95
Melting point (°C)	216	190	156	184	242	300

Draw a fully labeled phase diagram for the mixture and explain the shape of the graph.

Using the graph explain what would happen if a liquid mixture containing 25% condenium at 350°C was gradually cooled.

The graph curve is V. shaped.

Pure bismuth has a high freezing point of 271°C but the freezing point lowers along AE due to increase in the amount of cadmium which acts as a solute responsible for lowering the freezing point. 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 constant temperature and cooling beyond the eutectic temperature both solidify out.

No change in state is observed when the mixture is cooled from 350°C until a temperature 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. As it continues solidifying out as temperature is lowered until the eutectic-temperature is reached at point E, when both cadmium and bismuth start solidifying out together as an eutectic and they do so at a constant temperature until when all is converted into a solid.

Solidification of two mixtures of two liquids with compound formation eg Phase diagram for Magnesium-Zinc system.

Some times when two liquid mixtures react to form a compound, an abnormal phase diagram is obtained with three chemical species. When zinc is mixed with magnesium, they react to form a compound with a formula MgZn_2

Graph

A- Melting point of pure magnesium

B- Melting point of pure zinc

C- Melting point of pure compound formed between magnesium and solid compound solidifying out.

E₁- Eutectic point showing solid magnesium and solid compound solidifying out.

E₂- Eutectic point at which the compound formed and ZMC solidify out together.

Suppose a liquid mixture of composition X is cooled from a certain temperature the mixture cools with out change in state until a point along curve AE, is reached at which point solid magnesium remains in equilibrium with liquid mixture ie magnesium begins to solidify out.

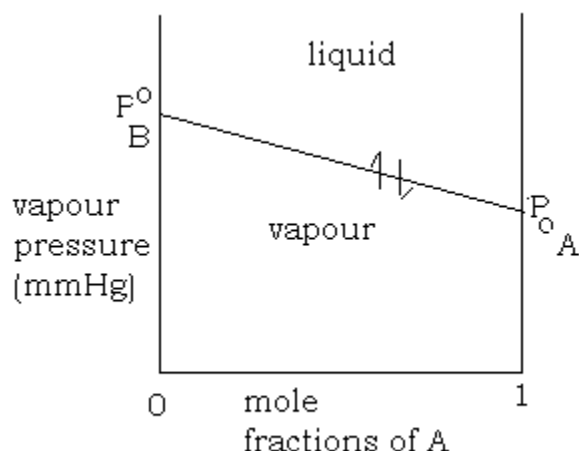
Further cooling up to point E₁, more solid magnesium is formed at point E, both magnesium is formed at point E, both magnesium and compound formed solidify out together as an eutectic and they do so at a constant temperature until when all is solid.

Supposing a liquid mixture y is cooled from a certain temperature cools with out change in state until a point is reached along curve CE₂ at this point the cpd begins to solidify out and an equilibrium is established between the solid compound and the liquid mixture.

Further cooling up to point E2 more and more compound solidifies out. At point E2 both the compound formed and Zinc solidify out together as an eutectic and they do so at a constant temperature until when all is a solid. The solid is left to cool up to room temperature.

LIQUID-VAPOUR EQUILIBRIUM

When a liquid mixture of two components A and B is boiled in a closed container, an increase in temperature causes evaporation and building up a vapour pressure above the boiling liquid. Further increase in temperature causes more and more vapour to build up in the space above the boiling liquid mixture. A point is reached when the number of molecules leaving the liquid mixture is equal to the number of molecules condensing from the vapour to form back the liquid. This established an equilibrium between the liquid and the vapour called the liquid-vapour equilibrium.



B is more volatile and in its pure form it exerts a high vapour pressure compared to A which is less volatile.

An increase in the amount of A in the mixture causes a decrease in the vapour pressure of B until a point is reached when it is only pure A that is exerting a vapour pressure which is less than that of pure B.

Binary ideal solution and Raoult's law

For binary ideal solution, Raoult's law is obeyed exactly. The law states that the partial vapour pressure of a component in an ideal solution is equal to the saturated vapour pressure of a pure component at that temperature multiplied by the mole fraction of a component in the liquid mixture, i.e.

$$P_1 = X_1 P_i \quad \text{where } P_i = \text{Partial vapour pressure of component}$$

In the liquid mixture P_i = Vapour pressure of the pure component

Consider a binary ideal solution made up of two components A, Q, B. If this mixture is boiled in a closed container, both A and B contribute to the

vapour above the boiling liquid. Their contributions are called partial vapour pressure which depend on their mole fractions in the liquid mixture at a particular temperature

By Raoult's law of ideal solutions.

$$P_A = X_A P_A^0 \text{ \& } P_B = X_B P_B^0$$

X_A = mole fraction of A

X_B = mole fraction of b

P_A^0 \& P_B^0 = Vapour pressures of pure A and B at a particular temperature.

But mole fraction of a component

$$X_A =$$

$$X_B =$$

If n_A \& n_B are the moles of A \& B respectively in the liquid mixture.

Then $X_A = \frac{n_A}{n_A + n_B}$ \& $X_B = \frac{n_B}{n_A + n_B}$

$$X_A + X_B = 1$$

The total vapour pressure above the boiling liquid is given as

$$P_1 = P_A + P_B$$

OR

$$P_T = X_A P_A^0 + X_B P_B^0$$

But for ideal solution

$$X_A + X_B = 1$$

OR

$$X_A + X_B = 100$$

$$P_1 =$$

$$X_A = (1 - X_B) + X_B P_B^0 / P_A^0$$

OR

$$P_1 = P_A^0 (1 - X_B) + X_B P_B^0$$

The magnitude of P_A and P_B above the boiling liquid depends on the mole of the components A and B respectively ie

$$P_A \propto X_A \text{ \& } P_B \propto X_B$$

Therefore a plot of partial vapour pressures of components A \& B Against their respective mole fractions X_A and X_B should be lineal.

When the partial vapour pressure s of A and B against their mole fractions are plotted using the same pair of axes, the graph below is obtained.

Graph

Curve a Is total vapour pressure of the mixture

Curve B is partial vapour pressure of component of B

Curve is partial vapour pressure of component A

NOTE: $P_A^0 > P_B^0$ therefore liquid A is More volatile than liquid B.

The above phase diagram shows how the vapour pressure varies with composition of the liquid being added.

Beginning with pure A (100% A, 0% B) the partial vapour pressure of A decreases as B is added it tends to 0 when B is 100%

This is because the molecules of B gradually replace the molecules of A above the liquid mixture.

Similarly beginning with pure B (100% B 0% A), the partial vapour pressure of B gradually declines as A is gradually added and the partial vapour pressure of B tends to 0 in 100% A. This is because molecules of A replace molecules of B above the liquid mixture at a given temperature.

The above phase diagram is only true for a binary ideal solution.

An ideal solution is one that obeys Raoult's law exactly such solutions are rare in nature and to obtain such a solution.

- (i) The molecules of the two liquids must exhibit similar inter molecular forces of attraction. Both in kind and magnitude such that when the two liquids are mixed the intermolecular forces of attraction cancel out. Because of this such liquid mixtures exhibit negligible intermolecular forces of attraction.
- (ii) On mixing the two liquids there should be no volume change.
- (iii) On mixing such liquids there should be no volume change.

Example

At 88°C the vapour pressures of benzene and toluene are 935 and 378 mmHg respectively. Calculate the vapour pressure of the benzene-toluene mixture containing 2 moles of benzene per mole of toluene assuming ideal behavior.

Solution

Moles of benzene = 2 moles

Moles of toluene = 1 mole

$$X_B = \frac{2}{2+1} = \frac{2}{3}$$

$$X_T = \frac{1}{2+1} = \frac{1}{3}$$

$$P_B = X_{\text{Ben}} \times P_B^0$$

$$= \frac{2}{3} \times 935$$

$$= 623.3$$

$$P_T = X_T \times P_T^0$$

$$= \frac{1}{3} \times (378)$$

$$= 126$$

$$P_{\text{total}} = P_T + P_B$$

$$= 126 + 623.3$$

$$= 749.3$$

Question

A mixture of liquid A & B obeys Raoult's law exactly. The vapour pressure of A and B are

10 kNm⁻² and 2.92 kNm⁻² respectively at 20°C. Calculate the vapour pressure of the mixture containing 0.5 mole of each liquid at 20°C

Solution

$$X_A = \frac{n_A}{n_A + n_B} = 0.5$$

$$X_B = \frac{n_B}{n_A + n_B} = 0.5$$

Moles of A = 0.5 Moles

Moles of B = 0.5 moles

$$P_A = X_A P_A^0$$

$$= 0.5 \times 10 \text{ kNm}^{-2}$$

$$P_A = X_A$$

$$= (0.5 \times 10)$$

$$= 5 \text{ kNm}^{-2}$$

$$P_B = X_B$$

$$0.5 \times 2.92 \text{ kNm}^{-2}$$

$$= 1.46$$

$$P_{\text{Total}} = P_A + P_B$$

$$= 1.46 + 5$$

$$6.46 \text{ kNm}^{-2}$$

Calculate the vapour pressure of the solution containing 50g of heptanes and 35g of octane at 200°C (the vapour pressure of heptanes and octane at 200°C are 473.2 Pa and 139.8 Pa respectively)

Solution

$$\text{RFM of Heptane (C}_7\text{H}_{16}) = (7 \times 12) + (16 \times 1) = 100$$

$$\text{Moles of heptanes} = \frac{50}{100}$$

$$= 0.5 \text{ moles}$$

Moles of octane

$$\text{RFM of octane (C}_8\text{H}_{18}) = (8 \times 12) + (18 \times 1) = 114$$

$$\text{Moles} = \frac{35}{114}$$

$$= 0.307$$

$$\text{Total moles} = 0.5 + 0.307 = 0.807 \text{ in mixture}$$

$$X_{\text{heptane}} = \frac{0.5}{0.807}$$

$$= 0.619$$

$$X_{\text{octane}} = \frac{0.307}{0.807}$$

$$= 0.381$$

$$P_H = X_H \cdot P_H^0$$

$$= (0.619 \times 473.2)$$

$$= 292.92 \text{ Pa}$$

$$P_O = X_O \cdot P_O^0$$

$$= (0.381 \times 139.8)$$

Vapour pressure of solution

$$P_1 = P_0 + P_H$$

$$55.92 + 283.92$$

$$= 339.84\text{Pa}$$

Note

For a binary ideal liquid mixture made of two components A and B, it follows that the forces of attraction between the molecules of A (Cohesive forces) and those of molecule by B (Cohesive forces) are equal in magnitude to the forces of attraction between the molecules forces of the liquid mixture (adhesive forces) ie.

A-A & B-B attractions are equal to A-B attractions molecules (Cohesive forces) are equal in magnitude and kind to the intermolecules forces of attraction between unlike molecules (adhesive forces).

Ideal miscible liquid mixture, are rare and many immiscible liquid mixture just approximately to ideal behavior actare and Nonane, hexane and heptane, methanol and water.

Question

Explain what is meant by the term ideal solution.

Explain why most solutions deviate considerably from ideal behavior.

Solution

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

Graph

The boiling point composition diagram for a binary ideal solution has two important curves ie the liquid composition curve and the vapour composition curve.

The liquid composition curve gives the composition of the components in the vapour phase. Starting with 100% B, the composition of B in the liquid keeps on decreasing until it is 100% A. usually A is found in the distillate since it is more volatile. boiling point composition diagram can be used to describe the changes that take place when miscible liquid mixtures are fractionally distilled.

Graph

Suppose a liquid mixture of composition 20% A and 80% B is heated, it boils at temperature T giving off a vapour b richer in the more volatile component A than the less volatile component B (60% A, 40% B). when the vapour is condensed into a liquid, it gives a liquid mixture of the same composition C.

When the liquid mixture is heated, it boils at a temperature T giving off a vapour B much richer in the more volatile component A leaving the residue in the flask riches in the less volatile component B (85% A, 15%B).

Finally pure A is isolated at its boiling point, therefore successive boiling and cooling results in isolation of the more volatile component at the boiling which is collected as the distillate leaving the residue in the flask as pure less volatile component. Hence pure A is obtained in the distillate and pure B is obtained as the residue.

Example

1(a) State Roults law for ideal solutions

(b) A mixture of liquids A and B obeys roults law the vapour pressures of A and B are 380, and 445mmHg respectively at 20°C.

(i) Calculate the composition fot he vapour containing equal moles of each component in the liquid mixture at 20°C.

(ii) Which of the two liquids is more volatile give a reason.

Solution

a. Partial vapour pressure of a component for an ideal solution is equal to the saturated vapour pressure of the pure component at that temperature multiplied by the mole fractions of the components in the liquid mixture.

b. Moles of A = 1 mole

Moles of B = 1mole

$$X_A = \frac{1}{2}$$

$$X_B = \frac{1}{2}$$

$$P_A = X_A$$

$$= \frac{1}{2} \times 380$$

$$= 190\text{mmHg}$$

$$P_T = P_A + P_B$$

$$= (190 + 222.5)\text{mmHg}$$

$$= 412.5\text{mmHg}$$

$$Y_A = \frac{P_A}{P_T} \times 100$$

$$= 46\%$$

$$P_B = X_B$$

$$\frac{1}{2} \times 445$$

$$= 222.5\text{mmHg}$$

$$Y_B = \frac{P_B}{P_T} \times 100$$

$$= 54\%$$

B is more volatile because it is more richer in vapour phase.

Qn: Two components A and B form an ideal solution. At 50°C the saturated vapour pressures of A and B are 200mmHg and 640mmHg respectively

(a) Calculate the composition of the vapour if the moe fraction of A in the liquid is 0.4

Solution

$$X_A = 0.4$$

$$X_B = 0.6 \text{ (1-0.4)}$$

$$P_A = X_A \cdot P_A^* = (0.4 \times 200) = 80 \text{ mmHg}$$

$$P_B = X_B \cdot P_B^* = (0.6 \times 640) = 384 \text{ mmHg}$$

$$P_T = P_A + P_B$$

$$= (80 + 384) \text{ mmHg}$$

$$= 464 \text{ mmHg}$$

$$Y_A = \frac{P_A}{P_T} \times 100$$

$$= 17\%$$

$$Y_B = \frac{P_B}{P_T} \times 100$$

$$= 83\%$$

(b) If the vapour in A above is condensed and then devolatilized at the same temperature, calculate the new composition of the vapour

Solution

$$X_A = 0.17$$

$$X_B = 0.83$$

$$P_A = X_A \cdot P_A^* = (0.17 \times 200) = 34 \text{ mmHg}$$

$$P_B = X_B \cdot P_B^* = (0.83 \times 640) = 531.2 \text{ mmHg}$$

$$P_T = P_A + P_B = 565.2$$

$$Y_A = \frac{P_A}{P_T} \times 100$$

$$= 6\%$$

$$Y_B = \frac{P_B}{P_T} \times 100$$

$$= 94\%$$

(c) Comment on the changes in the composition for the vapour in A and B

The vapour progressively becomes richer in the more volatile component B than the less volatile component A.

The diagram below shows the boiling point composition diagram of the mixture of liquids X and Y

Graph

(i) Identify the curves P and Q and the points M and N

P – vapour composition

Q – Liquid composition curve

M – Boiling point of pure Y

N – Boiling point of pure X

(b) Describe what happens when the liquid mixture of composition Z is boiled.

The liquid mixture of composition Z gives a vapour richer in Y and X because Y is more volatile. This leaves the residue in the flask richer in X because it is less volatile.

The vapour obtained condenses on cooling to form a liquid mixture of the same composition. The liquid obtained when re-volatilised gives a vapour which is much richer in Y than X and on cooling a liquid mixture of the same composition is obtained hence successive heating and cooling results in isolation of pure Y at its boiling point as the distillate and pure X as the residue.

(a) Explain how the principle in (b) above can be used to separate liquid mixtures by fractional distillation

Explanation

The principle is when a liquid mixture is heated a vapour richer in the more volatile component is obtained which if cooled forms a distillate.

Successive heating and cooling of the liquid mixture and the vapour respectively result into isolation of the more volatile component at its boiling point.

During fractional distillation a fractionating column consisting of glass beads which increase the surface area even when the vapour condenses and separates out the various components condenses around the glass beads but it is re-volatilised by the upcoming vapour and is led into the Liebig Condenser where it is cooled and obtained in the pure form as a distillate. The vapour due to the more volatile component condenses around the glass beads and drips back into the distillation flask obtaining the non volatile component in its pure form as the residue.

Using the fractionating column, the steps involving continuous volatilizations and condensations are performed automatically.

Question

1. Heptane and Octane form an ideal solution. Calculate vapour pressure of the solution containing 50g of heptane and 38g of Octane at 20°C
2. Hectare and Hexane form an ideal solution and at which they have saturated vapour pressures of 50 and 40 K.Pa respectively. Calculate the mole fraction of each component in the liquid mixture if their mole fractions in the vapour are equal.

Deviation from Roul't's law (ideal behavior)

Deviations arise when the two liquids A and B of the binary solution do not exhibit similar intermolecular forces of attraction. As a result of the deviation the vapour pressure composition diagram is no longer linear and the mixture does not obey Roul't's law such liquid mixtures form non ideal solution.

If the forces of attraction between like molecules in the mixture (cohesive forces) are stronger than the forces of attraction between unlike molecules (adhesive forces) then the liquid mixture is said to deviate positively from Roul't's law. The mixture forms more vapour compared to the vapour pressure of each component.

If the forces of attraction between unlike molecules (adhesive) are stronger than the forces of attraction between like molecules (cohesive forces), the liquid mixture deviates negatively from Roul't's law. Less vapour is formed by the mixture compared to the vapour pressure of each pure component.

During positive deviation each component vapourisation more easily in presence of the other than it was in pure state. The vapour pressure composition diagram shows a maximum.

Graph;

There is a certain composition X where the intermolecular forces of attraction between molecules of A and B are weakest and this corresponds to the highest vapour.

When the two liquids that deviate positively from Roulte's law are mixed there is an increase in volume and an increase in temperature.

During negative deviation there is a reduced tendency of molecules of A to escape into the vapour phase in presence of molecules of B since adhesive

forces are stronger than the cohesive forces. The net effect is lowered vapour pressure of either component in the pure state. The curve for negative deviation gives a minimum.

Graph

There is a certain composition X where the intermolecular forces of attraction between molecules of A and B are strongest corresponding to the lowest vapour pressure. At this point the tendency of molecules of A to escape in presence of molecules of B is lowest and therefore less vapour is formed.

On mixing liquids that deviate negatively from Raoult's law, there is a decrease in volume in temperature i.e. heat is given out and there is a decrease in volume.

The vapour pressure composition diagram below is for a liquid mixture of A and B that deviates positively from Raoult's law.

Graph

(a) Identify the points

X – Vapour pressure of pure B

Y – Vapour pressure of pure A

(b) Explain the shape of the graph in relation to ideal behavior

For ideal behavior the cohesive forces are equal in magnitude to the adhesive forces. However for the mixture of A and B the vapour pressure curve is above the expected for ideal behavior because the cohesive forces are stronger in magnitude than the adhesive forces. This causes an increased tendency of molecules of B to escape in the vapour phase in presence of molecules of A. therefore more vapour builds up.

B is more mixture first increases to a maximum where the forces of attraction between molecules of A and B are weaker. The vapour pressure slightly decreases as the mole fraction of A and increased because A is less volatile and molecules of A are replacing molecules of B.

Differences between mixtures that deviate negatively and positively from Roul't's law.

Positive deviation	Negative deviation
Cohesive forces are stronger than adhesive forces	Cohesive forces are weaker than adhesive forces
There is an increase in volume on forming the liquid mixture	There is a decrease in volume on forming the liquid mixture
The mixture has a higher vapour than expected from Roul't's law	The mixture has a lower V.P than expected from Roul't's law.
Heat is absorbed on forming the liquid – mixture therefore the liquid mixture therefore the container becomes cold	Heat is given off on forming the liquid mixture and the container becomes warm.

Examples of liquid mixtures that deviated positively from Roults law include Ethanol and water, propane 1-ol and water, propane – 2-0l and water, tetrachlomethane and Methanal, Ethanal and Hexane, Bnzene and Methanol, Cyclohexanel/Ethanol

Examples of liquid mixtures that deviate negatively from Roul't's law include

- Ethanoic acid/pyridine
- Nitric acid/water
- Hydrochloric acid/water
- Propanone/trichloromethane
- Trichlomethanelethoxyethane

Examples of mixtures that show ideal behavior include

- Hexane/heptane
- Bensene/methylbenzene
- Octane / Noname
- Methanol/Water

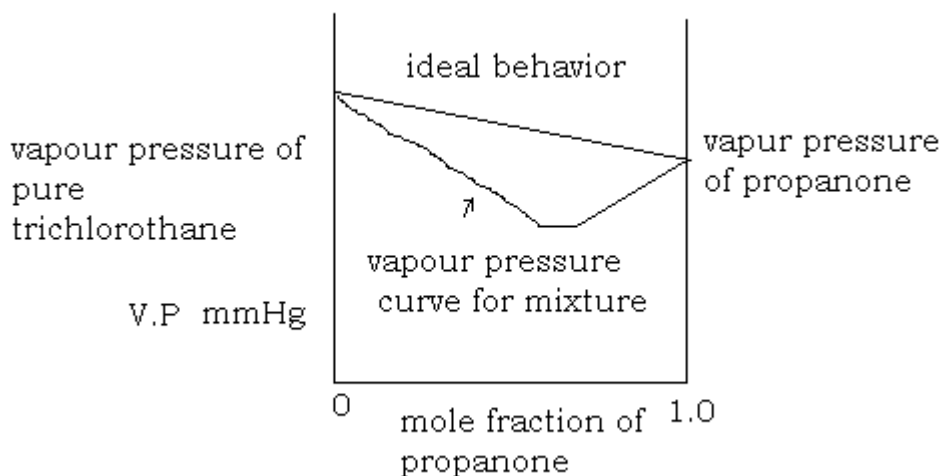
Question

A mixture of propanone (68-Bpt) and Trichloromethane (Bpt-62°C)

Shows negative deviation from Roul't's law

- i. Draw the vapour pressure comp. Curve for the mixture and indicate the line for ideal behavior
- ii. Explain the shape of the curve in relation to Roul't's law

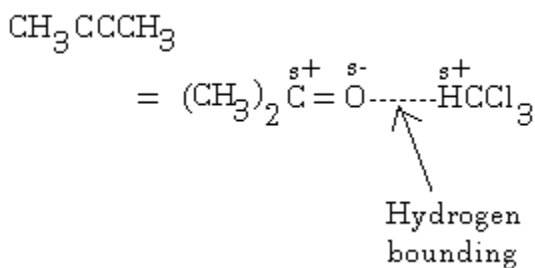
Solution



Explanation

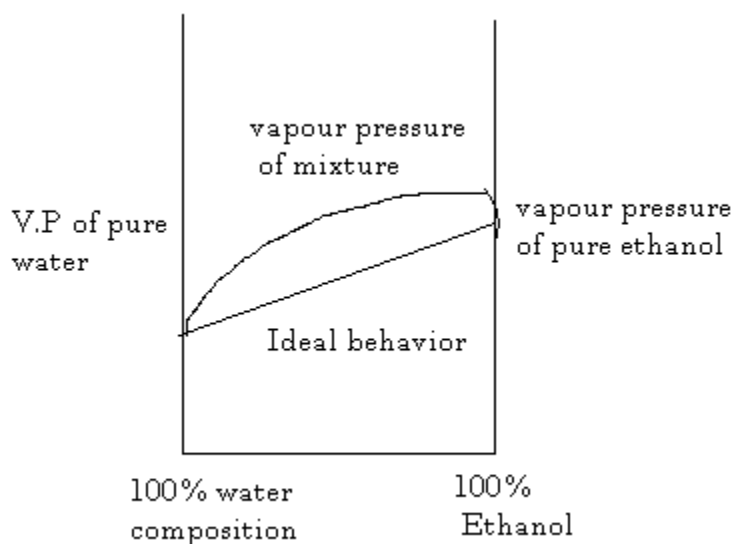
The curve of the mixture lies below the line of ideal behavior. For Raoult's law to hold true, the intermolecular forces between the unlike molecules in the mixture (adhesive forces) and those between the molecules in the pure components (cohesive forces) must be similar in magnitude and kind.

The forces of attraction between molecules of pure Trichloromethane and those between molecules of pure propanone are weaker than the forces of attraction between molecules of chloroform and propanone. Molecules of chloroform associate via weaker van der Waals forces similarly molecules of chloroform and propanone associate via strong intermolecular hydrogen bonding hence the escaping tendency of molecules of each component is reduced in presence of the other leading to a reduced vapour pressure of the mixture



Qn: A mixture of ethanol (Bpt-78°C) and water (Bpt – 100°C) deviates positively from Raoult's law

- (i) Draw the vapour pressure composition diagram for the mixture in relation to Raoult's law
- (ii) Explain the shape of the curve for the vapour pressure of the mixture in relation to Raoult's law.



The curve for the mixture is above the curve for ideal behavior. For Raoult's law to be true, cohesive forces must be similar to adhesive forces.

The adhesive forces between molecules of water and ethanol are weaker than the cohesive forces between molecules of pure ethanol and pure water. Molecules of pure water are held together by intermolecular hydrogen bonding. However, the magnitude of hydrogen bonding is greater in pure water than in ethanol; hence, water has a higher boiling point and lower V.P. as compared to ethanol.

When in solution, molecules of ethanol associate with molecules of water through intermolecular hydrogen bonding, but these are weaker than those in molecules of pure water and those in molecules of pure ethanol. Hence, the escaping tendency of molecules of each component is increased in the presence of molecules of the other, leading to an increase in the vapour pressure of the mixture.

Liquid mixtures that deviate from Raoult's law either positively or negatively cannot be completely separated by fractional distillation. The boiling point composition diagram either shows a minimum or maximum.

Boiling point composition diagram for a liquid mixture that deviates positively from Raoult's law

The composition x corresponds to the composition with the least or weakest intermolecular forces of attraction.

On the vapour pressure composition diagram, it shows a maximum, and on the boiling point composition diagram, it shows a minimum because it has the lowest boiling point. This mixture is called an azeotropic mixture.

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

- i. Its composition changes with changes in pressure, yet for compounds, their compositions are constant regardless of the pressure.

- ii. It can be separated by any physical means such as the technique of a azeotropic distillation yet compounds can not be separated by such physical means.

From the above graph X has the lowest boiling point and B has the highest boiling point therefore when a liquid mixture containing A and B is fractionally distilled, X distills off first because of its high volatility after isolation of X pure A is isolated at its boiling point leaving pure B as the residue in the flask since it is the least volatile.

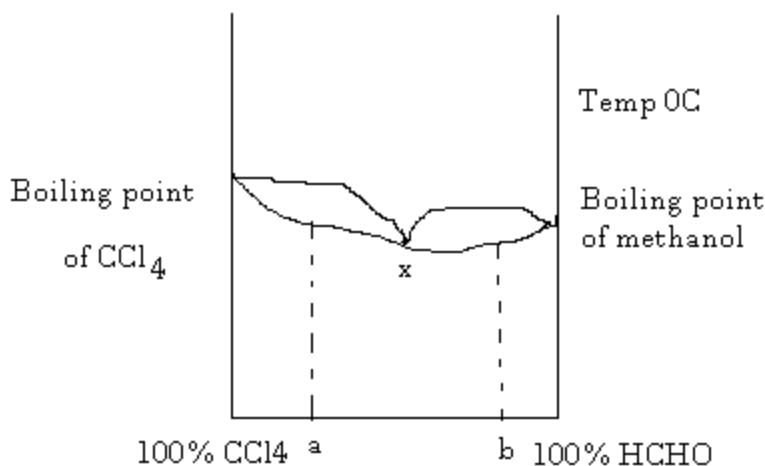
However what distills off first depends on the composition of the liquid mixture being distilled.

Suppose a liquid mixture of composition *h* is fractionally distilled, the azeotropic mixture X collects as a distillate leaving the residue in flask as pure A.

If a liquid mixture of composition *i* is distilled, it distills unchanged giving a constant boiling point mixture of both A and B as the distillate of the same composition.

If a liquid mixture of composition *y* is fractionally distilled the azeotrope X is collected as the distillate at a constant boiling point while pure B is obtained as the residue.

Consider the boiling point composition diagram for the mixture of carbon tetrachloride of water and methanol.



If a liquid mixture *a* is fractionally distilled, it boils to give a vapour which is richer in the Azeotropic mixture leaving the residue in the flask richer in carbon tetrachloride. Cooling this vapour produces a liquid mixture of the same composition which when heated produces a vapour richer in the azeotropic mixture while the residue is richer in CCl_4 .

Repeated heating and cooling finally produces the residue as pure carbon tetrachloride and the distillate as the azeotropic mixture containing 80% methanol and 20% carbon tetrachloride.

Similarly if a liquid mixture of composition *b* is fractionally distilled, pure methanol is obtained as the residue while the distillate is the azeotrope.

Note: Molecules of carbon tetrachloride associate via weak van der Waals forces similarly molecules of methanol associate via weak van der Waals forces. When

mixed the molecules of carbon tetrachloride associates via much weaker van der Waals forces increasing the escaping tendency of the molecules of either component in presence of the other. This builds a higher vapour pressure for the mixture compared to either component in their pure form.

The boiling point of carbon tetrachloride is higher than that of methanol because carbon tetrachloride is bulkier and the magnitude of van der Waals forces is greater in carbon tetrachloride than methanol.

The boiling point decreases gradually from point y to point X because at y the molecules of pure carbon tetrachloride have high van der Waals forces due to the high molecular mass so the boiling point is higher than that of the azeotropic mixture at point X.

A decrease in the mole fraction of carbon tetrachloride causes a decrease in the boiling pt of the mixture because the molecules of less volatile carbon tetrachloride are being replaced by the molecules of the more volatile methanol so molecules in the mixture escape more easily than the molecules of pure carbon tetrachloride. The decrease in boiling pt continues a liquid mixture of composition x which has the weakest van der Waals forces and the lowest boiling pt is attained.

Boiling point composition diagram for a liquid mixture that deviates negatively from Raoult's law.

When a liquid mixture that deviates negatively from Raoult's law is fractionally distilled, the distillate obtained first is pure A at its boiling pt because it is the most volatile on further distillation pure B is isolated at its boiling point because it is more volatile than X on isolation of pure B, the azeotrope X is obtained as the residue since it has the highest boiling pt so it is the least volatile.

However in principle what distills first depends on the composition of the mixture eg

If a liquid mixture of composition is fractionally distilled at its B_{pt} while the residue in the flask is the azeotropic mixture containing 40% A and 60% B.

If a liquid mixture of composition b is distilled fractionally pure B is obtained as the distillate at the B_{pf} leaving the residue in the flask as the azeotrope containing 40% A and 60% B.

If a liquid mixture of composition C is distilled, it gives a vapour of the same composition ie it distills unchanged giving a constant boiling point mixture containing 40% A and 60% B.

If a liquid mixture of composition C is distilled, it gives a vapour of the same composition ie it distills unchanged giving a constant boiling point mixture containing 40% A and 60% B.

Solution

The phase diagram below is for a mixture of two miscible liquids A and B.

(a) Identify the wires A and B, the phases X and Y and point Q

Solution

A- Vapour composition curve

B- Liquid composition curve

Phases

X-Vapour

Y-Liquid

Point Q – Azeotrope

(b) Describe briefly what happens when a liquid mixture

- i. Containing 50% A is fractionally distilled
- ii. 90% B is fractionally distilled
- iii. Explain the shape of the curve pQ.

Solution

The liquid mixture boils to form a vapour which is richer in A than the original mixture since A is more volatile leaving the residue in the flask richer in the a zeotropic mixture. The vapour cool to join a liquid of the same composition if boiling and cooling results in isolation of pure A at its Bpt leaving the residue in the flask as the a zeotropic mixture (80% B and 20%A)

The liquid containing 90%B when boiled gives a vapour richer in component B than the original mixture the residue in the flask richer in the a zeotropic because pure B is more volatile than the a zeotropic mixture. The vapour cools to give a liquid of the same composition. Successive boiling and cooling results in isolation of pure B at its boiling point and zeotrope is obtained as the residue.

At point p the boiling point is low because pure A is more volatile than the a zeotropic mixture at point Q. bo point increases gradually as molecules of the mole volatile component A are being replaced lowering the vapour pressure of the mixture.

At point Q, the composition has the strongest intermolecular forces of attraction corresponding to the highest boiling point.

Question

- (i) At standard pressure, HCl and water form an a zoetrope with boiling point 110°C.
- (ii) Sketch a labeled diagram of the boiling point composition for HCl and water system (Boiling pt of water is 100°C
- (iii) Describe what would happen if a mixture of 10% Hcl is fractionally distilled
- (iv) A constant boiling pt mixture of hydrochloric acid and water is 20% by mass of HCl and has a dervity of 1.18kg. calculate the volume of the acid needed to prepare 1 litre 2m HCl solution.

Solution

When a liquid mixture of 10% HCl is fractionally distilled, it boils to give a vapour which is richer in water than the original liquid mixture, cooling this vapour produces a liquid mixture of the same composition which when heated produces a vapour richer in water than the liquid mixture.

Repeated heating and cooling finally produces pure water as the distillate and the a zeotropic mixture containing 20% HCl as the residue.

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

Composition of a zoetrope = 20% HCl

Density of HCl alone (x 1.18)

$$= 0.236 \text{ g cm}^{-3}$$

Mass of acid in g l^{-1}

1 cm^3 of acid contain 0.236 g

1000 cm^3 of acid contain $\times 1000$

$$= 236 \text{ g l}^{-1}$$

RFM of HCl

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

$$= 36.3$$

Majority of original acid

=

=

$$= 647 \text{ M}$$

647 moles are contained in 1000 cm^3 of acid

2 moles are contained in

$$= 309.1 \text{ cm}^3$$

So to prepare 2 M solution of hydrochloric acid measure 309.1 cm^3 of the original acid and transfer into 1 litre volumetric flask then top up to the mark with distilled water.

Question

- a. State Raoult's law of ideal solutions
 - i. What is meant by a zeotropic mixture
- b. . Explain with the aid of a boiling point composition diagram how can ideal liquid mixture of two liquids with different boiling points can be separated by fractional distillation.
- c. Explain why
 - i) With a small amount of cyclomethane is added to methanol the boiling point is lowered.
 - ii) When a small amount of non volatile solid is dissolved in methanol the Bpt is raised
- d. The following data were obtained for a mixture cyclohexane (Bpt = 81°C) in methanol (Bpt = 65°C)

Bpt ($^\circ\text{C}$) of the mixture	Mole fraction of methanol in	
	Liquid mixture	Vapour above the mixture
70	0.12	0.27
60	0.31	0.47
55	0.50	0.56
57	0.82	0.69
61	0.94	0.83

Plot a graph of boiling pt against composition for the solution of cyclohexane in methanol

State the type of deviation from Raoult's law

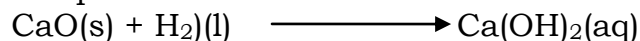
Use your graph to obtain the composition of the azeotrope and explain why it can not be separated into pure components by fractional distillation.

Explain what would happen if a liquid mixture containing 40% methanol is fractionally distilled.

Methods used to separate a zeotropic mixture

1. Separation by chemical methods

A mixture where one of the components is water can be separated by addition of quick lime (CaO) which removes the water and leaves behind the other components.



Distillation using a third component

An a zeotropic mixture of ethanol and water may be separated by addition of benzene and there distilled. Here the first distillation yields a ternally a zoetrope made up of the three composnents then ethanol and Benzene. On distilling the binary zoetrope ethanol is obtained in its pure form at its boiling point.

Separation by adsorption

This is affected by adding charcoal or siled get which absorbs one of the components.

By solvent extraction

Here a third component is added and the solute more soluble in the fluid component is removed from the a zeotropic mixture.

IMMISCIBLE LIQUIDS

Immuncible liquids are liquids that donot mix uniformly there by forming separate layers each of the liquists in the mixture acts independently of the other liquid and the vapour pressure above the heated mixture of immiscible liquids at a given temperature is equal to the sum of the vapour pressures of individual liquids at the same temperature heating of the mixture is necessary to enable each liquid to establish its own V.P at a given temperature.

The VP of the mixture is independent of the amount of each liquid present in the mixture as long as there is enough liquid to form a saturated V.P at a given temperature. Each component exerts a V.P independent of the other because of the mixture is higher than the vapour pressure of the individual liquids at a given temperature. When the total VP of the mixture becomes equal to the atmospheric pressure (760mmHg) the mixture boils and becomes each component exerts a vapour pressure independent on the other, the atmospheric pressure at a lower temperature and the boiling point of the mixture is lower than the boiling point of either liquid in the pure state.

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

Reason

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

The above principle of immiscible liquids is the basis of steam distillation (distillation under reduced pressure).

STEAM DISTILLATION

Steam distillation depends on the properties of immiscible liquid and atechnique for separating a liquid or solid from a mixture.

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

The technique enables separation of immiscible liquids which have boiling points that differ greatly from each other. The two the liquids must be immiscible with water.

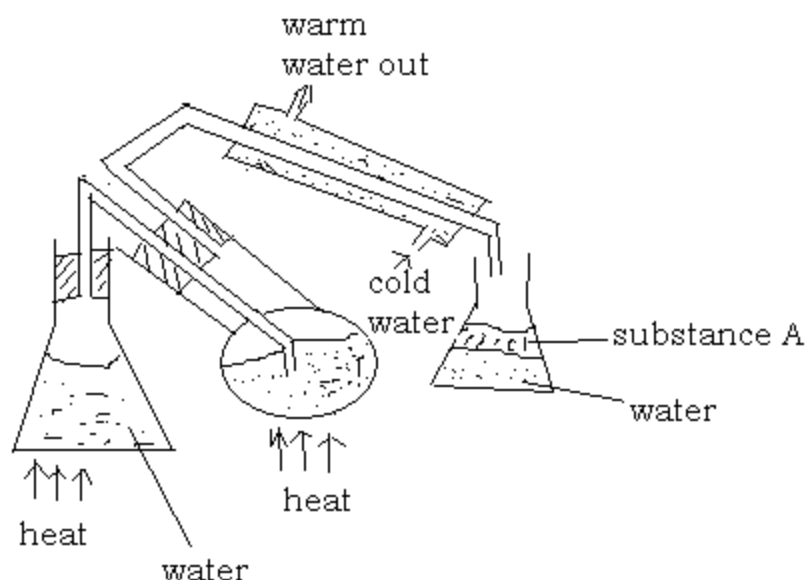
Steam is passed in the heated mixture of two miscible liquids and the component with the lowest boiling point (most volatile) is first isolated with water as the distillate. The other component with a high boiling point remains in the distillation flask as the residue eg a mixture of 2-nitro phenel and 4 Nitro phenol is separated by steam distillation. 2 Nitrophenenol is isolated first with water because it has a lower boiling point (more volatile) than 4 Nitro phenol (less volatile)

2-Nitrophenol and water are then separated using a separating funnel.

Advantages of using steam distillation

It enables isolation of organic compounds with high boiling points when ordinary distillation is carried out. In this case the substance is isolated at a lower temperature because the mixture of the substance and steam boils at a lower temperature than the boiling point of the substance and water since each component exerts a vapour pressure independent of the other.

It enables separation of miscible liquids whose components have high boiling points which are not close to each other. In this case the component with the lowest Bp is isolated first with water as the distillate.



Composition of distillate

During steam distillation the distillate obtained consists of the substance being isolated and water. The composition of the distillate can be obtained using the expression.

Mass of substance =

The mass of the substance can be expressed in gas as a percentage. The above expression can be used to determine molecules mass of the substance isolated using steam distillation.

Principle of steam distillation

- i. The substance to be isolated must be immiscible with water. This has two advantages
- ii. It enabled the components of the mixture to exert their own vapour pressure independent of vapour pressure and a lower boiling point.
- iii. The substance can easily be separated from water when it selects as a distillate using a separating funnel.

The substance to be isolated must have a high molecular mass this enables a reasonable mass of the substance to be obtained in the distillate (Rmm of substance x mass of the substance at a given temperature).

The substance to be isolated must exert a high vapour pressure near the boiling point of water. This enables the substance to exert a reasonable vapour pressure at a given temperature.

The impurities must be non volatile this ensures that they are not part of the distillate.

Examples

Compound x was steam distilled at 80°C and 760mmHg the distillate was found to contain 9m0% by mass of X (VP of H_2O at 80°C = 240). Calculate the formular mass of X

=

For the mixture to boil

$$P_A + P_w = 760\text{mmHg}$$

$$P_A = (760 - 240)$$

=

Molar mass of X =

$$= 74.8\text{g}$$

When asp y was distilled at standard atmospheric pressure and 96°C, The VP of the H₂O at this temperature was 730mmHg and the distillate contained 74% water. Calculate the molar mass of y.

Solution

=

RMM of y =

Qn: Amino hydroxyl benzene is usually contaminated with some impurities to remove the impurities it was steam distilled at 96°C and standard atmospheric pressure. At this temp, the VP of water was 654mmHg. Calculate the percentage composition of the distillate.

Solution

$$\text{RFM of H}_2\text{O} = 18$$

$$= (12 \times 6) + (1 \times 7) + (10 \times 1) = 109$$

$$\text{Vapour of 2-nitro phenol} = (760 - 654)$$

$$106\text{mmHg}$$

=

=

=

$$\% \text{ of substance} = x \times 100$$

$$= 49.5\%$$

$$\text{Total mass} = 0.981 + 1$$

$$= 1.981$$

$$\% \text{ of water} = = 50.5\%$$

Assignment

Paper2 2004

Distribution / partition of

Question 4: The melting point of 4-nitro phenol is much higher than that of 2-nitrophenol. The compounds can be separated by steam distillation.

Explain why the boiling of 4-nitro phenol is higher than that of 2-nitro phenol
For 4 nitro phenol its functional groups are far apart from thus weakening hydrogen bonds hence the forces of attraction are weaker this results into higher melting point while 2-nitro phenol the function groups form hydrogen bonds since they are close this leads to strong intramolecular forces of attraction between the molecules thus a lower melting point.

Explain the principles of steam distillation

The substance to be isolated must be immiscible with water.

The substance to be isolated must have a higher molecular mass to enable a reasonable mass of the substance to be contained.

It must exert a higher vapour pressure near the boiling it must be volatile.

The impurities must be non-volatile

2-nitro phenol and 4-nitrophenol are miscible liquids with boiling points that greatly differ from each other. This technique enables steam distillation to take place steam is passed through the heated mixture of the two miscible liquids and 2-nitro phenol which is the most volatile (low boiling point) is isolated first with water as the distillate 4-nitro phenol with a high boiling point and therefore less volatile remains in the distillation flask as the residue.

2-nitrophenol and water are then separated using a separating funnel since they are immiscible. In this way steam distillation has occurred.

When a substance y was distilled at 93°C and 750mmHg the distillate contained 55% of y by mass. Calculate the relative molecular mass of y (the partial vapour pressure water at 95°C is 65.4mmH)

Let the total mass of the distillate be x

=

$$= 149.875$$

184

The relative molecular mass of y is 149900

$$= 149.9\text{g}$$

Question: When 490g of an organic compound x containing carbon and hydrogen only was burnt in oxygen, 15.78g of carbondioxide and 5.38g of water were formed. Calculate the empirical formula of X

$$X = 3 \text{ Rem of CO}_2 (12 \times 2) + (16 \times 2) = 44$$

$$-1 \text{ Composition of carbon} = x \ 15.78$$

$$Y = 2 \text{ RFM of H}_2\text{O} = (1 \times 1) + (16 \times 1) = 18$$

$$\text{C}_3 \text{ composition of hydrogen} = x \ 5.38 = 0.598$$

No of moles: carbon Hydrogen

$$\begin{array}{cc} 1:1.7 & x3 \\ 3:3 & \end{array}$$

X was steam distilled at 80°C and 760mmHg and the distillate was found to contain 90.8% by mass of X (The vapour pressure of water at 80°C is 240mmHg).

Calculate the formula mass of x

=

=

$$(\text{Rmm})_x =$$

$$= 81.993$$

82

The formula mass of X is 82

Reduce the formula of X

$$(C_3H_5)_x = 82$$

$$[(12 \times 3) + (1 \times 5)]_x = 82$$

$$41x = 82$$

$$(C_3H_5)_2$$

$$= C_6H_{10}$$

Question 1: The vapour pressure (V.P) of water and of an immiscible liquid x at different temperature are given in the table below.

Temp/ $^{\circ}C$	92	94	96	98	100
V.P of x/KPa	6	8	12	15	17
V.P of H_2O /KPa	74	80	88	94	101

On the same axes, plot graphs of vapour pressure against temperature

Determine the vapour pressures of the mixture of X and water at the temperature given in the table above

On the same axes as the graph in (a), plot a graph of the vapour pressure of the mixture versus the temperature

The distillate obtained from the mixture at 101Kpa contains 1.6g of water and 1.1g of x

Calculate the relative molecular mass of X using the information from the graphs you have drawn.

Explain the principle of separating of mixture by steam distillation

State any two advantages of steam distillation

Solution

The substance to be isolated must be a higher molecular mass to enable a reasonable amount of mass of substance to be obtained.

It must exert a higher vapour pressure near the boiling point of water

Impurities must be non volatile

Advantages of steam distillation

- It enables isolation of organic compounds with higher boiling points which would otherwise decompose near their normal boiling points when ordinary distillation is carried out
- It enables separation of miscible liquids whose boiling points are higher but not close together.

The vapour pressure of the mixture is determined by summing up the vapour pressure of the components (x and water) at a particular temperature.

$$\text{Vapour pressure of X} = 12 \text{ KPa}$$

$$\text{Vapour pressure of } H_2O = 88.5 \text{ KPa}$$

$$\text{Mass of x} = 1.1 \text{ g}$$

$$\text{Mass of } H_2O = 1.6 \text{ g}$$

$$=$$

$$=$$

$$x =$$

$$= (V.P) H_2O$$

$$M_r = 91.27$$

The three component system;

Distribution / partition of a solute between two immiscible solvents.

This is a case of three component system if a solute (solid or liquid) is added to a mixture of 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 an equilibrium is established. At equilibrium, the ratio of the conc of the solute in one solvent to the conc of a solute in another solvent is constant and is referred to as the partition coefficient. Partition or distribution coefficient (K_D) is defined as the ratio of the conc of the solute, between two immiscible solvents at equilibrium whether solute is soluble in both solvents at a given temperature.

Suppose a solute x is shaken with a mixture of two immiscible solvents A and B at a given temperature, then at equilibrium.

$\frac{x}{y} = \text{constant}$

OR $x \propto K_D$

The partition coefficient K_D is derived from the partition law which states that *when a solute is miscible in two immiscible solvents in the same system is shaken in a constant ratio at constant temperature when equilibrium is attained.*

The partition law has some limitations

- i). Temperature must be kept constant.
- ii). The solute must be soluble in both solvents.
- iii) The solute must not dissociate or associate in either solvent it should remain in the same molecular state
- (iv) It should not react with either solvent
- (v) The solvents must be immiscible
- (vi) The solution used must be fairly dilute i.e. solute should not saturate either solvents.

Determination of K_D between solvent

Determination of K_D of Ammonia between water and trichloromethane

Procedure;

- A given volume of a standard solution of Ammonia is shaken with a given volume of a mixture of water and trichloromethane in a stopper separating funnel at a given temperature for about 15 minutes. This ensures that equilibrium is attained.
- The mixture is allowed to stand to let the layers separate out. Equal volume of either layer is piped and separately titrated with a standard solution of HCl using phenolphthalein indicator. Ammonia reacts with HCl according to the equation

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$
- The volume of HCl required to reach end point is noted and the concn of ammonia in either layer can be calculated. The value of K_D is obtained from the expression.

$K_D =$

- Ammonia is much more soluble in water than 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.

Determination of K_D Ethanoic acid between tetrachloromethane and water.

Procedure;

- A known volume of CCl_4 and a known volume of H_2O are reduced in a separating funnel. A known volumes of standard solution of ethanoic acid is added to the mixture. The funnel is stopped 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 volume of either layer are pipetted and titrated separately with standard solution of sodium hydroxide using phenolphthalein as the indicator.
- Ethanoic acid reacts with sodium hydroxide according to the equation.
$$\text{CH}_3\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow \text{CH}_3\text{COONa}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- The volume of sodium hydroxide required to reach end point for the separate layers is noted and the concn of ethanoic acid in either layer is then determined from which the partition coefficient of ethanoic acid can be calculated as.

$K_D =$

- Ethanoic acid is much more soluble in tetrachloromethane than 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 tetrachloromethane and water.

Procedure;

- A given mass of iodide is shaken with a given volume of a mixture of tetrachloromethane and water in a stopped separating funnel at a given temperature until the equilibrium of iodide between the two layers is attained.
- The mixture is allowed to stand to let the two layers separate at equal volumes of each layer are pipetted in separate conical flask and separately titrated with a standard solution of sodium thiosulphate using starch indicator.
- The volume of standard sodium thiosulphate required to reach end point is noted for each layer.
- Sodium thiosulphate reacts with iodine according to the equation



Note: Iodine is a covalent solute, non-polar with limited interaction between its molecules and water so it has a very low solubility in water.

APPLICATIONS OF PARTITION LAW; The main applications include;

- (i) Solvent attraction.
- (ii) Determination of formula of complexes.

(iii) Chromotography.

1. Solvent extraction.

This is a technique used to gradually isolate a solute from one solvent in which it is less soluble into another solvent in which the solute more soluble by shaking the mixture of the solute and the solvent in which it is less soluble with another solvent where it is more soluble provided the two solvents are immiscible and the solute dissolves in each of the solvents. Solvent extraction is normally used to remove solutes from their aqueous solution by shaking with an organic solvent in which the solute is more soluble at a given temperature.

During solvent extraction the process can be performed at once using all the available solvent ie extract the solute or it can be done using successive portion of the solvent using separate portions in more economical and preferred during solvent extraction since much amount of the solute is extracted.

Examples;

1. 100cm³ of a solution contain 30g of substance Z. calculate the mass of Z that can be extracted by shaking the aqueous solution with Portions of ether (the KD of Z ether and water is 5)

Solution

KD =

5 =

150-5a-a

a =

= 20g

The mass extracted by 100Cm³ of t is 20g

Using the two 50cm³ portion of ether

First portion

Let b the mass extracted by the first portion of 5cm³

The mass of a remaining aqueous layer is (30-b)_g

K_D =

S =

S =

150-5b = 2b

b =

2143g

Mass remaining in aqueous layer = (30 – 2143)

8.57g

KD =

S =

S =

2c = 5 x 8.57. 5c

7c = 40.85

C = 6.12g

= 27.55g

2. 100cm³ of an aqueous solution containing 20g of w was shaken once with 50cm³ of ether.

- (a) Calculate the mass of w extracted by either (KD of between ether water is 4)
 (b) Calculate the mass of w that would be extracted by shaking the solution twice with 25cm³ of ether.

Solution

Let the mass of w extracted by 50cm³ of ether be xg

Mass of w remaining in water = (20 - x)g

KD =

S =

4 =

$$80 - 4 - x = 2x$$

$$X = 13.3g$$

First partition

Let the mass of w extracted by the first 25cm³ portion be y

Mass of w remaining (20-y)

KD =

$$80 - 4y = 4y$$

Y =

$$Y = 10g$$

Mass remaining in aqueous layer = (20-10)

$$= 10g$$

2nd portion

Let z be the mass of w extracted by the second portion. Then mass of w remaining in aqueous layer = (10-z)

y =

y =

$$40 - 4z = 4z$$

z =

$$z = 5g$$

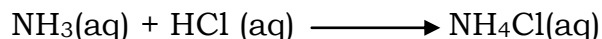
total mass extracted by using portions

$$= (5 + 10)g$$

$$= 15g$$

3. 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 12.75cm³ 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

100cm³ of solution contain 0.1 moles of HCl

5 cm³ of solution contain () moles of HCl

Moles of ammonia reacted () moles

25cm³ of solution contain () moles of ammonia

100cm³ of solution contain x

$$= 2 \times 10^{-2}M$$

Aqueous layer

1000cm³ of solution contain 0.1 moles of HCl

827.5cm³ of solution contain (x 127.5) moles of HCl

1 mole of HCl reacts with 1 moles of NH₃

Moles of NH₃ reacted

=)moles

25cm³ of solution contain)moles of NH₃

1000cm³ of solution contain)moles

= 51 x 10²M

K_D =

K_D =

K_D = 0.04

4. 50cm³ of 1.5M ammonia solution were shaken with 50cm³ of trichloromethene in a separating funnel. After the layers had settled, 20 cm of the chloroform layer were pipetted and titrated with 0.05m HCl. If 23ml of the acid were required for neutralization, calculate the value of K_D of Ammonia between water and chloroform at that temperature.

Solution

1000cm³ of solution contain 0.05 moles of HCl

23cm³ of solution contain (x 23) moles of HCl

1 mole of HCl reacts with 1 mole of NH₃

Moles of NH₃ reacted

= ()

20cm³ of solution contain ()moles of NH₃

1000cm³ of solution contain () x

= 0.0575M

Conc NH₃ remaining in aqueous solution layer

= (1.5-0.0575)

= 1.4425M

K_D =

=

= 251

5. 50cm³ of an aqueous solution of iodine was shaken with an equal volume of carbon tetrachloride in a separating funnel at 298K. when equilibrium was established the two layers were left to separate out. 20cm³ 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 7.2cm³ of the same solution of sodium thiosulphate. Calculate the value of K_D of I₂ between the organic layer and the aqueous layer.

Solution

Equation

I₂(aq) + 2S₂(aq) ————— 2I⁻(aq) + S₄(aq)

Organic layer

1000cm³ of solution contain 0.05moles of S_{2(aq)}

47.5cm³ of solution contain x 475 moles of S_{2(aq)}

(x 47.5) moles of S_2 react with $\frac{1}{2}$ (x 475) moles I_2

20cm³ of solution contain $\frac{1}{2}$ () moles of I_2

1000cm³ of solution contain (x x)moles of I_2

= 0.0475M

Aqueous layer

1000cm³ of solution contains 0.05moles of S_2

75cm³ of solution contain () moles of S_2

2 moles of S_2 react with 1 moles of $I_2(aq)$

(moles of S_2) moles of I_2

1000cm³ of solution will contain ($\frac{1}{2}$ x x) moles of I_2

K_D =

= 6.3

2.Determination of formula of complex ions

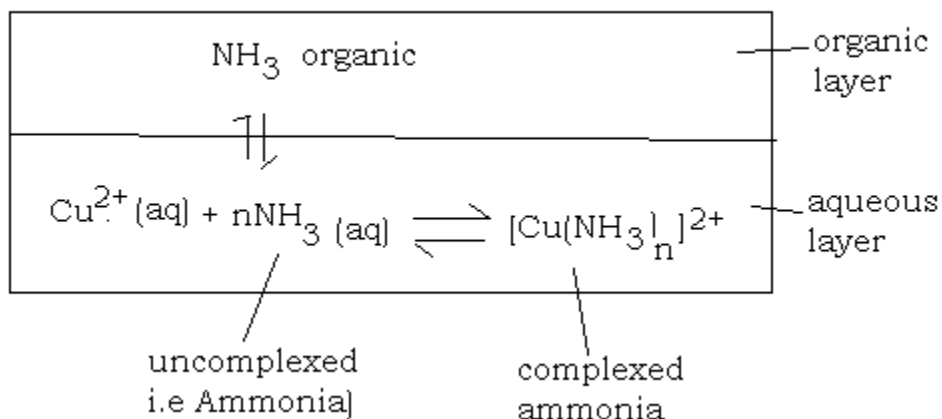
Eg the number of ligands in the complex $[Cu(NH_3)_n]^{2+}$. The partition law can be used to determine the formular of the complex ion, found in one of the layers ie aqueous or organic layer depending on the nature of the complex eg the partition law can be used to determine the formular of the complex between Cu^{2+} ions and Ammonia (NH_3). Cu^{2+} ions react with NH_3 to form the complex according to the equation.



Excess NH_3 is shaken with a mixture of standard aqueous solution NH_3 of Cu^{2+} ions and trichloromethane is a stoppered separating funnel at a given temperature until equilibrium is established.

The mixture is left to stand to allow the two layers separate out. Equal volumes of either layer are pippeted and separately titrated with a standard solution of HCl using phenolphthalan indicator.

The concn of ammonia in ether layer is then determined free and ammonia complexed.



From the partition coefficient of ammonia between water and aqueous layer can be determined

$$K_D =$$

In the aqueous

$$[\text{NH}_3]_{\text{total}} = [\text{NH}_3]_{\text{free}} + \text{complex } [\text{NH}_3]_{\text{free}}$$

$$[\text{NH}_3]_{(\text{aq}) \text{ complexed}} = [\text{NH}_3]_{\text{total}} - [\text{NH}_3]_{\text{free}}$$

Knowing the total concn of Ammonia in the aqueous and Ammonia concn free in the aqueous layer, the concentration of complexed Ammonia can be determined.

$$[\text{NH}_3]_{(\text{aq}) \text{ complexed}} = [\text{NH}_3]_{\text{total}} - K_D [\text{NH}_3]_{\text{organic}}$$

By comparing the concn of Cu^{2+} ions and complexed Ammonia in the aqueous layer, the formula of the complex formed between Cu^{2+} ions and Ammonia is obtained i.e.

$$[\text{Cu}^{2+}], [\text{NH}_3]_{\text{fixed}} = 1:n$$

Question: Excess NH_3 was shaken with an aqueous solution of 0.05 molar Cu^{2+} ions and trichloromethane in a stoppered separating funnel.

The funnel was allowed to stand for the two layers to separate out

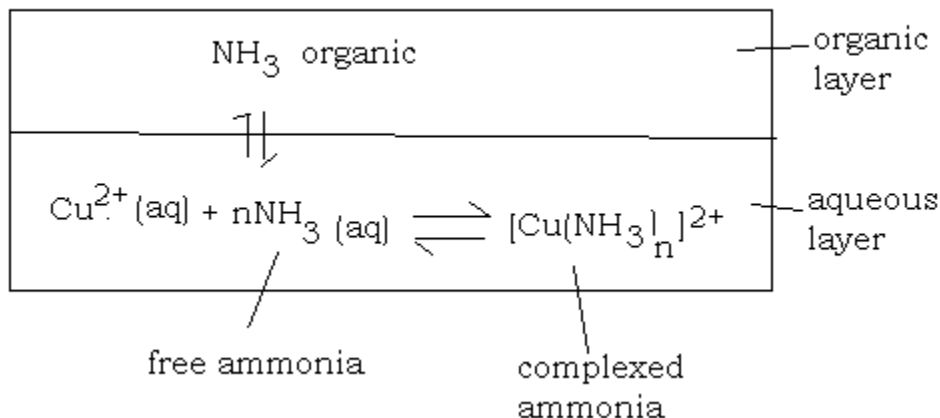
Some ammonia reacted with Cu^{2+} ions in the aqueous layer to form the complex $[\text{Cu}(\text{NH}_3)_n]^{2+}$

At equilibrium the concn of Ammonia in the trichloromethane and the aqueous layer were 0.021 and 0.725 mol l^{-1} respectively. (The partition coefficient of CHCl_3 between water and trichloromethane is 25 cm^3).

Calculate

- (i) The concn of free Ammonia in the aqueous layer
- (ii) The concn of Ammonia that formed the complex with Cu^{2+} ions
- (iii) The values of n in the complex and write the formula of the complex.

Solution



$$K_D =$$

$$25 =$$

$$[\text{NH}_3]_{\text{free}} = 25 \times 0.021$$

$$= 0.525\text{m}$$

Concentration of $[\text{NH}_3]$ complexed

$$= [\text{NH}_3]_{\text{total}} - [\text{NH}_3]_{\text{free}}$$

Volume of n

$$[\text{Cu}^{2+}(\text{aq})] : [\text{NH}_3]_{\text{fixed}}$$

:

$$n=40$$

$$n = 40$$

Alternatively, the value of m in the formula of the complex $[\text{Cu}(\text{NH}_3)_2]^{2+}$ can be obtained from the graph

$$\text{From } [\text{NH}_3](\text{aq})_{\text{total}} = [\text{NH}_3]_{\text{free}} + [\text{NH}_3](\text{aq})_{\text{fixed}}$$

$$\text{But } [\text{NH}_3](\text{aq})_{\text{free}} = K_D[\text{NH}_3]_{\text{organic}}$$

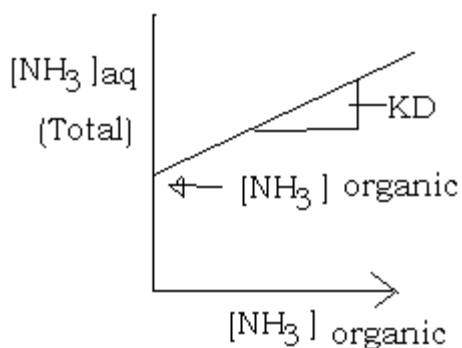
Substituting for $[\text{NH}_3]_{\text{aq free}}$

We get

$$[\text{NH}_3](\text{aq})_{\text{total}} = K_D[\text{NH}_3]_{\text{organic}} + [\text{NH}_3](\text{aq})_{\text{fixed}}$$

$$y = Mx + C$$

A plot of $[\text{NH}_3]_{\text{aq total}}$ against $[\text{NH}_3]_{\text{organic}}$ gives a straight line graph with K_D as the gradient and $[\text{NH}_3]_{\text{aq fixed}}$ as the intercept on the y-axis



The concn of fixed Ammonia is obtained as the intercept for which the value of n can be obtained using the ratio $\text{Cu}^{2+} [\text{NH}_3]_{\text{fixed}} = 1:n$

Example

The table below shows the results of partition of Aminomethane between trichloromethane and 0.1 CuSO_4 .

Solution

CH_3NH_2 in 0.1M CuSO_4	0.87	1.10	1.33	1.57	1.80
CH_3NH_2 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 no. of moles of Ammonia methane that have formed a complex with Cu^{2+} ions.

Qn: A solution of 25ml of 0.1M Cu^{2+} ions was added to 25ml of Ammonia and the resultant solution was shaken with trichloromethane and the mixture allowed to settle 20cm³ of the chloroform layer needed 10.2cm³ of 0.05M HCl and needed 16.5cm³ of the acid to reach end point, if the K_D of Ammonia between water and trichloromethane at that temperature is 25. Calculate the value of n in the complex.

Solution

Date

Aq. Layer (complexed + free Ammonia) = Total ammonia

Pipetted 10ml 0.5M HCl Vol required = 16.5cm

Organic layer

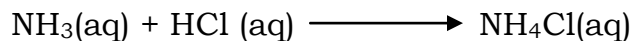
Pipetted

2cm³ 0.05M HCl vol required 10.2cm³

Organic layer

1000cm³ of solution 0.05moles of HCl

10.2cm³ of solution contain (x 10.2) moles of HCl



1 mole of NH_3 reacts with 1 mole of HCl

Moles of NH_3 reacted = (x 10.2) moles

20cm³ of solution contain (x 10.2) moles

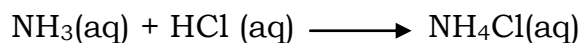
1000cm³ of solution contain (x 10.2 x) moles of NH_3
 = 0.025M

Aq. Layer

This contains complexed and free Ammonia

1000cm³ of solution contain 0.5 moles of HCl

16.5cm³ of solution contain (x 16.5) moles of HCl



1 mole of HCl reacts with 1 mole of NH_3

Moles of NH_3 reacted (x 16.5) moles

10cm³ of solution contain (x 16.5) moles of NH_3

1000cm³ of solution contain (x 16.5 x
 = 0.825M

But from K_D =

$[\text{NH}_3]_{\text{free}} = K_D \times [\text{NH}_3]_{\text{aq organic}}$

= (25 x 0.025)

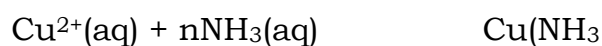
= 0.652

$[\text{NH}_3]_{\text{aq complexed}} = [\text{NH}_3]_{\text{aq total}} - [\text{NH}_3]_{\text{aq free}}$

= 0.825 – 0.625

= 0.2M

From the equation leading to the formation of the complex



1000cm³ of solution contain 0.1 moles of Cu^{2+} ions

25cm³ of solution contain (x 25) moles of Cu^{2+} ions

50cm³ of solution contain () moles of Cu²⁺ ions

1000cm³ of solution contain () moles of Cu²⁺ ions

= 0.05M

[Cu²⁺] : [NH₃] complex

1 : 4

The formula is Cu(NH₃)₄

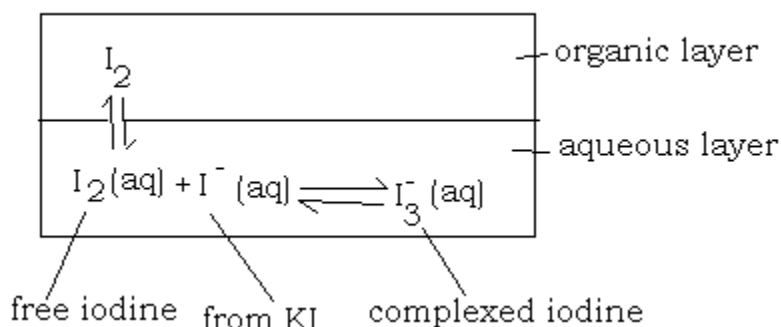
Determination of the equilibrium constant K_c

Partition can be used to investigate an equilibrium in aqueous solution between a covalent species and an ionic species of the equilibrium.

Partition can be used to investigate an equilibrium in aqueous solution between a covalent species and an ionic species of the equilibrium.

I₂(aq) + I⁻(aq)

Only the covalent iodine molecules I₂ will dissolve in the organic solvent. If an aqueous solution of Iodine in Iodide ions is shaken with an organic solvent such as carbon disulphide. The equilibria below are established.



A sample from the organic layer is pipetted and titrated with standard sodium thiosulphate using starch indicator.

The concentration of Iodine in the organic layer can be determined. Eqn for reaction between iodine and sodium thiosulphate (S₂(aq))



Knowing the concn of I₂ in the organic layer, the concn of free iodine in the aqueous layer can be obtained from the expression.

K_D =

$[I_2](aq) \text{ free} =$

The value of $[I_2](aq) \text{ free}$ is obtained from the data on K_D values at a particular temperature.

Another sample of the aqueous layer is pipetted and titrated with standard sodium thiosulphate ($2S_2O_3^{2-}$) using starch indicator this gives the concentration of Iodine in the aqueous layer which includes the free iodine and the complexed Iodine. The complexed iodine

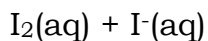
$[I_2](aq) \text{ free}$ is obtained by subtracting the free iodine from the total iodine

$[I_2](aq) \text{ free} = [I_2](aq) \text{ total} - [I_2](aq) \text{ free}$

The concentration of iodide ions is obtained by subtracting

$[I_2](aq) \text{ free}$ from the original Iodide ions

Example: Iodine is dissolved in water containing 0.16M potassium iodide and the solution is shaken with tetra chloromethane. The concentration of iodine in the aqueous layer was found to be 0.08M and that in the organic layer 0.1M. the partition coefficient for Iodine between tetrachloromethane and water is 85. Calculate the equilibrium constant for the reaction.



Solution

$[I_2] \text{ in } CCl_4 = 0.1M$

$K_D =$

$[I_2]_{\text{free}} =$

$[I_2]_{\text{aq}} = 0.08M$

$[I_2]_{\text{aq}} = [I_2]_{\text{aq Total}} - [I_2]_{\text{aq free}}$

$= 0.08 - 1.176 \times 10^{-3}$

$= 0.0788$

Initial $[I^-] = 0.16M$

$[I^-] \text{ reacted} = 0.0788$

$[I^-] \text{ at equilibrium} = (0.16 - 0.0788)$

$= 0.0812M$

$K_D =$

$=$

$= 825.21 \text{ mol}^{-1} \text{ dm}^3$

1. X is 12.0 times more soluble in trichloromethane than water. What mass of X will be extracted from 1.00 dm³ of an aqueous solution containing 25.0 g by shaking with 100 cm³ of trichloromethane.

2. The partition coefficient of y between ethoxyethane (ether) and water is 80. If 200 cm³ of an aqueous solution containing 5 g of y is shaken with 50 cm³ of ethoxyethane. What mass of y is extracted from the solution.

Z is allowed to reach an equilibrium distribution between the liquids ethoxyethane and water. The ether layer is 50 cm³ in volume and contains 4.00 g of Z. the aqueous layer is 250 cm³ in volume and contains 1.00 g of z. what is the partition coefficient of Z between ethoxyethane and water. (20.0)

500 cm³ of aqueous solution of concentration 0.120 mol dm⁻³ is shaken with 50.0 cm³ of ethoxyethane. The partition coefficient of the solute between ethoxyethane and water is 60.0. calculate the amount (in mol) of the solute which will be extracted by ethoxyethane (0.0154 mol)

The distribution coefficient of A between ethoxyethane and water is 90. An aqueous solution of A with a volume of 500 cm³ contains 5.00 g. what mass of A will be extracted by

- i. 100 cm³ of ethoxyethane and
- ii. Two successive portions of 50.0 cm³ of ethoxyethane

An organic acid is allowed to reach an equilibrium in a separating funnel containing 50 cm³ of ethoxyethane and 500 cm³ of water. On titration, 25.0 cm³ of the ethoxyethane layer required 22.5 cm³ of 1.00 mol dm⁻² sodium hydroxide. Solution and 25.00 ml of the aqueous layer required 9.0 cm³ of 0.0100 mol dm⁻³ Sodium hydroxide solution. Calculate the partition coefficient for the acid between ethoxyethane and water.

7. A small amount of Iodine is shaken in a separating funnel containing 50.0 cm³ of tetrachloromethane and 500 cm³ of water. On titration 25 cm³ of an aqueous layer required 6.7 cm³ of a 0.0550 mol dm⁻³. Solution of sodium thiosulphate 250 cm³ of the organic solvent require 27.2 cm³ of 1.15 mol dm⁻³ sodium thiosulphate solution. Calculate the distribution coefficient for iodine between water and tetrachloromethane.

8. A solid A is three times as soluble in solvent x as in solvent y. A has the same relative molecular mass in both solvents. Calculate the mass of n that would form a solution of 4 g in 12 cm³ of y by extracting it with

- a. 12 cm³ of x
- b. Three successive portions of 4 cm³ of x

9. The partition of T between ethoxyethane and water at room temperature with 100 cm³ of ethoxyethane at room temperature. What mass of T will be present in the ethoxyethane layer.

(b) What would be the total mass of T extracted if the ethoxy...were used in the separate 50cm³ portions, instead of the single 100cm³ portion.

Solution

$$= 12 =$$

Let mass of x extracted be Z

$$12 =$$

$$12 = .$$

$$12 =$$

$$22z = 300$$

$$t =$$

$$z = 13.6g$$

$$KD = 80 =$$

Let mass of y extracted from solution be x

$$80 =$$

$$80 = .$$

$$50(5-x) = 4x$$

$$400 = 84x$$

$$X = 4.76$$

$$KD =$$

$$K_D =$$

$$K_D = x \ 250$$

$$K_D = 20.0$$

No. 5 Let mass of A extracted be x

$$90 =$$

$$90 = x$$

$$90 =$$

$$95x = 90 \times 5$$

$$X = 4.74g$$

Mass of A extracted by 100cm³ of Ether is 4.74g

Let the mass extracted by first portion be x

$$90 = x$$

$$90 =$$

$$X_1 = 4.5g$$

Mass of A remaining in aqueous solution = 5.45

$$= 0.5$$

X₂ be mass extracted by second portion

$$90 =$$

$$90 = x$$

$$45 = 100x_2$$

$$X_2 = 0.45$$

Total mass extracted = 0.457 + 45

$$= 4.95g$$

Aqueous layer

100cm³ of solution contain 1 mole of NaOH

22.5cm³ of solution contain (x 22.5) moles

Mole 1:1

25cm³ of solution contain (x 22.5) moles of organic acid

1000cm of solution contain (x 22.5 x)

= 0.9M

Aqueous layer

1000cm³ of solution contain oil of NaOH

9cm³ of solution contain (x 0.9) moles of NaOH

1 mole of NaOH reacts with 1 mole of organic acid

23cm³ of solution contain (x 0.9) moles of organic acid

1000cm³ of solution contain (x 0.9 x)

= 0.036M

K_D =

K_D =

K_D = 25

I₂(aq) + 2S₂(aq) \longrightarrow 2I⁻(aq) + S₄(aq)

Aqueous layer

1000cm² of solution contain 0.0550 moles of S₂

6.7cm³ of solution contain (x 6.7) moles of S₂

1 mole of iodine reacts with 2 moles of S₂

(x 6.7) moles of S₂ react with (x x 6.7)

25cm³ of solution contain (½ x x 6.7 x)

= 7.37 x 10⁻³M

Aqueous layer

1000cm³ of solution contain 1.15 moles of S₂

27.2cm³ of solution contain (x 27.2) moles of S₂

1 mole of Iodine reacts with 2 moles of S₂

Moles of iodine reacted = ½ (x 27.2) moles

25cm³ of solution contain (½ x x 27.2) moles of I₂

1000cm³ of solution contain (½ x x 27.2 x) moles of I₂

= 0.6256

K_D =

= 1.18 x 10²

K_D =

The mass of A that form a solution of 4g is 12cm³ of y be E

3 =

3 = -

12-3t = t

4z = 12

Z = 3y

The mass that would form a solution of 9g

Let the extraction of first portion be x

3 =

3 = -

12 - 3x₁ = 3x₁

X₁ = 2

Mass of remaining 4-2

$$= 2$$

Mass extracted by 2nd portion X_2

$$3 = -$$

$$3 = .$$

$$6 - 3x_2 = 3x_2$$

$$X_2 = 1$$

Mass of y remaining = 2-1

$$= 1$$

Let mass extracted of 3rd portion be x_2

$$3 =$$

$$3 = .$$

$$3 - 3x_3 = 3x_3$$

$$6x_3 = 3$$

$$X_3 = 0.5$$

Total mass extracted = $x_1 + x_2 + x_3$

$$2 + 1 + 0.5$$

$$3.5g$$

$$K_D = 19 =$$

Let mass extracted by Ether be K

$$19 =$$

$$. = 19$$

$$19(5 - k) = k$$

$$20K = 95$$

$$K = 4.75g$$

Mass extracted = 4.75g

First portion

Let mass extracted be K_1

$$19 = .$$

$$95 - 19k_1 = K_1$$

Mass of I remaining in H_2O = 5.452

$$= 0.45$$

Mass extracted by 2^d portion be K_2

$$19 = .$$

$$19(0.48 - K_2) = 2K_2$$

$$=$$

$$K_2 = 0.43$$

Total mass extracted = $K_1 + K_2$

$$9.52 + 0.43$$

$$4.95g$$

3. Chromatography

BONDING AND STRUCTURE.

Atoms combine with others to complete their octet. They do so by either transferring of electron or sharing of electrons. Transfer of electrons results into ionic bond while sharing of electron results into covalent bond.

There are 5 types of bonds which include

1. Ionic bonds
2. Covalent bonds
3. Co-ordinate covalent relative bonds
4. Metallic bonds
5. Hydrogen bonds

Ionic bonds

An ionic bond is formed when (an electron is formed) when an electron is transferred from one atom to another it is also known as an electrovalent bond.

By losing an electron, an atom gains a positive charge and becomes an ion.

The two oppositely charged cation and anion attract each other with a very strong electrostatic forces thus ionic compounds have very high melting points.

Eg include Na^+Cl^- , $\text{Mg}^{2+}\text{Cl}^-$, $\text{Zn}^{2+}\text{O}^{2-}$

Properties of ionic compounds

- They exist as solid at room temperature
- They have very high melting point and boiling point
- They are good conductors of electricity in molten state or in solution.
- The distortion of the electron cloud of an anion is called polarization

Properties of covalent bonds

1. They are normally liquid or gas in room temperature
2. They have low boiling point and melting point
3. They are insoluble in polar solvents but soluble in non – polar solvents
4. They do not conduct electricity

Polarization and its effect on bonding

(a) Effect on covalent bonding

When a covalent bond is formed between two similar atoms, bonding electrons are shared equally. However this isn't true when a covalent bond is formed between two different atoms.

The more electronegative atom attracts bonding electrons towards itself thus creating electric dipoles within the molecule. The molecule is said to be polarized.

Eg a molecule of phosphorous tri-chloride (PCl_3) is because chlorine is more electronegative than phosphorous likewise SO_2 , H_2O , NH_3 , HI and HCl .

However carbon tetrachloride and carbon dioxide molecules are non-polar because their bonds are symmetrically arranged which gives the molecules a dipole moment of zero. Covalent compounds which are polar have physical properties different from what is expected from true covalent compounds eg some of them conduct electricity.

(b) EFFECT OF POLARIZATION OF IONIC BONDS

When a cation approaches an anion during an ionic bond formation it tends to displace the electron cloud of the anion towards itself. The electron then tends to be more or less shared hence

Factors affecting polarization

(a) Ionic radius

Polarization increases with decrease in ionic radius of the cation however it increases with increase in ionic radius of an anion.

This is because in a cation, a decrease in ionic radius leads to an increase in charge density due to high charge density, electrostatic attraction of electrons by the cation increases thus a high polarizing power.

For anions, a large ionic radius implies that the outer most electrons are very far away from the nucleus. These electrons can therefore be easily polarized (attracted) by the cation.

Example

For the compounds NaCl , LiCl and KCl , melting point increases from lithium chloride (LiCl) to potassium chloride (KCl) in the order

$\text{LiCl} < \text{NaCl} < \text{KCl}$

Why?

Explanation

Ionic radii of the cations increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+$. the higher the charge density the higher is the polarizing power of the cation. The higher the polarizing power of the cation, the higher is the degree of covalency in its compounds.

Therefore the covalent character of the above chlorides decrease in the order

$\text{LiCl} < \text{NaCl} < \text{KCl}$

The higher the covalent character the lower is the melting point

Similarly the melting point of Aluminium chloride is lower than that of Aluminium oxide. This is because the chloride ion has a bigger ionic radius than the oxide ion. The chloride ion is therefore more easily polarized than the oxide ion. Consequently Aluminium chloride has a greater covalent character than aluminium oxide.

(b) Ionic charge

Polarization increases with increase in ionic charge. This is because in ionic charge leads to an increase in charge density. Consequently, aluminium chloride has a lower melting point than calcium chloride due to a high charge of the Aluminium ion (Aluminium^{3+} Al^{3+}) compared to calcium ion [Ca^{2+}].

Question

Below are the melting points of some compounds

Compound	M.P (R)
Al_2O_3	2290
AlCl_3	451
CaO	2850
CaCl_2	1051

Explain why

(a) The melting point of Aluminium chloride is much lower than that of calcium chloride.

(b) Melting point of Aluminium chloride is lesser than of Aluminium oxide

Solution

- AlCl_3 has a high ionic charge and hence increase in charge density this leads to a high polarizing power this leads to an increase in covalency character hence a low melting point.
- The chloride ion has a bigger ionic radius than the oxide ion and therefore the chloride ion is easily polarised than the oxide ion and hence increase in covalence character this leads to low melting points.

The diagonal relationship

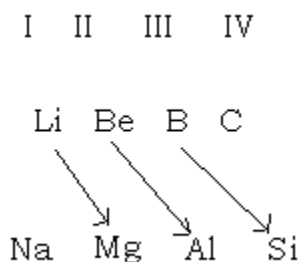
Down any group of the periodic table, charge density and electro negativity reduce therefore polarizing power reduces down the group.

Across any period ionic charge increases but ionic radius reduces therefore polarizing power increases across the period and also electro negativity i.e. charge density = .

Consequently an increase in polarizing power across the period is offset by a decrease in polarizing power down the group hence diagonal elements have similar polarizing power and electro negativity.

Similarity in polarizing power and electronegativity bring about similarity in chemical properties.

Consider part of the periodic table below.



From Lithium to beryllium polarizing power increases while from beryllium to magnesium polarizing power reduces.

The increase from Li to Be is offset by a decrease from power and therefore similar chemical properties.

Like wise Be and Al as well as Boron and Silicon have similar Chemistry (chemical properties) such elements are said to exhibit a diagonal relationship.

Diagonal relationship is defined as the relationship in which two elements diagonally opposite to each other in period 2 and 3 share similar chemical properties due to similarity in their polarizing power and electronegativity.

Because of the diagonal relationship, the chemistry magnesium and Lithium is similar in the following ways.

1. Both lithium and magnesium combine directly with nitrogen to form nitrides other Alkali metals do not react with nitrogen.
2. Both lithium and magnesium form normal oxides only ie Li_2O and MgO . Other metals form normal oxides and also peroxides eg Na_2O_2 .
3. Carbonates and hydroxides of magnesium and Lithium decomposes on heating and are sparingly soluble. Carbonate of other alkali metals are soluble and do not decompose heating.
4. Nitrate of Lithium and Magnesium decompose on bonds ie form an oxide, nitrogen dioxide and oxygen. Nitrates of other Alkali metals only form a nitrate and oxygen on heating.
5. Hydroxides of Lithium and Magnesium are not deliquescent.
6. Hydrogen carbonates of Li and Mg only exist in solution
7. Their fluorides are soluble in organic solvents
8. Both magnesium and Lithium form carbides when heated in carbon.

Exercise

State properties in which the chemistry of the following element is similar.

- (a) Beryllium and Aluminium
- (b) Boron and silicon

Solution

Beryllium and Aluminium

Both metals are made passive by nitric acid

Both metals react with NaOH to evolve H_2

Both oxides and hydroxides of beryllium and aluminium are amphoteric.

The chlorides are covalent polymeric solids when anhydrous $(\text{BeCl}_2)_x$ and $(\text{AlCl}_3)_x$ which readily dissolve in organic solvents they are readily hydrolyzed by water, with the evolution of hydrogen chloride.

Beryllium carbide, Be_2C , aluminium carbide Al_4C_3 give methane on treatment with water, unlike the ionic carbides of the group.

2 metals, they are therefore referred to as methides.

Similar complexes of beryllium and aluminium have similar stabilities eg BeH_4^{2-} and AlH_4^- . The shape is in agreement with the simple theory of electron pair repulsion.

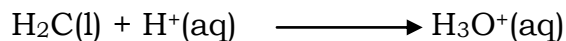
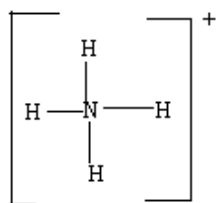
COORDINATE BOND (DATIVE BOND)

This is a covalent bond in which only one atom or group of atoms provides a pair of electrons being shared. The donor atom must have at least one lone pair of electrons i.e. a pair of electrons not being used for bonding.

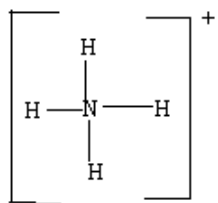
The acceptor atom must have at least a vacant orbital.

Examples

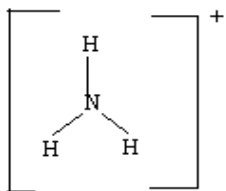
Ammonia

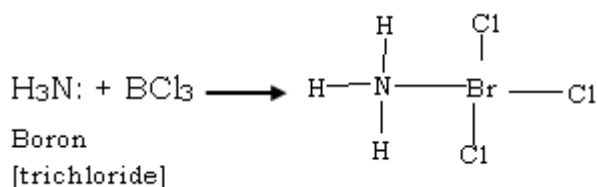


A dative bond is represented by an arrow pointing from the donor atom



Or





METALIC BOND

In metallic bonding, each metal atom pools (loses) its valency electrons forming metal cations which are attracted together by the lost electrons. This results in a strong metallic bonds.

The lost electrons are delocalized and free to move through out the entire metal structure thus metals conduct electricity and heat.

When atoms approach each other, their outer shell orbitals overlap forming molecular orbitals.

Because of a larger number of outer shell orbitals, many molecular orbits are formed which are non degenerate ie they are at different energy levels.

When light is shown on a metal, electrons absorb energy and transitions occur from lower energy molecular orbitals to higher energy molecular orbitals.

When electrons return to lower energy molecular orbitals.

When electrons return to lower energy molecular orbitals they emit energy in form of light. This explains why metals appear shinny.

Intermolecular forces

Covalent bonds have directional properties ie they are polar thus intermolecular forces exist between opposite poles of covalent molecules. The magnitude of intermolecular forces will determine whether the molecules are bond into solid state, liquid state a gaseous state.

Common intermolecular forces among covalent molecules include

Dipole-Dipole interactions, vander wool's forces and hydrogen bonds, hydrogen bonds are strongest among the intermolecule forces.

Intermolecular forces are generally weak compared to other bonds like covalent bonds or ionic bonds.

(i) Dipole-Dipole interactions

In solid state, polar molecules arrange themselves in such a way that opposite charges are adjacent to each other. This results into dipole-dipole attractions between the molecules.

Consequently ionic compounds dissolve in polar solvents because the energy required to break up the ionic crystal lattice is re-copued (recovered) by the energy released when dipole-dipole interactions occur between polar solvent molecules and ions of the ionic compound.

Vander waals forces

These are sometimes called molecular bonds, they are forces of attraction between electrical dipoles of different molecules. These forces exist in non – polar molecules eg mobile gas molecules, hydrogen gas molecule. This is when non – polar molecules approaches each other, temporally dipole, moments are created between the moles. The opposite dipoles attract each other creating vander waal's forces.

Magnitude of vander waal's forces increase with increasing molecular mass and this explains why melting point an boiling point of alkanes increase with increase in molecular mass eg lower members are gases while higher alkanes are either liquids or solids at room temperature.

Hydrogen bonds

A hydrogen bond is dipole- dipole attraction between a hydrogen atom attached to a strongly electringly to a strong electronegative atom and other electronegative atom in another molecule.

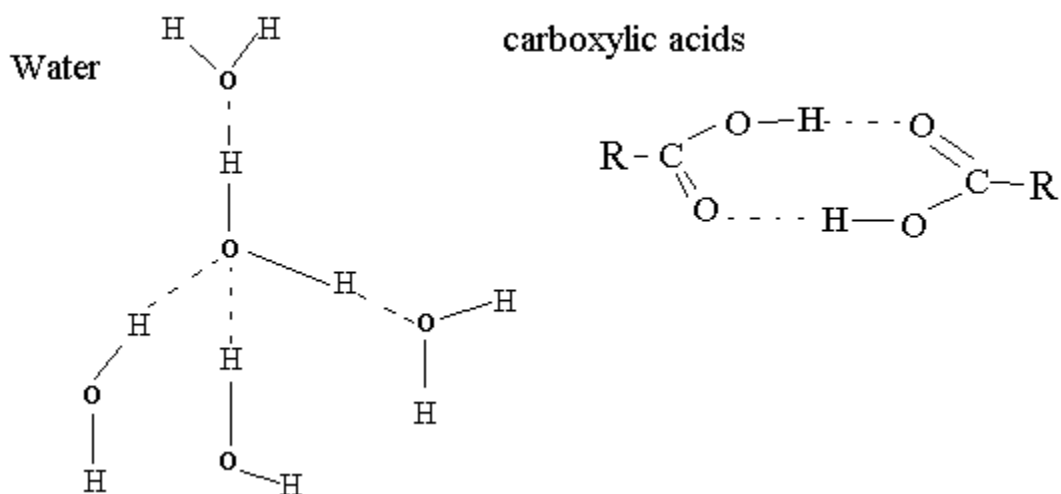
NOTE

Highly electronegative atoms that can easily induce hydrogen bonds include fluorine, oxygen and nitrogen. Therefore molecules kin which a hydrogen atom is attached to one of these electronegative atoms normally contain hydrogen bonds eg HF, HN₃ and H₂O.

Hydrogen bonds are stronger than other intermolecular forces thus compounds having hydrogen bonds are characterized by unexpected physical properties eg melting point, boiling, density etc.

Dehydrogen bond is represented by a dotted line as shown in the compounds below.

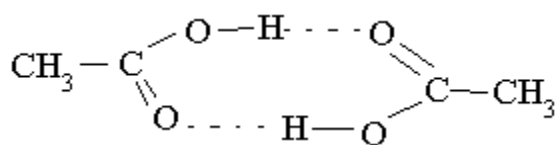
Hydrogen fluoride----- - - - - -



Effects of hydrogen bonding on physical properties of some compounds.

1. Ice floats of water
2. The formula mass of ethanoic acid as determined by freezing point depression method in benzene is twice the theoretical formular mass.
This is because ethanoic acid associates in benzene through bonding to form dimmers.

Ethanoic acid



Question

Explain the following observations

Boiling points of hydrides of groups (vii) increase in the order $\text{HCl} < \text{HBr} < \text{HI} < \text{HF}$

The fluorine atom is highly electronegative thus hydrogen fluoride molecules are held by strong hydrogen bonds. This gives hydrogen fluoride an abnormally high boiling point. The rest of the hydrides (HCl , HBr , HI) are held by weak vander waals forces.

Magnitude of vander waals forces increase with increasing the order to that of $\text{HCl} < \text{HBr} < \text{HI}$. The higher the molecular mass, the higher is the magnitude of vander-waal forces and the higher is the boiling point.

Ice floats on water

In ice, each oxygen atom is tetrahedrally bonded to four hydrogen atoms through covalent bonding and hydrogen bonding. This gives ice an extremely open tetrahedral structure thus a low density.

When ice melts the water molecules are in constant motion the hydrogen bonds in water therefore progressively form and break over and over again. This enables close packing of water molecule thus water has a high density than ice.

Boiling points of alcohols are higher than those of alkanes of approximately the same molecular mass.

Alcohols are held by strong hydrogen bonds while alkane molecules are held by weaker vander-waals forces.

Intermolecular forces in alcohols therefore are stronger than those in alkanes thus alcohol require more energy for these forces to be broken such that alcohol can boil.

Evidence for existence of hydrogen bonds

Existence of hydrogen bonds can be confirmed by comparing properties of some compounds with similar compounds. These include.

- a. Ice has a lower density than water
- b. Boiling points of alcohol and carboxylic acids are higher than those of alkanes of approximately the same molecular mass.
- c. Amines have higher boiling points than alkanes of approximately the same molecular mass.
- d. Molecular masses of carboxylic acids determined by cryoscopic method in organic solvents are observed to be twice the theoretical molecular masses. This is because carboxylic acid dimerise through hydrogen bonding when placed in organic solvents.

- e. Ammonia, water and hydrogen fluoride have higher boiling points than other hydrides of group 15 and 17 respectively.
- f. 2-hydroxy benzoic acid has a lower boiling point than for hydroxy benzoic acid.

Similarly 2 nitro phenol has a lower boiling point than 4-nitrophenol.

Questions

Define the term hydrogen bond?

Give the term hydrogen bond?

Give example, discuss the effects of hydrogen bonds on physical properties of some compounds

Explain why ice has a lower density than water

Bonding and structure

- Bonding
- Electrovalent (ionic) bonding
- Coordinate bonding
- Vander Waals bonding
- Hydrogen bonding

Structures

- ❖ Structure of simple molecular Compounds
- ❖ Structure of oxoanions
- ❖ Structures of ionic Compounds
- ❖ Structure of macromolecular covalent Compounds
- ❖ Metallic structures
- ❖ Structure of diamond and graphite

Bonding

Atoms of different elements or same elements combine to acquire stable electronic structures similar to those of noble gases which have full outer quantum shells such noble gases include: Helium, Neon, Argon, Krypton, Xenon.

The atoms combine in two types of bonding ionic bonding or covalent bonding ionic bonding or covalent bonding.

Atoms of the same metal come together through metallic bonding.

Vanderwaals bonding, coordinate bonding and hydrogen bonding come as a result of covalent bonding has taken place.

Electrovalent bonding

Electrovalent bonding is the type of bonding which there is transfer of electrons from outer most shells of the metal atoms to outer most shells of non – metal atom. The metal atom lose electrons and become cations while non metal atom, gain electron and become anions.

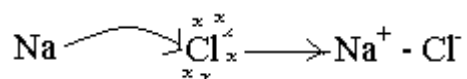
After the ions are formed, they are strongly attracted to each other through electrostatic forces of attraction which constitute ionic bond and the energy required to break the, ionic bonds, is called lattice energy and its magnitude depends on two factors i.e ionic radius and ionic charge. If ions of opposite charge have small ionic radii they approach each other strongly i.e electrostatic force of attraction between the ions is high and this leads to high lattice energy.

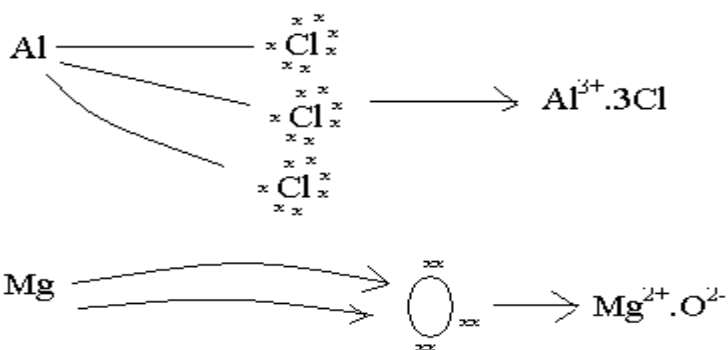
If the ions of opposite charge have high charge density eg X^{5+} & Y^{2-} or X^{3+} & Y^{3-} they approach each other strongly with a very high electrostatic force of attraction and thus the ionic bonds will be very strong leading to high lattice energy.

Therefore lattice energy can be defined in two ways.

Lattice energy it is the enthalpy change or heat change that occurs when 1 mole of a crystal ionic solid is broken down to form free gaseous ions or it is the enthalpy change or heat change that occurs when one mole of ionic crystal lattice is formed from its constituent gaseous ions. This is an exothermic process heat given out.

Eg





Properties of ionic C'pds

- ❖ They are crystalline solids at room temperature
- ❖ They conduct electricity either in molten state or in aqueous state.
- ❖ They are soluble in polar solvent such as water but insoluble in organic solvents such as benzene, ethanol, carbon disulphate
- ❖ They have very high melting points and very high boiling points

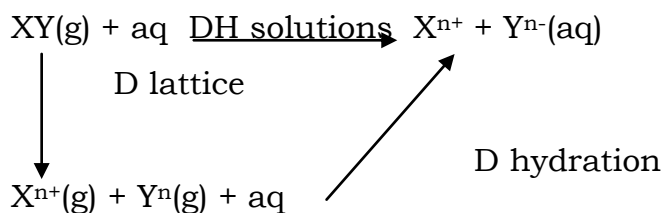
Note

Some ionic C'pds may acquire covalent character particularly those formed from small cations eg Lithium chloride and Aluminium Chloride possess some covalent character and therefore can easily dissolve in organic solvents such as ethanol, benzene etc

This is because Li^+ and Al^{3+} have very small ionic radii and this makes them to have very high charge density and very high polarizing power and this leads to formation of covalent compounds with low melting point and boiling point.

When an ionic cpd is dissolved in water there are three energy terms involved.

- ❖ Enthalpy of solution
- ❖ Enthalpy of lattice
- ❖ Enthalpy of hydration



Covalent bonding

This is the type of bonding that takes place when non metal ions combine they can be of the same element or different elements. This type of bonding involves sharing of electrons and each atom contributes the same number of electrons for sharing.

They can share either a part of electrons or two or three pairs

When a pair of electrons is shared a single covalent bond is formed. When two pairs of electrons are shared a double covalent bond is formed and when three pairs of electron are shared then a triple covalent of electrons constitute a covalent bond is formed.

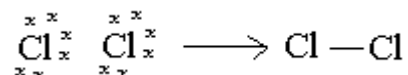
Note: Each pair of electrons constitute a covalent bond.

Show how the bonding takes place in the following C'pds.

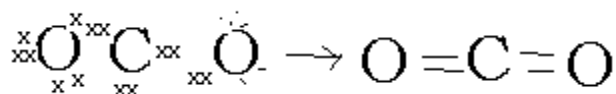
Note: each pair of electrons constitute a covalent bond.

Show how the bonding takes place in the following C'pds

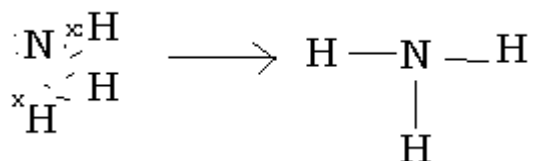
(a) Chlorine gas Cl_2



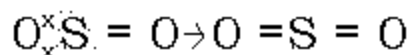
Carbondioxide



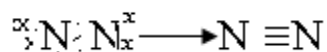
Ammonia gas



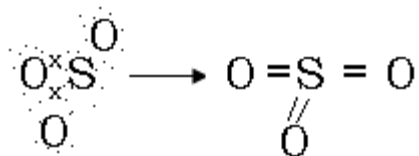
Sulphur dioxide gas



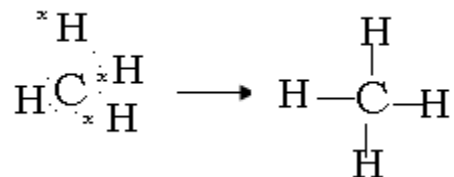
Nitrogen gas N_2



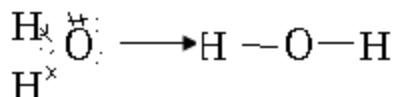
Sulphur trioxide gas



Methane gas



Water

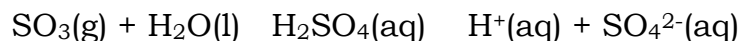
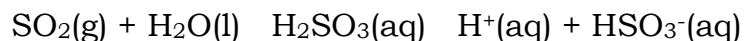
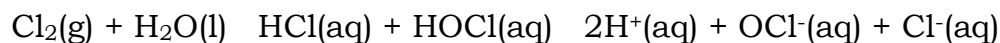
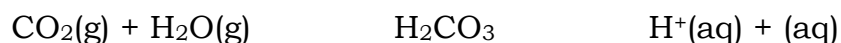
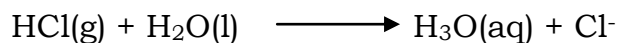


Properties of covalent C'pds

Covalent cpds are mainly gases and volatile liquids with low melting points and boiling points except silicon (iv) oxide which has again a covalent structure and it is a solid with high melting point and high boiling.

Covalent C'pds are non conduction of electricity ie they are non electrolytes except some gases which dissolve in water to form some ions and are able to conduct electricity. Such gases include HCl, Cl₂, NH₃, SO₂, CO₂.

Equations



Most of the covalent Cpds consist of discrete molecules

Most covalent C'pds are insoluble in water but soluble in organic solvents eg CCl₄ is insoluble in water but very soluble in ether.

Coordinate bonding

Coordinate bond is a type of covalent bond in which the shared pair of electrons is provided by only one of the bonded atoms. One atom is the donor and the other is the acceptor.

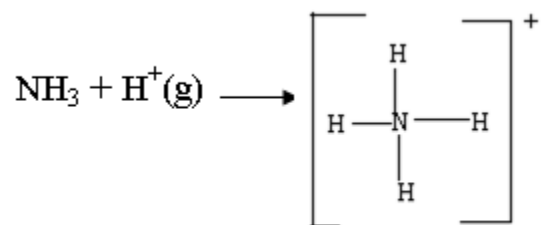
A coordinate bond is sometimes called a dative bond. Once a dative bond is formed it has the same characteristics as a covalent bond.

A coordinate bond is differentiated from a normal covalent bond where the electrons are coming from and where they are going.

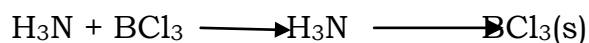
For the atom to act as a donor, it must have at least one pair of unsaturated electrons (a lone pair of electrons).

The acceptor atom should lack a pair of electrons. Compounds or ions which exhibit coordinate bonding are as follows.

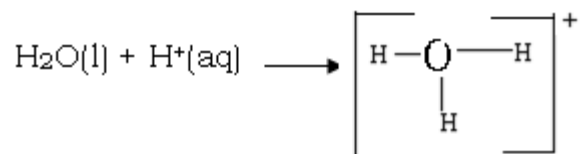
(a) Ammonium ion



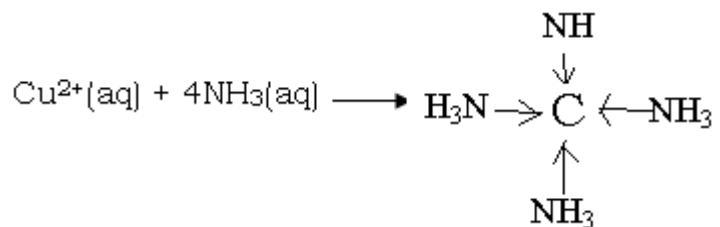
(b) Ammonium boron chloride $\text{H}_3\text{N} \cdot \text{BCl}_3$



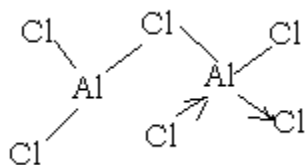
(c) Hydronium ion (H_3O^+)



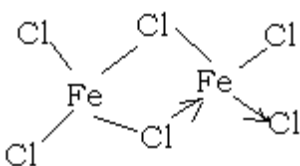
(d) Tetra amine copper (ii) ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$



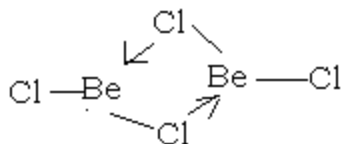
(e) Aluminium chloride in the vapour phase has a formula Al_2Cl_6 which is a dimer of AlCl_3 through coordinate bonds.



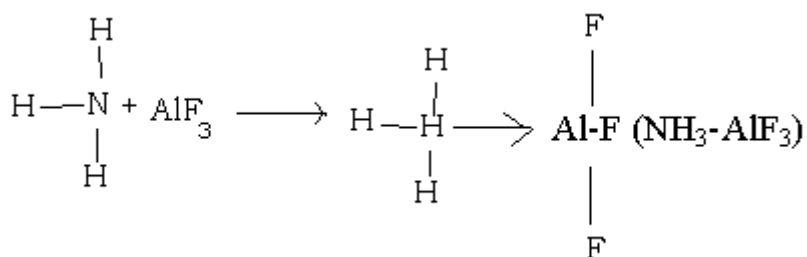
Iron (iii) chloride in vapour phase a formula FeCl_6 which is dimer of FeCl_3 through coordinate bonding.



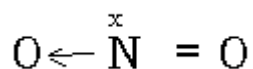
Beryllium chloride in the vapour phase has a formula Be_2Cl_4 which is a dimer of BeCl_2 through coordinate bonding.



Ammonium aluminium fluoride ($\text{NH}_3 \cdot \text{AlF}_3$)



Nitrogen Chloride (NO_2)



Shapes of simple covalent molecules and ions

The shapes of simple covalent molecules or ions are predicted by a theory called valence shell electron pair repulsion theory which was advanced by Sidwick and Powell (VSEPR theory).

The theory is based on the following principles

The arrangement of the electron pairs around the central atom in a molecule or ion depends on the number of electron pairs of the central atoms

The stable structure adopted by a molecule or ion is the one in which the electron pairs around the central atom are distributed so as to minimize the repulsion and hence to minimize the energy of the molecule or ion.

Any lone pair of electrons on the central atom will occupy the top position and will repel the bond pairs more greatly and can influence the geometry of the molecule.

Note: lone pair of electrons is a pair of electrons which do not take part in bonding.

A bond pair is a pair of electrons that form a single covalent bond.

According to the theory, repulsion decreases in the

- a. Order; lone pair – lone pair > lone pair – bond pair > pair-bond pair.
- b. Triple bond (X Y) > double bond (X Y) > single bond (X-Y)
- c. The repulsion decreases with the decrease in the electronegativity of the central atom. This affects the bond angles.

Steps to follow when working out the shape of the molecule or ion

- i. Write the electronic configuration of the central atom in terms of SPDF notation
- ii. Determine the number of electrons in the outer most quantum shell
- iii. Determine the number of bond pairs and lone pairs of electrons in the central atom
- iv. Write the formula of the C'pd in the form AX_mE_n where

A-Central atom

X- Ligands (surrounding atoms)

M – number of ligands

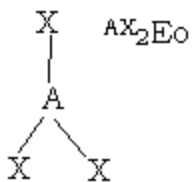
E- Lone pair of electrons

n - Number of lone pairs of electrons

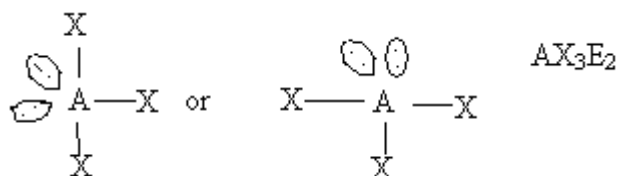
The molecule or ion can adopt any of the following shapes / structures

Linear structure $X-A-X^{AX_2E_0}$

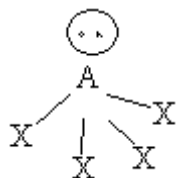
Triagonal planor (triangular) structure



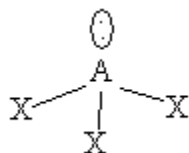
T – shaped structure



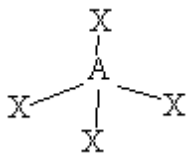
Sea saw (AX_4E_1)



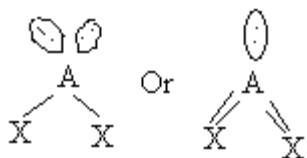
Pyramidal (AX_3E_1)



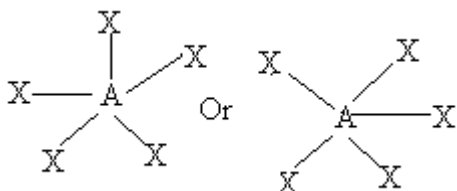
Tetra hedral (AX_3E_1)



V- Shaped structure AX_2E_2 or AX_2E_1

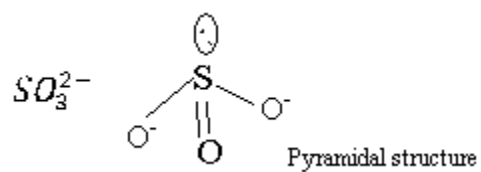
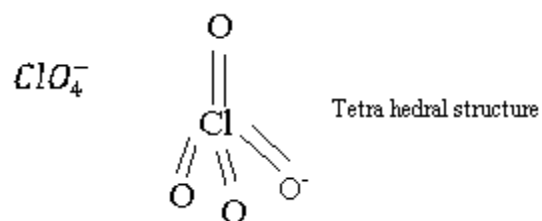
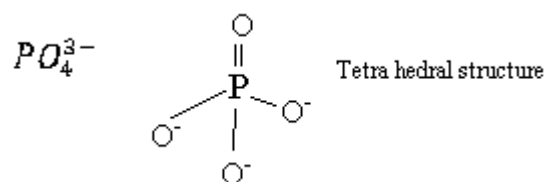
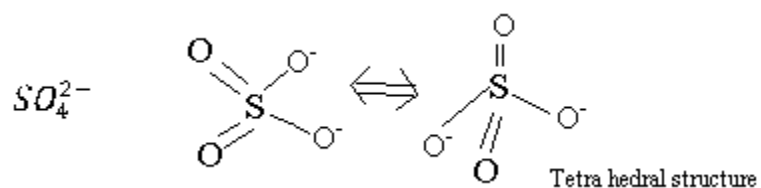
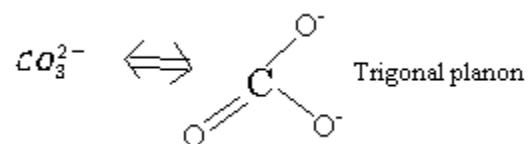


Trigonal bipyramidal (AX_5E_0)



Note

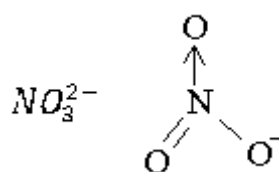
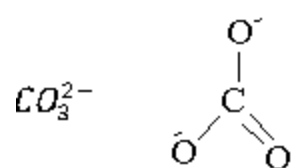
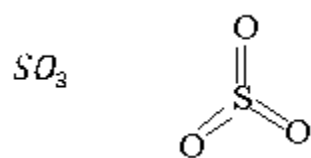
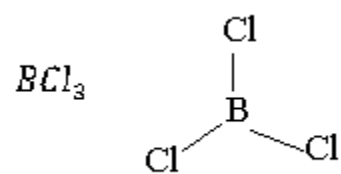
- When a central atom has atleast alone pair of electrons, the molecule can adopt any of the following shapes or structures.
 - ❖ v-shaped structure
 - ❖ T- shaped
 - ❖ Pyramidal
 - ❖ Sea-saw
- When a central atom has no lone pair of electrons then the molecule can adopt any of the structures.
 - ❖ Linear
 - ❖ Trigonal planar
 - ❖ Tetrahedral
 - ❖ Trigonal bipyramidal
- Oxygen atom forms a double bond with the central atom except when the oxygen has a charge of negative that is when it forms; a single bond with the central atom
- An oxo anion (shows that M oxygen atoms with negative charge and thus forms single bonds with the central atom and the rest of the oxygen atoms form double bonds with the central atom eg



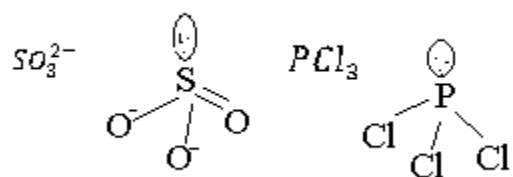
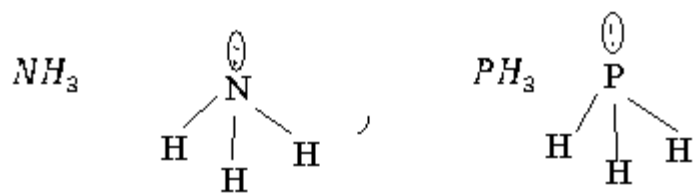
Linear structure

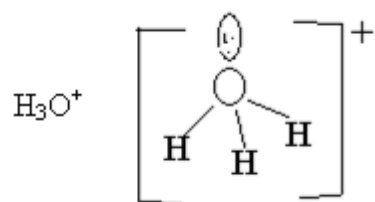


Trigonal planor structure AX_3E_0

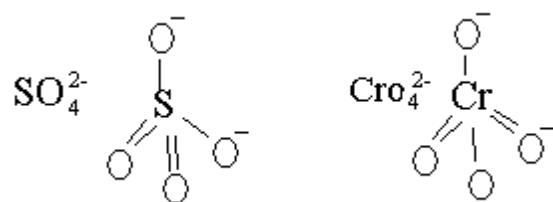
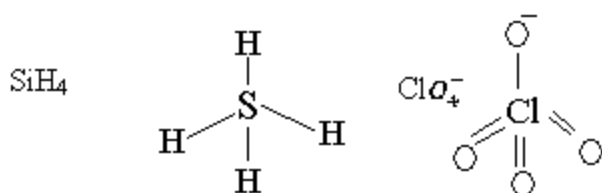
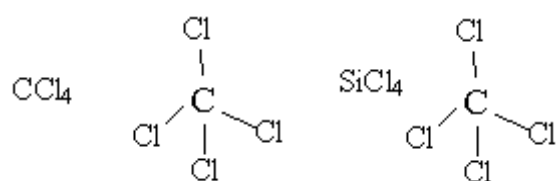
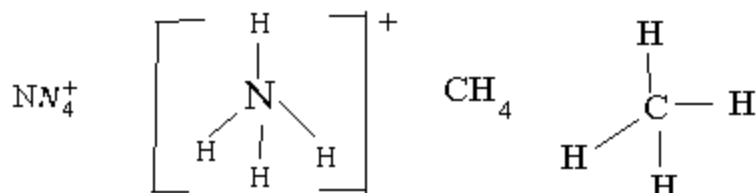


Pyramidal structure (AX₃E₁)

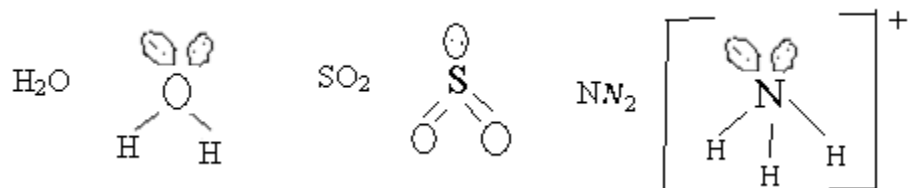




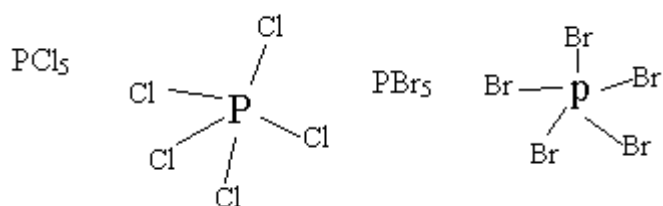
Tetrahedral structure (AX₄E₀)



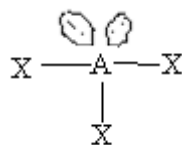
V- Shaped structure



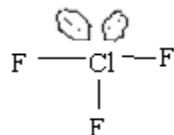
Trigonal bipyramidal (AX_5E_0)



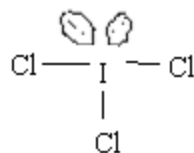
T- Shaped structure (AX_3E_2)



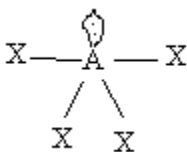
Eg CCF_3



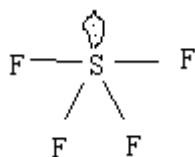
ICl_3



See-saw AX_4E_1



Eg SF₄, Sulphur tetra fluoride

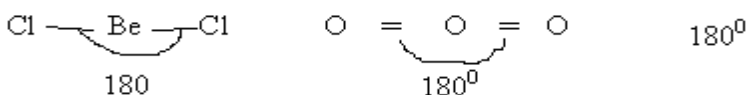


Effect of electro negativity of the central atom on the bond angle

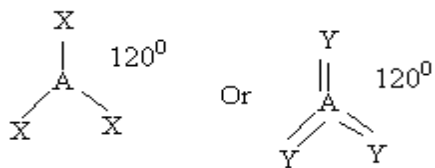
Electro negativity can be defined as the ability of an atom to attract bond electron towards itself when combined in a C'pd.

Bond angle is the angle formed between two covalent bonds.

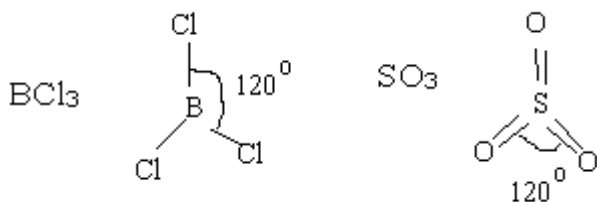
Linear structures have a bond



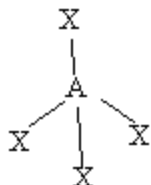
Trigonal planor structures have a bond angle of 120°



Eg



Tetrahedral structures are expected to have a bond angle of 90° but some time it is either less or greater than 90° due to the differences in the electronegativity of the central atom and the ligands eg



When the electronegativity of the central atom is high then there is a strong attraction of the bonding electrons towards itself and this results into a high concentration of bonding electrons around the central atom and this increases the repulsion between the bonding electron pairs and thus the bond angle is bigger than expected.

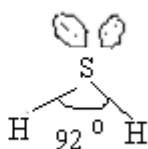
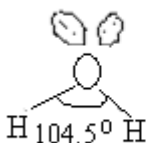
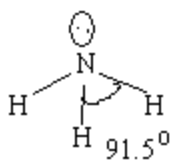
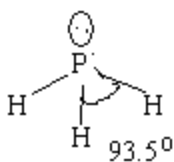
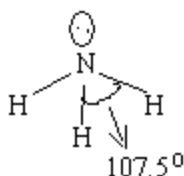
But if the electronegativity of the central atom is smaller than the ligands then the bonding electrons will be attracted towards the ligands and there will be a low concentration of bonding electrons around the central atom and thus the repulsion between bond angle to be smaller.

The effect of electronegativity of the central atom on bond angles is much felt in pyramidal structures and V-shaped structures where there is at least a lone pair of electrons on the central atom.

Considering the hydrides of group V and group VI

Group V: NH_3 , PH_3 , AsH_3 (pyramidal)

Group VI: H_2O , H_2S , SeH_2 (V-shaped structure)



The hydrides of gpV adopt a pyramidal structure because the central atom has a lone pair of electrons but the bond angle decreases from the hydride of nitrogen to the hydride of Arsenic. This is because the electronegativity of nitrogen is higher than that of phosphorous which in turn is higher than that of Arsenic.

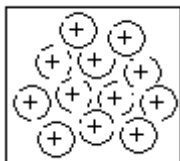
In ammonia there is a high conc of bonding electrons around the central atom making the repulsion greater and thus making the bond angle to be bigger.

In phosphine (hydride of phosphorous) the electronegativity of phosphorous is smaller than that of nitrogen and there is a low concentration of bonding electrons around the phosphorous atom and the repulsion between bond pairs reduces making the bond angle to be smaller. NB the same explanation applies to the hydrides of group VI elements.

Metallic bonding

A metallic bond is a strong attraction between the metal ion and the delocalised electrons

In a metal structure positive ions of the metal are packed in a regular array with in a sea of electrons liberated from the metal atoms.



The more the no. of valency electrons of the metal, the stronger the metallic bond.

GpI metals are very soft and can easily be cut with a knife because their metallic bond is weak because each atom contributes one electron to the metallic bond formation (charge cloud).

Gp II metals are harder than gpI metals and therefore their boiling and melting points are higher than those of gpI metals

This is because each atom of a group II metal contribute two electrons to the charge cloud and thus the metallic bond is stronger.

Transition metals are very hard eg iron, manganese , chromium etc because their metallic bonds are very strong because they have many valency electrons contributed to the metallic bond.

Properties of metals

They are conductors of heat and electricity because of the delocalized electrons.

They have high luster (they have shiny surfaces)

They have high density

They have high melting and boiling points

They are malleable and ductile ie their metal ions can slide relative to one another when under stress without shattering.

Vander waals forces

Vander waals forces are the kind of attraction between polar covalent molecules or non polar covalent molecules due to dipole- dipole interaction.

In polar covalent molecules and non polar covalent molecules vander waal's increase with increase in relative molecular mass.

Among the group VII (halogen) the vander waals forces increase down the group due to the increase in relative molecular mass of the halogens, chlorine and fluorine are gases at room temperature, bromine is a volatile liquid while iodine is a volatile solid which sublimes on warming.

The vander waals forces become progressively stronger as one moves down the group and therefore the boiling points of the halogens increase down the group.

Among alkanes the vander waal's forces increase with increase in relative formula mass eg methane, ethane, propane and butane are gases at room temp, although their boiling points are different. From pentane to hexadecane are liquids at room temperature.

Those alkanes with 17 carbon atoms and above are solids (waxy solids)

In alcohols there are vander waals forces existing in their molecules in addition to hydrogen bonds.

The boiling points of alcohols are higher than those of alkanes.

Branching in organic C'pds both polar and non polar reduce vander waal's forces and the branched isomers have a relatively lower boiling points than unbranched isomers.

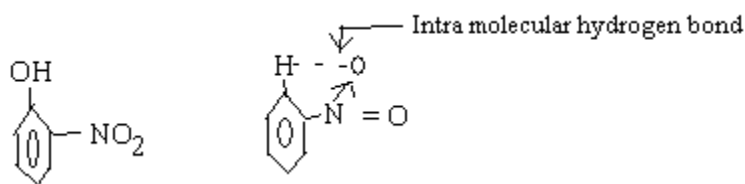
Hydrogen bonding

A hydrogen bond is a permanent dipole-dipole interaction (attraction) between a hydrogen atom in one molecule and a more electronegative atom in another molecule or the same molecule.

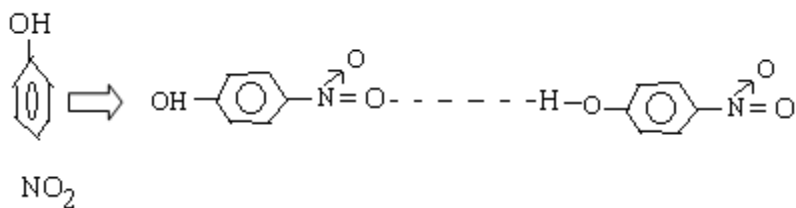
There are two types of hydrogen bonding:-

Intra molecular hydrogen bonding which exists in the same molecule and inter molecular hydrogen bonding which exists in different molecules.

2-nitro phenol is the best example where intra molecular hydrogen bonding takes place.



4- nitro phenol exhibits inter molecular hydrogen bonds



Intermolecular hydrogen bonding is stronger than intra molecular hydrogen bonding because there are many molecules involved in the hydrogen bond formation while intra molecular hydrogen bonding there is only one molecule.

The more electronegative atoms include oxygen, fluorine, sulphur and nitrogen.

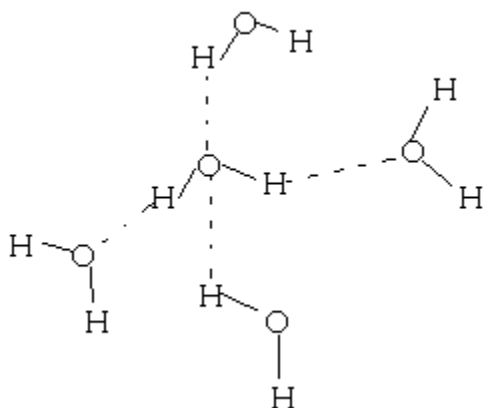
Effect of hydrogen bonding on the physical properties of some compounds (covalent)

Physical properties of some covalent c'pds such as solubility in water, melting and boiling points, density are affected by the presence of hydrogen bonds.

When a c'pd contains a more electronegative atom such as atom, its physical properties will be different from those of the group members eg the hydrogen of gpVI and gVII are generally gases at room temperature but water and hydrogen fluoride are liquids at room temp.

This is because water molecules associate together through strong hydrogen bonds and to break these bonds, more energy is needed and therefore water boils at 100°C but hydrogen sulphide its boiling point is -60°C .

Hydrogen sulphide molecules associate together through weak vander waal's forces which require less energy to break and therefore it is a gas at room temperature.



Similarly the boiling point of hydrogen fluoride is 20°C while that of hydrogen chloride is -80°C . this is because fluorine is more electronegative than chlorine and therefore hydrogen fluoride molecules associate through strong hydrogen bonds which require a lot of energy to break while hydrogen chloride molecules associate through weak vander waal's forces which require less energy to break and that is why HCl exists as a gas at room temperature while HF exists as a liquid at room temperature.

Ammonia (NH_3) and phosphine (PH_3) are hydride of gpV elements and their boiling points are -35°C and -86°C respectively. The boiling point of ammonia is much higher than that of phosphine. This is because nitrogen atom is smaller and more electronegative than that of phosphorous ammonia molecule associate through stronger hydrogen bonds which requires more energy to

break while PH_3 molecules associates through weak vander waals forces which require less energy to break.

Among the Hydrides of gpV, gpVI and gpVII elements water has the highest boiling point because it forms extensive hydrogen bonds and each water molecule forms 4 hydrogen bonds which require more energy to break.

When water is cooled up to 0°C it forms ice which is solid water because the hydrogen bonds are very strong at this temperature and they hold water molecules in their liquid positions and the ice formed is less dense than liquid water (it has a lower density than water) because the 4 hydrogen bonds around the water molecule will give ice a tetra hedral structure which is open and therefore will occupy more space/volume and with the same mass of the water the density reduces. But when the ice melts the hydrogen bonds are progressively broken and this facilitates the close plucking of the water molecules and there is a decrease in volume and therefore the density increases.

The table below shows the boiling points of the hydrides of group V, groupVI and group VII.

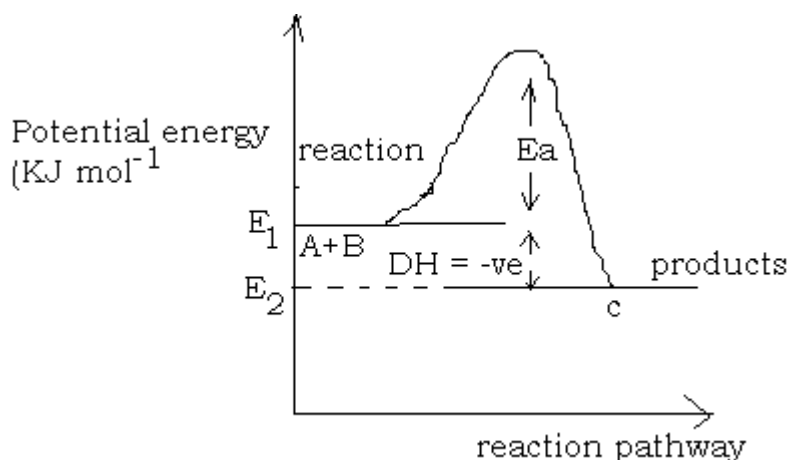
	Gp IV					GpV		
Hydride	CH_4	SiH_4	GeH_4	SnH_4	NH_3	AgH_3	SbH_3	PH_3
Bpt($^\circ\text{C}$)	-161	-112	-95	-52	-35	-56	-20	-86
Period No.	2	3	4	5	2	4	5	3

	Gp VI					GpVII		
Hydride	H_2O	H_2S	H_2	HiTc	Hp	HCl	HBr	HT
Bpt($^\circ\text{C}$)	100	-60	40	-5	20	-80	-60	-35
Period No.	2	3	4	5	2	3	4	5

Question

- On the same axes, plot graphs of boiling points of the hydrides of gp IV, gpV, gp IV and gp VII against period number.
- Explain the shape of the graph.

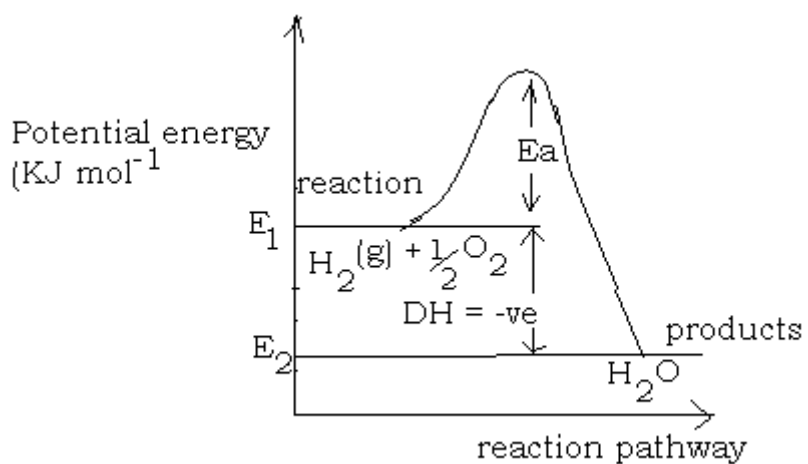
THERMOCHEMISTRY



For endothermic reactions, since the products are at a higher energy are at a higher energy content than the reactants, the products are energetically unstable compared to the reactants from which they are made.

For exothermic reactions, products have less energy than the reactants and are energetically more stable than the reactants.

Consider the exothermic formation of water from its elements.



Since water is formed exothermically it is more stable relative to its elements.

All chemical reactions proceed after overcoming an energy barrier called activation energy. It greatly limits reactions from proceeding and a catalyst is usually employed which provides an alternative pathway with a lowered activation energy.

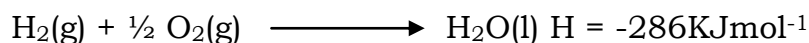
For endothermic reactions, activation energy can be overcome by increasing temperature which activates many molecules that can overcome the activation energy

Standard conditions for heat of reaction

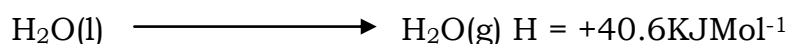
Physical state

In transforming to products the heat evolved or absorbed depends on the physical state of the participating species. Since in transforming one physical state to another heat is either evolved or absorbed therefore it is important to specify the physical state of the participating species in a chemical reaction by adding (L), (s), (g) for liquid, solid or gas respectively.

Consider the formation of liquid water and gaseous water.



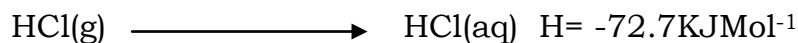
Less heat is given out when water is formed in form of a gas or vapour because some of it is used in the transformation of liquid water into gaseous water.



Similarly in the reactions



More heat is given out when hydrogen chloride gas is used instead of hydrochloric acid. The difference is because hydrogen chloride gas dissolves in water to form aqueous hydrochloric acid with evolution of heat.



2. Concentration of the participating species. If the reacting species are in aqueous solution, their concentration should be 1 molar (1M)

3. Temperature and pressure

The standard conditions of temperature and pressure are 298K 1 atmosphere.

Pressure affects reaction involving gaseous species.

Note: if conditions 1-3 are satisfied, then the symbol H bears superscript and a subscript and is written.

Note: if conditions 1-3 are satisfied, then the symbol H bears a superscript and a subscript and is written.

Or simply

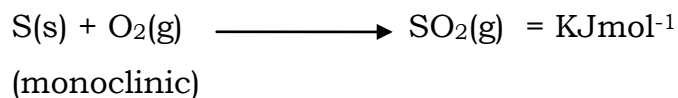
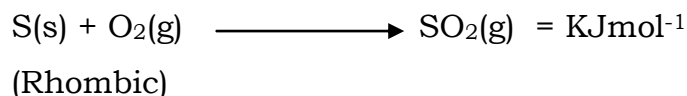
. This means that the energy change accompanying such a reaction is under standard conditions i.e. standard physical states, concentration of 1. If solutions are involved, pressure of 1 atm and temperature of 298K.

Other factors affecting enthalpy changes accompanying a reaction include.

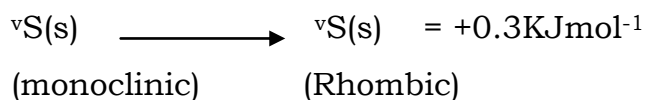
1. Allotropic modifications

An enthalpy change is involved in conversion of one allotrope into another such that the allotrope used affects the value of the enthalpy accompanying reaction.

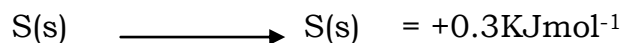
Consider the formation of sulphur dioxide.



More heat is absorbed when rhombic sulphur is used than monoclinic sulphur showing that the transformation of monoclinic to rhombic is endothermic.



Similarly less energy is absorbed when monoclinic sulphur is used to form sulphur dioxide showing that a conversion of Rhombic to monoclinic sulphur is exothermic.



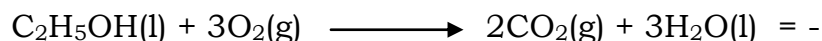
An increase in the amount of reacting substances increases the heat evolved or absorbed during the course of a reaction.

Types of enthalpies/heat of reaction

1. Enthalpy of combustion

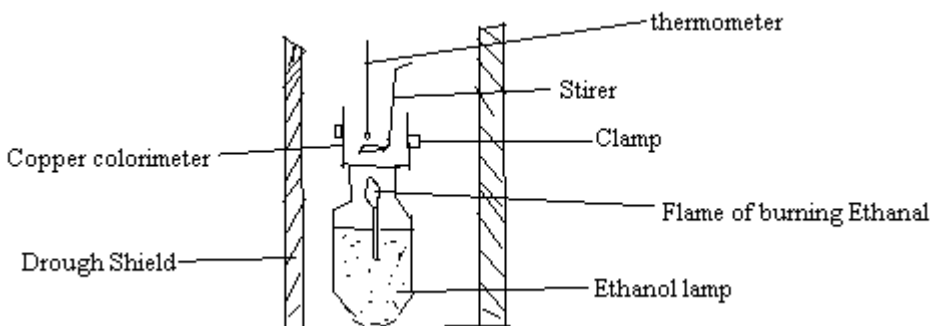
This is the heat evolved when 1 mole of a substance is completely burnt in excess oxygen under standard conditions.

Consider the reaction



For all combustion reactions the enthalpy of reaction is negative since heat is given out when a sample is burnt in excess oxygen.

Experimental determination of enthalpy of combustion of a liquid fuel eg Ethanol.



A known volume of water is put in a copper calorimeter fitted with a thermometer and a stirrer.

The calorimeter is damped and put in a shield which minimizes heat losses to the surroundings.

The initial temperature of water is noted. A given volume of ethanol is put in the ethanol lamp and weight of the lamp is noted.

The lamp is lit and the ethanol burnt is used to raise the temperature of water which is stirred continuously.

The final temperature of water is noted the lamp is removed.

The lamp is weighed again and its weight again and its weight noted. The mass of ethanol burnt can be determined.

Treatment of results

Let initial temperature of H_2O be $^{\circ}\text{C}$

Final temperature of water be $^{\circ}\text{C}$

Initial weight of lamp be $W_1\text{g}$

Final weight of lamp be $W_2\text{g}$

Weight of ethanol burnt = $(W_1 - W_2)g$

Volume of water used = $V\text{cm}^3$

Water g/cc

Heat given out in burning $(W_1 - W_2)g$ of ethanol = Heat gained by water.

= $M_w C_w$

$M_v = \text{density} \times \text{Vol}$

= $(\text{Density} \times \text{Vol}) \times C_w(2-1)J$

Heat given out in burning 1g of ethanol = J

$C_2H_5OH = (12 \times 2) + (1 \times 6) + (16)$

= 46g

Heat given out in burning = J

46g of ethanol

KJmol^{-1}

Example

Use the following information to calculate the heat of combustion of ethanol

Mass of ethanol + bottle before burning = 24.63g

Mass of ethanol + bottle after burning = 24.40g

Initial temperature of $H_2O = 18^\circ\text{C}$

O_2 temperature of $H_2O = 33.0^\circ\text{C}$

Density of $H_2O = 1\text{g/cc}$

Vol of H_2O used = 100cm^3

SHC of $H_2O = 4.27 \text{ mol}^{-1}\text{K}^{-1}$

Solution

Mass of ethanol burnt = $24.63 - 24.4$

= 0.23g

Temperature rise = $33 - 18$

= 15°C

Molar mass of $C_2H_5OH = (12 \times 2) + 1 \times 6 + (16 \times 1)$

= 46g

Heat given out in burning = heat gained by water 0.23g of ethanol

= mass of \times SHC of \times temp

Water H_2O rise

$(100 \times 1) \times 4.2 \times 15$

6300J

Heat given out in burning = [] J

1g of ethanol

Heat given out in burning = [$\times 46$] J

46g of ethanol

= $1.26 \times 10^6 \text{ Jmol}^{-1}$

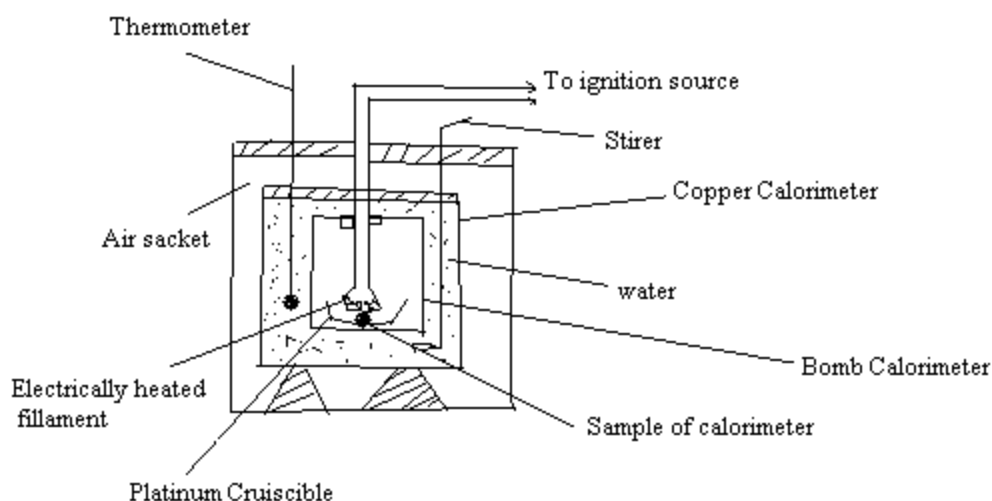
KJmol^{-1}

= $1.26 \times 10^3 \text{ KJmol}^{-1}$

= 1260 KJmol^{-1}

Enthalpy of combustion of 0.23g of ethanol is -1260 KJmol^{-1}

Determination of heat of combustion of a solid sample eg carbon graphite



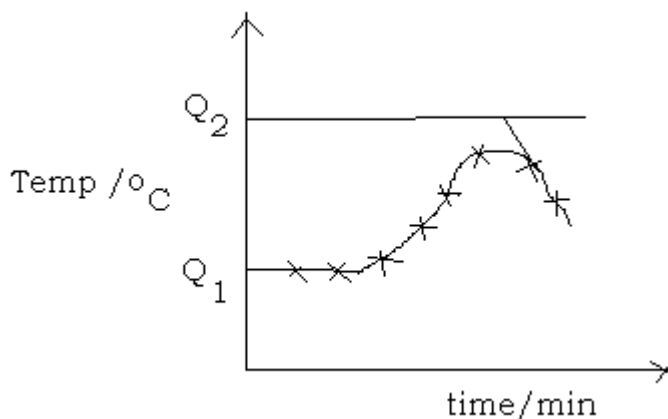
A known mass of the sample whose heat of combustion is under investigation is put on the plantinum cruiscible in a tomb calorimeter.

Oxygen under pressure is pumped into the bomb calorimeter and the calorimeter is made air tight.

The bomb is immersed in water of known volume fit with a thermometer and a stirrer. The initial temperature water is noted using the thermometer.

The sample is then ignited and the temperature of water is noted continuously on the thermometer and is recorded until when it has started falling.

The results are rendered as a graph



The final maximum temperature is obtained by extrapolation.

Treatment of results

Let volume of water be $V \text{ cm}^3$

Density of water be $\rho \text{ g/cc}$

Specific heat capacity of water be $C \text{ J g}^{-1} \text{ K}^{-1}$

Initial temperature of water be $\theta_1 \text{ } ^\circ\text{C}$

Final temperature of water be $\theta_2 \text{ } ^\circ\text{C}$

Heat given out in burning = Heat gained by water a grammes of the sample neglecting the small amount of heat taken up by the thermometer, stirrer and calorimeter.

= Mass of x specific heat \times temperature water capacity of water change.

$V.C (\theta_2 - \theta_1) \text{ J}$

Heat given out in burning /g of sample

Heat given out in burning 1 mole of sample $= m \times r$

J mol^{-1}

$\times M_r \text{ KJ mol}^{-1}$

Therefore heat of combustion of the sample

KJ Mol^{-1}

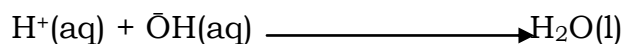
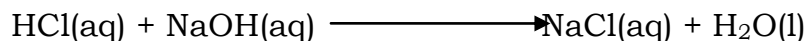
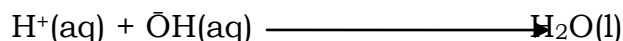
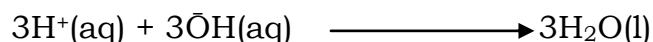
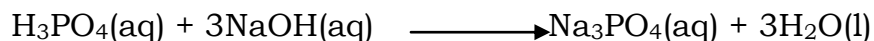
NEUTRALISATION

ENTHALPY OF NEUTRALISATION

A neutralization reaction occurs between an acid and a base forming water and a salt.

The heat of neutralization of an acid is the heat evolved when an acid reacts with a base completely to form 1 mole of water. Similarly the heat of neutralization of a base is the heat evolved when acid completely neutralizes the base to form 1 mole of water under standard conditions, the solutions involved should be 1 molar and in this case the acid or base is completely neutralized forming 1 mole of water. Therefore standard enthalpy of neutralization is the heat evolved when an acid of concentration 1 molar reacts with a base of the same concentration 1 molar reacts with a base of the same concentration forming 1 mole of water at 25°C and 1 atmosphere pressure.

Consider the following neutralization reactions



The above neutralization reactions show that in neutralization of a strong acid by strong base, the same ionic equation can be used to represent the reaction and if the acid and base in question are of concentration 1 mole dm^{-3} the same amount of heat is evolved and is approximately 57.3KJmol^{-1}

I.e



This is only true for strong acid strong base neutralizations but if the acid is weak the heat evolved is less eg the neutralization ethanoic acid by sodium hydroxide.



Ethanoic acid is weak acid and only slightly ionizes in solution releasing few hydrogen ions in solution

Secondly the salt formed during the course of the titration (Sodium Ethanoate) is a strong salt and fully ionizes.

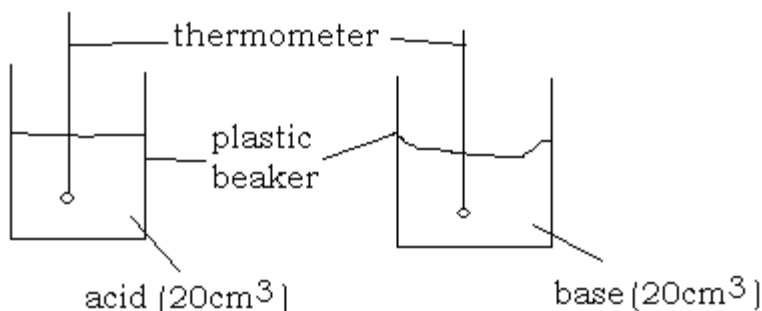


Ethanoate ions from the salt suppress the ionization hydrogen ions (H^+) in solution. Since a neutralization reaction occurs between hydrogen ions and hydroxyl ions, this reduces the heat evolved.

Experimental determination of heat of neutralization of 1M $\text{HCl}(\text{aq})$ by 1M $\text{NaOH}(\text{aq})$

In this experiment known volumes of the acid and base each of concentration 1 mol dm^{-3} are taken and put in separate plastic beakers.

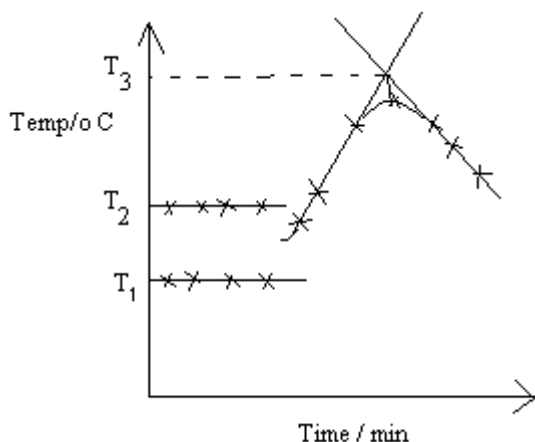
Thermometers are inserted into each of the solution and the stop clock started.



The temperature of the two solution are noted at 1 minute interval for about 5min.

The solutions are mixed together and stirred continuously using the thermometer noting the temperature of the mixture at 1 minute interval until when it has shown a fall for about 3 consecutive minutes.

The results are plotted on a graph



The final maximum temperature is obtained by extrapolation of the curves

Treatment of results

Volume of acid and base be $V \text{ cm}^3$ each

Total vol of solution $(V_1 + V_2)$

Initial temperature of base $T_2 \text{ } ^\circ\text{C}$

Initial temperature of acid $T_1 \text{ } ^\circ\text{C}$

Initial average temperature = $\theta \text{ } ^\circ\text{C}$

Final temperature of solution = $T_3 \text{ } ^\circ\text{C}$

Change in temperature $T_3 - \theta \text{ } ^\circ\text{C}$

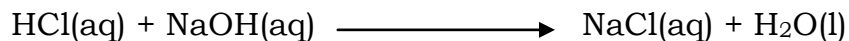
Density of the salt solution g/cc

S.H.C of solution = $C \text{ Jg}^{-1}\text{K}^{-1}$

Conc of acid and base = 1 mol dm^{-3} each

$$(V_1 + V_2)C (T_3 - \theta) \text{ J}$$

From the reaction



Moles of NaOH used to neutralize the acid

$$= (x \times V)$$

From the equation 1 mole of NaOH reacts with 1 mole of acid forming 1 mole of H_2O .

Moles of water formed = $(x \times V)$

Heat evolved in neutralizing the acid by the base to form

$$(V_1 + V_2)C [T_3 - \theta] \text{ J } \theta \text{ moles of water}$$

Heat evolved in neutralizing the acid by the base to form 1 mole of water

$$\frac{(V_1 + V_2)C [T_3 - ()] \text{ J}}{1.0V}$$

$$\frac{(V_1 + V_2)C [T_3 - ()] \text{ K.Jmol}^{-1}}{1.0V}$$

Qn. Find the heat neutralization of reaction (HCl + NaOH) from the following experimental data

Vol of 2M HCl = 20cm³

Vol of 2M NaOH = 35cm³

Initial temperature eg NaOH = 15.5°C

Initial temp of HCl = 15.0°C

Final temperature of the mixture = 28.3°C

SHC of water = 42Jg⁻¹K⁻¹

Density of water = 1g/cc

Solution

Total vol of solution = (20 + 35) = 55cm³

Average initial temperature =) = 15.4°C

Change in temperature = 28.5 – 15.4

= 12.9°C

Hea given out in neutralizing NaOH by HCl is = heat gained by salt solution

= Mass of X SHC X Temperature

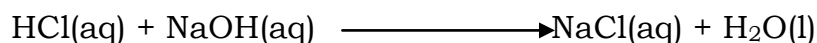
Soln Soln Change

(55x1) x 42 x 12.9

= 2979.97

Moles of HCl used in neutralization = x 20

= 0.04



1 mole of HCl neutralizes 1 mole of NaOH forming 1 mole of water.

0.04 moles of water are formed with evolution of 2979.9J of heat

1 mole of water is formed by evolution of

=

$$= 74497.5 \text{ Jmol}^{-1}$$

$$\text{Heat of neutralization} = - 74.4975 \text{ KJmol}^{-1}$$

Qn. 25cm³ of 2M sodium hydroxide at a temperature of 13.4⁰C were mixed with 50cm³ of 2M sulphuric acid at a temperature of 12.9⁰C. if the maximum temperature of the solution was 15.2⁰C. Calculate the heat of neutralization of sodium hydroxide by H₂SO₄ (SHC of soln = 4.2 Jg⁻¹K⁻¹, ρ = 1g/cc)

Solution

Total volume of solution

$$= 25 + 50$$

$$= 75\text{cm}^3$$

Average initial temperature =

$$= 13.15^{\circ}\text{C}$$

Change in temperature

$$= 15.2 - 13.15$$

$$= 2.05^{\circ}\text{C}$$

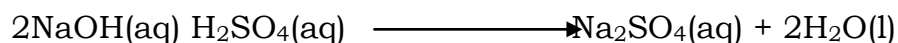
Heat given out in neutralizing of NaOH by H₂SO₄ = Heat gained by salt solution

$$= \text{mass} \times \text{SHC} \times \text{Temperature}$$

Of soln of soln rise

$$= (75 \times 1) \times 4.2 \times 2.05$$

$$= 645.75\text{J}$$



Moles of NaOH used = () = 0.05moles

Moles of H₂SO₄ reacted = () $\times \frac{1}{2}$

$$= 0.025 \text{ moles}$$

1 mole of H₂SO₄ reacts with 2 moles of NaOH forming 2 moles of H₂O

Moles of water formed

$$= 0.025 \times 2$$

$$= 0.05 \text{ moles}$$

0.05 moles of water are formed with evolution of 645.75J of heat

1 mole of water is produced with evolution of $\times 1) \text{ Jmol}^{-1} = 12915 \text{ Jmol}^{-1}$

=

=

$12.915 \text{ KJmol}^{-1}$

Heat of neutralization

$= -12.915 \text{ KJmol}^{-1}$

ENTHALPY OF FORMATION

The molar enthalpy of formation of a compound is the enthalpy change that occurs when 1 mole of a compound is formed from its elements in their normal physical states under standard conditions.

Compounds that are formed exothermically are more stable relative to their elements while as stable compared to their elements.

Not: It is important to specify the elements to which a compound is stable or unstable eg hydrogen peroxide is formed exothermically from its elements.



Hydrogen peroxide is expected to be very stable but it readily decomposes each in absence of a catalyst. This shows that hydrogen peroxide is stable relative to its elements but unstable relative to water and oxygen to which it readily decomposes.

Stability of compounds

The value of the standard enthalpy of formation of compounds gives a measure of their stability. All those that have positive values of enthalpy of formation are unstable eg



All those compounds that are formed exothermically are very stable eg



Stability can also be measured by using the entropy of the reaction.

The entropy of reaction is the measure of the degree of randomness, disorderliness, mixed upness of the reaction.

It is given the symbol S

If q is the heat absorbed by 1 mole of a substance only used to raise the entropy, then

$$DS = \text{ or }$$

$$q = TDS$$

In any reaction, the heat accompanying a reaction is called its enthalpy (h) of this only part is used to do useful work called free energy change (g) such as movement of piston in an engine whose a fuel is burnt, the remainder is turned into the entropy.

If the enthalpy of the reaction at the start H_1 is the free energy charge is G_1 . The difference $H_1 - H_2$ is H and the difference $G_1 - G_2$ is DG. The difference between DH and DG is called the entropy TDS.

$$\text{Ie } DH - DG = TDS$$

$$\text{Or } DG = DH - TDS$$

The reaction is possible if DG is negative at OK the entropy is 0 but an increase in temperature increases the entropy which becomes more positive since atoms begin to vibrate and the degree of randomness increases. An increase in temperature increases the entropy such that TDS becomes a larger negative value solution that free energy change becomes negative.

The degree of randomness can also be increased by dissolving the solute in water.

In the solid state the crystal lattice of the solutes has a regular arrangement of ions or atoms and their entropy is 0 (zero) which dissolved in water the ions go into solutions increasing their degree of randomness and hence increasing their entropy. This makes the value TDS a large negative making the free energy change negative.

This explains why readily soluble salts such as Sodium chloride, NaCl, sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$ and NaNO_3 have positive enthalpies of solution would

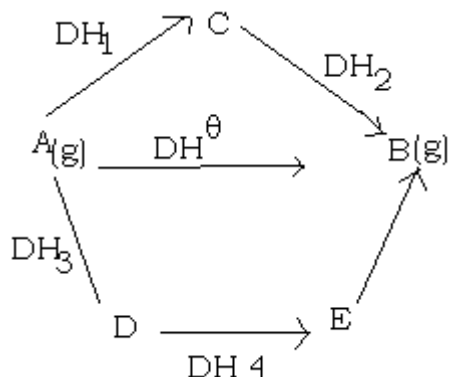
expect to be insoluble if enthalpy of solution would depend on ΔH alone but also depends on the entropy.

Measurements of standard heats of formation

The standard enthalpies of formation of many oxides such as carbon dioxide, magnesium oxide, copper oxide, calcium oxide etc can be measured directly using a bomb calorimeter because their enthalpies of formation are the same as the heats of combustion of the respective elements. However there are many compounds whose heat of formation can be measured directly eg heat of formation of carbon monoxide can not be detected using a bomb calorimeter because some carbon dioxide is also formed when carbon burns in a limited supply of air.

For such compounds their heats of formation are determined indirectly using Hess's law of constant summation.

It states in transforming reactants into products the total heat change is the same regardless of the path taken provided the initial and final states are the same eg in transforming A and B it can be done at once or it can be in stages.



By Hess's law

= +

OR

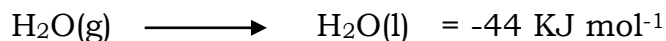
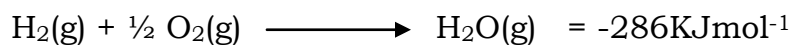
= + +

Example's using Hess's law

1. Consider the formation of gaseous water

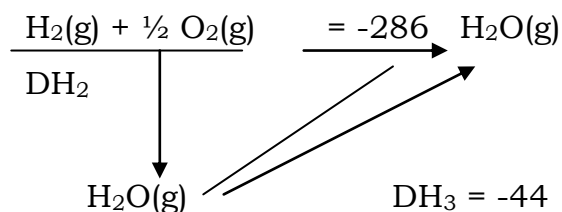


The value above can be obtained from



Solution

By Hess's law



By Hess's law

$$\text{DH}_1 = \text{DH}_2 + \text{DH}_3$$

$$-286 = \text{DH}_2 + -44$$

$$\text{DH}_2 = -242 \text{ KJ mol}^{-1}$$

The above diagram is called an energy cycle alternatively an energy level diagram can be used in using the energy level diagram all elements in their normal physical states are given a heat content of

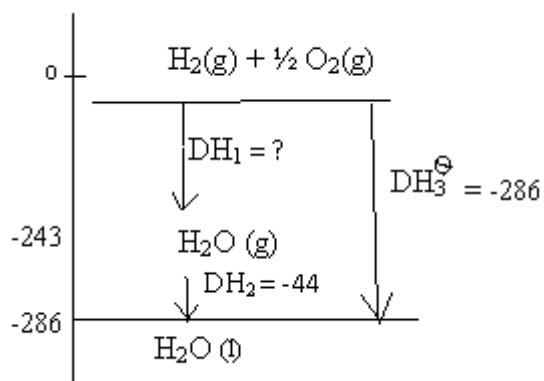
Questions

Define the term hydrogen bond

Giving examples, discuss the effects of hydrogen bonds on physical properties of some compounds.

Explain why Ice has a lower density than water

Energy level diagram



By Hess's law

$$DH_1 = DH_2 +$$

$$DH_1 = -286 - (-44)$$

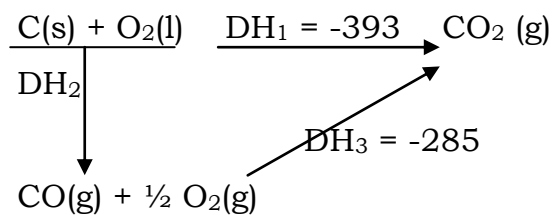
$$-242 \text{ KJ mol}^{-1}$$

Example 2

Use the following data to calculate the heat of formation of carbon monoxide.

Heat of combustion of CO = 285 KJ mol^{-1}

Heat of formation of CO_2 = -393 KJ mol^{-1}



$$= DH_2 + DH_3$$

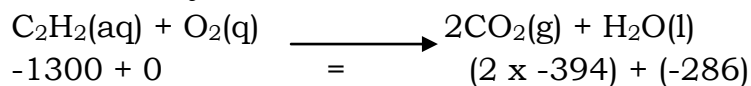
$$DH_2 = -DH_3$$

$$= -393 + 285$$

$$= -108 \text{ KJmol}^{-1}$$

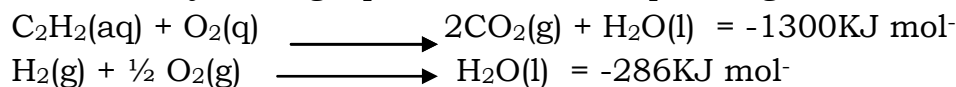
$$= 226 \text{ KJ mol}^{-1}$$

Alternatively



$$\begin{aligned} \text{of C}_2\text{H}_2 &= (\text{heat content of reactants}) - (\text{heat content of product}) \\ &= (-1300) - (-1074) \\ &= -226 \text{ KJ mol}^{-1} \end{aligned}$$

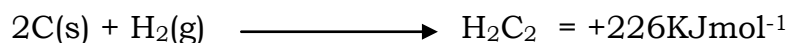
Alternatively writing equations and manipulating them



Required equation is

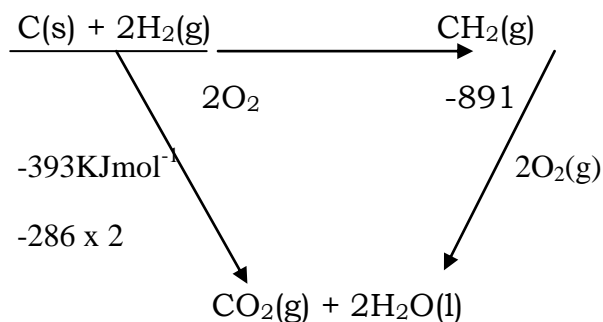


Multiplying (iii) x 2, then reverse eqn (i) and sum up all the eqns.



Example

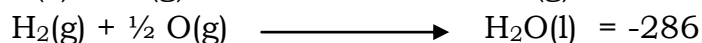
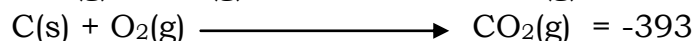
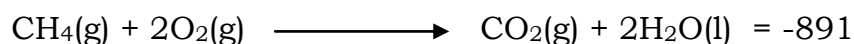
Calculate the enthalpy of formation of ethene given that its combustion is -891 KJ mol^{-1} and those in carbon and hydrogen are -286 KJ mol^{-1}



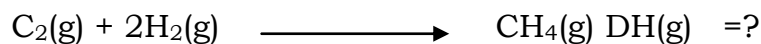
$$= (-393 + (-286 \times 2) + 891$$

$$= -74 \text{ KJ mol}^{-1}$$

Method 2

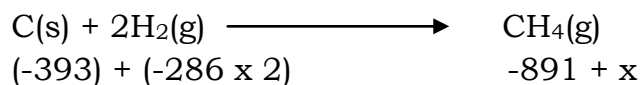


Required eqn



Multiplying (eqn) (iii) by 2 and reverse eqn (i) then sum up all equations.

Or



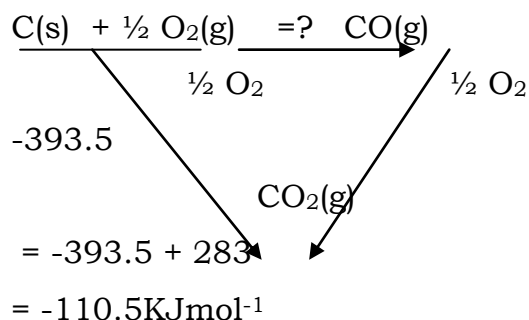
Introduce an unknown on the side where we want to get the energy term.

$$X = 891 + (-393) + (-286 \times 2)$$

$$X = -74 \text{KJmol}^{-1}$$

Example 4

Given the enthalpies of combustion of carbon graphite and carbon monoxide as -393.5 and -283 KJmol⁻¹ respectively. Calculate the enthalpy of formation of carbonmonoxide.



Or

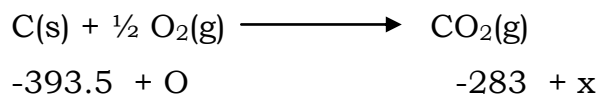


Reversing eqn (ii) and suming up both eqns

$$+286 + -393.5$$

$$= -110.5 \text{KJmol}^{-1}$$

Or



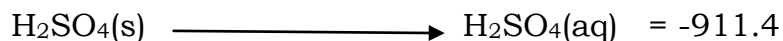
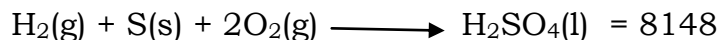
$$X - 283 = -393.5$$

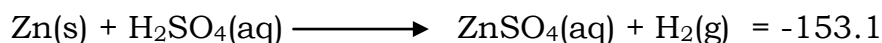
$$X = -393.5 + 283$$

$$X = -110.5 \text{KJmol}^{-1}$$

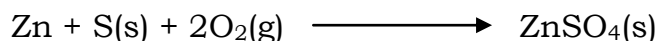
Question

The heat changes for some reactions are given below all in KJmol⁻¹





Calculate the heat of formation of hydrous zinc sulphate

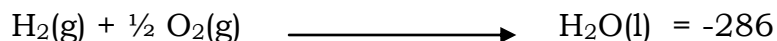
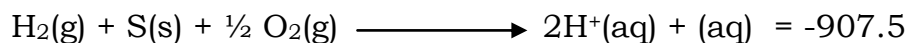
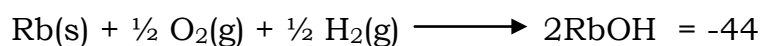
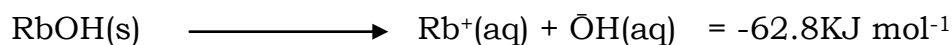


Reversing equation (ii) and summing up all the equations

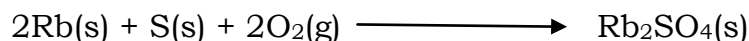
$$-814.8 + -911.4 + 81.9 + -153.1$$

$$= -1797.4 \text{ KJ mol}^{-1}$$

Given the data below, calculate the enthalpy of formation of Radium sulphate (Rb_2SO_4)



Solution

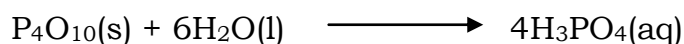


Multiplying eqn (iii) (vi) by 2 then reverse (viii) and (vi) gives

$$(-57.382) + (-62.8 \times 2) + -929.3 + (414 \times 2) + -907.5 + (286 \times 2)$$

$$= -2335 \text{ KJ mol}^{-1}$$

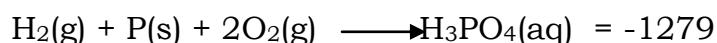
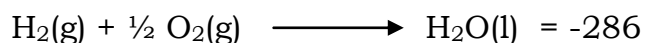
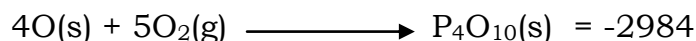
Calculate the enthalpy change for the reaction



Given that the DH_f of H_3PO_4 , P_4O_{10} , H_2O are $-1279 \text{ KJ mol}^{-1}$,

-2984 , -286 respectively

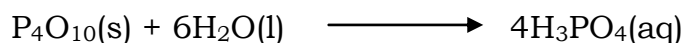
Solution



Multiply equation 11 by 6 eqn (iii) by 4 then reverse equation (i) and (ii) and sum up all equations.

$$+2984 + 286 \times 6 - 1279 \times 4$$

$$= -416 \text{ KJ mol}^{-1}$$

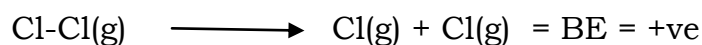


$$4 \times -12798 \text{ kJ}$$

BOND ENTHALPIES

This is defined as the energy change that occurs in forming a bond from free gaseous atoms or breaking the bond to form free gaseous atoms. When the bond is broken, heat is supplied but when the bond is formed heat is given out. The bond formed is a covalent bond and is from free gaseous atoms.

Bond enthalpy (energy) is the energy required to break 1 mole of a covalent bond forming free gaseous atoms eg



Or

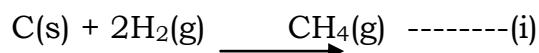
It is the energy given out by free gaseous atoms when they combine to form 1 mole of a covalent bond.

The free gaseous atoms possess potential energy of atomisation which is given out when they combine to form 1 mole of a covalent bond and this explains why bond enthalpies are negative when the bond is being formed.



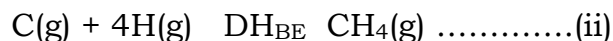
Calculating bond energies

Consider formation of methane

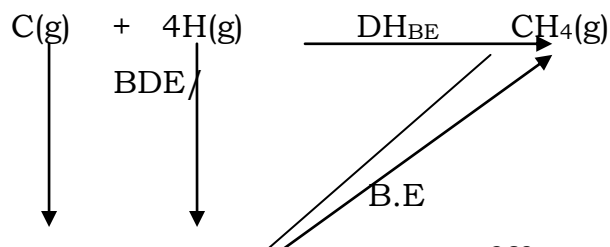


Alternatively

It can be formed from its gaseous atoms



Combining eqn (i) and (ii)





The BE is given out in forming 4 (C-H) bonds

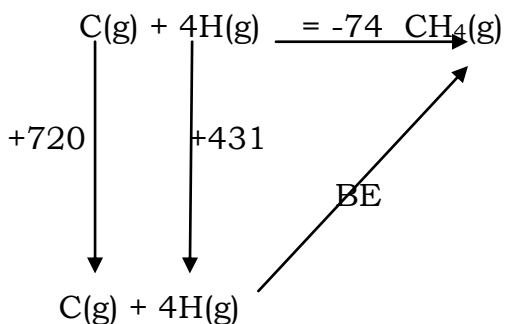
For every C-H bond, the energy given out is

Qn: use the following data to calculate the average C-H bond energy methane.

Enthalpy of atomisation of carbon = +720

Bond dissociation of hydrogen molecule = +431

Enthalpy of formation of $\text{CH}_4 = -74$

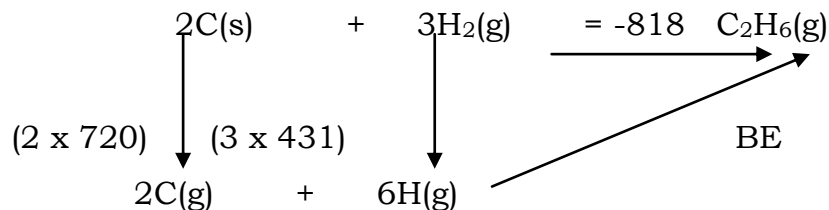


By Hess's law

$$-74 = +720 + (431 \times 4) + \text{BE}$$

$$\text{BE} = -1656 \text{ kJ mol}^{-1}$$

Qn: Determine the C to C bond energy in ethane assuming the C-H bond energy in ethane is the same as that in methane and the enthalpy of atomisation of carbon and hydrogen molecules are +720 and +431 kJ mol^{-1} .



$$-818 = (2 \times 720) + (3 \times 431) + \text{BE}$$

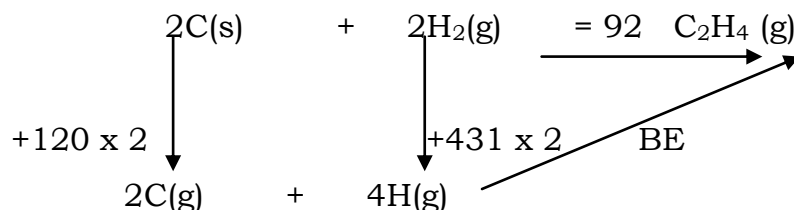
$$\text{BE} = -2821 \text{ kJ mol}^{-1}$$

$$-2821 = 6(\text{C-H}) + 1(\text{C-C})$$

$$-2821 = (6 \times -414) + (\text{C-C})$$

$$(\text{C-C}) = -337 \text{ kJ mol}^{-1}$$

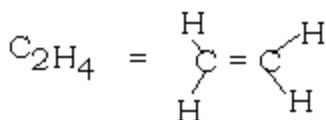
Similar calculation can be used to determine the bond enthalpy of carbon to carbon double bond and $\text{C}=\text{C}$ eg in ethene given the enthalpy of formation of ethene as -92 kJ mol^{-1}



By Hess's law

$$-92 = (720 \times 2) + (431 \times 2) + \text{BE}$$

$$\text{BE} = -2394 \text{ kJ mol}^{-1}$$

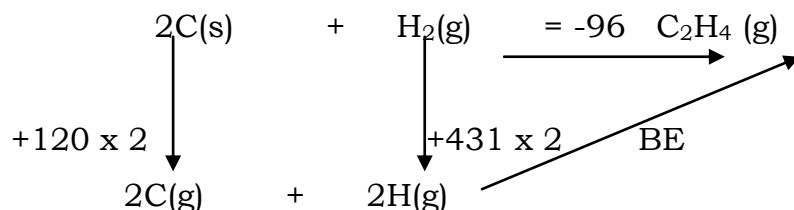


$$4(5-H) + (\text{C}=\text{C}) = -2394$$

$$4x - 44 + \text{C} = \text{C} = -2394$$

$$(\text{C} = \text{C}) = -738 \text{ kJ mol}^{-1}$$

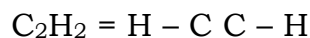
For C C as in ethyne given the enthalpy of formation of ethyne of formation of ethyne as -96 kJ mol^{-1}



By Hess's law

$$-96 = (720 \times 2) + (431 \times 1) + \text{BE}$$

$$\text{BE} = -1967 \text{ kJ mol}^{-1}$$



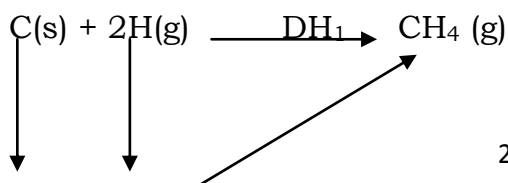
$$-1967 = 2(\text{C-H}) + 1(\text{CC})$$

$$-1967 = 2(-414) + (\text{CC})$$

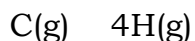
$$(\text{CC}) = -1139 \text{ kJ mol}^{-1}$$

(a) What is meant by the term bond energy.

(b) The figure 1 nbelow represents energy diagram for the formation of methane.



DH₃ DH₂ DH₄



Identify the following energy changes DH₃ DH₂ DH₄

Given that DH₁ = -75 KJmol⁻¹ DH₂ = +218KJ mol⁻¹ of hydrogen atom, DH₃ = +715KJ mol⁻¹. Calculate the

- (i) Value of DH₄
- (ii) Bond energy for carbon hydrogen bond

Solution

(b) DH₁ enthalpy of formation of 1 mole of methane

DH₂ Atomisation energy of hydrogen atoms (bond desociation energy of hydrogen molecule)

DH₃ Atomisation energy of carbon atoms

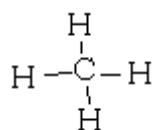
By Hess's law

$$\text{DH}_1 = \text{DH}_2 + \text{DH}_3 + \text{DH}_4$$

$$\text{DH}_4 = \text{DH}_1 - \text{DH}_2 - \text{DH}_3$$

$$= -75 - (218 \times 4) - 715$$

$$\text{DH}_4 = -1662 \text{ KJ mol}^{-1}$$



$$4(\text{C-H}) = -166.2$$

$$\text{C-H} =$$

$$= -415.5 \text{ KJmol}^{-1}$$

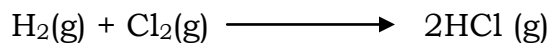
Calculating heats of reaction from bond energies atomisation energies

Given the following data

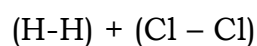
Bond	Bond energies/ KJmol ⁻¹
Cl – Cl	242
H-H	436

H-Cl	431
O=O	496
C-H	414
C=C	345
O-H	463
C≡C	616
C-Cl	315
C=O	605

Calculate the enthalpy change for the following reactions



Bonds broken



$$436 + 242 = +678 \text{ KJmol}^{-1} \text{ (Bond broken +) (form bond -1)}$$

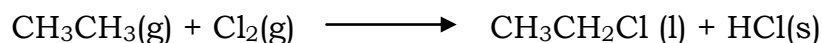
Bonds formed

$$2(\text{H}-\text{Cl}) = 2 \times 431$$

$$= -862 \text{ KJmol}^{-1}$$

$$\text{Heat of reaction} = +678 - 862$$

$$= -184 \text{ KJmol}^{-1}$$



Bond broken

$$= 1(\text{C}-\text{H}) + (\text{Cl}-\text{Cl})$$

$$= (414 \times 1) + (242 \times 1)$$

$$= +656 \text{ KJmol}^{-1} \text{ (breaking bond+)}$$

Bonds formed

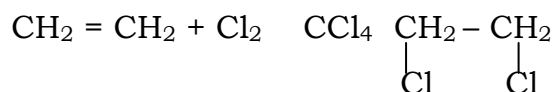
$$1(\text{C}-\text{Cl}) + (\text{H}-\text{Cl})$$

$$= 315 \times 1 + (431 \times 1)$$

$$= -746 \text{ KJmol}^{-1}$$

$$\text{Heat of reaction} = -746 + 656$$

$$= -90 \text{ KJmol}^{-1}$$



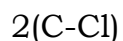
Bonds broken

$$1(\text{C}-\text{C}) + 1(\text{Cl}-\text{Cl})$$

$$(348 \times 1) + (242 \times 1)$$

$$= +590 \text{ KJ mol}^{-1}$$

Bonds formed



$$= 2 \times 315$$

$$= -630 \text{ KJmol}^{-1}$$

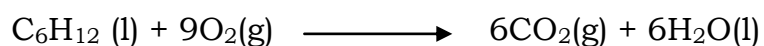
$$\text{Heat of reaction} = -630 + 590$$

$$= -40 \text{ KJmol}^{-1}$$

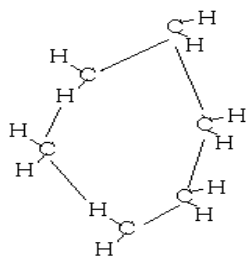
Question

Calculate the heat of combustion of cyclohexane using the above bond energies.

Soln



Bonds broken



$$6(\text{C-C}) + 12(\text{C-H}) + 9(\text{O=O})$$

$$(348 \times 6) + 414 \times 12 + (496 \times 9)$$

$$= +11520 \text{ KJmol}^{-1}$$

Bonds formed



$$2 \times 6 (\text{C}=\text{O}) \qquad 2 \times 6 (\text{O-H})$$

$$12 (\text{C}=\text{O}) \quad + \quad 12(\text{H-O})$$

$$= (12 \times 605) + (12 \times 463)$$

$$= -12816 \text{ KJ mol}^{-1}$$

$$\text{Heat of reaction} = +11520 + -12816$$

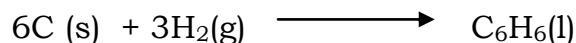
$$= -1296 \text{ KJmol}^{-1}$$

Question

Calculate the heat of formation of benzene from the above data.

Given that the enthalpy of atomisation of carbon

= +720 KJmol per atom of carbon



Bonds broken

Atomisation energy

= 3(H-H) + 6C(g)

(3 x 436) + (6x720)

= +5628 KJmol⁻¹

Bonds formed

6(C-H) + 3(C-C) + 3(CC)

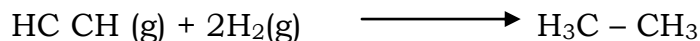
(6 x 414) + (3 x 348) + (3 x 615)

= -5373 KJmol⁻¹

Heat of reaction = +5628 – 5373

= +255KJmol⁻¹

Calculate the heat of hydrogenation of ethyne to ethane using the data



Bonds broken

(C=C) + 2(H-H)

(615 x 1) + (2 x 431)

= +1487 KJmol⁻¹

Bonds formed

4(C-H)

4 x 414

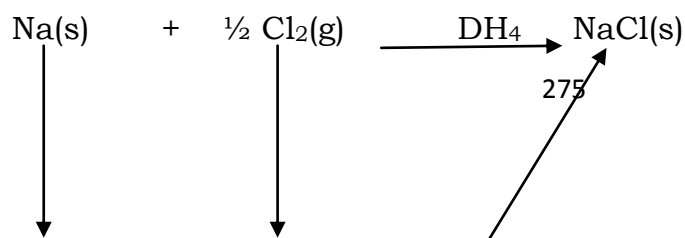
= -1656 KJmol⁻¹

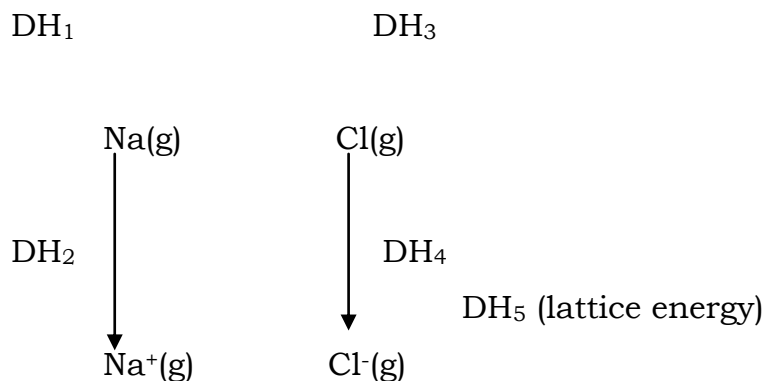
Heat of hydrogenation = +1487 KJmol⁻¹ – 1656 KJmol⁻¹

= 169 KJmol⁻¹

BORN HARBER CYCLES

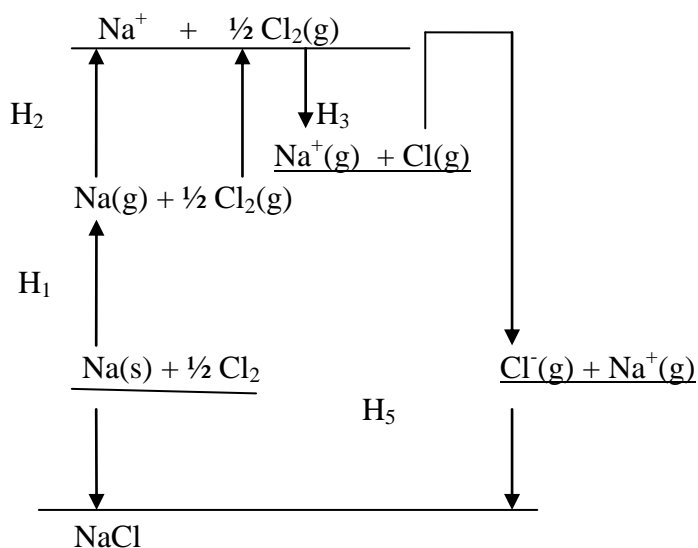
Energy cycle





Born harber cycle is a complete energy cycle linking many enery terms and can be used to determine the latice energyof an ionic crystal which can not be determined experimentally it can be represented as either anenergy cycle or an energy level diagram.

Energy level diagram



To construct the energy level diagram, enthalpy changes that are negative are idicated by an arrow pointint downwards while those that are positive are idicated by an arrow pointing upwards

DH_1 is called the enthalpy of atomisation and is defined as the heat required to form 1 mole of gaseous atoms from the solid metal under standard conditions.

DH₂ is called ionisation energy and is defined as the energy required to remove 1 mole of an electron from gaseous atoms forming 1 mole of unipositive cations.

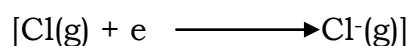
DH₃ is bond dissociation energy for chlorine molecules defined as the energy required to break 1 mole of a covalent bond into free gaseous atoms.

Or it is the atomisation energy of chlorine atoms which is defined as the energy required to form 1 mole of gaseous atoms from gaseous molecules.

DH₄ is called electronic affinity and is the energy given out when 1 mole of an electron is added to gaseous atoms forming negatively charged ions.

The first electron affinity is negative but the second is positive because after addition of the first (1st) electron the atom acquires a negative charge which repels the second electron.

DH₅ is called lattice energy defined as the potential energy possessed by free gaseous ions which is given out when they combine to form 1 mole of an ionic crystal in the solid state.



Or

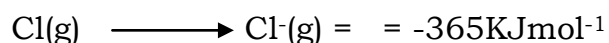
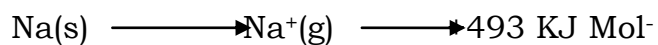
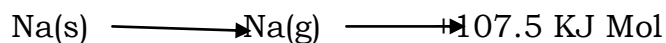
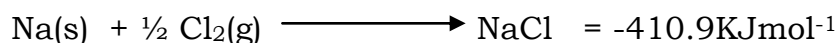
It is the energy required to split 1 mole of an ionic crystal in the solid state into free gaseous ions.

By Hess's law, lattice energy can be obtained

$$= \text{DH}_1 + \text{DH}_2 + \text{DH}_3 + \text{DH}_4 + \text{DH}_5$$

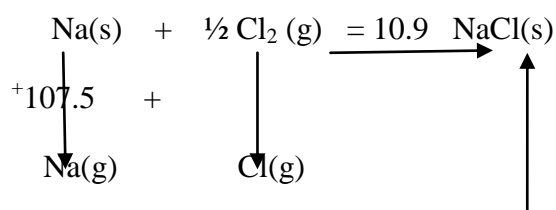
$$\text{DH}_5 = -(\text{DH}_1 + \text{DH}_4 + \text{DH}_3 + \text{DH}_2)$$

Qn: Using the following information to work out the lattice energy of sodium chloride.



Solution

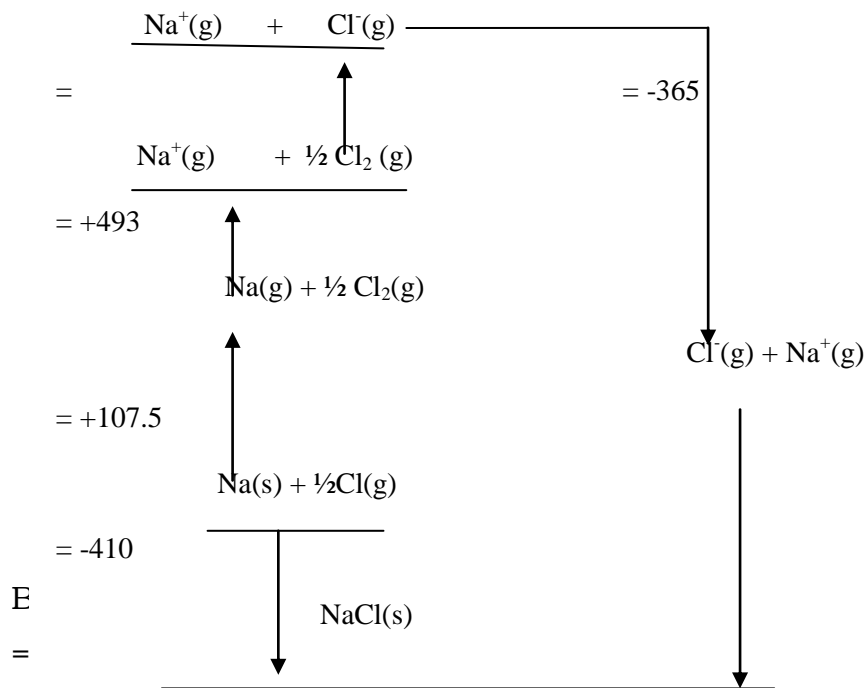
Using an energy cycle



By Hess's law

$$\begin{aligned}
 &= + + + + \text{lattice} \\
 &= 40.9 - (102.5 + 493 + + -365) \\
 &= 775.9 - 716.5 \\
 &= +59.4 \text{ KJ mol}
 \end{aligned}$$

Using an energy level diagram



Use the following data construct a energy cycle and use it to calculate the value of lattice energy of copper (ii) oxide.

Atomisation energy of copper = +339

1st ionisation energy of copper = +716

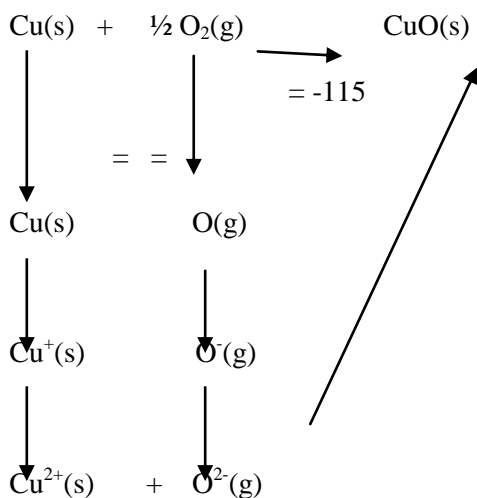
Atomisation energy of oxygen molecule = +245

2nd electron affinity of oxygen = +791

Enthalpy of formation $\Delta_f H^\circ = -115$

Copper (ii) oxide

3rd electron affinity of oxygen = -141

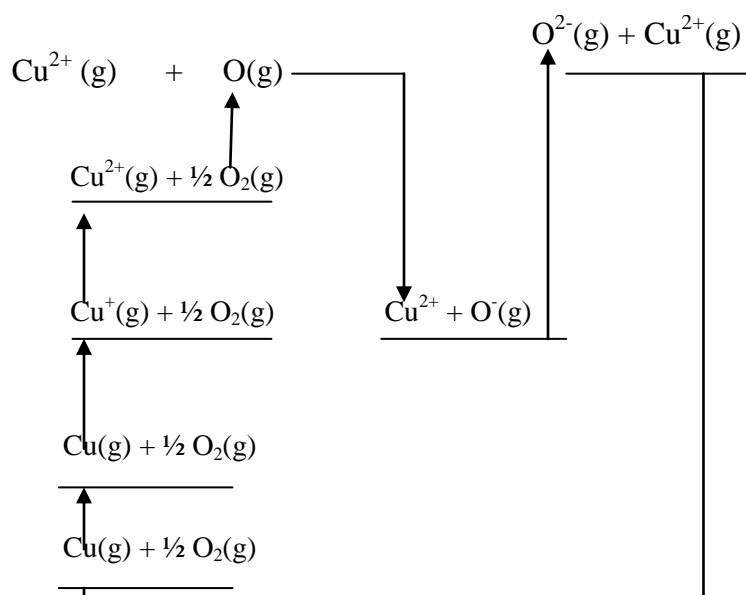


By Hess's law

$\Delta_f H^\circ = -(\Delta_{\text{ion}} + \Delta_{\text{ion}} + \Delta_{\text{EA}} + \Delta_{\text{EA}})$

$(339 + 716 + 791 + 1225 - 141)$

$= -1942.5 \text{ kJ mol}^{-1}$



$$= - (+ + + + +)$$

$$-115-[339+746+1960++791 + -141$$

Use the thermochemical data below to determine the lattice energy of copper (ii) chloride)

$$\text{CuCl}_2 = -220 \text{ KJmol}^{-1}$$

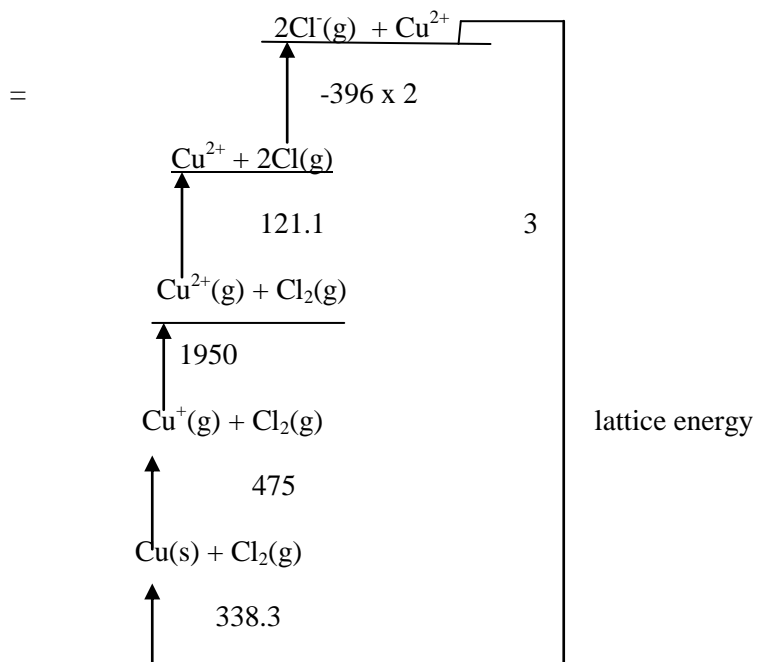
$$\text{Cu} = +338.3 \text{ KJmol}^{-1}$$

$$1^{\text{st}} \text{ IECu} = +475 \text{ KJmol}^{-1}$$

$$2^{\text{nd}} \text{ F.E Cu} = +1958 \text{ KJmol}^{-1}$$

$$1^{\text{st}} \text{ EA of Cl} = -346 \text{ KJmol}^{-1}$$

Bond dissociation energy of chlorine molecule = 121.1 KJmol



$$= - (+ + + +)D$$

$$= -220 = (338.3 + 475 + + -346 + 121.1)$$

Factors affecting the magnitude of lattice energy

Lattice energy

The minimum energy required to break 1 mole of an ionic crystal into free gaseous ions. Lattice energy is influenced by the following factors.

1. Charge on each ion (ionic charge)

Lattice energy increases with increase in ionic charge because increased ionic charge decreases the electrostatic attraction between oppositely charged ions.

The force between a pair of ions of charge Q^+ and Q^- is given by

$$F = Q^+Q^-$$

$$F = 1$$

+

When the charge on the ions decreases, the lattice energy is reduced due to reduced electrostatic attraction between the oppositely charged ions. This explains why sodium chloride (Na^+Cl^-) has a lower lattice energy than calcium oxide ($Ca^{2+}O^{2-}$).

2. Ionic radius

Lattice energy increases with a decrease in ionic radius because charge density increases in ionic radius.

The higher the charge density the higher is the electrostatic attraction between oppositely charged ions. Therefore the force between two oppositely charged ions is given as

$$F =$$

Therefore the lattice energy will increase as the distance ($r^+ + r^-$) between the ions decreases. Lattice energies are therefore higher for compounds of small group II cations with small than larger group II cations with larger anions by calcium fluoride has a higher lattice energy than Barium Chloride ($\text{Ba}^{2+}\text{Cl}^-$).

Lattice energy decreases in magnitude from lithium Fluoride (LiF) to Calcium Fluoride since in both cases the distance between the ions is increasing.

The extent to which the bonding deviates from fully ionic mode.

For example aluminum chloride has a lower lattice enthalpy than sodium chloride because the degree of covalency is higher in Aluminium Chloride.

Applying lattice energy

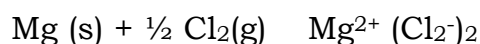
1. Determining the stoichiometry of salts

Eg Magnesium Chloride is MgCl_2 and not MgCl_6

2. Solubility of ionic compounds
3. Thermo decomposition of salts

Stoichiometry of salts

Stoichiometry refers to the ratio in which atoms react. Consider the Born-Haber cycles $\text{Mg}^{2+}\text{Cl}^-$



Sublimation energy of magnesium = 150 KJ/mol

1st I.E of magnesium = +736

2nd IE of magnesium = +1450 KJmol⁻¹

Bond dissociation energy per = +242

Moles of chloride

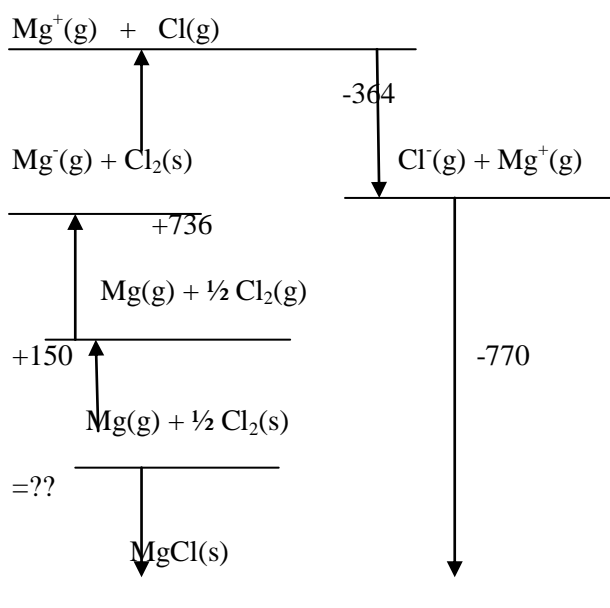
EA of chlorine = -364

Lattice energy of MgCl_2 = -770 KJ/Mol

Lattice energy of $\text{Mg}^{2+}\text{Cl}^-)_2$ = -2493

From the above data MgCl_2 has a more negative lattice energy and therefore stable.

Alternatively the values of enthalpies of formation of p/gCl and MgCl_2 can be determined using energy level diagram



$$= 150 + + -364 - 770 + 736$$

$$= 127 \text{ KJ mol}^{-1}$$

MgCl_2 is formed more exothermically and is more stable

SOLUBILITY OF IONIC COMPOUNDS

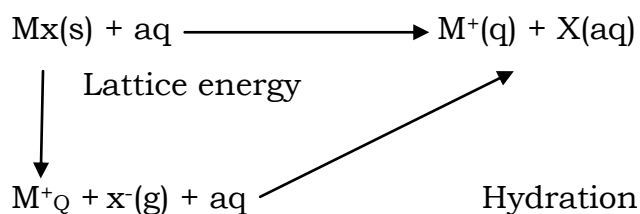
For an ionic compound to dissolve the enthalpy change depends upon 2 factors
ie

- Lattice energy of the solid
- Hydration enthalpy of the ions

Hydration energy is defined as the heat change per mole for the hydration of the gaseous ion with energy water molecules until there is further heat change on dilution.

For a soluble to be soluble, lattice enthalpy should be less than hydration energy but for a sparingly soluble or insoluble salt lattice enthalpy is higher than hydration energy.

For an ionic solute MX_2 its solubility is shown by the energy cycle below.



By Hess's law

solution = lattice energy + hydration energy

The hydration of ions occurs because the polar water molecules are attracted to the charge on the ion.

The extent of hydration depends on the charge density i.e. its charge and the smaller are less the more isothermally the hydration enthalpy.

Solubility trends for group II sulphates and hydroxides

(a) Sulphates

The solubility of sulphate depends on charge on the cation since that of the anion remains constant and the lattice energy of the compound.

As you move down the group the size of the cation increases keeping the anion radius constant. This causes a decrease in both lattice energy and hydration energy.

The hydration enthalpy of the cation has the most important effect since the anion is large and does not change, therefore lattice enthalpy does not change significantly as the cation radius increases. However the hydration energy of the cation falls significantly as the cation gets larger. Therefore as you move down the group hydration energy decreases more rapidly than lattice energy causing a decrease in solubility.

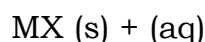
Hydroxide

For the hydroxides lattice energy is more important because the hydrogen ion is small and the sum of the radius of the cation and anion is influenced on the ionic size. The lattice enthalpy decreases more rapidly as the cation gets larger. This causes an increase in the solubility of hydroxides.

Thermostability of enthalpy of solution

Is the heat charge that occur when 1 mole of an ionic compound dissolves in water to form an infinitely dilute solution with no further heat charge.

Enthalpy of solution of an ionic salts depends on lattice energy and hydration energy can easily be overcome by the hydration energy



Experimental determination of Enthalpy of solution

A known volume of water say $V\text{cm}^3$ is put into a plastic beaker and its temperature noted.

A known mass of the ionic salt whose enthalpy of solution being investigated is added.

The mixture is stirred continuously using the thermometer until a constant temperature reached.

The final temperature is noted at steady state

Treatment of salts

Let

Volume water be $V\text{cm}^3$

Mass of solution be $a\text{ g}$

Initial temperature of water be $T_1\text{ }^\circ\text{C}$

Final temperature of solution be $T_2\text{ }^\circ\text{C}$

Assuming heat capacity of the solution to be $4.2\text{ Jg}^{-1}\text{K}^{-1}$

Density of solution is 1g/cm^3

Neglecting the heat capacity of the beaker and the thermometer.

Then volume of solution = $(V + a)\text{cm}^3$

Mass of the solution = $(V + a) \times 1 = (V + a)\text{g}$

Heat change for the solubility of $a\text{ g}$

= mass of solution \times SHC \times Temperature

$$= (V + a) \times 4.2 \times (T_2 - T_1)$$

$$\text{Heat change for Mrg of solute} = x \text{ Mr Jmol}^{-1}$$

$$= \text{KJ mol}^{-1}$$

Example

15.95g of anhydrous copper sulphate were dissolved in 1 litre of water. The temperature of water was 17°C and that of solution 18.5°C. What is the heat of solution of anhydrous copper sulphate (density of solution 1g/cc and specific heat capacity of solution is 9.2 Jg⁻¹K⁻¹)

Total volume of solution = Volume of water + Mass of solute

$$= (1000 + 15.95) \text{ cm}^3$$

$$1015.95 \text{ cm}^3$$

Mass of solution 1015.95 x 1 (volume x density)

$$= 1015.95 \text{ g}$$

Enthalpy of solution of

$$\begin{array}{l} 15.95 \text{ g of solute} \\ \text{(anhydrous copper (ii) sulphate)} \end{array} = \begin{array}{l} \text{Mass of X SCH of X Temperature} \\ \text{solution solution change} \end{array}$$

$$= 1015.95 \times 4.2 \times (18.5 - 17)$$

$$= 1015.95 \times 4.2 \times 1.5$$

$$= 6400.85$$

$$\text{CuSO}_4 = (64 \times 1) + (32 \times 1) + (16 \times 4)$$

$$= 160 \text{ g}$$

Enthalpy of solution for 1 mole of anhydrous CuSO₄

$$= \frac{6400.85}{160}$$

$$= 40.0053 \text{ KJ mol}^{-1}$$

$$= 40.0053 \text{ KJ mol}^{-1}$$

Thermo-stability of salts

The larger the lattice energy the more thermally stable the compound is and can not easily dissociated.

The compound is more likely to be is and cannot easily be dissociated. The compound is more likely to be decomposed in heating of the cation polarises the Anion lowering the lattice. This is possible with cations having a high

change density group II salts decompose more readily than group I salts and BeCO_2 is thermally less stable.

HEAT OF COMBUSTION AND MOLECULAR STRUCTURES

The heats of combustion of organic compounds sharing the same molecular structure are the same for example the heats of combustion of normal butane.

$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3)$ and methyl propane CH_3CHCH_3 are



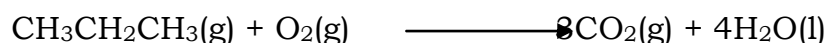
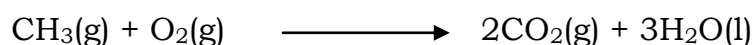
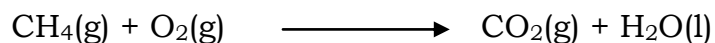
2877 and 2870 KJmol^{-1} respectively. The close similarity in there values is because both isomers have the same number of moles of carbon atoms and hydrogen atoms and the same number of carbon – carbon and carbon hydrogen bonds. This shows that each kind of bond makes anxed contribution to the total enthalpy change. This idea is confirmed when heats of combustion of simple alkanes are examined.

Alkane	Heat of combustion	Change in heats of combustion
CH_4	-890	-670
CH_3CH_3	-1560	-670
$\text{CH}_3\text{CH}_2\text{CH}_3$	-7220	-660
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	-2872	-652

In moving from one member to the next, there is an almost fixed increment in the amount of heat of combustion because of addition of a methylene (CH_2) group which has a fixed number of bonds. Each bond makes a fixed contribution to the energy content of a substance.

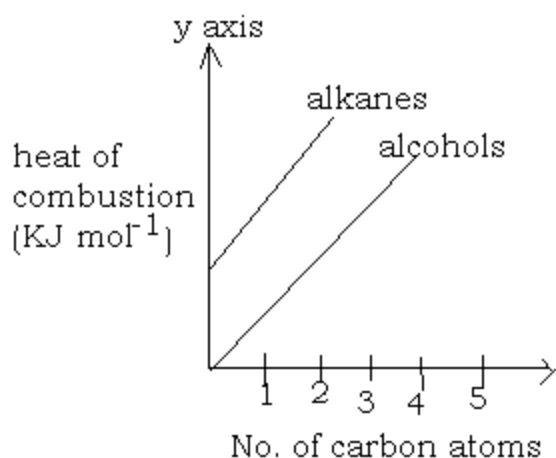
During combustion bonds are broken between the atoms of the alkane and new bonds are formed in carbondioxide and water. The alkane molecules gets larger more energy is required to break the bark between atoms and more energy is released when CO_2 and H_2O are formed.

In burning each alkans molecule, 1 molecule of CO_2 and water is closed more than the previous alkane.



The heat of combustion gets larger by constant amount as you progress along homologous series not only for alkanes but other organic compounds.

The idea is confirmed by plotting heats of combustion against number of carbon atoms for alkanes and alcohols.



The graph for alcohols passes through the origin while that of alkanes has the intercept along the y-axis for alcohol, using the general formular.

$C_nH_{2n+1}OH$ of $n = 0$, remaining molecule is liquid water. Water does not burn in air so its enthalpy of combustion is 0.

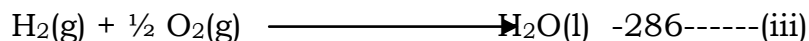
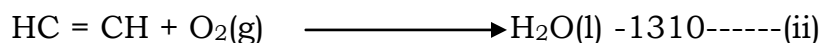
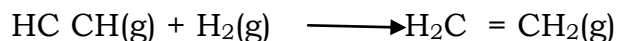
For alkanes using the general formula C_nH_{n+2} if n is 0 the remaining molecule is hydrogen gas. Hydrogen readily burns in air giving out molecule giving out 286 KJmol of heat corresponding to the intercept along the y – axis.

Qn: Calculate the heat of hydrogen of Ethyne to Ethene from the following data.

of ethene = $-1393 \text{ KJ mol}^{-1}$

of ethyne = $-1310 \text{ KJ mol}^{-1}$

of $H_2O(l)$ = -286 KJ mol^{-1}



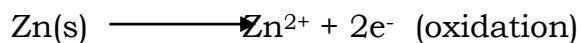
ELECTRO – CHEMISTRY

Electro chemical cells

An electrochemical cell is a device which allows a chemical reaction to proceed in such a way that the flow of electrons is produced. An electrochemical cell has two half cells with one involving an oxidation reaction and another involving a reduction reaction. A redox reaction involves simultaneous loss and gain of electrons. A reducing agent loses electrons. A reducing agent loses electrons while an oxidizing agent gains electrons.

Consider the zinc and copper half cell reactions, zinc involves electron loss while copper gains electrons. The flow of electrons from the zinc half cell to the copper half cell causes a current to flow in the opposite direction.

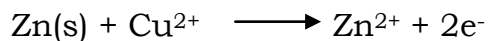
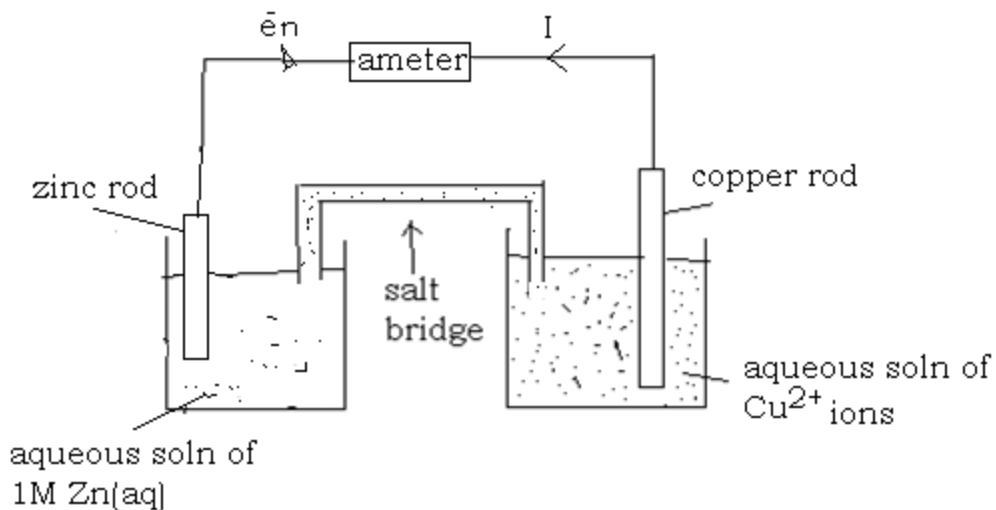
The half cell reaction



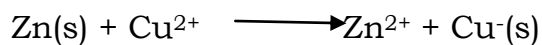
Copper half cell reaction



A cell diagram can be used to represent the above



Write the equation for the reaction

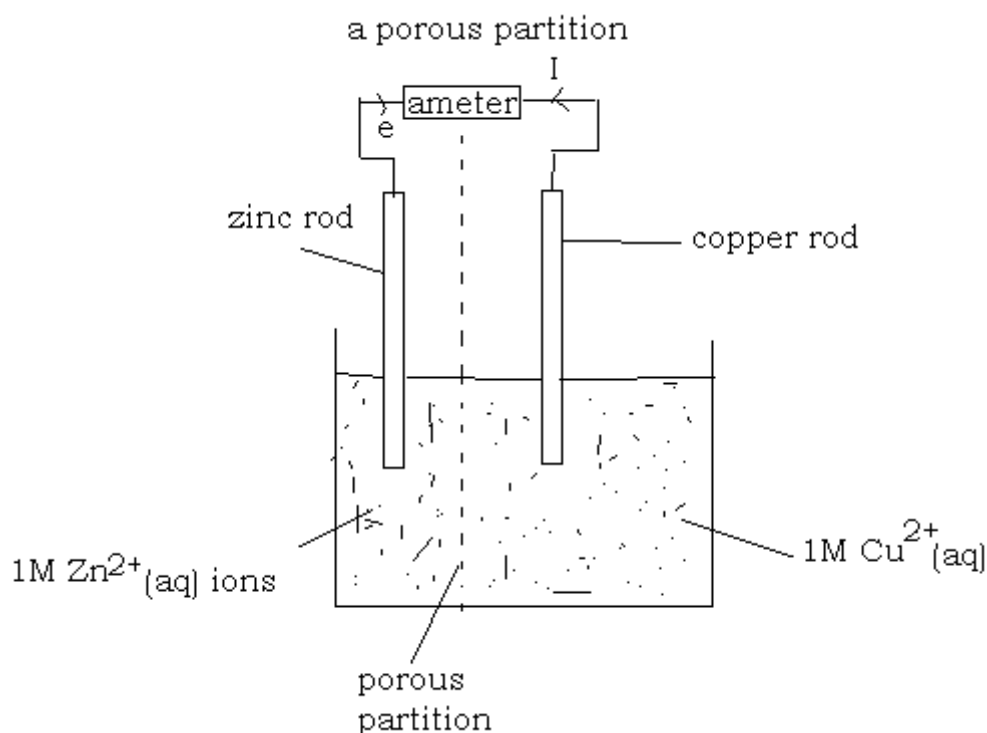


Electrons flow from the zinc cell to the copper half cell through the wire the external circuit this creates a current in the wire which shows in the opposite direction and measured using an Ammeter. This current can be used to do some work like lighting bulbs.

The redox reaction can be proceeded.....are in isolation so the salt bridge completes the internal circuit and is made up of an electrolyte such potassium chloride or potassium nitrate which does not interfere with the reaction.

The simplest salt bridge can be a strip of a filter paper soaked in other an aqueous solution of potassium nitrate in KCl

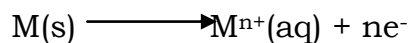
Alternatively a porous partition can be used to separate the two solutions instead of the salt bridge.



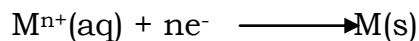
Electrode potential

When a metal rod is dipped into a solution of its ions thing may happen
The metal and may use electrons to form ion which point.

Solution

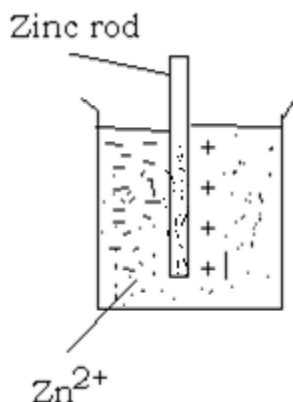


The ions in solution may gain electrons and are deposited as metal on the rod.



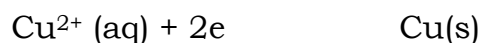
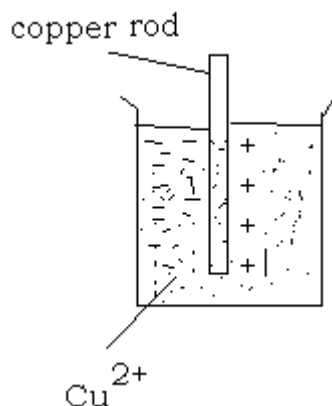
Whether the metal loses electrons to go into solutiongaining electrons to deposit as metal depends on the ele.....

Consider the zinc and copper electrodes dipping in their aqueous solutions of concentration 1 molar. Zinc being electropositive goes into solution forming zinc ions. The tendency of the zinc rod to lose electrons and its ions to go into solution is called its electrolytic solution pressure. The zinc rod requires a negative charge relative to the outside.



An electric double layer is created called electric pressure difference between the inside of the electrode and the solution. This is called the electrode potential.

Copper being more electronegative, the copper ions solution accepts electrons depositing as copper metal the tendency for ions to deposit on the metal from the solution is called deposition pressure. When Cu^{2+} ions deposit on the metal it acquires a positive charge relative to the solution.

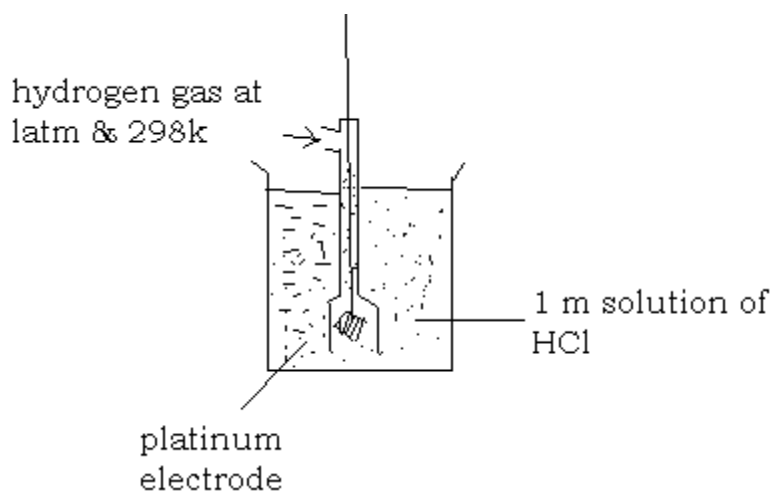


Similarly an electric double layer is created between the electrode and the solution giving the electric pressure difference called an electrode potential.

Electrode potential is therefore defined as the potential of an electrode which is dipped in a solution of its ions.

Measurement of standard electrode potential

In order to measure the electrode potential of an electrode dipped in a solution of its ions, the standard hydrogen electrode is used. It consists of hydrogen gas bubbling over an inert electrode dipped in a solution of an acid preferably hydrochloric acid platinum electrode at a pressure of 1 atmosphere and a temperature.



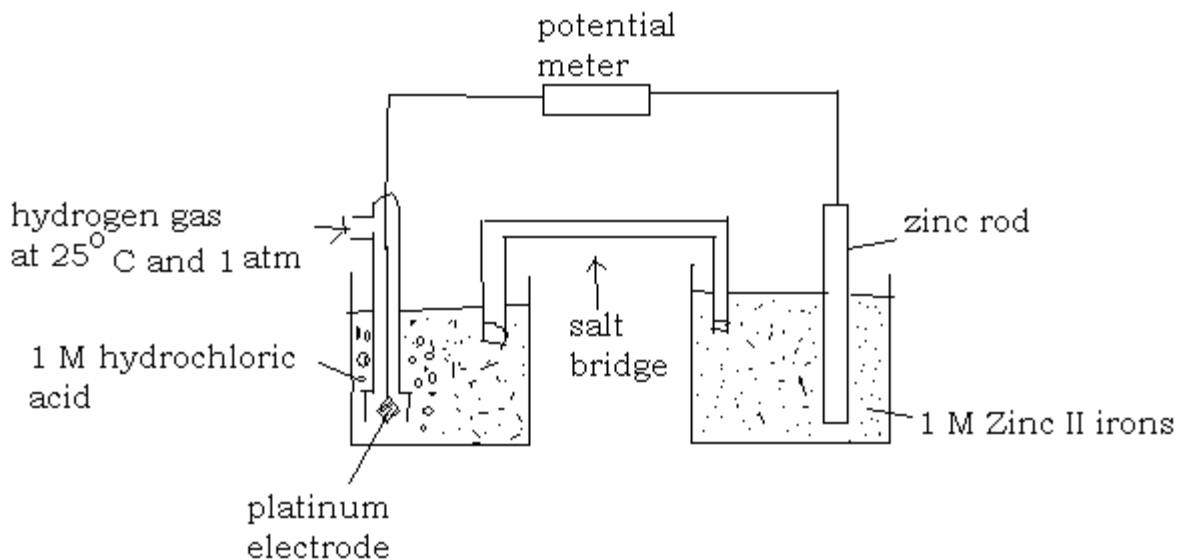
On the platinum electrode



This gives the standard hydrogen electrode (SHE) half cell reaction.

Under standard conditions of temperature 298K, pressure 1 atm and concn of acid 1M, the electrode potential of the hydrogen half cell is 0.00v

Measuring standard electrode potential of zinc.



The zinc half cell is constructed from a zinc rod dipped into a solution of zinc II ions of concentration 1M as shown above. The standard hydrogen electrode is constructed by bubbling pure hydrogen gas at a temperature of 298K and a pressure of 1 atm over a platinum electrode dipping in a solution of HCl bridge. The potential difference between the two half cells, the potential difference between the two zinc electrode since the SHE is given a potential of 0.00v under standard conditions.

The standard electrode potential of a metal is therefore defined as the potential difference between the SHE and a metal electrode dipping in solution of the ions of concn 1 M of temp 298k and a pressure of atmosphere.

If these conditions are satisfied the of a standard electrode potential of a metal is given a symbol . The superscript means all standard conditions are satisfied.

Factors affecting the magnitude of electrons potential of a metal

Sublimation energy of a metal

This is the energy required to converted 1 mole of a metal in a solid state into gaseous atoms eg

Zn(a) Zn(g)

Metals with low sublimation energy have high value of electrode potentials. Group I metals are soft and can easily be cut through by knife so they have low sublimation energies and high values of electrode potentials.

Ionization energy of the metal (IE)

This is the energy required to detach an electron from gaseous atoms forming gaseous ions. The lower the value of IE, the higher is the magnitude of electrode potential. Therefore group I metals have low ionization energies and high electrode potentials.

Hydration energy of the metal ion

$M^{2+}(s) + aq \rightarrow M^{2+}(aq)$

This is the energy given out when a gaseous ion is surrounded by a sphere of an infinite number of water molecules. The higher the hydration energy, the greater is the value of the electrode potential.

Concentration of the solution

At low concn the deposition pressure is low reducing the value of electrode potential but an increase in concn causes a corresponding increase in the deposition pressure hence higher value of electrode potential. Under standard conditions the concentration of all solutions must be 1 M.

Temperature

For standard electrode potential temperature should be 298K.

Pressure

The pressure should be 1 atmosphere under standard conditions.

The convention used are those recommended by the IUPAC

A cell made up of two half cells

The emf of the cell is given by

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}}$$

The standard hydrogen electrode (SHE) is defined to have an electrode potential of 0.00V

A standard electrode potential is measured with a SHE as the left hand cell.

The negative electrode shall be the left and the positive the right therefore electrons flow from the left to the right.

If both potentials are positive the less positive is the left and if both are negative the more negative is the left.

Question

Given the following half cell reactions



Calculate the emf of the cell

$$\text{cell} = \text{LHS}$$

$$= 0.80 - 0.34$$

$$= +0.46\text{v}$$

Given the following reaction potentials, calculate the

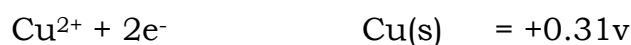


$$\text{cell} = \text{LHS}$$

$$= -1.66 - (-2.37)$$

$$= +0.71\text{v}$$

Using the Daniel half cell reactions



Calculate the cell

$$\text{cell} = \text{LHS}$$

$$= 0.34 - (-0.76)$$

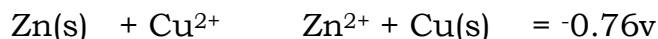
$$= +1.10\text{V}$$

Combining half cells

Consider the Daniel cell made up of copper and zinc half cells



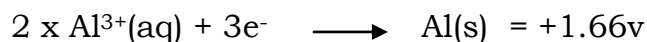
In combining the two half cells the equation with a negative potential is reversed and an overall equation obtained with a corresponding emf of the cell.



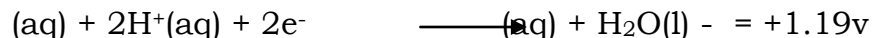
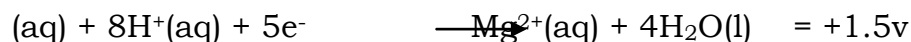
If both half cell reactions are having negative potentials. The more one with a more negative potential is reversed eg the galvanic cell based on the half reactions.



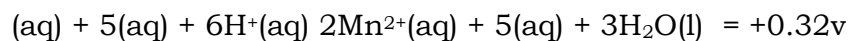
Reversing eqn (3) and multiplying eqn (1) by 2 and eqn (2) by 3



If both half cell reactions have positive electrode potentials, the half cell reaction with less positive electrode potential is reversed eg for the half cell reactions.




Reversing eqn (s) + multiplying eqn (1) by 2



Note

In combining two half eqns, 1 or both of them may be multiplies by intergers but the electrode potential value (f) is not affected because the magnitude of the electrode potential does not depend on the number of times the reaction occurs.

Table of standard electrode potentials

$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li(s)}$	-3.03		Strongest reducing agent (electropositive)
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K(s)}$	-2.92		
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca(s)}$	-2.87		
$\text{Na}^+(\text{g}) + \text{e}^- \rightarrow \text{Na(s)}$	-2.71		
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg(s)}$	-2.37		
			Weakest reducing agent

$\text{Al}^{3+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{l})$	-0.76
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{l})$	-0.13
$\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2(\text{g})$	-0.00
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80

The more negative the potential the easier is for oxidation to take place ie

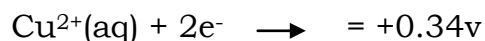
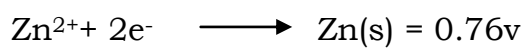


This is true for highly electropositive metals with loosely attached electrons. These are mainly group I elements which are electron donors, making them strong reducing agents.

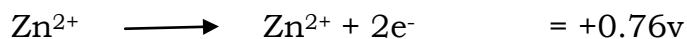
CATHODE AND ANODE IN ELECTRO CHEMICAL CELLS

In electrochemical cells the negative electrode is the anode and the positive electrode is the cathode. Therefore oxidation occurs at the anode while reduction occurs at the cathode.

For the Daniel cell made up of Zinc and copper.

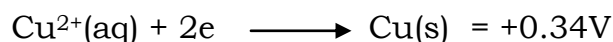


The zinc electrode is the negative electrode therefore it is the anode and oxidation takes place at this electrode according to the equation.



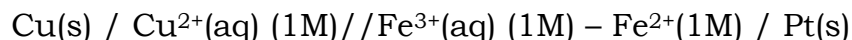
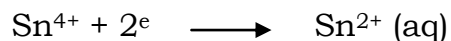
In the process electrons are given a way to the electrode which acquires a negative charge relative to the solution.

The copper electrode is the positive electrode and is the cathode on the electrode giving it a positive charge relative to the solution. The cathode reaction is therefore;

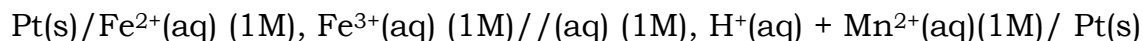


THE PLANTINUM ELECTRODE (PE)

Consider half cell reactions below involving ion –ion type without a metal



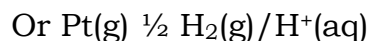
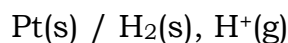
Again for the reaction



(oxidation)

(Reduction)

If one of the electrodes is the SHE then it is used as the left hand side electrode.

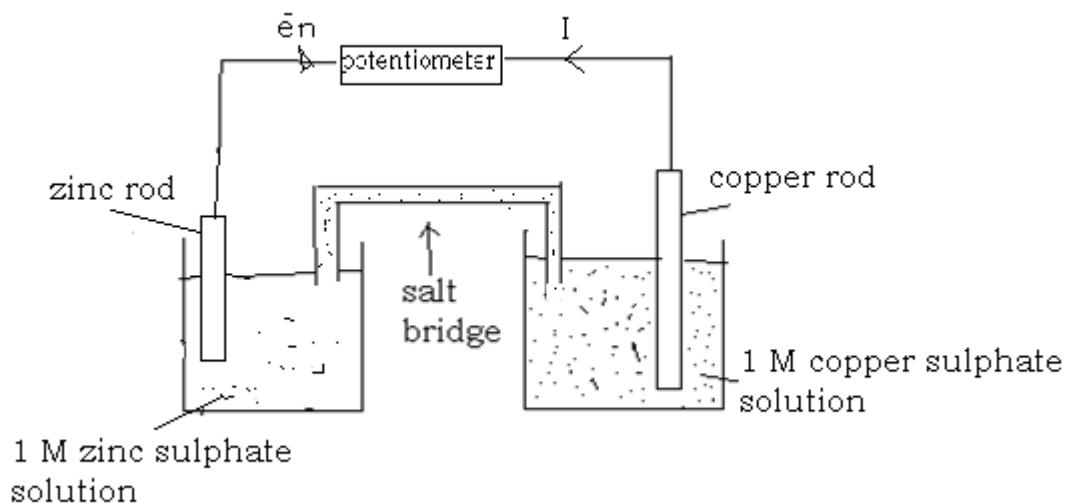


Emf of cell /

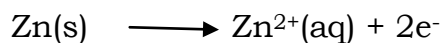
This is defined as the potential difference between two half cells each with its electrode dipping in its aqueous solution of concentration. 1M at a temperature of 298K and a pressure of 1 atmosphere.

Electrochemical cells generate an emf by causing electrons to flow from left to right and the current to flow in the opposite direction.

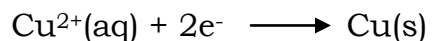
Consider the Daniel cell made up of zinc and copper.



Zinc being higher in the electrochemical series (more electropositive) ionizes faster than copper. Zinc atoms then dissolve in solution forming zinc ions, leaving electrons in the rod, giving it a negative potential.



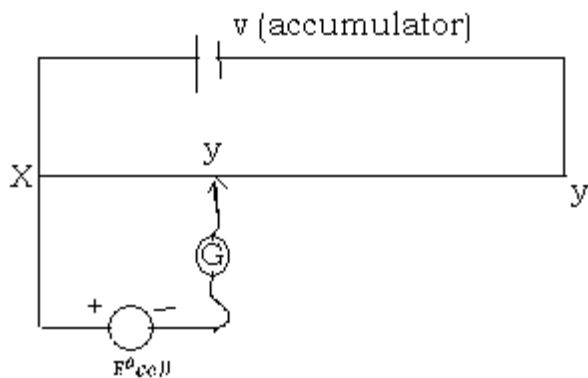
These electrons flow in the external circuit connected to the copper electrode. The copper ions gain electrons to deposit as copper metal. As more copper ions deposit on the electrode, the electrode acquires a positive charge relative to the solution giving it a positive potential.



The flow of electrons from the zinc half cell to the copper half cell causes a current to flow in the opposite direction generating an emf which can be measured using a potentiometer.

Measuring e.m.f ()

This is done by using a potentiometer. In simplest form it is made up of a standard cell or an accumulator of known potential differences (p.d) and a centre zero galvanometer which determines the null point with a jockey moved along a wire of uniform diameter and a length of 1m.



A jockey J is moved on a uniform wire xy(100cm) until when a condition of a current flow in the galvanometer is achieved (null point) or balance point. At balance point the ratio of the length $\frac{xy}{xy} =$ to the ratio of emf of the standard cell y to the emf of the cell under investigation.

=

=

Emf and free energy change

The emf of a cell under standard conditions represents the maximum amounts of work obtained from the cell.

An emf of cell can do useful work like lighting a bulb or driving a motor. The measure of how much work is done by the cell is called the free energy change (DG) it is given the expression

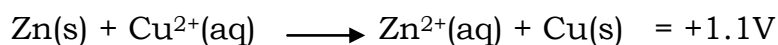
$$= -n, \text{ where}$$

N = number of moles of electrons transferred

F = Faraday's constant

$$= \text{Emf of a cell}$$

Consider the Daniel cell



=

$$= -2 \times 96500 \times 1.10$$

$$= -212300\text{J mol}^{-1}$$

$$-212.3 \text{ kJmol}^{-1}$$

Feasibility of a reaction

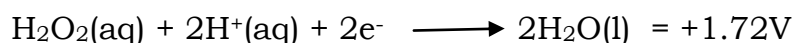
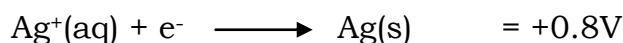
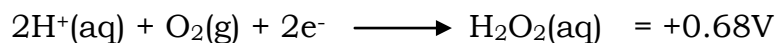
A reaction can be predicted to be feasible or spontaneous of

Calculating the emf of a cell

A feasible or spontaneous reaction is one whose cell is positive and the free energy change is negative.

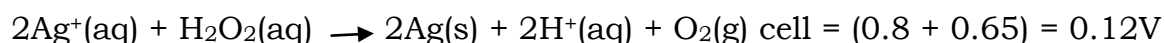
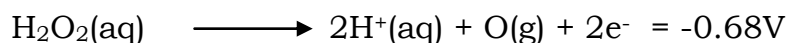
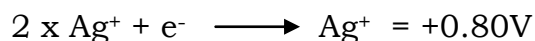
Qn

The electrode potentials for some reactions are given below



Write an equation for the reaction between silver nitrate and H₂O₂ and work out the cell and state whether the reaction is feasible or not give a reason.

Solution

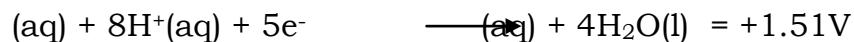


$$\begin{aligned}\text{Or cell} &= - \\ &= (+0.80 - +0.68) \\ &= +0.12\text{V}\end{aligned}$$

The reaction is feasible because of the cell is positive

Question

Below are half cell reactions



- Write the equation for the spontaneous cell reaction
- Calculate the emf of the cell made by combining the two half cell reactions
- Using four result in (b) explain why HCl is not used to acidify potassium permanganate titration

Solution

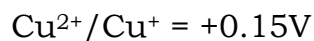
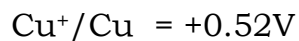
For a feasible reaction, cell should be positive so reversing equation 2.



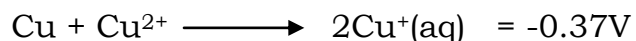
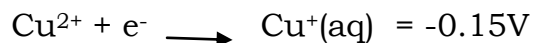
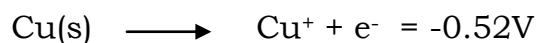
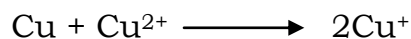
$$\begin{aligned}\text{cell} &= \\ &+1.51 - +0.75 \\ &= +0.76\text{V}\end{aligned}$$

Since the oxidation of chloride ions to chlorine by the permanganent ions gives a positive then the process is feasible so during the titration the chloride ions from hydrochloric acid are oxidized to chlorine which interferes with the titration.

Qn Given the standard electrode potentials



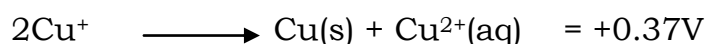
Calculate the cell voltage of the reaction and state whether the reaction is feasible or not.



The reaction is not feasible because the emf of the cell is negative.

Which ion is more stable in the aqueous solution and why.

Copper (ii) is more stable in the aqueous solution because the forward reaction is not feasible so copper (ii) can not be reduced to copper (ii). However copper (i) is very unstable and the feasible reaction is

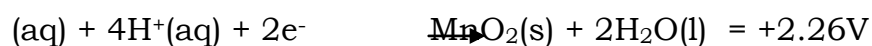


Therefore Cu^{2+} readily despoportianates into element copper (ii)

A disproportionation reaction is one involving self oxidation and reduction of a chemical species.

Question

Given

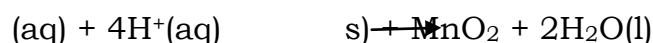
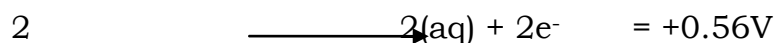


Comment on the feasibility of the reaction

$(\text{aq}) + 4\text{H}^+(\text{aq}) \xrightarrow{\text{s})} \text{MnO}_2 + 2\text{H}_2\text{O}(\text{l})$ and the stability of the (aq) ion. (F = 96500C)

Solution

Reverse equation (2)



=

$$= +2.26 - 0.56$$

$$= +1.70\text{V}$$

$$= +1.70\text{V}$$

=

$$= -2 \times 96500 \times 1.70$$

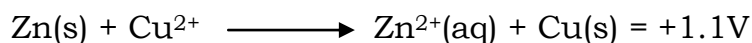
$$= -328.1 \text{ kJ mol}^{-1}$$

The reaction is feasible because the free energy change for the cell reaction is negative.

Since the forward reaction is feasible the Mn^{2+} ion is very unstable therefore manganese (vi) ions readily disproportionate into manganese II and Manganese (iv) in acidic solution.

Emf and concentration changes

Consider the Daniel cell

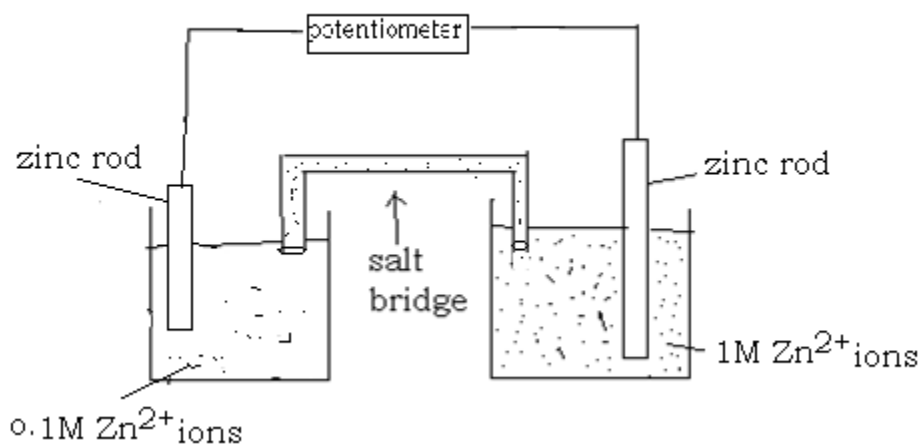


The above cell reaction generates an emf of 1.10V under standard conditions and any ions involved having a concn of 1 molar.

Consider if the concn of copper ions is greater than 1M the cell potential will be increased.

This increases the driving force on electrons hence increasing the cell potential.

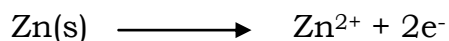
Concentration cell



A concentration cell is one in which both compartments have the same chemical species but at different concentrations, the difference in concentration is the only factor that produces a cell voltage.

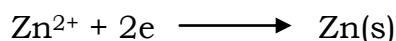
Equilibrium is achieved when the two concentrations are equal.

The higher concentration is reduced and the lower concentration is increased therefore a dilute solution undergoes oxidation i.e. more of the zinc electrode dissolves releasing zinc ions in solution.



Therefore the dilute compartment forms the left half cell

The concentrated solution undergoes reduction where by the zinc ions in solution deposit on the electrode as Zinc solid on the electrode reducing their concentration.

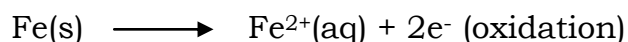


Therefore the concentrated compartment forms the right half cell. The convention used here is electrons flow from the less concentrated to the more concentrated and the less concentrated is the negative half cell while the more concentrated is the positive half cell.

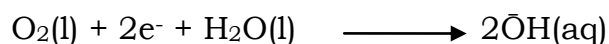
Corrosion/Rusting

This is an electro-chemical process when iron is heated scratched or stressed, water collects in the pit and some areas become anodic while, others cathodic. In the presence of water and oxygen the following reactions take place.

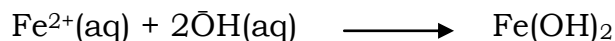
At the anodic area iron atoms become oxidized and lose 2 electrons.



The electrons travel to the cathodic area and reduce oxygen so at the cathodic area the following reaction takes place.

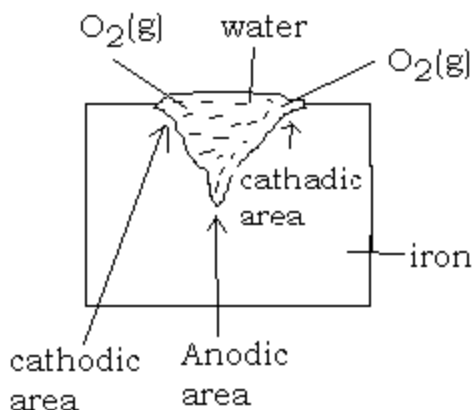


The iron (ii) ions and hydroxyl ions meet and iron (ii) hydroxide is precipitated



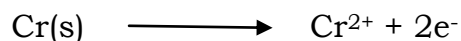
Finally oxygen oxidizes the iron (ii) hydroxide to iron (iii) oxide which is rust.



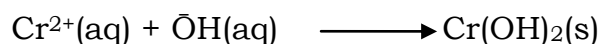


Stainless steel is iron containing a high proportion of chromium which forms a protective layer of chromium (iii) oxide over the whole surface of the metal. If the surface is scratched, a new protective layer of chromium (iii) oxide is formed and iron does not rust.

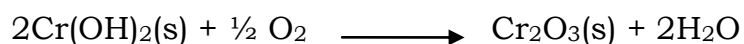
It scratched, at the anodic area chromium atoms became oxidized since chromium is more electropositive than iron.



At the cathodic area water splits into $\bar{\text{O}}\text{H}$ and hydrogen ions the hydrogen ions are discharged as hydrogen gas at the cathode but the $\bar{\text{O}}\text{H}$ ions meet with the Cr^{2+} ions forming Cr^{2+} hydro chromium (ii) hydroxide.



Finally chromium (ii) hydroxide undergoes oxidation aerial oxidation to form chromium (iii) oxide.



The chromium (iii) oxide forms the protective covering and the steel doesnot rust.

Prevention of rusting

1. Placing a physical barrier between steel and the environment such barriers include paint, tin, zinc or chromium plating.
2. Adding a sacrificial metal. This can be done by coating with zinc (galvanizing).

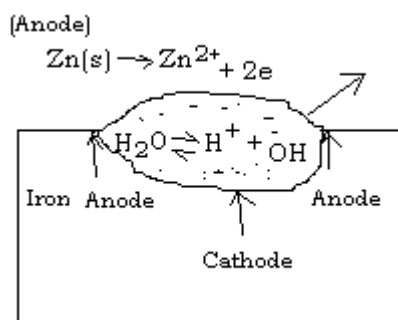
Comparison of tin and zinc as protective coverings

Zinc and tin are commonly used to protect iron from rusting but they are not equally effective.

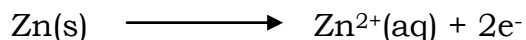
If galvanized iron becomes scratched so as to expose the iron below, rusting does not occur.

If the surface of tinned iron is broken rusting of the exposed iron is rapid and is facilitated by the presence of tin.

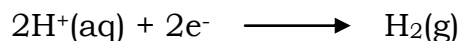
Suppose part of zinc is removed and the depression is filled with water as shown below.



Anode reaction

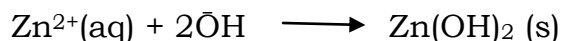


Cathode reaction



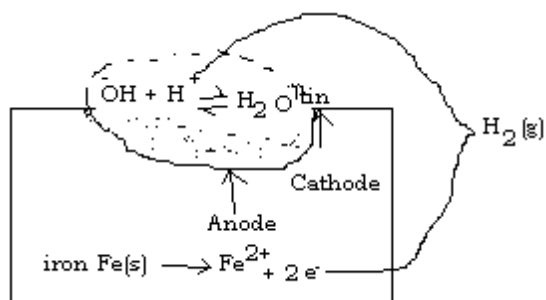
Zinc is more electropositive than iron so it goes into solution liberating zinc ions and electrons. This surface becomes the anodic area where oxidation takes place.

Iron acts as a cathode where water splits into hydrogen ions and OH^- ions the hydrogen ions combine with electrons from the anode to liberate the hydrogen gas. This disturbs the water equilibrium such that more hydroxide ions are released. These combine with the zinc ions forming zinc hydroxide.



This solid forms a protective covering that prevents iron underneath from rusting. During this process zinc is sacrificed hence acts as a sacrificial metal.

Suppose tin plated iron is scratched creating a depression where water fills, the following reactions take place.



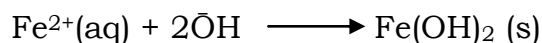
Iron is more electropositive than tin so it undergoes oxidation and forms the anodic area.



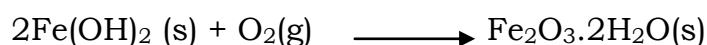
Tin forms the cathodic area where reduction takes place. The electrons from iron reduce hydrogen ions obtained by splitting of water at the cathode liberating hydrogen gas at the cathode area.



Discharge of hydrogen gas at the cathode at the cathodic area encourages more hydroxide ions to be released which combine with iron (ii) forming iron (ii) hydroxide.



The hydrogen undergoes aerial oxidation to form hydrated iron (iii) oxide which is rust.



Therefore tin can not protect iron from rusting.

Conductivity

This is concerned with the effective of passing an electric current into solutions. Some solutions conduct when electrolyzed and others do not.

Terms used

1. Electrolyte

Substances which do conduct electricity in aqueous or molten state eg salts, acids, alkalis etc.

2. Non – electrolytes

Substances which do not conduct electricity in aqueous solution or molten state eg glucose, sucrose and many organic compounds.

3. Weak electrolytes

Substances which only slightly ionize in aqueous solution eg organic acids and bases. They release few ions in solution conducting to a lesser extent.

4. Strong electrolyte

Substances which almost completely ionize in aqueous solution eg salts of metals and all mineral acids

5. Covalent electrolytes

These only ionize when only in aqueous solution eh hydrochloric acid, sulphuric acid etc and in their pure state they do not conduct electricity. They exist as covalent molecules.

6. Ionic electrolytes

These exist as ions in solid state and conduct electricity when molten.

Electrolytes conduct electricity because of the existence of ions hence they are called ionic conductors as opposed to metals which conducts electricity due to flow of electrons hence they are called electronic conductors.

Evidence for the existence of ions in electrolytes

1. When solid sodium chloride is tested for conductivity, it does not conduct electricity but on aqueous solution of water provides the necessary hydration energy to break down the crystal lattice into free gaseous ions which can conduct electricity. Again dissolving sodium chloride in water increases the entropy which breaks down the solid into ions.
2. Ionic solids when fused or molten conduct electricity because during melting the ions are set free and can migrate to the respective electrodes.
3. From the studies of colligative properties eg when sodium chloride is dissolved in water, it elevates the boiling point twice when compared with the same amount of glucose. Therefore sodium chlorides dissociates in solution releasing ions while as glucose does not dissociate.

Electrolysis

This is the decomposition of an electrolyte by passing an electric current through it.

During electrolysis the positive ions (cations) migrate to the cathode and the negative ions (anions) migrate to the anode.

The products of electrolysis are deposited or discharged at the electrodes. The amount of the substances liberated or deposited are governed by two laws known as Faraday's laws of electrolysis ie

1. The amount of the substance deposited or discharged at the electrodes during electrolysis is proportional to the quantity of electricity that has passed ie $M \propto Q$

Where M-is mass of substance

Q is quantity of electricity

Or

$$M = ZQ$$

Z – constant

But quantity of

Electricity = current x time

$$= It$$

$$M = ZIt$$

If a current of 1 Ampere is used for 1 second

$$M = Z$$

Z is a proportionality constant called the electrochemical equivalent

It is defined as the mass of a substance liberated or deposited when a current of one ampere is passed through an electrolyte for 1 second.

2. The second law states that; the number of faraday's required to deposit or discharge, 1 mole of a substance is proportional to the number of moles of electrons used.

After careful experiments faraday found out that the quantity of electricity of electricity required to deposit 1 mole of a substance is constant. It was given the value 96500C and is called a faraday.

For unipositive cations, 1 mole of electrons is required hence one faraday is needed.

Doubly charged cations require 2 faradays etc

Question

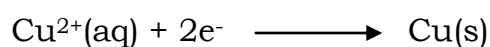
Calculate the mass of copper deposited when a current of 3A is passed through a solution of copper sulphate for 25 minutes

Solution

$$Q = It$$

$$= 3 \times 25 \times 60$$

$$= 4500\text{C}$$



2F deposit 64g of Cu

4500C will deposit ($\times 4500$)

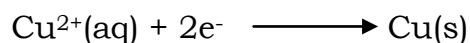
$$= \times 4500$$

$$= 1.49\text{g}$$

Assume that during the electrolysis of 250cm² of 0.1m copper (ii) sulphate solution all the copper (ii) ions are reduced to copper metal at the negative electrode.

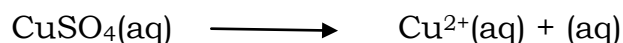
(a) What quantity of electricity must pass during this reduction

Solution



Moles of CuSO₄ used = ($\times 250$)

$$= 2.5 \times 10^{-2} \text{ moles}$$



1 mole of CuSO₄ gives 1 mole of Cu²⁺aq

Moles of Cu²⁺

$$=()$$

$$= 0.025\text{moles}$$

And moles of Cu(s) deposited = 0.025 moles

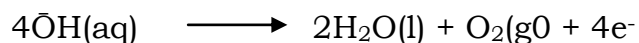
1 mole of Cu is deposited by 2 x 96500C

0.025 will be deposited by (2 x 96500 x 0.025)6

$$= 4825\text{C}$$

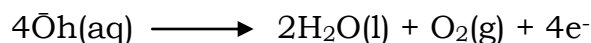
$$= 4825$$

Name the gas obtained at the positive electrode and write the equation to its release.



(c) calculate the volume of the gas at stp obtained at the positive electrode (I= 96500Cmol⁻¹, molar gas volume of stp = 22.4 dm³)

Solution



4F are required to discharge 1 mole of O₂

(4 x 96500)C are required to discharge 22.4dm³ of O₂

1C will discharge of oxygen

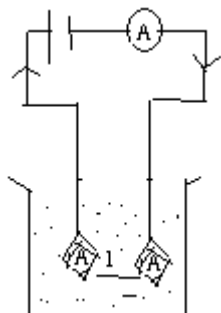
4825C will discharge [x 4825] dm³ of oxygen

= 0.28dm³ of oxygen

Conductivity of solutions of electrolytes

Electrolytic conductivity

Electrolytes conduct electricity because of the ions they contain. Consider two electrodes of cross sectional area. A separated of a distance in an electrolyte as shown.



The resistance offered by a given volume of the electrolytic solution between the two electrodes to the flow of current is in line with the one offered by metallic conductors.

At constant temperature, the electrical resistance offered by the electrolyte is

- (i) Directly proportional to the distance of separation l between the two electrodes.

(ii) Inversely proportional to the cross-sectional area of the electrodes ie

$$R \propto \frac{1}{A} \quad (1)$$

$$R \propto l \quad (2)$$

Combining (1) and (2)

$$R \propto \frac{l}{A}$$

Or

$$R =$$

Where ρ is proportionality constant called resistivity

$$\text{Resistivity } (\rho) = R \frac{A}{l}$$

The electrodes are of a unit cross – sectional area and the distance of separation between two electrodes is a unit length.

$$\text{Then } \rho = R$$

Therefore resistivity of an electrolyte is defined as the resistance of given volume of an electrolyte between two electrodes of a unit cross-sectional area separated by a unit length.

$$\text{From } R =$$

$$= \frac{\rho l}{A}$$

The reciprocal of resistance is the conductance electrolyte. It is given the symbol G

$$G = \frac{1}{R}$$

It is defined as the conductivity of a given volume of an electrolyte between two electrodes of unit cross sectional area separated by a unit length.

The reciprocal of electrolyte resistivity is called electrical conductivity (κ) and is given the symbol κ .

$$\text{From } \kappa = \frac{1}{\rho}$$

$$\bullet \quad \kappa = \frac{1}{\rho}$$

$$\bullet \quad \kappa = \frac{1}{\rho}$$

If $l = 1 \text{ unit}$, & $A = 1 \text{ unit}$

$$\kappa = \frac{1}{\rho}$$

Electrolytic conductivity K is defined as the reciprocal of resistivity or. The conductance of a given volume of an electrolyte between two electrodes of a unit cross – sectional area separated by a unit length.

The value

If l is in metres and A is square metres

$$\bullet = .$$

And if $l = \text{cm}$ and A in cm^2

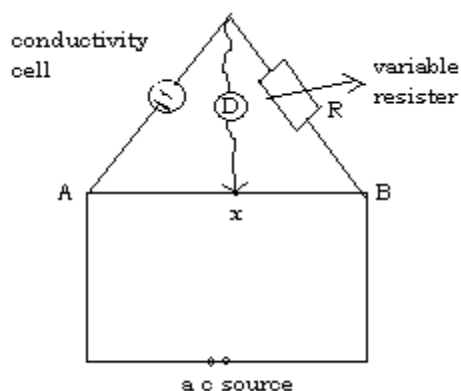
Then

$$\bullet = \text{Ohm}^{-1}\text{cm}^{-1}$$

Siemen metre⁻¹ (sm^{-1}) or siemen centi metre (S cm^{-1}) are also used since = Siemen.

$$(1 \text{ Scm}^{-1} = 100\text{Sm}^{-1})$$

Measurement of conductivity of solutions



A wheatstone bridge circuit is used be.

Because direct current causes back emf, an alternating current must be used. The set up is as shown above. The variable resistor R and the jockey at point x are moved until no current passes through the detector D . at this point or the balance point.

Resistance offered by conductivity

$$=$$

Resistance of the variable of the conductivity cell is obtained and the conductivity K can be determined using the expression $K =$.

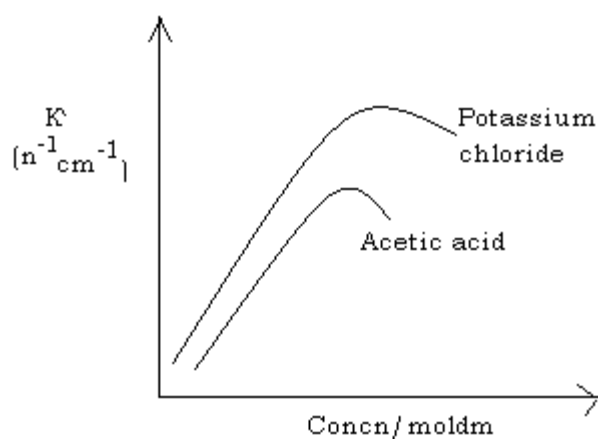
The value of the cell constant is read from the cell used.

Variation of conductivity with concentration

Conductivity increases with increase in concn of the electrolyte. This is true for both weak and strong electrolytes because an increase in concn increases the number of conducting ions per unit volume. Strong electrolytes give greater values of conductivity than weak electrolytes.

Concn	0.0001	0.001	0.01	0.1	1.0	1.0	2.0	3.0
K (KCl)	0.013	0.12	1.1	11.2		98.2	185.2	246.9
K(CH ₃ COOH)	0.0107	0.041	0.143	0.46		1.32	1.60	1.62

This is shown graphically below



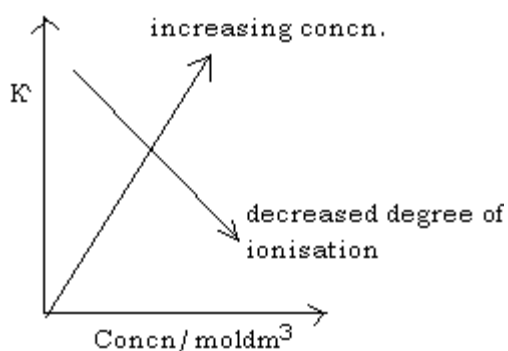
Strong electrolytes are fully dissociated in solution releasing many conducting ions per unit volume showing a higher conductivity.

Weak electrolytes are only slightly ionized releasing few conducting ions in solution hence a lower conductivity.

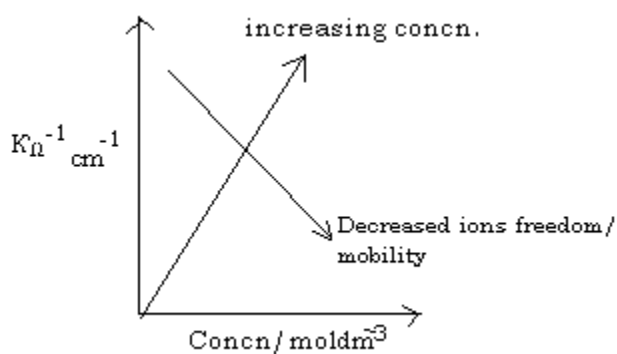
For both weak and strong electrolytes, conductivity decreases at very high concn because

1. A reduced degree of ionization for weak electrolytes
2. Increased ionic interference or reduced ionic freedom for strong electrolytes.

Weak electrolytes



Strong electrolytes



For weak electrolyte the degree of ionization is high at low concentration, so many conducting ions per unit volume. The degree of ionization decreases with increase in concentration reducing the number of conducting species per unit volume. Therefore the conductivity K is lowered at high concentration. For concentration because of a lowered ionic interference or increased ionic freedom.

At high concn there is an increase in ionic interference lowering ionic freedom reducing the conductivity.

Molar conductivity Λ_m

This is defined as the conductance of a given volume of an electrolyte containing 1 mole of a solute between two electrodes of 1cm^2 cross-sectional area separated by a length of 1 cm.

Molar conductivity $\Lambda_m =$

=

$$C = \text{mol dm}^{-3}$$

$$\bullet = \Omega^{-1} \text{cm}^{-1}$$

$$\bullet =$$

$$10 \text{cm} = 1 \text{dm}$$

$$10^{-3} \text{cm}^3 = 1 \text{dm}^3$$

$$=$$

$$1000 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\text{Units are } \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\Lambda_m = \text{Or molar conductivity} =$$

$$10 \text{dm} = 1 \text{m}$$

$$1 \text{ dm} = (10^{-1}) \text{m} = 10^{-1} \text{m}$$

$$1 \text{ dm}^3 = (10^{-1})^3 \text{m}^3$$

$$1 \text{ dm}^3 = 10^{-3} \text{m}^3$$

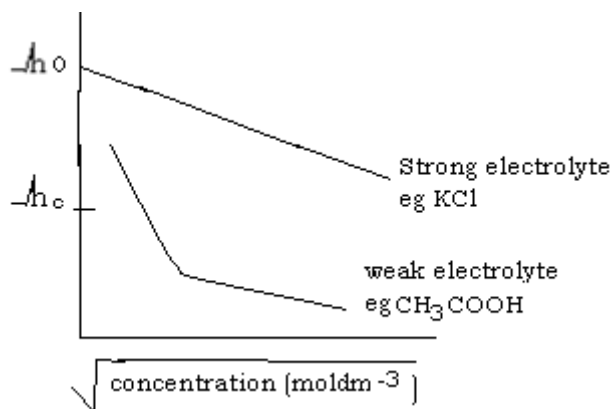
$$\bullet =$$

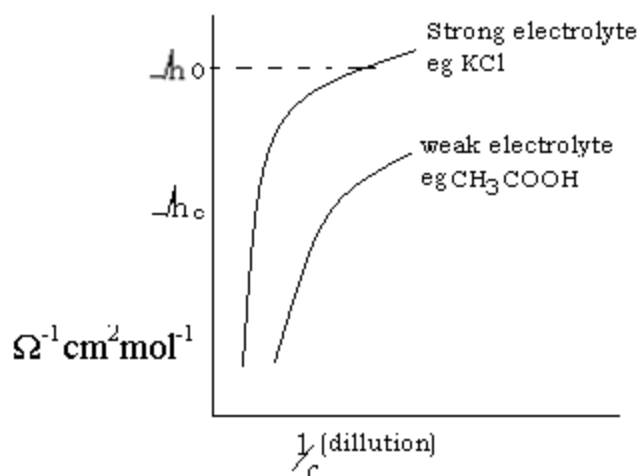
$$=$$

$$\text{Units are } \Omega^{-1} \text{m}^2 \text{mol}^{-1} \text{ and}$$

$$\Lambda_m =$$

Variation of molar conductivity with concentration





(a) Strong electrolytes

Molar conductivity decreases with increases in concentration or molar conductivity increases with dilution

Reason

At low concn there is increased ionic freedom which independent of each other due to reduced ionic interference. This makes molar conductivity high.

At high concn or low dilution molar conductivity is low because there are many ions per unit volume increasing ionic interference reducing ionic freedom. This reduces the molar conductivity.

Ionic interference a rises because a solution of an ionic salt has positive ions and negative ions. A positive ions becomes surrounded by ionic atmosphere of negative ions.



While a negative ion is surrounded by an ionic atmosphere of positive ions.



This effects (ionic interference) is greatest in concentrated solution but in dilute solution the ionic atmosphere breaks down reducing ionic interference but increasing ionic freedom and hence increasing molar conductivity.

Kohlrausch found out that for a strong electrolyte;

$$\bullet \quad \Lambda_c = \Lambda_c^\infty - K\sqrt{C}$$

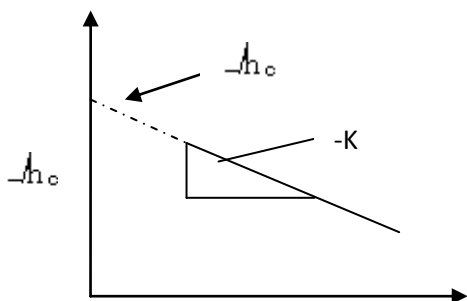
Where

- Λ_c - molar conductivity at a given concn of the solution.

K – proportionality constant

C – concn of the solution

A Plot of Λ_c Vs \sqrt{C} gives



A strong electrolyte molar conductivity is highest at zero concn at infinite dilution because at this point positive and negative ions are very free from each other. The value of molar conductivity at zero (0) concn or infinite dilution is called the molar conductivity at zero concentration and is obtained by extrapolation.

(b) Weak electrolytes

The molar conduct is high at very low concn or at high dilution and the molar conductivity decreases with increase in concentration or a decrease in dilution. This is because at very low concentration (high dilution) the degree of

ionisation is very high and almost complete. This releases many conducting ions in the solution.

At high concentration (low dilution), the degree of ionization is greatly reduced reducing the number of conducting ions in solution and reducing the molar conductivity.

For a weak electrolyte, Arrhenius found out that the degree of ionization is given by

=

And at zero concn (infinite dilution) is proximately equal to 100% or 1 but at a high concentration is less than 100% or 1

The value of Λ° at a given concentration is got from conductivity measurement by using an electrolyte of a known concentration (Λ° -) while for Λ° it is got indirectly by using Kohlrausch's law of independent.

Ionic migration

The law states that "The molar conductivity at zero concentration of an electrolyte or at infinite dilution is equal to the sum of the molar conductivities at Zero concentration of the ions produced by the electrolyte"

At infinite dilution ions are free from each other and they migrate to the electrodes independently eg for NaCl.

$(\text{NaCl}) = \Lambda^\circ \text{Na}^+ + \Lambda^\circ \text{Cl}^-$ therefore the molar conductivity at zero concn for a weak electrolyte such as ethanoic acid can be obtained from the values of the molar conductivities of the individual ions ie

$$(\text{CH}_3\text{COOH}) = \Lambda^\circ(\text{CH}_3\text{COO}^-) + \Lambda^\circ(\text{H}^+)$$

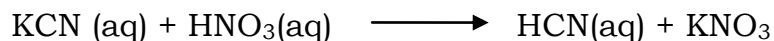
Alternatively the value of Λ° for ethanoic can be obtained from the molar conductivity at zero concn for selected strong electrolytes eg NaCl, HCl and $\text{CH}_3\text{COONa}^+$

i.e $\text{HCl(aq)} + \text{CH}_3\text{COONa}^+(\text{aq}) \longrightarrow \text{NaCl(aq)} + \text{CH}_3\text{COOH(aq)}$

$$\text{CH}_3\text{COOH} = (\Lambda^\circ \text{HCl} + \Lambda^\circ \text{CH}_3\text{COONa}^+) - \Lambda^\circ \text{NaCl}$$

The molar conductivity of KNO_3 , KCN and nitric acid at infinite dilution are, respectively 145, 156 and $425 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Calculate the molar conductivity of hydrocyanic acid at infinite dilution.

Solution



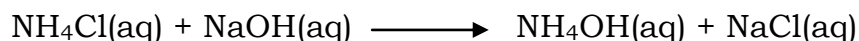
$$\Lambda^\circ_{\text{HCN}} = (\Lambda^\circ_{\text{KCN}} + \Lambda^\circ_{\text{HNO}_3}) - \Lambda^\circ_{\text{KNO}_3}$$

$$= (156 + 421) - 145$$

$$= 432 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

Worked example

The molar conductivities of Ammonium chloride NaOH and NaCl are respectively 141, 252, $280 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Calculate the Λ° of ammonium hydroxide.



$$\Lambda^\circ_{\text{NH}_4\text{OH}} = (\Lambda^\circ_{\text{NH}_4\text{Cl}} + \Lambda^\circ_{\text{NaOH}}) - \Lambda^\circ_{\text{NaCl}}$$

$$= (141 + 252) - 280$$

$$= 113 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

Worked examples

The resistance of a cell containing 0.1 mold m NaCl at 25°C is 50.6. in the cell a 0.02M KNO_3 has a resistance of 185 ohms at the same temperature. If the conductivity of NaCl at the temperature is

- The cell constant
- The conductivity of KNO_3
- The molar conductivity of a 0.0116M solution of KNO_3

Solution

$$P =$$

$$= R$$

$$= .$$

$$\kappa = .)$$

$$() = \kappa R$$

$$= 1.3 \times 10^{-2} \times 50.62$$

$$= 0.65806\text{cm}^{-1}$$

$$\kappa(\text{KNO}_3) =$$

$$= 0.65806$$

$$= 3.55708 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$$

$$\Lambda_m(\text{KNO}_3) =$$

$$=$$

$$= 306.645 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

The electrolytic conductivity of a solution of 0.1m of aqueous amino ethane is $1.5 \times 10^{-1} \Omega^{-1} \text{m}^{-1}$. If the molar conductivity of solution of infinity is $2.04 \times 10^{-2} \Omega^{-1} \text{m}^2 \text{mol}^{-1}$.

Calculate

The percentage dissociation of amino ethane

The basic dissociation constant of amino ethane

Solution

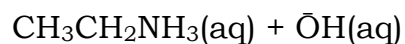
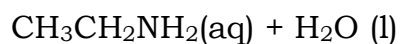
$$= \times 100$$

$$\text{CH}_3\text{CH}_2\text{NH}_2 =$$

$$= 1.5 \times 10^{-3} \Omega^{-1} \text{m}^2 \text{mol}^{-1}$$

$$= \times 100$$

$$= 7.35\%$$



Initially 1

0

0

If in degree C (1-)

C

$$K_b =$$

$$=$$

$$K_b =$$

$$=$$

$$583 \times 10^{-4} \text{ mold m}^{-3}$$

$$583 \times 10^{-4} \text{ mold m}^{-3}$$

$$K_b =$$

At equilibrium]

$$K_b =$$

$$[\text{OH}] =$$

=

$$= 7.63 \times 10^{-3} \text{ Mold m}^{-1}$$

$$[\text{H}^+] =$$

=

$$= 1.3097 \times 10^{-11} \text{ mold m}^{-3}$$

$$\text{PH} = -\log(\text{H}^+) = -\log(1.3097 \times 10^{-11})$$

$$= 10.88$$

$$\text{pH} = 10.88$$

FACTORS AFFECTING CONDUCTIVITY OF AN ION

Size of the ion

The smaller the size of the ion the higher the conductivity. This is because smaller ions are highly mobile and therefore highly conducting. This explains why the most highly conducting ions is the hydrogen ions because it is the smallest ion.

Charge on the ion

The greater the charge on the ion the higher is its conductivity because a highly charged ion is more readily attracted to the electrodes than a less charged ion. This explains why the conductivity of magnesium ion ($\text{K}^\circ = 106 \Omega^{-1} \text{cm}^{-1}$) is higher than that of sodium.

Similarly the surrounding of a sulphate ion is higher than that of a chloride ion (Cl^-).

Charge density

The higher the charge density the lower is the conductivity of ions with a higher charge density because their mobility is hence reduced, reducing their conductivity. This explains why Lithium has the lowest conductivity among all cations of group I.

because it has the highest charge density and attract the largest sphere of water molecules in solution so it is the heaviest.

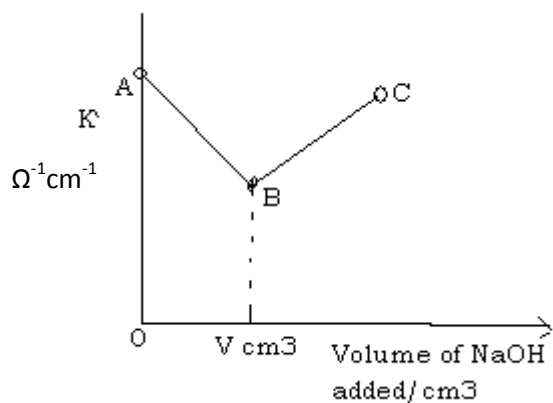
APPLICATION OF CONDUCTANCE MEASUREMENTS

Conductimetric titrations

This is the application of conductance to follow the course of an acid-base titration in which there is a significant difference between the conductivity of the original solution and that of the resultant mixture. At the end point there is a sharp change in conductivity and the vol required to reach end point is noted.

To minimize dilution effect the solution being titrated with should be 10 times more concentrated than the one in the beaker.

Changes in conductivity as a strong acid is titrated with a strong base eg HCL and NaOH.

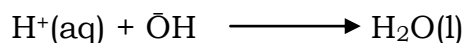


The conductivity decreases rapidly along AB and increases gradually along BC. Initially the conductivity is high because HCl is a strong acid and completely dissociates into many and by highly conducting hydrogen ions.



The conductivity then decreases with the addition of the basis because hydrogen ions are being neutralized by the hydroxide ions to form the neutral water molecules which do not conduct.

According to the equation

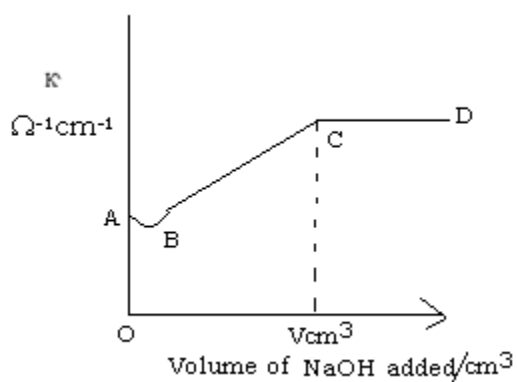


The fast moving and highly conducting H^+ ions are being replaced by the slow moving and less conducting Na^+ ions.

Point B gives the conductivity of the solution at end point and the volume of the base required is $V\text{cm}^3$. At the end point is the minimum conductivity due to conductivity of Na^+ conc and Cl^- ions only from the salt formed. The two have very low conductivities.

Beyond the end point conductivity increases due to excess highly conducting hydroxide ions.

Changes in conductivity when a weak acid is titrated with a strong base eg ethanoic acid, sodium hydroxide pair.

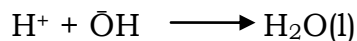


Initially the conductivity is low because ethanoic acid is a weak acid which enters slightly ionized, releasing few highly conductivity and fast moving hydrogen ions.



Conductivity decreases along AB due to

- (i) Removal of the few hydrogen ions in the neutralization reaction by the hydroxide ions in the solution.

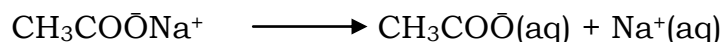


- (ii) Suppression of ionization of ethanoic acid by the strong salt formed due to a common ion effect, addition of a small amount of sodium hydroxide to

ethanoic acid forms sodium ethanoate that suppresses the ionization of ethanoic acid.



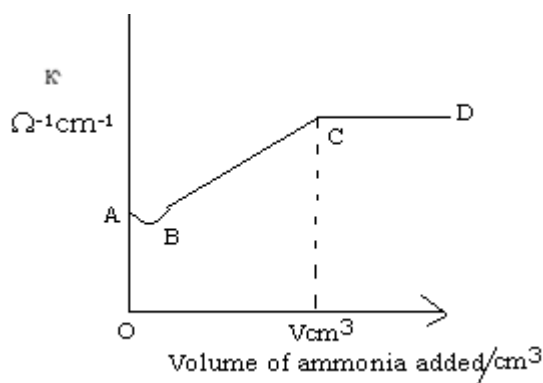
There is a sharp increase in conductivity in the region BC due to the salt formed which fully ionizes releasing many sodium ions in solution.



Point C is the end point of the titration and the volume required to reach end point is $V \text{ cm}^3$. The conductivity at the end point is higher than the initial conductivity because the solution at the end point has more conductivity ions than the initial solution.

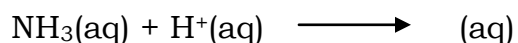
The further gradual increase in conducting in region CD is due to excess highly conducting hydroxide ions being added after all the ethanoic acid has been neutralized.

(a) Variation in conductivity when a weak acid such as aqueous acid is titrated with a weak base such as ammonia



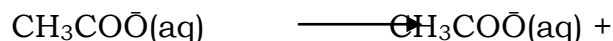
At point A conductivity is low because ethanoic acid is weak and only slightly ionizes in solution releasing few hydrogen ions in solution.

Neutralization of the hydrogen ions by ammonia (OH^- from NH_4OH). The fast moving hydrogen ions are being replaced by the less moving ammonia ions with formation of neutral water molecules.



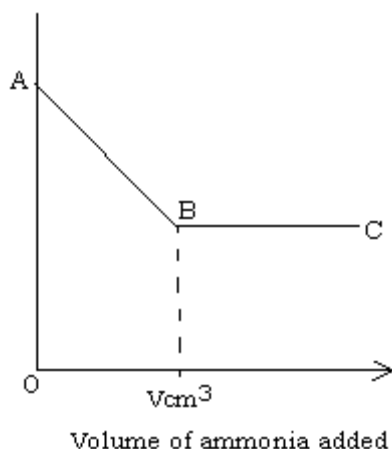


Suppression of the ionization of ethanoic acid due to common ion effect

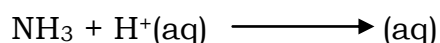


Atom BC conductivity increases due to formation of a strong electrolyte ethanoate which fully dissociates releasing many conducting ions. The end point is at point C and the volume of ammonia needed to reach end point is V_{cm^3} . The conductivity at all the end point is high due to strong electrolyte formed compared to the original ethanoic acid which is a weak electrolyte. At the end point all ethanoic acid has been neutralized so on more formation of ammonium ethanoate and any ammonia added from the burette does not contribute to conductivity because it is suppressed from ionizing due to common ion effect and the conductivity remains constant along CD.

Changes in conductivity when a strong acid is titrated with a weak base eg HCl and Ammonia



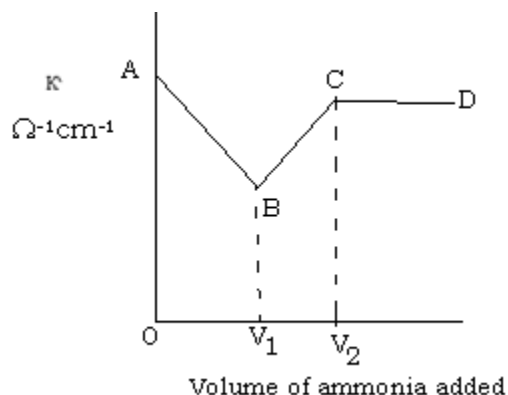
The initial conductivity is high because the acid is a strong electrolyte and fully dissociated releasing many and highly conducting hydrogen ions. Conductivity decreases along AB because of the removal of the hydrogen ions due to their neutralization by ammonia. The hydrogen ions are being replaced by the ammonia ions which are less conducting.



Point B is the end point of the titration and the volume of ammonia required to reach end point is $V\text{cm}^3$. Any increase in conducting after the end point would be due to excess ammonium hydroxide added but its ionization is suppressed by the ammonium ions from the strong ion effect to conducting remains constant along BC.



Changes in conductivity when a mixture of a strong acid and a weak acid is titrated with a weak base eg a mixture by HCl and CH_3COOH with Ammonia.



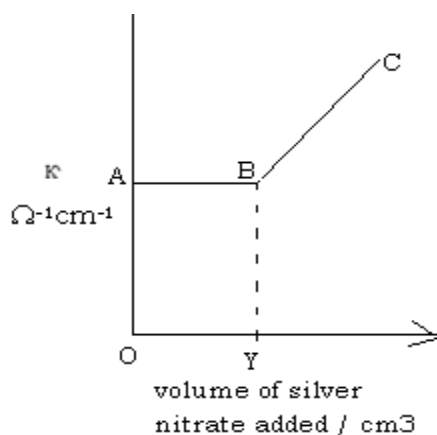
It is the strong acid that titrates fast. The initial conductivity is high because HCl is a strong electrolyte and releases many hydrogen ions in solution. The fall in conductivity along AB is due to neutralization of the H^+ ions from strong acid.

At point B all strong acid has been neutralized and volume required is $V_1\text{ cm}^3$

The conductivity along BC raises because of the titration of the weak acid and the rise is due to the production of strong salt ammonium ethanoate. The end point of the titration with a weak acid is marked by $V_2\text{ cm}^3$ and the volume required for only ethanoic acid is $(V_2 - V_1)\text{cm}^3$.

Conductivity remains constant after the end point because of suppression of ionization of ammonium hydroxide due to common ion effect.

Changes in conductivity during a precipitation reaction eg sodium chloride silver nitrate.



The initial conductivity is high because sodium chloride is a strong electrolyte and fully dissociated releasing many conductivity ions in solution.

In the initial solution the conducting ions are chloride ions and sodium ions.

Addition of silver nitrate precipitates out chloride ionic but they are replaced by an equal number of nitrate ions so conductivity remains constant along AB.

At point B the end point has reached and all the chloride ions have been precipitated and any excess silver nitrate contains silver ions that remain in the solution. So the...in conductivity along BC is because of excess silver nitrates. The volume of silver nitrate required to reach end point is $V \text{ cm}^3$.

Determining the solubility of a sparingly soluble salt.

This electrolytic conductivity of a solution is equal to the conductivity of the solution and that of the solvent ie

Solution = solute + solvent and

- Solution = κ solution - κ solvent.

Then molar conductivity of the solute is and for saturated solutions the concentration of the solute is equal to its solubility in mol per litre.

solute =

Solubility =

Example

Calculate solubility of a saturated solution of AgCl at 25°C whose electrolyte conductivity is $4.36 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ and that of water is $2.50 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ given that the molar conductivity of silver chloride at the same temperature is $1.46 \times 10^{-2} \Omega^{-1}\text{cm}^{-2} \text{mol}^{-1}$.

Solution

$$\begin{aligned} \bullet \quad \text{Solution} &= \kappa \text{ solution} - \kappa \text{ solvent.} \\ &= (4.36 \times 10^{-6} - 2.50 \times 10^{-6}) \end{aligned}$$

$$= 1.86 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$$

$$\text{Solubility} =$$

$$=$$

$$= 0.1274 \text{ mol dm}^{-3}$$

$$\text{Molar mass of AgCl} = 108 + 35.5$$

$$= 143.5$$

$$\text{Solubility in g/l}$$

$$= 143.5 \times 0.1274$$

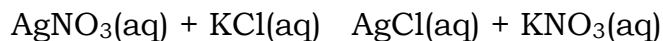
$$= 18.2819 \text{ g l}^{-1}$$

Question

At 25°C the molar conductivity of silver nitrate, potassium nitrate and potassium chloride are 133.4, 145.0 and 149.9 $\Omega^{-1}\text{ohms}$ respectively. At the same temperature the conductivity of a saturated solution of silver chloride is $3.1 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ while that of pure H₂O is $1.6 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$.

- (i) Calculate the solubility of silver chloride in mols l⁻¹ at this temperature.
- (ii) Determine the solubility product of silver chloride at this temperature.

$$(\text{AgCl}) =$$



$$\begin{aligned} \Lambda(\text{AgCl}) &= \Lambda(\text{AgNO}_3) + \Lambda(\text{KCl}) - \Lambda(\text{KNO}_3) \\ &= (133.4 + 149.9) - 145.0 \\ &= 138.3 \, \Omega^{-1}\text{cm}^2\text{mol}^{-1} \end{aligned}$$

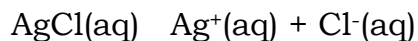
$$\kappa(\text{AgCl}) = \kappa_{\text{solution}} - \kappa_{\text{solvent}}$$

$$\begin{aligned} &= 3.14 \times 10^{-6} - 1.6 \times 10^{-6} \\ &= 1.54 \times 10^{-6} \, \Omega^{-1}\text{cm}^{-1} \end{aligned}$$

Solubility of AgCl

=

$$1.11 \times 10^{-5} \, \text{mol dm}^{-3}$$



$$K_{\text{sp}}(\text{AgCl}) = (\text{Ag}^+)(\text{Cl}^-)$$

1 mole of AgCl gives 1 mole of Ag^+ ions and 1 mole of Cl^- ions.

$$[\text{Ag}^+] = 1.11 \times 10^{-5} \, \text{mol dm}^{-3}$$

$$[\text{Cl}^-] = 1.11 \times 10^{-5} \, \text{mol dm}^{-3}$$

$$K_{\text{sp}}(\text{AgCl}) = (\text{Ag}^+)(\text{Cl}^-)$$

$$= (1.11 \times 10^{-5}) \times (1.115 \times 10^{-5})$$

$$= 1.2321 \times 10^{-10} \, \text{mol}^2 \, \text{dm}^{-6}$$

Question

Given that the mole conductivity at infinite dilution of ionic species below

Ion	$\Lambda \, \Omega^{-1}\text{cm}^2\text{mol}^{-1}$
-----	--

Na^+	50.1
---------------	------

OH^-	198.6
---------------	-------

H^+	349.8
--------------	-------

Cl^-	76.4
---------------	------

0.1M HCl solution was titrated with 1M NaOH solution. Calculate the changes in conductivities.

(i) Before the titration is started

(ii) When the end point was attained

(iii) when twice as much NaOH has been added as compared to the volume required for the end point.

Sketch a graph to show the changes in conductivity during the course of the titration.

Explain the shape of the graph

Solution

Conductivity before the titration is due to 0.1M HCl

HCl =

$\text{HCl} = \text{H}^+ + \text{Cl}^-$

$= (349.8 + 76.4)$

$= 426.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

• HCl =

$= 4.262 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$

$\text{NaOH(aq)} + \text{HCl(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$

At the end point the conductivity solution is salt solution of NaCl

Since 1 mole of HCl gives 1 mole of NaCl the $[\text{NaCl}] = 0.1\text{M}$

$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$

$50.1 + 74.6$

$= 124.7 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$

• NaCl=

$= 1.247 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$

When twice as much NaOH been added conductivity is due to the salt formed and the excess NaOH

But from

$\text{HCl(aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$

1 mole of HCl reacts with 1 mole of NaOH at the end point.

$[\text{HCl}]$ reacted at end point = 0.1M

$[\text{NaOH}]$ reacted at end point = 0.1M

[NaOH] which would react when twice as much has reacted, been added.

The excess [NaOH] = $0.2 - 0.1$

$\text{NaOH} = \text{Na}^+ + \text{OH}^-$

$= 50.7 + 198.6$

$= 245.7 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$

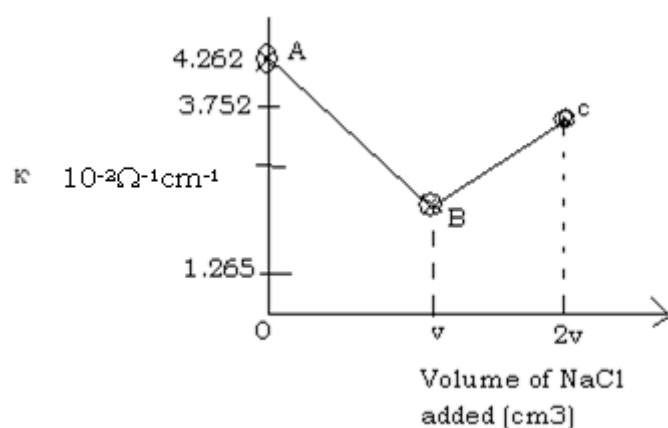
• $\text{NaOH} =$

$=$

$= 2.487 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$

Total $K = K_{\text{NaCl}} + K_{\text{NaOH}}$

$= 3.752 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$



Initially the conductivity is very high because hydrochloric acid is a strong electrolyte and fully dissociated in solution releasing many fast moving and highly conducting hydrogen ions. The conductivity decreases along AB because of the removal of hydrogen ions by the hydroxide ions forming molecules of water which are not conducting and the hydrogen ions are being replaced by the less mobile and less conductivity sodium ions. Point B is the end point of the titration and the volume NaOH required is $y \text{ cm}^3$.

The increase in conductivity along BC is because of the excess out ions from the base and the sodium chloride formed after the neutralization.

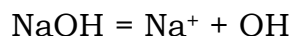
Conductivity of the resultant solution is less than that of the mutual solution because the salt formed and the excess sodium hydroxide are less conducting compared to the hydrochloric acid.

Calculate the electrolytic conductivity for (i) 0.01M NaOH

Solution

Solution made by mixing 50cm³ of 0.01M sodium hydroxide and 50cm³ of 0.02 hydrochloric acid.

Solution



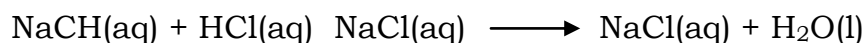
$$= (50.1 + 198.6)$$

$$248.7 \Omega^{-1} \text{cm}^{-1} \text{mol}^{-1}$$

$$\kappa = \frac{1}{0.01} \times 248.7$$

$$=$$

$$= 2.487 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$$



Conductivity is due salt formed and excess HCl

Moles of NaOH used = (0.01 x 50) moles

Moles of HCl used = (0.02 x 50) moles

Moles of excess HCl acid = (0.02 x 50) - (0.01 x 50)

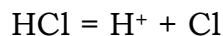
$$=$$

$$= 5.0 \times 10^{-4} \text{ moles}$$

100cm³ of solution contains 5.0 x 10⁻⁴ of excess HCl

1000cm³ of solution will contain 5.0 x 10⁻³

$$= 5.0 \times 10^{-3} \text{M}$$



$$349.8 + 76.4$$

$$= 426.2 \Omega^{-1} \text{cm}^{-1} \text{mol}^{-1}$$

$$\kappa = \frac{1}{0.005} \times 426.2$$

$$= 2.13 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$$

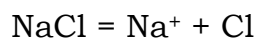
Since 1 mole of NaOH completely reacts with the acid to form 1 mole of NaCl then moles of NaCl formed.

$$= (0.01 \times 50) \text{ moles of NaCl}$$

100cm³ of solution will contain x50 moles of NaCl

1000cm³ of solution will contain x

$$= 5.0 \times 10^{-3} \text{M}$$



$$= 50.1 + 16.4$$

$$= 126.5 \Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$$

$$\kappa_{\text{NaCl}} =$$

$$=$$

$$= 6.325 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$$

Total conductivity

$$\kappa_{\text{NaCl}} + \kappa_{\text{HCl}}$$

$$6.325 \times 10^{-4} + 2.131 \times 10^{-3}$$

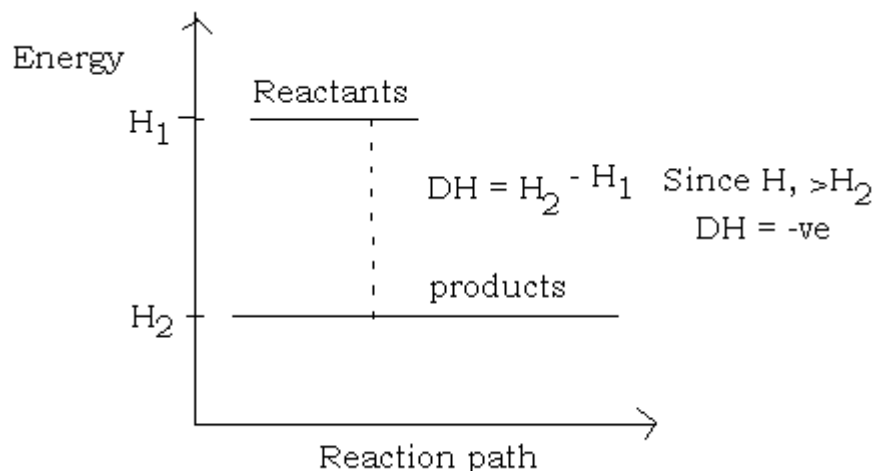
$$= 2.7635 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$$

THERMOCHEMISTRY [ENERGETICS]

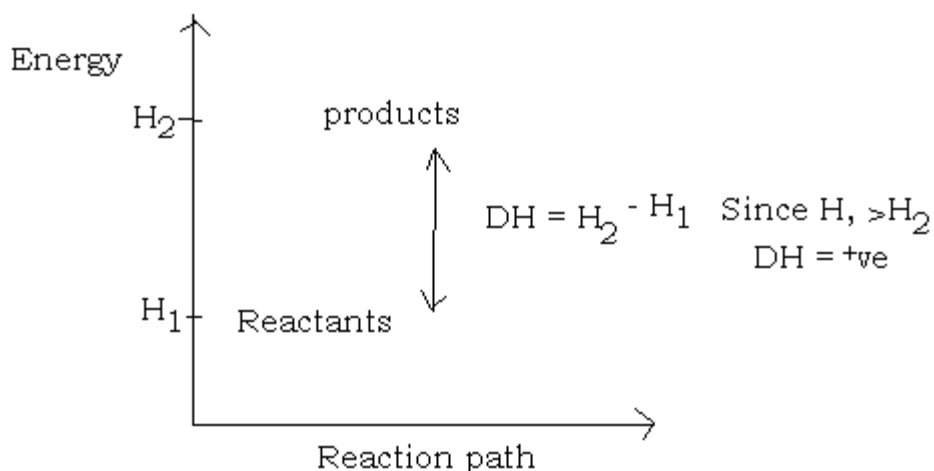
All chemical reactions are accompanied by energy changes which are usually observed as heat changes. The chemical involved in a reaction forms the system and the system may lose heat to the surrounding or may gain heat from the surrounding.

A system that loses heat to the surrounding is called an exothermic reaction while the one that absorbs heat from the surrounding is called an endothermic reaction.

Exothermic reaction



Endothermic reaction



Note

An exothermic reaction liberates heat to the surrounding and there is always temp rise.

An endothermic reaction absorbs heat from the surrounding and there is always a temperature fall.

The quantity of heat evolved or absorbed during a chemical reaction will depend on the following factors.

- ❖ The physical states of the reactants and products must be specified because to convert a substance from one physical state to another involves an energy change. Therefore it is important to indicate the state of each of each substance by the appropriate letter placed in brackets

after the formular (s) for solid, (l) for liquid, (g) for a gas (aq) for acqueous.
(dissolved in water)

- ❖ The amount of chemical substances involved in a reaction will affect the magnitude of the heat change.
- ❖ The temp at which the reaction is carried out must be specified
- ❖ The pressure at which the reaction is carried out must also be specified.

STANDARD ENTHALPY CHANGES

Such enthalpy changes are measured at standard conditions ie temps of 25°C or 298K. pressure of 1 atmosphere or 760mmHg or 101325 pa or 101325NM⁻². Therefore standard enthalpy of reaction is denoted by

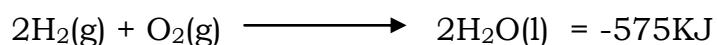
Standard enthalpy of formation is denoted by

Standard enthalpy of combustion is denoted by

Standard enthalpy of neutralization is denoted by

Standard enthalpy of reaction

It is the enthalpy change that occurs when molar quantity of reactants are stated in equation react together under standard conditions of one atmosphere and 298K.



Standard enthalpy of formation standard enthalpy of combustion.

Standard enthalpy of formation (Δ_f) is the enthalpy change that occurs when one mole of the substance (cpd) is formed from its elements in their standard states under the standard conditions of one atmosphere and temperature of 298K.

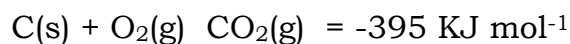
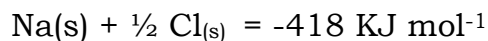
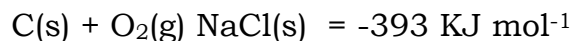
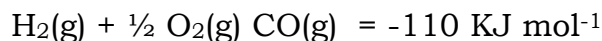
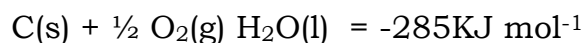
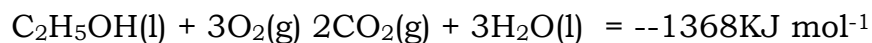
Note

Standard enthalpy of formation of elements such as Cl, Na, Ca, N₂(g) O₂(g) there standard states are zero.

The standard state of a substance is the most stable physical state of a substance under standard conditions of pressure of one atmospheric and temperature at 298K.

Standard enthalpy of combustion is the enthalpy change that occurs when one mole of substance is completely burnt in O₂(g) under standard conditions





Experiment: Determination of heat enthalpy of combustion

Using solid substances

This determination is carried out in a bomb calorimeter. A typical example of a bomb calorimeter is made of steel. It is nickel plated on the outside and protected on the inside by a coating of non oxidisable material eg platinum.

A known mass of the substance under investigation is placed in the pt cap.

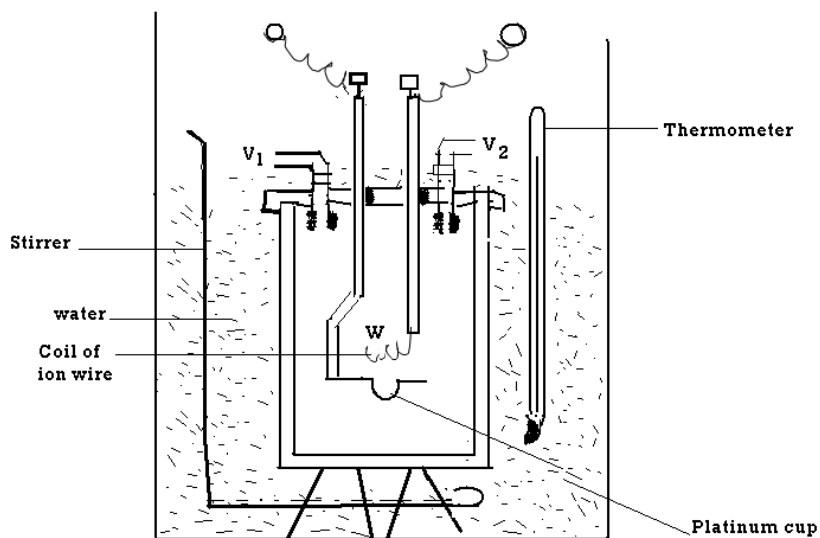
Air is displaced by oxygen which is allowed to reach a pressure of 20-25 atmospheres.

The bomb calorimeter is then closed by screw valve placed in a known mass of water which is being stirred and the water is placed in the calorimeter which is filtered with a stirrer and an accurate thermometer and is well lagged to minimize heat losses.

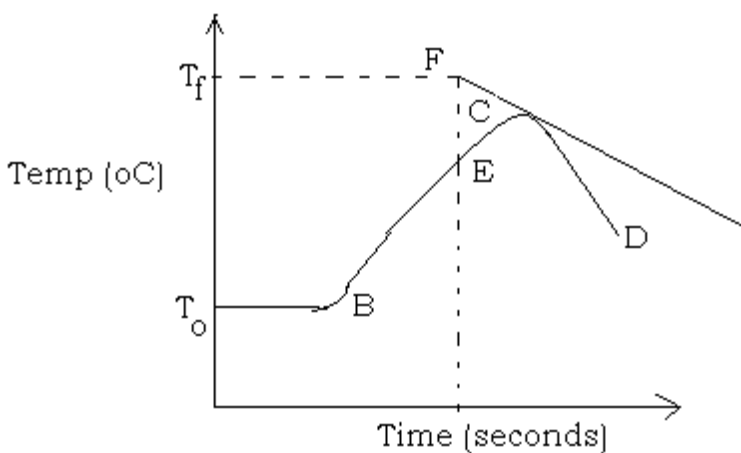
With the stirrer operating temp reacting are taken at regular intervals of time.

Current is then passed, the iron wire becomes red hot and fires the substance and combustion occur. This brings a sudden rise of temp, and the temperature readings are taken until the system is cooling slowly and regularly.

The diagram of a bomb calorimeter.



A graph of temp against time is plotted and the graph can be used to determine the max temperature as follows.



A tangent is drawn on the cooling curve, if E is the mid point of BC and EF is parallel the temp axis the highest temp reached can be taken as for T_f .

Treatment of results

Let a_g be the mass of the substance under investigation.

b_g be the mass of water

T_0 – initial temp of the water

T_f – final temp of the water

Let the S.H.C of water be $4.2 \text{ Jg}^{-1}\text{K}^{-1}$

Let the heat capacity of bomb calorimeter be C_{JK}^{-1}

DT absorbed by the water = $M_w C_w DT + C_D T$

$$= (b \times 4.2) (T_f - T_0) + C(T_f - T_0)$$

ag of the substance produce $(b \times 4.2) (T_f - T_0) + (C T_f - T_0)^J$

about Mr of the substance

Mr of the substance will produce

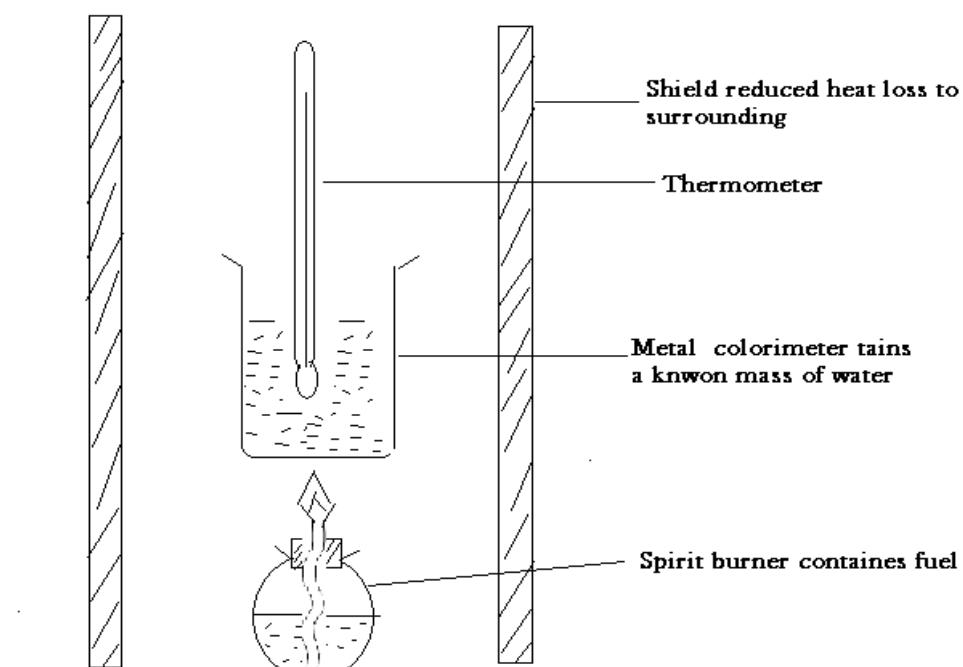
Enthalpy of combustion of the substance

- $[KJ Mol^{-1}]$

Using a liquid substance such as ethanol

In this experiment we use an improvised spirit lamp.

- A spirit lamp is half filled with ethanol and its mass determined.
- A known mass of water is measured and transferred into a thin walled metal can which is fitted with a thermometer.
- The set up of the apparatus is shown below.



- The initial temperature of water is read and recorded as T_0 °C.
- The spirit lamp is lit and the flame is placed in position so that it just touches the bottom of the metal can and is allowed to heat up the water.
- A stirred is arranged to allow the flame to remain steady

- When the temperature of the water has risen by 25°C , the flame is put out and the final temperature of the water is quickly read and recorded as $T_1^{\circ}\text{C}$.
- The spirit lamp is allowed to cool and the final mass of the spirit and its contents is taken.

Treatment of result

Let the initial mass of the lamp and its content be M_1 g

Let the final mass of the spirit lamp and its content be M_2

Let the shc of the 4.2 $\text{Jg}^{-1}\text{K}^{-1}$.

Let the mass of the water be a g

$$\Delta T = (T_1 - T_0) ^{\circ}\text{C}$$

Mass of ethanol that burnt = $M_1 - M_2$

Heat absorbed by the water = mass of water \times ShCw \times ΔT

$$= a \times 4.2 \times (T_1 - T_0)$$

RFM of ethanol = 46

$(M_1 - M_2)\text{g}$ of ethanol produce $a \times 4.2 \times (T_1 - T_0)\text{J}$ of heat

46g of ethanol will produce X 46

$$\text{of Ethanol} = -[\text{KJ mol}^{-1}]$$

NOTE

- The ΔH of any substance is negative (ie it is an exothermic reaction)
- The ΔH of ethanol in the above experiment will be less than the material rate because heat is lost to the surrounding and some heat is absorbed by the metal can.

QN

- When 1.5g of ethanol was burnt, the heat produced raised the temperature of 500g of water from 25 to 44.5
Calculate the ΔH of ethanol (Shc of water = 4.2
 $= 44.5 - 25$

2. What mass of methane (natural gas) must be burnt to raise the temperature of 2kg of water from 20°C to 100

Assume no heat is lost (C_p of water = 42J

of methane = -890 Jmol⁻¹)

No. 1

Heat absorbed by water = $500 \times 42 \times 19.5 = 40950 \text{ J}$

1.5g of ethanol produce 40950J

46g of ethanol produce $x \times 46 \times$

$= -6255.8 \text{ kJmol}^{-1}$

$$1. \text{ RFM} = 12 + 4 = 16$$

$$= 672000.5$$

$$\text{of} = -890 \text{ kJmol}^{-1}$$

612kJ are produced by $x \times 672$

$$= 12.1 \text{ g}$$

Determining standard enthalpies of formation from standard enthalpies of combustion

There are two methods of calculating standard enthalpies of formation from combustion enthalpies

1. Cancellation method
2. Born Haber cycle

Cancellation method

It involves writing various equations at the combustion reactions. Some equations cancel out to obtain the required equation

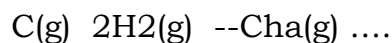
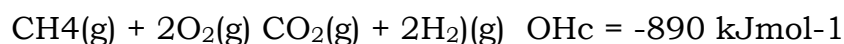
i. When an equation is multiplied by a certain factor, the enthalpy is also multiplied by the same factor.

ii. When an equation is reversed the sign of the enthalpy also changes

Note: The purpose of reversing the equation is to obtain the required product which was originally the resultant.

Calculate the standard enthalpy of formation of methane from the following thermodynamic data

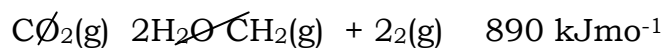
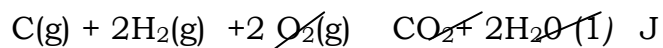
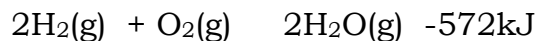
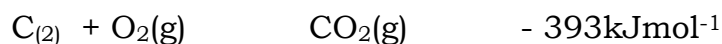
$$+ 393 \text{ kJmol}^{-1} \text{ --- 2}$$



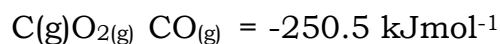
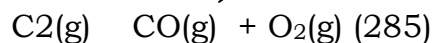
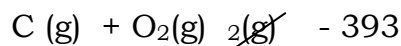
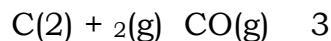
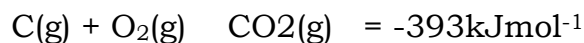
iii. When the equations are added or subtracted

iv. The enthalpies are also added or subtracted

$$\text{Eqn 4} = (1) + x(\text{ii}) + -(\text{iii})$$

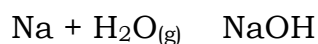
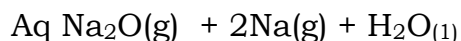
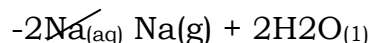
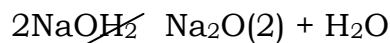


2. Find the standard enthalpy of formation of carbon monoxide. If the standard enthalpies of combustion of carbon and carbon monoxide are -393 kJmol^{-1} and -285 kJmol^{-1} respectively.

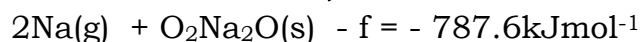
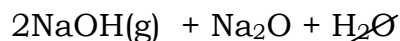
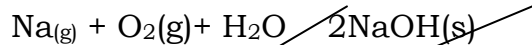
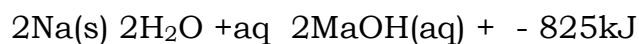
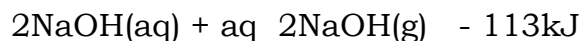


Calculate the standard enthalpy of formation of sodium oxide from the following data

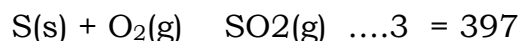
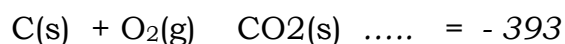
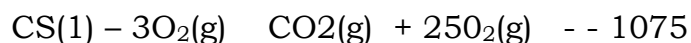
1. $\text{Na}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{s}) \rightarrow 2\text{NaOH}(\text{g}) = -205 \text{ kJmol}^{-1}$
2. $\text{NaOH}(\text{g}) + \text{aq} \rightarrow \text{NaOH}(\text{aq}) = -56.5 \text{ kJmol}^{-1}$
3. $\text{Na}(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{aq} \rightarrow \text{NaOH}(\text{aq}) (\text{G}) = -410 \text{ Jmol}^{-1}$
4. $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) = -285.6 \text{ Kmol}^{-1}$
5. $2\text{Na}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{Na}_2\text{O}(\text{g})$



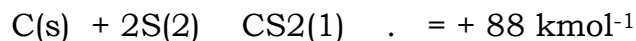
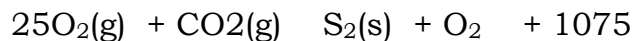
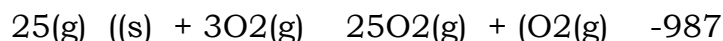
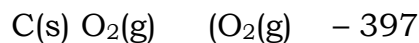
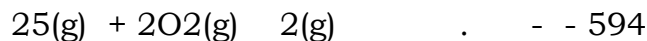
$$5 = 2 - (2) + 2(\text{s}) + 4 - (1)$$



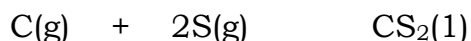
Find the standard enthalpy of formation of carbondisulphide
 burns in air to form carbondioxide and sulphur dioxide. The $\Delta_f H^\circ$ of
 carbondisulphide, sulphur and carbon are -1075 , -297 & -393 kJmol^{-1}
 respectively

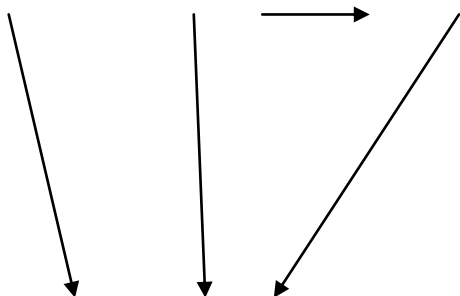


$$4 = 2(3) + (2) - (1)$$



Born Haber cycle





$$+ 2$$

$$= 85 \text{ kJmol}^{-1}$$

Calculating enthalpies of reactions from standard enthalpies of formation

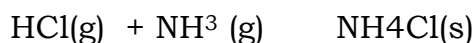
reaction = (reactants)

1. Given the standard enthalpies of formation of some prds

$$(\text{NH}_3) = -46 \text{ kJmol}^{-1}$$

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

$(\text{NH}_2(1)) = -315 \text{ kJmol}^{-1}$ Calculate the standard enthalpy of the following reaction



$$= -315 - (-46 + -92.3)$$

$$= 196.7 \text{ kJmol}^{-1}$$

2. Given the standard enthalpies of formation of some prods

$$(\text{H}_2\text{O}_{2(l)}) = -20 \text{ kJmol}^{-1}$$

$$(\text{CO}_2(\text{g})) = -393 \text{ kJmol}^{-1}$$

$$(\text{CH}_3\text{NHNH}_2(1)) = -53 \text{ kJmol}^{-1}$$

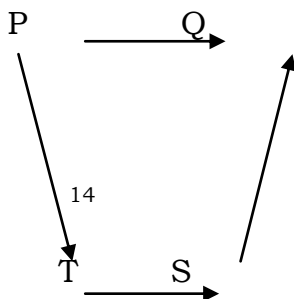
$$(2\text{C}_{(s)}) = -286 \text{ kJmol}^{-1}$$

Calculate the standard enthalpy of the following reaction



$$= (\text{products}) - (\text{reactants})$$

Hess's law states that if a reaction can have place by more than one route, the overall change in enthalpy is the same which ever route is followed



By Hess's law

$$1 = 2 + 3 + 4$$

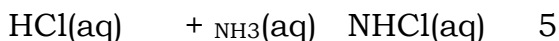
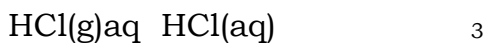
The closed energy cycle is what we call a born – haber cycle

e.g

Ex starting from ammonia gas and hydrogen chloride gas, an aqueous solution of ammonium chloride can be formed from the two cpds in two ways
in one way, the gases are allowed to react to form $\text{NH}_4\text{Cl(g)}$ which when dissolved in water an agent solution of ammonium chloride is formed.
The other, the two gases are separately dissolved in water and their aqueous solution mixed to form an aqueous solution of NH_4Cl



$$\text{Total enthalpy} = 1 + 2$$



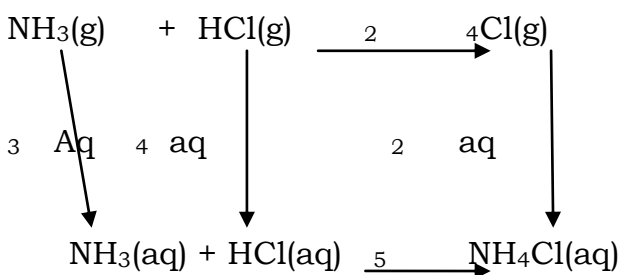
Total enthalpy change

33

By Hess's law

$$1 + 2 = 3 + 4 + 5$$

Born – haber cycle



By Hess's law

$$1 + 2 = 3 + 4 + 5$$

Indirect determination of enthalpy changes by application of Hess's law

The enthalpy changes of some reactions can not be determined directly by expts, but by the application at Hess's law

They can be calculated from other experimental results eg it is possible to determine experimenting the enthalpies of combustion of CH_2 , C Hydrogen and these results can be used to calculate the standard enthalpy of formation of methane which can not be determined directly.

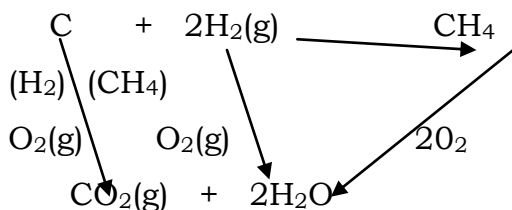
e.g

$$(\text{CH}_4) = -890 \text{ kJ mol}^{-1}$$

$$(\text{H}_2) = -286 \text{ kJ mol}^{-1}$$

$$(\text{CO}_2) = -393 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy of formation of methane



By Hesse's law

$$(\text{CH}_4) + (\text{CH}_4) = (\text{c}) + (\text{H}_2)$$

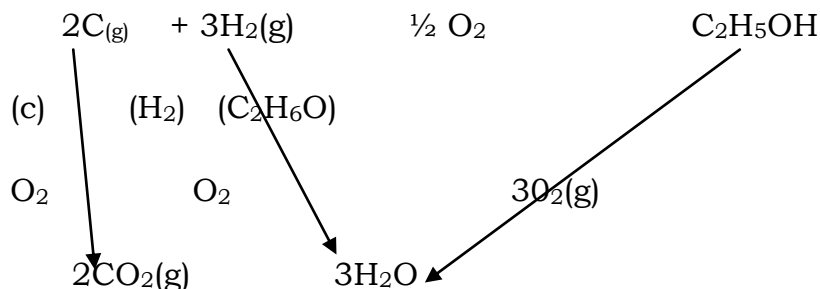
$$= (\text{C}) + (\text{H}_2) - (\text{CH}_2)$$

$$= -393 + 2(-286) - (-890)$$

$$= -75 \text{ kJmol}^{-1}$$

Calculate the standard enthalpy of formation of ethanol given that the $\Delta_f H^\circ(\text{C}_2\text{H}_2\text{O}) = -393 \text{ kJmol}^{-1}$

$$= -286 \text{ kJmol}^{-1}$$



$$+ \Delta_f H^\circ(\text{C}_2\text{H}_6\text{O}) = \Delta_f H^\circ(\text{H}_2) + \Delta_f H^\circ(\text{C}_2)$$

$$= \Delta_f H^\circ(\text{H}_2) + 3 \Delta_f H^\circ(\text{H}) - \Delta_f H^\circ(\text{C}_2\text{H}_6\text{O})$$

$$= 2(-393) + 3(-286) - (-136 \dots)$$

$$= -276 \text{ kJmol}^{-1}$$

Standard enthalpy of atomization and based energy

Standard enthalpy of atomization of an element is the heat required to convert the element in its normal state and under standard conditions into one mole of gaseous atoms.

When the element is a metal, the enthalpy of atomization is sometimes called the enthalpy of subtraction

$$\text{e.g. } \text{Na}_{(\text{g})} - \text{Na}_{(\text{s})} = +108 \text{ kJmol}^{-1}$$

$$\text{H}_{2(\text{g})} - \text{H}_{(\text{g})} = +218 \text{ kJmol}^{-1}$$

$$\text{Cl}_{2(\text{g})} - \text{Cl}_{(\text{g})} = 121 \text{ kJmol}^{-1}$$

$$\text{C}_{(\text{g})} - \text{C}_{(\text{s})} = 717 \text{ kJmol}^{-1}$$

Bond energy

This is the heat required to break one mole of a covalent bond between two atoms in gaseous state



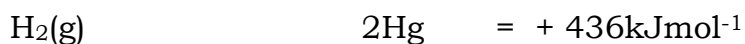
This bond energy is some times called, bond dissociation energy which is an endothermic process.

Bond energy is the heat required when one mole of a revalent bond is formed from two atoms in gaseous state

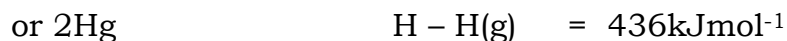
This is an exothermic process



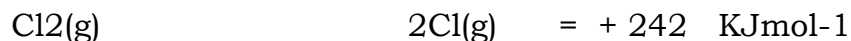
e.g



H-H



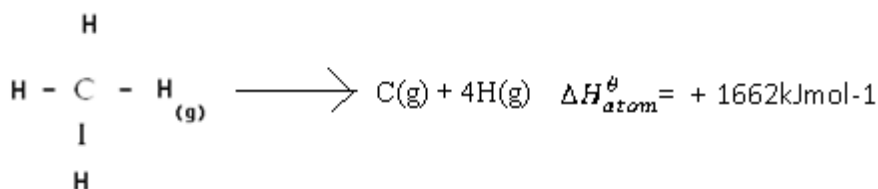
$H_2(g)$



Enthalpy of atomization and bond energy are related by the fact that bond energy is hence enthalpy of atomization.

AVERAGE BOND ENERGY

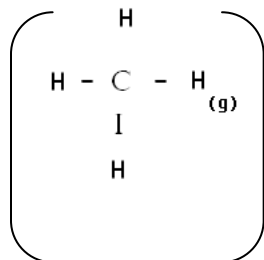
This is the energy of one covalent bond obtained by the dividing the total bond energies of the cpd by the no of bonds in that cpd



$$4 \times E(C-H) = 1662$$

$$E(C-H) = \frac{1662}{4} = 415.2 \text{ kJmol}^{-1}$$

$$- 1662 kJmol^{-1}$$



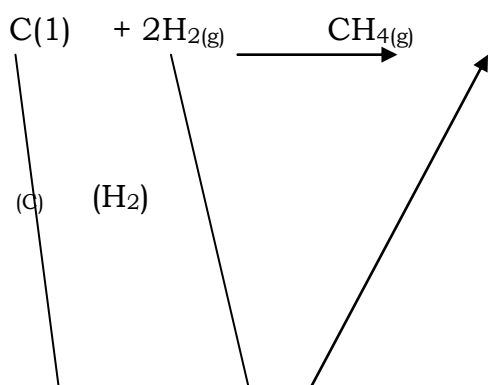
Calculating bond energies from standard enthalpies of atomization and formation

1. The standard enthalpy of formation of methane is -74.8 kJmol^{-1}

And the standard enthalpy of atomization of graphite and hydrogen are $+715 \text{ kJmol}^{-1}$ and $+218 \text{ kJmol}^{-1}$ respectively.

Construct a Born-Haber cycle for the standard enthalpy of formation of methane.

Determine the average bond energy of C-H bond in methane.



$$+ 715 + 421 +$$

$$- - 1661.5 \text{ kJmol}^{-1}$$

(b) Average bond energy =

$$= - 415.45 \text{ kJmol}^{-1}$$

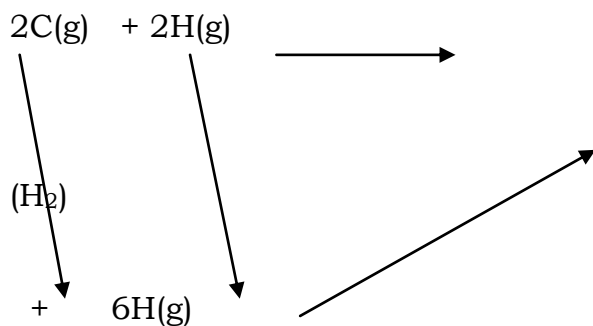
2. Calculate the average C-C bond energy in ethane from the following thermodynamic data

(c) $= + 715 \text{ kJmol}^{-1}$

$(\text{H}_2) = - 218 \text{ kJmol}^{-1}$

$(\text{H}_2) = 84.6 \text{ kJmol}^{-1}$

$$= 415.45 \text{ kJmol}^{-1}$$



$$\begin{aligned} \text{C}_2\text{H}_2 &= \text{C}_2 + \text{H}_2 + \text{C} \\ &= + 6 \times 218 + 2 \times 715 \\ &= 6(218) + 2(715) + 84.6 \\ &= -2822.6 \text{ kJmol}^{-1} \\ &= -415.45 \text{ kJmol}^{-1} \end{aligned}$$

$$E(\text{C}-\text{H}) = -2492.7 \text{ kJmol}^{-1}$$

$$2 E(\text{C}-\text{C}) = -2822.6 - (-2492.7)$$

$$2 = -329.9 \text{ kJmol}^{-1}$$

Determination of enthalpy of reaction from the bond energies

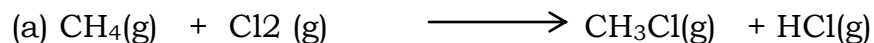
$$= -$$

In resistant for bond formation products

The table below shows some bond energies for the selected bonds.

Bond	Bond energy kJmol ⁻¹		Bond
C - C	345	146	O - O
C = C	610	463	O - H
C - H	415	562	F - H
C - O	360	890	C \equiv N
C = O	740	276	C - Br
C \equiv C	835	484	C - F
N \equiv N	945	238	C - I
C - Cl	339	318	C - I
H - H	435	264	S - H
Cl - Cl	242	390	S - S
N - N	163		N - H
Br - Br	193		
F - F	158		
H - Br	365		
H - Cl	431		

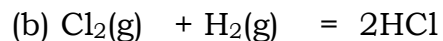
Using the bond energies from the table, calculate the enthalpies of the following reactions.



$$= -$$

$$= (415 + 242) - 431 + 339)$$

$$= -167\text{kJmol}^{-1}$$



$$= (242 + 435) - 2(431)$$

$$= -185\text{kJmol}^{-1}$$



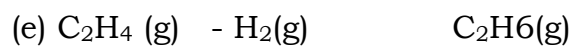
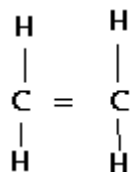
$$= 945 + 3(435) - 2(390)$$

$$= 1479\text{KJmol}$$



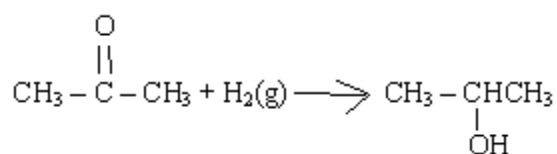
$$= 2(163) + 4(380) - 4(562)$$

kJmol^{-1}



$$= (435 + 610) - (345 + 2(415))$$

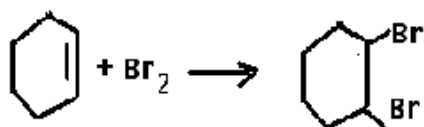
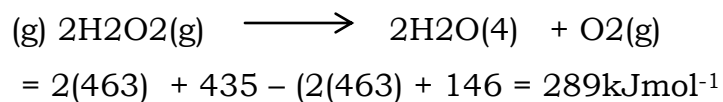
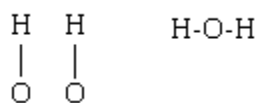
kJmol^{-1}



$$= 740 + 435 - 463$$

$$= 712 \text{ kJmol}^{-1}$$

kJmol^{-1}

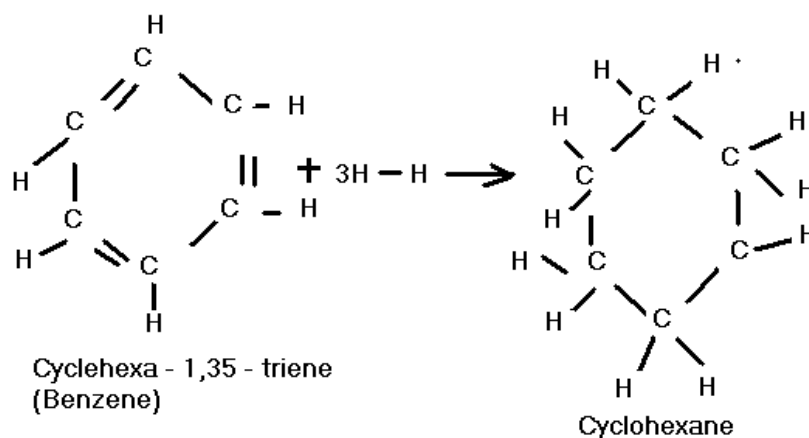


$$= 610 + 193 - [(276) \times 345]$$

$$= -94 \text{ kJmol}^{-1}$$

Delocalization energy in Benzene

If the structure of benzene is assumed to consist of alternate double and single bonds, then, the enthalpy of hydrogenation of benzene can be calculated as follows;



$$\begin{aligned}
 &= \quad - \\
 &= 3E(C+C) + 3E(H-H) - C.E(C-H) + 3E(C-C) \\
 &= 3(610 + 3(435) - 6(415) + 3(345) \\
 &= 645 \text{ kJmol}^{-1} \\
 &= -3390 \text{ kJmol}
 \end{aligned}$$

The experimental determined value for benzene is approximately = 210 kJmol⁻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 390 – 210

$$= 180 \text{ kJmol}^{-1}$$

the extra stability of the benzene ring is attributed to the delocalisation of the bonding electrons over all six carbon atoms.

Prediction of the feasibility of a reaction

The enthalpy change of a reaction is sometimes used as a rough guide to show whether the reaction is feasible or not or the likelihood that the reaction will occur.

If for a reaction is negative then the reaction is feasible and the products are more stable than the reactant. But when the enthalpy of reaction is positive then the reaction is not feasible and such a reaction needs external energy to have place.

Therefore reactions which occur spontaneously are often exothermic reactions. However, some endothermic reactions can also occur spontaneously.

This is due to increase in the entropy of the reaction.

Entropy can be defined as the degree of disorder of a system

e.g. dissolving potassium iodide in water is an endothermic process and the reaction does not need any heating. This means that such a reaction has high entropy.

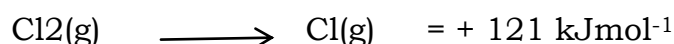
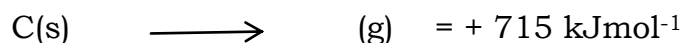
Born-Haber cycle and lattice energies

The Born-Haber energy cycle considers the energy changes which occur during the formation of an ionic crystal (ionic compound) from its elements.

We can form the ionic compound directly or we can use other enthalpies to reach the ionic compound. Such enthalpies include atomization energy, ionisation energy, electron affinity and lattice energy.

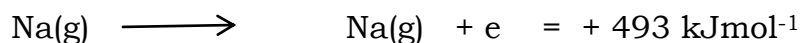
Atomisation energy

It is the enthalpy change that occurs when an element (metal) is converted into one mole of gaseous atoms



Ionisation energy

It is the enthalpy change that occurs when one mole of electrons is removed from one mole of gaseous atoms to form one mole of positively charged gaseous ions

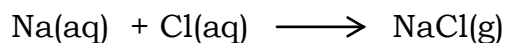


Electron affinity

This is the enthalpy change that occurs when one mole of gaseous atoms of a non-metal gain one mole of electrons to form one mole of negatively charged gaseous ions.

Lattice energy

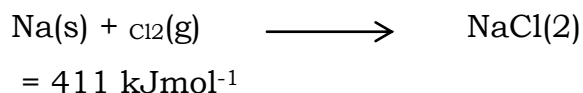
It is the enthalpy change that occurs when one mole of an ionic crystal is formed from its constituent gaseous ions.



Enthalpy of solution

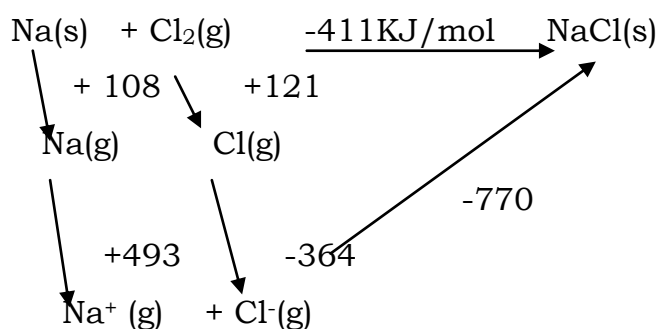
It is the that formed when one mole of an ionic crystal lattice is broken into its constituent gaseous ions.

Standard enthalpy of formation is the heat react.. when one mole of a compound is formed from its physical state from its construent elements



Born – Haber cycle for formation of sodium chloride

From its elements



ENERGY DIAGRAM FOR FORMATION OF AN IONIC (PD) FROM IT'S ELEMENTS

An energy level diagram is an improved born-huber cycle which follow the energy terms.

For endothermic reaction, the energy level increases but an exothermic reaction the energy level decreases.

Energy level diagram for the formation of sodium chloride from its lements using the following energy changes.

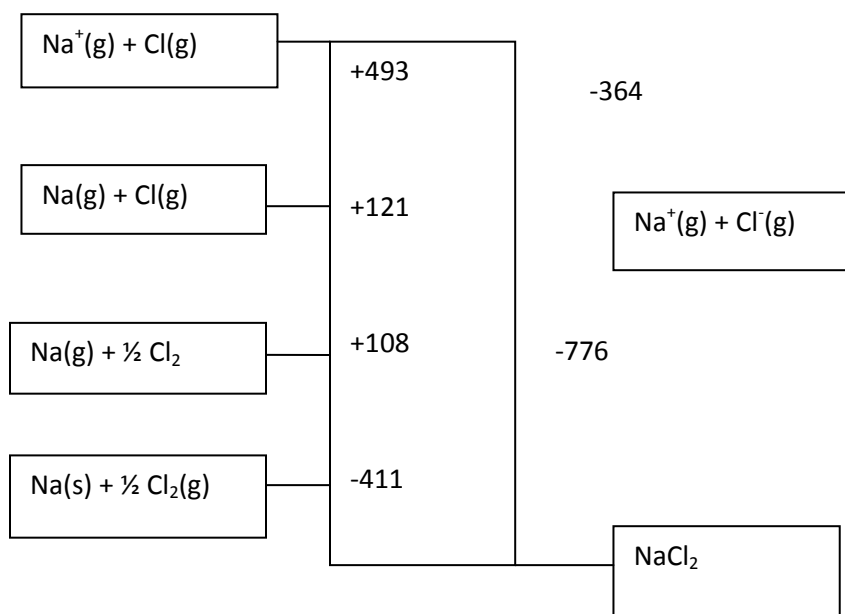
$$(\text{NaCl}) = -411 \text{ kJmol}^{-1}$$

$$(\text{Na}) = +108 \text{ kJmol}^{-1}$$

$$(\text{Na}) = +493 \text{ kJmol}^{-1}$$

$$(\text{Cl}) = -364 \text{ kJmol}^{-1}$$

$$\Delta_f H^\circ(\text{NaCl}) = -776 \text{ kJ mol}^{-1}$$



By Hess's law

$$\Delta_f H^\circ(\text{NaCl}) = \Delta_f H^\circ(\text{Na}) + \Delta_f H^\circ(\text{Cl}) + \Delta_f H^\circ(\text{NaCl})$$

$$= 108 + 121 + 493 + -364 + 776$$

$$= -418 \text{ kJ mol}^{-1}$$

Construct an energy level diagram for the formation of calcium chloride from its elements.

Calculate the lattice energy of calcium chloride using the following thermodynamic data.

$$\Delta_f H^\circ(\text{CaCl}) = -795 \text{ kJ mol}^{-1}$$

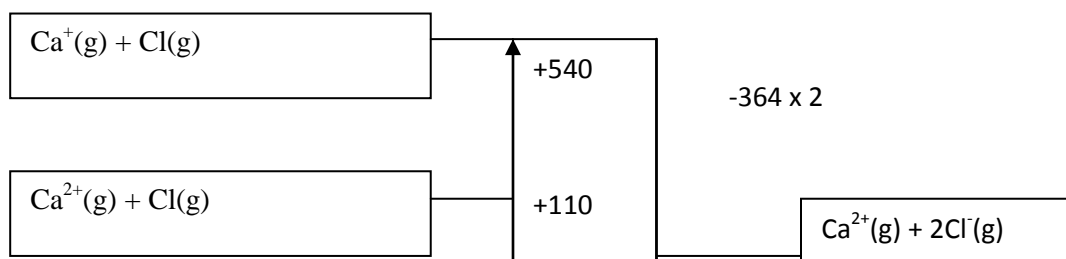
$$\Delta_f H^\circ(\text{Ca}^+) = +177 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{Cl}) = +121 \text{ kJ mol}^{-1}$$

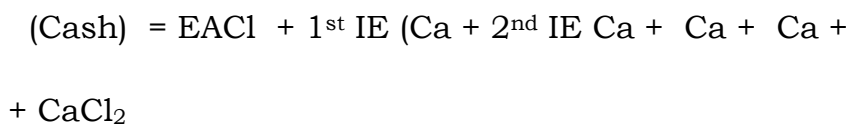
$$\text{1st IE of Ca} = 590 \text{ kJ mol}^{-1}$$

$$\text{2nd IE of Ca} = +1100 \text{ kJ mol}^{-1}$$

$$\text{1st EA of Cl} = -364 \text{ kJ mol}^{-1}$$



By Hess's law



$$-795 = 364 + 590 + 1100 + 177 + 121.4 - x$$

$$x = -2176 \text{ kJmol}^{-1}$$

$$\Delta H_{\text{f}}^\circ(\text{CaCl}_2) = 2176 \text{ kJmol}^{-1}$$

Factors affecting lattice energy of an ionic cpd

There are two factors that affect the lattice energy of an ionic cpd:-

- Ionic radius (size of ion)
- Ionic charge (charge on ion)

When the ionic radius of the ions of the opposite charge are small, then the ions approach each other closely and electrostatic forces of attraction between the ions are very high and this results in the formation of strong ionic bonds moving the lattice energy to be very high. But when the ionic radii of the ions of opposite charge are big, then the ions do not approach each other more closely and the electrostatic force of attraction is weak leading to weak ionic bonds and therefore the lattice energy will be small.

(c) Ionic charge

When the ions of opposite charge have high charge they will approach each other more closely resulting into strong electrostatic forces of attraction and thus the ionic bonds, will be very strong making the lattice energy to be very high. But when the ions of opposite charge have low charge density then they do not approach each other more closely and the electrostatic forces of attraction between the ions becomes weak leading to weak.

Ionic bonds and thus the lattice energy becomes small

Compound	lattice kJmol ⁻¹	
N ⁻		
Na ⁺		
·		
·		
· 3		
·		
·		
·		
CaF ₂	-2602	
CaCl	-2237	
CaO	-3310	

From the table, it is seen that when the size of the ion (i) small lattice energy is high F.

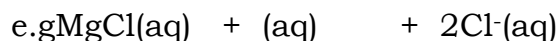
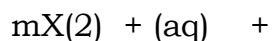
Fluoride ion is smaller than chloride ion and therefore CaF₂ has a higher lattice energy than CaCl₂

Oxygen ion is doubly charged which chloride ion is singly charged therefore CaO has a higher lattice energy than CaCl₂.

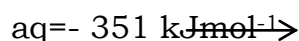
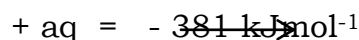
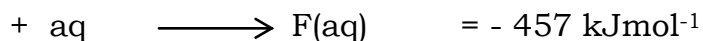
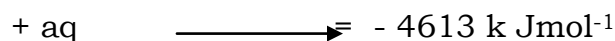
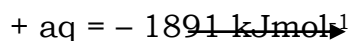
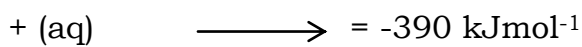
Standard enthalpy of solution and standard enthalpy of hydration.

Standard enthalpy of solution is the enthalpy change that occurs when one mole of an ionic compound is dissolved in specified amount of water to form an infinitely

dilute solution containing the ions of the cp'd infinitely dilute solution containing the ions of the cp'd



standard enthalpy of hydration (hydration energy is the enthalpy change that occurs when one mole of gaseous ions is completely surrounded by water molecules, such that further dilution causes no enthalpy change the enthalpy of hydration is always, an exothermic process because there are partial bond formed between the ions and water molecules .



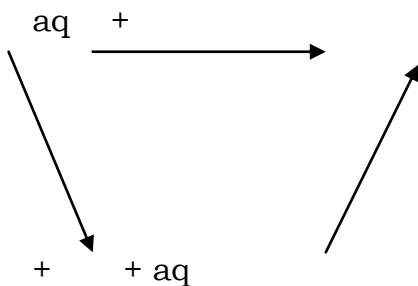
From the values above of the hydration energies, the smaller the ion the higher the hydration energy.

This is because when the ion has smaller ionic radius the charge density is very high and therefore strongly attracts the water molecules , leading to higher hydration energy.

Also when the charge on the ion is big, it will experience high charge density and therefore it will attract water molecules strongly leading to higher hydration energy.

When an ionic solid is dissolved in water the three energy terms come into play.. ie enthalpy of solution enthalpy of lattice and enthalpy of hydration.

The three energy terms are related by the born-haber cycle below;



By Hess's law

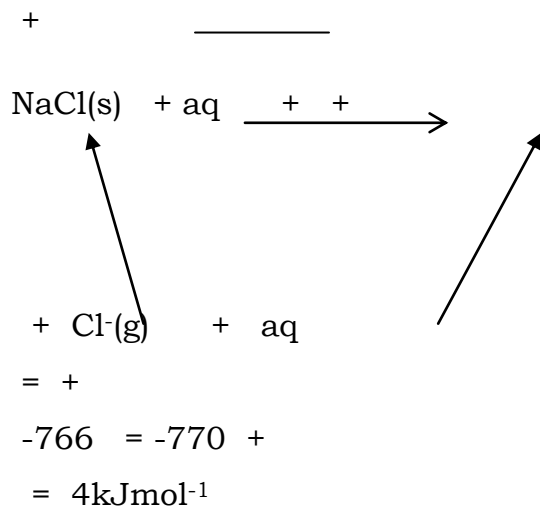
+

The lattice energy in this case is positive and it is greater than hydration energy, then the enthalpy of solution will be positive

But if the enthalpy of hydration is greater than lattice energy, the enthalpy of solution will be negative ie an exothermic reaction.

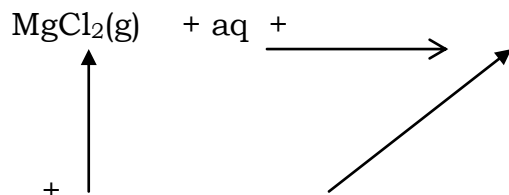
Qn.

1. Given that the lattice energy of sodium chloride is -770 kJmol^{-1} and the hydration energy of $\text{Na}(\text{g})$ is -766 kJmol^{-1} . Calculate the enthalpy of solution of sodium chloride.



The lattice energy of MgCl_2 is -2484 kJmol^{-1}

The hydration energies of Mg^{2+} and Cl^{-} are -1891kJmol^{-1} and -381kJmol^{-1} respectively. Calculate the enthalpy of solution of MgCl_2 .



$$\begin{aligned} \Delta H_{\text{sol}} &= \Delta H_{\text{hyd}}(\text{Mg}^{2+}) + 2\Delta H_{\text{hyd}}(\text{Cl}^{-}) \\ &= -1891 + -381 \times 2 = -2484 \text{ kJmol}^{-1} \\ &= -2652 + 2489 = -164\text{kJmol}^{-1} \end{aligned}$$

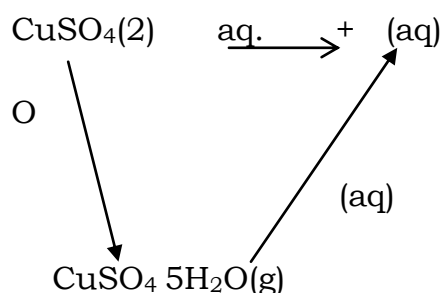
NOTE

The balance between lattice energies and enthalpies of hydration accounts for the observation that certain hydrated cpds dissolve endothermically, where as the corresponding anhydrous cpds dissolve

Exothermically

This is because the ions in the crystals of the hydrated cpd are already partially hydrated so that when they are dissolved in water, the lattice energy easily outweighs the enthalpy associated with further hydration, but for the anhydrous cpd the hydration energy is more than lat energy and therefore the enthalpy of solution is negative e.g. anhydrous copper (ii) sulphate dissolves in form a dilute solution and the enthalpy of solution -66.3kJmol^{-1} where as the enthalpy of solution of hydrated copper (ii) solution is $+11.4\text{kJmol}^{-1}$

The following energy cycle can be constructed



By Hess's law

= +

-66.5 + + 11.4

= -66.3 - 11.4

-77.7 kJmol⁻¹



Explain the determines the enthalpy of solution of an ionic salt.

A known mass of water is placed in a plastic breaker or an insulated calorimeter which is filled with a stirrer and thermometer.

The water is stirred for some time until the temperature remains steady and the initial temperature of the water read and recorded as T_i,

A known mass of the salt is added to the water and stirred to dissolve completely to form the solution.

The final steady temperature of the solution is read and recorded as T_f.

Assumption

The density of the solution is assumed to be equal to that of water = 1gcm³.

The sp. heat of a solution is assumed to be equal to that of water = 4.2 J/g°C

Treatment of results

Let m_w be the mass of the water.

m_s be the mass of the salt

M be the relative formula mass of salt.

Temp change ΔT = (T_f - T_i)

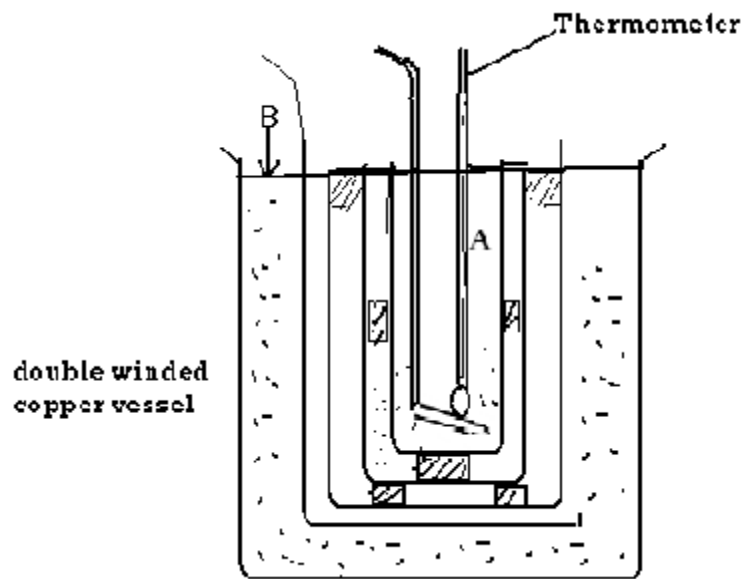
Heat absorbed by the solution = M x sp. heat x ΔT

= m_s x 4.2 x (T_f - T_i)

m_s g of the salt produce a c (T_f - T_i)

Molar heat of the produce

Determination of enthalpy of solution of (NH₄Cl)



To find the heat

Water is placed in a copper calorimeter titled with a silver and thermometer reading to...

The calorimeter is surrounded by an empty copper cylinder, by a doubled walled copper vessel containing water.

The vessel s are prevented from houching by cork.

The purpose of the outer vessel is to prevent heat loss or ... by radiation.

Ammonium Chloride is provided to enable rapid dissolving and weighed amount in action scaled but it is able to water in A.

The results broken in the water by means of the thermometer and the solution ins stirred until there is no further changes in temp.

The .. of the solution is determined (of dilute this may be assumed to be equal to that of water. Heat of solution is calculated after allowing for the heat c,... orby the calorimeter and the given results.

Treatment of results

Let a g be the mass of the water

b g be the mass of ammonium chloride

Mabe the relative formular mass of NH_4Cl

RFM of $\text{NH}_4\text{Cl} = 14 + 4 + 35.5 = 53.5$

Enthalpy of neutralis Temp change be $(T_1, - T_1)^\circ\text{C}$

Heat absorbed by the solution in Mass x She X DT

$$= a \times 4.2 \times (T_2 - T_1)$$

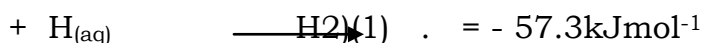
By of NH_4Cl produce $a \times 11.2 \times (T_2 - T_1)$

5353 of NH_4Cl produce $4.24 (T_2 - T_1) .55.5$

$$= - \times 224.7 (T_2 - T_1) \text{ kJmol}^{-1}$$

Enthalpy of neutralization

It is enthalpy change that occurs when one molecule of hydrogen low from the acid reacts with one mole hydroxide ions from the alkali to form one mole of water under standard conditions of 298k and 1 atom.

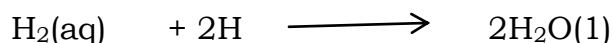
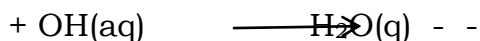
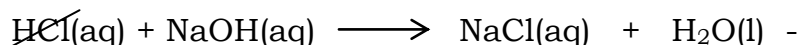


NOTE:

All enthalpies of neutralization are negative neutralization reaction is an exothermic reaction.

The heat of neutralization of a strong acid and a strong alkalis constant and the value is Z

This is because strong acid and strong alkali dissolute completely to form cons and the reaction is always between hydrogen ion and hydroxide ion to form one mole of water .



The enthalpy of neutralization of a weak acid such as CH_3COOH . HF, hydrogen Propanoil acid ($\text{CH}_3\text{CH}_2\text{COOH}$) and strong alkali e.g NaOH and KOH solution and vice versa is less than -57.3 KJ/mol because weak electrolytes dissolute particularly to form fewer ions and therefore the reaction is not complete and therefore a lower enthalpy is obtained .

Also ionization of weak electrolytes is an endothermic process i.e. that is absorbed and this reduces on the over all heat at neutralization.

If both electrolytes are weak ie a reaction between a weak acid and a weak alkali, the enthalpy of neutralization is mass lower -5.3 kJmol because weak electrolytes absorb a lot of energy for the dissociation reaction to take place which counter acts the enthalpy of neutralization.

ACID	ALKALI	neutrralisaiton kJmol ⁻¹
Hco	NaOH	-57.4
Hcl	KOH	-57.3
Hno3	NaOH	-57.3
H ₂ SO ₄	NaOH	-01.3
HCN	KOH	-11.7
HCI	NH ₃	-52.2
HCN	NH ₃	-5.4
CH ₃ COOOH	NaOH	-55.2

EXPERIMENT TO DETERMINE THE ENTHALPY OF NEUTRALIZATION OF STRONG ACID AND STRONG ALKALI

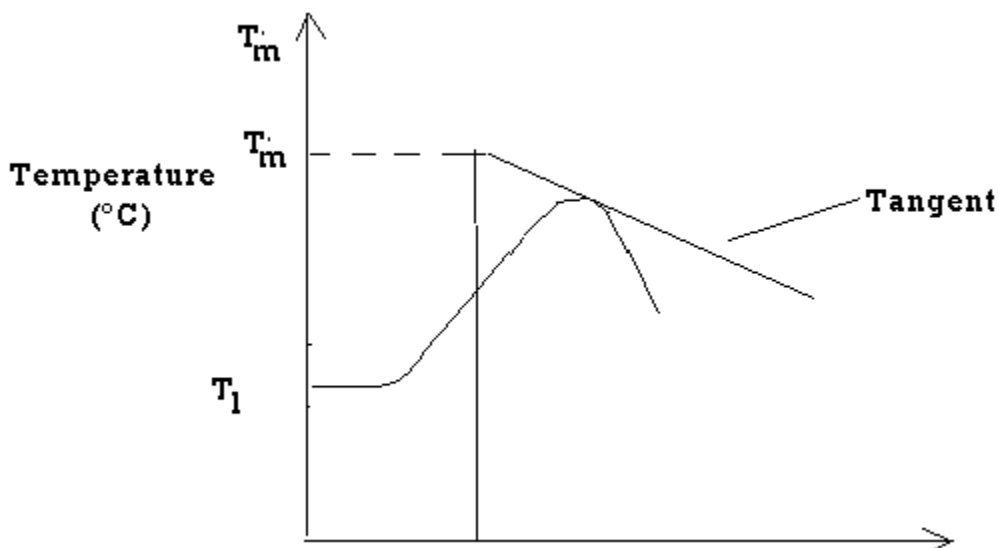
A known volume V1cm³ of a strong acid known conc M, is placed in a thermes flask or in a plastic beaker or in a well lagged calorimeter fitted with a thermometer.

The initial temp of the acid solution is read and recorded as T₁

A known volume V2cm³ of a strong alkali of known concentration whose initial temp is read and recoded as T1 is mixed with the acid in a well lagged (in soluted) container and the mixture well stirred.

The maximum temp of the mixture is read and recorded as T₂ or the temp of the mixture is taken at regular time intervals until the system starts to cool.

A graph of temp against time is plotted and the graph is used to determine the maximum temp by drawing a tangent on the cooling curve and a point at which the tangent cuts the temp axis is the max temp.



Treatment of results

Initial temp $T_1 =$

Final temperature of the mixture = T_m

Temperature change = $[T_m - T_1]$

Let the density of mixture be ρ

Let the sp. heat of the mixture be C

Total volume of the solution = $V_1 + V_2$

Mass of the solution = density \times volume

= $\rho(V_1 + V_2)$

Heat absorbed by the solution = MC

= $\rho(V_1 + V_2) \times [T_m - T_1]$

No. of moles of the acid =

=

moles of acid produced = C

1 mole of the acid produced $(V_1 + V_2) C (T_m - T_1)$

Enthalpy of neutralization =

qns

1. When 25cm^3 of 2M HCl were mixed with 25cm^3 of 2M sodium hydroxide solution but at initial temp of 24.5°C . The final temp of the mixture was 37.0°C . Calculate the enthalpy of neutralization of hydrochloric acid

Total volume of the solution = $25 + 25 = 50\text{cm}^3$

Mass of the solution = $1 \times 50 = 50\text{g}$

Heat absorbed by the solution = MC

= $50 \times 4.2 \times 12.5$

= 2625J

No of mole of acid 1000cm^3 of acid contain 2moles

25cm^3 of acid contain $\times 25$

= 0.05 moles

C.C. Heat of acid produced 2625J

1 mole of acid produced $\times 1$

= 52500J

Enthalpy of neutralization = 52.5kJmol^{-1}

NOTE:

The heat of neutralization determined by the above experiment is less than the theoretical values because some heat is lost to the surroundings.

50cm^3 of $2\text{M H}_2\text{SO}_4$ were mixed with 50cm^3 of 2M NaOH solution and the temp of the mixture rose by 13.6°C . Calculate the enthalpy of neutralization of Sulphuric acid.

Total mass of the solution = $50 + 50 = 100\text{cm}^3$

Mass of solution = $1 \times 100 = 100\text{g}$

Heat absorbed by the solution = MC

= $100 \times 4.2 \times 13.6$

5712J

100cm^3 of H_2SO_4 contain 2 moles

50cm^3 of H_2SO_4 contain $\times 50 = 0.1$ mole

0.1moles of acid produced 5712J

1 mole of acid produces = 571205 114.24 kJ

Enthalpy neutralization of H_2SO_4 = kJmol^{-1}

Thermometric titration Method II

This type of titration involves volumes and temp. Changes

A known volume of the acid is pipetted into a plastic beaker or a well lagged container fitted with a stirred and thermometer

Known portions of the alkalis are added to the acid and at each addition, the mixture is well stirred and the temp of the mixture determined.

The initial temp of the acid must be known

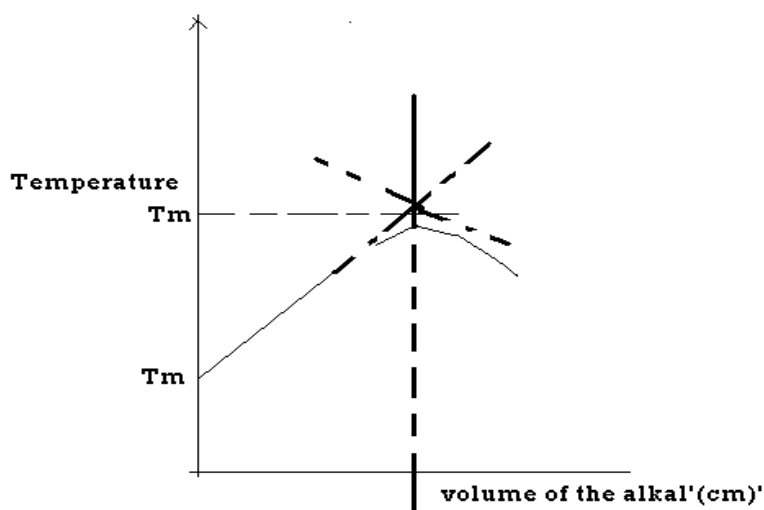
A graph of temp (Temp change) is plotted against the volume of the alkali.

The graph assumes the maximum

Tangents are drawn at either side of the maximum where the tangents meet gives the maximum temp of the reaction mixture and the volume of the alkali that corresponds to the maximum temp is the volume that neutralize the acid completely i.e. the maximum temp correspond to the neutralization point or end point of the titration

The graph can be used to determine

- (a) Enthalpy of neutralization of the acid or alkali
- (b) Stoichiometry of the reaction (reaction mole ratios)



Example

50cm³ of HCl was placed in a plastic beaker and the initial temp read and recorded as 22.5

5cm³ portions of 2M sodium hydroxide solution were added to the acid and the temp of the mixture recorded on each addition. The results of the exp't were shown in the table below;

Volume of NaOH/cm ³	0	5	10	15	20	25	30	35
Temperature/	22	27.5	31.3	34	35	34	32	28.5

Plot a graph of temp against volume of sodium hydroxide added.

Use the graph to determine the molarity of HCl the heat of neutralization of HCl

Maximum temp reached is 36.2

Mass of solution 50 x 85 = 85

mass

55 x 4.2 x 13.1

4676.2J

HCl + NaOH → NaCl + H₂O

Sodium of NaOH Contain 2m

35cm³ of NaOH contains x 35 = 0.07

0.07moles produce heat change of 4617 J

1 mole of HCl produce

= 66.21kJmol⁻¹

Heat of displacement reaction

It is the heat change/enthalpy change that occurs when one mole of metal ion in solution is displaced by a more reactive metal

e.g Zn(s) + Cu²⁺(aq) → Zn²⁺(aq) + Cu(s)

Fe (s) + Cu²⁺(aq) → Fe²⁺(aq) + Cu(s)

½ Cu(s) + Ag⁺(aq) → ½ Cu²⁺(aq) + Ag(s)

1. When 0.1 mole of Zinc powder was added to 250cm³ of 0.2 CuSO₄ solution in a plastic cup and the mixture is stirred gently using the thermometer and

the temp changed from 19 to 25C. calculate the moles heat of the displacement reaction.

2. Excess Zn powder was added 25cm³ of 1m solution of CuSO₄ in a plastic beaker and the temp of the solution recorded at regular intervals. Data obtained is shown in the table below;

Time (min)	0	2.5	3	35	5.0	60	7.0
temp	27.7	66.0	69.5	68.5	68.5	62	59.5

Plot a graph of temp against time.

Use the graph to determine the moles heat of displacement reaction

20 – 19.9

Mass of solution 250g

Heat absorbed by solution = MC

= 250 x 4.2 x 4

= 9650J

$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu (g)}$

1000cm of Calcium 0.2mole

250cm of calcium x 250 = 0.05mole

Mole of ratio of Zn : = 1:1 moles of Zn = 0.05

1.05 mole of Zn 9450J

1 mole produce = 189 kJmol⁻¹

2. Maximum Temp. = 105

= 70.5 – 27.2 = 43.5

Mass of the solution 1 x 25 = 25g

Heat absorbed by the solution = m.

= 25 x 4.2 x 43.3

4546.5J

1000cm³ calcium 1 mole

25cm³ of contain x 25 = 0.025 mole

Mole Zn(g) + Cu²⁺ → Moles of Zinc ions reacted = 0.025 moles

Moles of Zn ions reacted 0.025 moles

0.025 moles of produce 4546kJ

LM04 of Produce kJ = 181.864kJmol⁻¹

Heat of displacement of the production is 181.86kJmol⁻¹

Heat of precipitation

It is the heat change that occurs when one mole of a solid compound (rpt) is formed from the two aqueous solutions under standard conditions, of 298K and atmosphere 1994

Determination of heat of precipitation of AgNO₃ measure out 25cm³ of silver Nitrate solution and pour it into the polystyrene bottle.

Insert the temp. fitted with the thermometer and not the temp of the bond to the liquid. Initial temp is 6.0

Measure out 25cm³ of 0.5M NH₄Cl and add it to silver nitrate solution in the polystyrene bottle/

Quickly replace the bung in the bottle and shake gently, to allow mixing of solution. Maximum temp = to .

Repeat (a) and (b) using 0.5M instead of NH₄(1)

Treatment of results

25cm³ of 0.5M AgNO₃ react with 25cm³ of NH₄(1)

25cm³ of 0.5M AgNO₃ contain

= 0.0125 moles

of 0.5M NH₄Cl or KCl

0.0125 mole of - -

Mass = 1 x 50 = 50g

Heat absorbed = MC

= 50 x 4.2 (t₂ - t₁)

What is meant by the following?

- i. standard state of a substance
- ii. Standard enthalpy of formation
- iii. Standard enthalpy of combustion

(b)(i) Describe an exp't determine the enthalpy of combustion of sulphur.

(ii) the standard enthalpies of combustion of sulphur from carbon dioxide and carbon disulphide are 297- 3994 & - 1075 kJmol⁻¹ respectively.

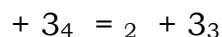
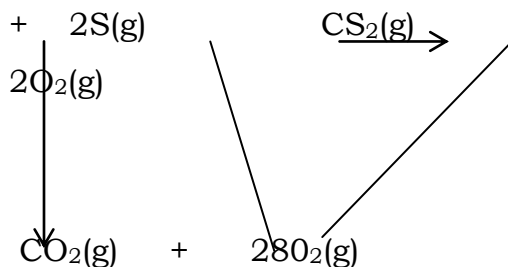
Calculate the standard enthalpy of formation of carbon disulphide

(c) The standard enthalpies of combustion of the first form straight chain alkanes and the first five straight .. alcohols are shown in the table below;

No of carbon atom	1	2	3	4	5
enthalpy of combustion of alkane (KJ mol)	-950	-1560	-7224	2871	-3509
Enthalpy of combustion of alcohol (kJ mol)	-715	-1371	-2010	-2673	-3305

1. On the same axis, put a graph of enthalpy of combustion against the number of carbon atoms for both alkanes and alcohols.

2. Explain the shape of the graph



The enthalpy of combustion of alcohol increases steadily as the number of carbon atoms increases.

The enthalpy of combustion of alkane increase steadily from 950 to 3509 as the number of carbon atoms increases.

However the enthalpy of combustion of alkane increases at a hither rate than that of alcohols.

This is because alkane excurate hydro compounds

