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 Kc.
- Gaseous equilibrium and Kp.
- The heterogeneous system and Kp.
- Factors affecting equilibrium and lachetelier's principle.

4. Ionic equilibrium.
4.1 Ionic equilibrium.
- Acidity and alkalinity as properties of a system Ka & Pka
- PH and its calculation.
- PH scale.
- The relationship between K_b and PK_b; Kw, 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, Ks_P
- 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 Ka & Kw

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
- Roault's law and its applications.
- Negative and positive deviations from Roault'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 it 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 Kohroausch'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, $CuSO_4$, NaCl, $PbBr_2$, CuCl, NaCl, NaBr etc.
- Faraday's laws and calculations.
- Applications electrolysis e.g corrosion of non, 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.
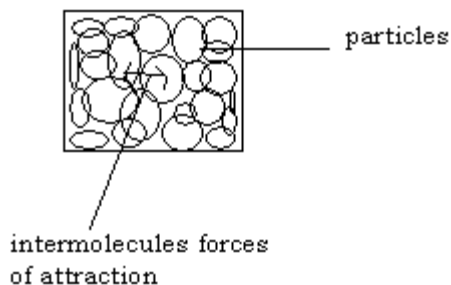

Behavior of particles in liquids.
In liquid, the particles are far apart with weak forces of attraction, they are therefore a free to move from 1 point to another within the bulk of the liquid. When liquids temp increase they gain kinetic energy move faster with higher velocities. When the temperature the system is lowered, the liquid cooled down and the vapour condenses back to liquid in the process called condensation.
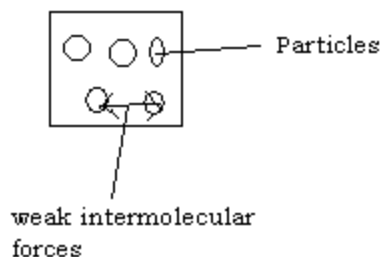
In Gases.
The particles are very far apart with very weak inter molecular forces between them. The gas particles move almost independent of one another and tend to move faster than those in liquid. When the temperature of a gas increased the particles move even faster but they tend 2 collide with one another.
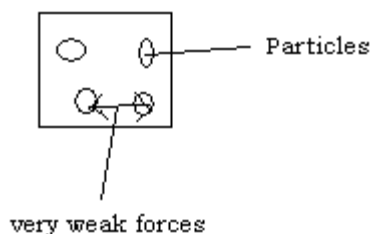
Fundamental differences between all the three states of matter.

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
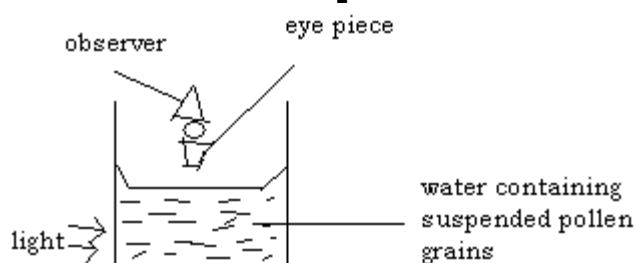
Method
Pollen grains suspended in water and observed under a microscope
Observe.
Yellow particles are seen moving around randomly
Conclusion
Yellow particles move randomly because were colliding with water particles which were moving randomly because liquid particles show random motion.
Random motion is gases.
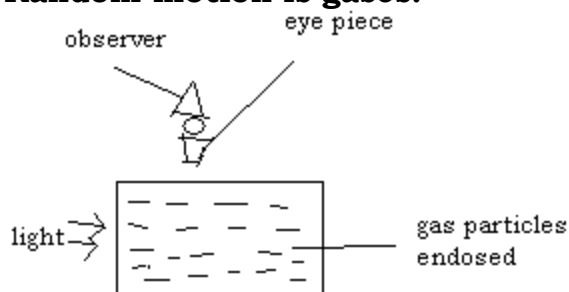
Method
White smoke from burning paper is enclosed in smoke cell and observed under a microscope.
Observation
The white specks are seen moving about randomly
Conclusion
Gases exhibit random motion.
**What is observed when a smoke cell is cooled or its temperature is raised?**

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

crystal of CuSO4 / POH
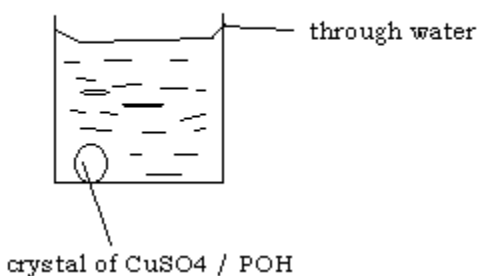
Method

A crystal of $CuSO_4$ is dropped in water in a trough
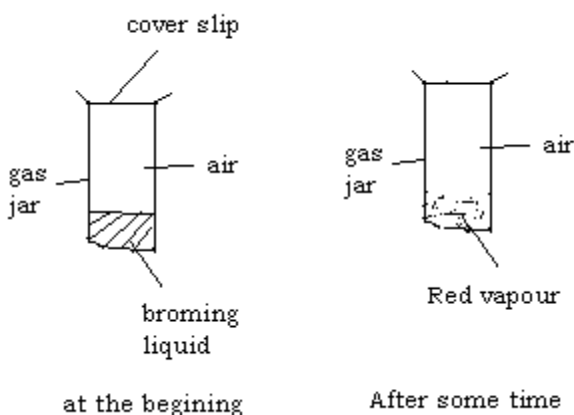
Observation
- The crystal sinks in the water in the trough.
- The crystal sinks and dissolves producing one solution at the base of the trough.
- The blue colour migrates upward in the trough and after some period of time, the entire mixture appears uniformly blue in colour.

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 because uniformly blue kin colour because the rate of down ward diffusion of the same ion had reached equilibrium so even diffusion continue to occur the colour of the mixture will not change.

Diffusion in gases

Example

cover slip

gas jar — air

gas jar — air

Red vapour

broming liquid

at the begining   After some time

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

Observation
- Bromine vaporizes giving a red vapour
- The red vapour slowly but steadily disperse in a gas jar
- At the beginning the red vapour is concentrated at the bottom of a gas jar but after sometimes, 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 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 have low densities
- The diffuse rapidly
- They expand on heating and contract on cooling
- Most gas 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.

$V \propto \dfrac{1}{\rho}$ ------------- (i)

$V = \dfrac{k}{p}$ ------------- (ii)

$Pv = k$ ---------- (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

$V_1 P_1 = V_2 P_2.$

Examples.

1. The volume of fixed mass of a gas of pressure of 4 atmospheres is 200cm³. Calculate volume at the pressure of 1.25 at 4 atm0sphere.

From $V_1 P_1 = V_2 P_2$

$\dfrac{200\ x\ 4}{1.25} = \dfrac{1.25\ x\ V_2}{1.25}$

V₂ = 640cm²

Graphical representation of Boyle's law
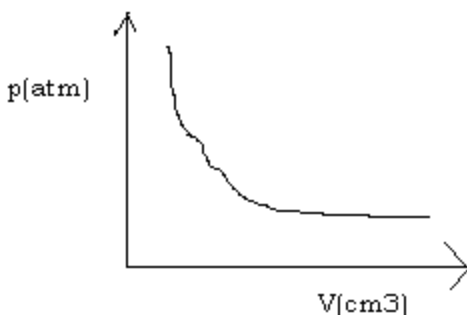
If $\dfrac{1}{p}$ is plotted against V a straight line graph is given out.
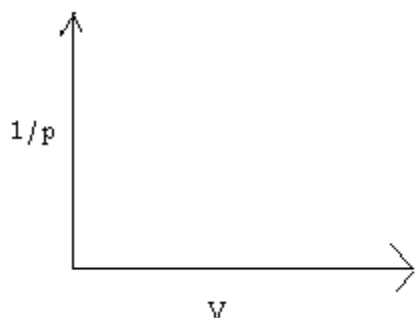
CHARLES LAW

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.

$V \propto Y$ ------------(i)

V = KT----------(ii)

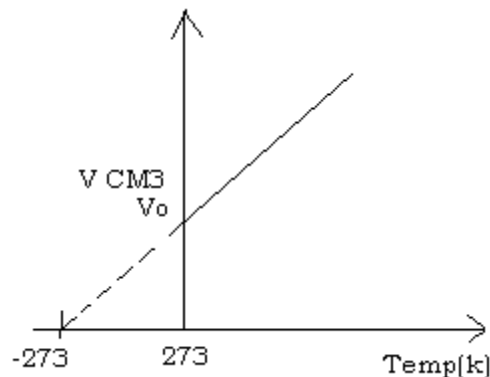$\frac{V}{T}$ = K ------------(iii)

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.

$V_1T_1 = V_2T_2$

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

Graphically, Charle's law is expressed as follow

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

From $V_1T_1 = V_2T_2$

100 x 25 = V_2 x 10

$\frac{2500}{10} = \frac{10V_2}{10}$

V_2 = 250CM³

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 ∝ T ------------(i)

P = KT----------(ii)

$\frac{P}{T}$ = K ------------(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.

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$

The equation of state

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

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

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;

$\frac{RV}{T}$ = 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 = $\frac{PV}{nT}$

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

R = $\frac{PV}{nT}$

R = $\frac{1.0132 \ x \ 10^5 \ x \ 22.4 \ x \ 10^{-3}}{1 x 273}$

R = 8.3145K^{-1} $mole^{-1}$/ $NM^{-1}K^{-k}$ mole **OR** R = 0.082 litres $Atm^{-1}K^{-1}$ 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 PT= PA + PB where;

PT – is the total pressure

PA – is the partial pressure of gas A

PB – 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; PA = XA. PA where PA is the partial pressure.

XA is the mole fraction of gas A

PA is the pressure exerted by pure gas A

The partial pressure for B is given by PB = X_{13} x P^0B where PB is the partial pussure of B.

XB- is the mole fraction of gas B

P^0B – 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.

XA = $\frac{nA}{nA+nB}$ also the mole fraction of B

XB = $\frac{nB}{nA+nB}$

Avogadro's law

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

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

1. Calculate the pressure exerted by mixing 5 moles of hydrogen and 2 moles of neon (P^0Ne = 200mmHg, P^0H_2 = 100mmHg).

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 Iussac's laws of combining volume.If $20cm^3$ of H_2 react with $10cm^3$ of O_2 to produce $20cm^3$ 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. !5cm³ of H_g 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 dm³ 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 atm = 101.325 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. $P_T = P_H + P_{Ne}$

$P_H = \frac{nH}{nH+nNe} = \frac{5}{7}$

$X_{Ne} = \frac{2}{7}$

$P_H = \frac{5}{7} \times 100 = \frac{500}{7}$

$P_{Ne} = \frac{2}{7} \times 200 = \frac{400}{7}$

$P_T = \frac{500}{7} + \frac{400}{7} = \frac{900}{7}$

=128.5mmHg

2. $C_6H_{14} = (12 \times 6) + 14 = 86$

86g of C_6H_{14} occupy 1 mole

43g of C_6H_{14} occupy $\frac{43 \times 1}{86} = 0.5$ moles

$C_7H_{16} = (12 \times 7) + 16 = 100g$

100g of C_7H_{16} occupy I mole

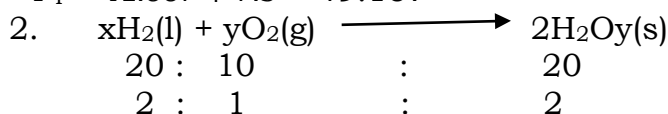10g of C_7H_{16} occupy $\frac{10 \times 1}{100} = 0.1$ moles

0.1 + 0.5 = 0.6 moles

$XC_6 = \frac{0.5}{0.6}$ $XC_7 = \frac{0.1}{0.6}$

$P_{C6} = \frac{0.5}{0.6} \times 50 = 41.667$

$P_{C7} = \frac{0.1}{0.6} \times 45 = 7.5$

$P_T = 41.667 + 7.5 = 49.167$

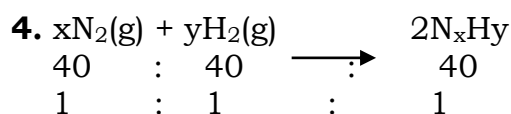2. $xH_2(l) + yO_2(g) \longrightarrow 2H_2Oy(s)$

        20 : 10   :   20

        2 :   1   :   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

4. $xN_2(g) + yH_2(g) \longrightarrow 2N_xHy$

  40   :   40   :   40

  1   :   1   :   1

X moles of N_2 reacts with y moles of H_2O to produce 2 moles of N_xHy

1 mole of N_2 reacts with 1 mole of H_2 to produce

1 mole of N_xHy . X =1 y = 1

Molar mass of NH = 14 + 1 = 15

N_2H_2

Therefore X = 2 y=2

5. $CxH_y(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(s)$

$CxHy (s) + \frac{y}{2}O_2 (g) \longrightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$
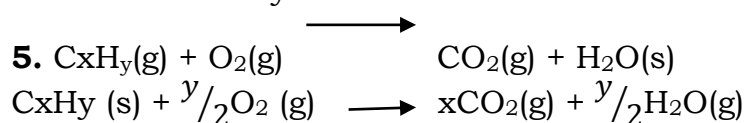
Let the volume of O_2 be Zt

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

Reaction rate 1 $\frac{t}{15}$ 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 $\frac{t}{15}$ moles of O_2 to

give 6 moles of CO_2 and 7 moles of H_2O is $\frac{y}{t} = \frac{7}{1}$ = y =4   x =6.

Therefore molecular formula = C_6H_4

$\frac{x+y}{4}$ $\frac{6+14}{4}$ $\frac{24+14}{4} = \frac{38}{4}$

= 38

1 volume of C_xH_y react with $(x + \frac{y}{4})$ volume of O_2

15 volume of C_xH_y reacts with $(\frac{x+y}{4})$ x 15 O_2

$(\frac{35}{4}$ x 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 $(\frac{4 \times 1}{36})$ moles

If 14 moles of N_2 contains 1 mole

Therefore 1 dm^3 of N_2 will contain $(\frac{1 \times 1}{14})$ moles

$XO_2 = (\frac{4 \times 1}{36}) = 0.111$ $\qquad$ $XN_2 = 0.71$

$(\frac{0.111 \times 200}{0.111 \times 200 + 0.071 \times 200}) = \frac{22.2}{22.2 + 14.2} = \frac{22.2}{36.4}$

= 0.61

8.

N_2	CO_2	O_2
$\frac{65}{28}$	$\frac{15}{44}$	$\frac{20}{32}$
$\frac{2.3}{0.34}$	$\frac{0.34}{0.34}$	$\frac{0.625}{0.34}$
6.8	1	1.8

$P_{N2} = \frac{7}{10} \times 101.325$

$PCO_2 = \frac{2}{10} \times 101.325$

= 20.3Kpa

9(a)

O_2	N_2	H_2
26.64	34	42.66
$\frac{26.64}{103.3} \times 100$	$\frac{34}{103.3} \times 100$	$\frac{42.66}{103.3} \times 100$
25.8%	32.9	41.3

(b)

O_2	N_2	H_2
$\frac{26.64}{26.64}$	$\frac{34}{26.64}$	$\frac{42.66}{26.64}$
1	1.28	1.60

$= {}^1/_{3.88}$

Mole fraction of $O_2 = {}^1/_{3.88}$

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.
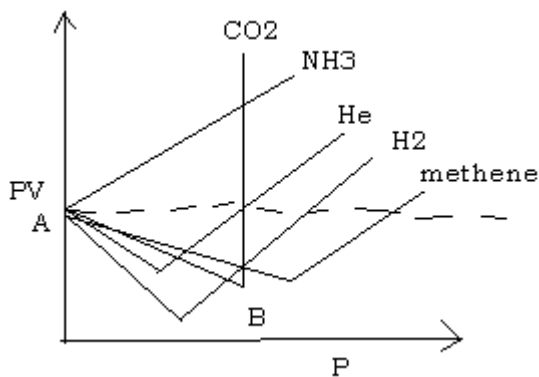**Non ideal gases/ real gases.**
These are gases which don't obey the gas laws and equations expectedly.
Assumption made for non ideal gases.
- Gas particles exert any inter molecular forces of attraction/repulsion between them.
- Particles occupy a particular volume compared to total volume.
- Real 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, Vcm^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) cm^3 if there is any number of molecule of the real

gas in the container, then the volume becomes (V- nb)cm³. Therefore from the expression

Pv – nRT

But V= (v-nb)

P(V-nb) =nRT.

A real gas has inter molecular forces of attraction causing the pressure reduction. Van da 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 $\propto$ concentration of molecules the wall x ie concentration of molecules in the interior of the container.

Pressure reduction $\propto \dfrac{n}{v} - \dfrac{n}{v}$

$$\propto \dfrac{n^2}{v^2}$$

The actual pressure would be;

P + $\dfrac{an^2}{v^2}$

From the expression PV = nRT, it becomes (P + $\dfrac{an^2}{v^2}$) (v-nb) = nRT.

It becomes (P + $\dfrac{an^2}{v^2}$) (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

$\dfrac{n^2}{v^2}$ - a factor of collection of deviction in a vol exerted by the gas when attractive forces become significant.

LIQUEFACTION / CONDENSATION OF GASES.

At high temperature,t_3 carbondixide 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 Boyles' law. The vapour remains in equilibrium with the liquid and this state happens when a certain temperature called **critical temperature** is applied.
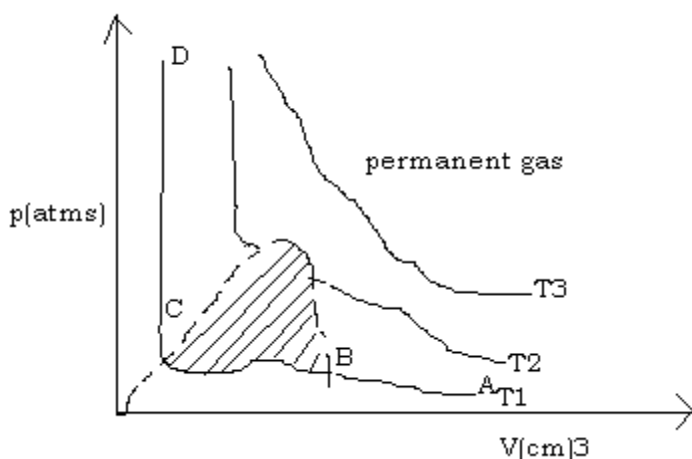
Taking the curve ABCD, between A & B CO_2 is a gas. A decrease in volume causes an increase in pressure in accordance with Boyle's law. At point B CO_2 begins to liquefy, along BC there is a sharp decrease in vol. with no change in pressure showing that liquids do not exert pressure. At point C liquefaction is complete and all CO_2 wall 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 an affected 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.
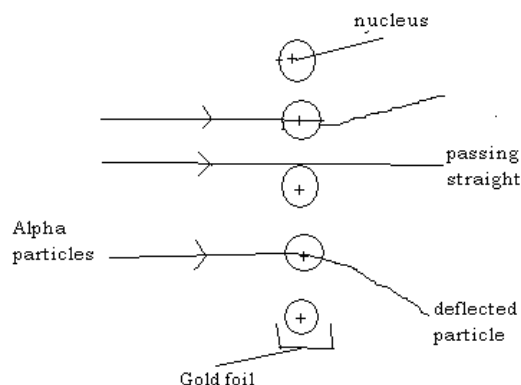
(b) Neutrons

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 prostitulate 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	$\dfrac{1}{1840}$	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 $_{12}^{24}\text{Mg}$, $_{11}^{23}\text{Na}$.
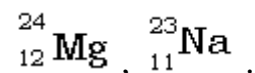
Isotopes there are different atoms of the same element with the same atomic number but if this mass number. Or are atoms of the same number of electrons and protons but of different electrons e.g

$$_{17}^{35}\text{Cl} \qquad _{17}^{37}\text{Cl} \qquad _{6}^{12}\text{C}$$
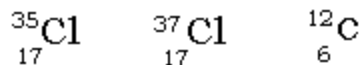
Since the chemical properties are determined by the number of electrons which are the same of in all isotopes. Therefore isotopes have got the same chemical properties. In order to evidence the existence of isotopes in atoms a mass spectrometer is used to detect the various isotopes on a mass spectrometer 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 Gram. Radioactivity substances affect photographic materials due When they disintegrate they release a lot of heat energy.

Results of radioactivity charges 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 H_e particles (^4_2He) 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 $^0_{-1}e$

Gamma rays
- These are neutral particles and are never deflected by either magnetic or electric field.
- They are electromagnetic radiation similar to e 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 destroy 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 $\frac{n}{p} = 1$.

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

$$\frac{n}{p} \neq 1$$

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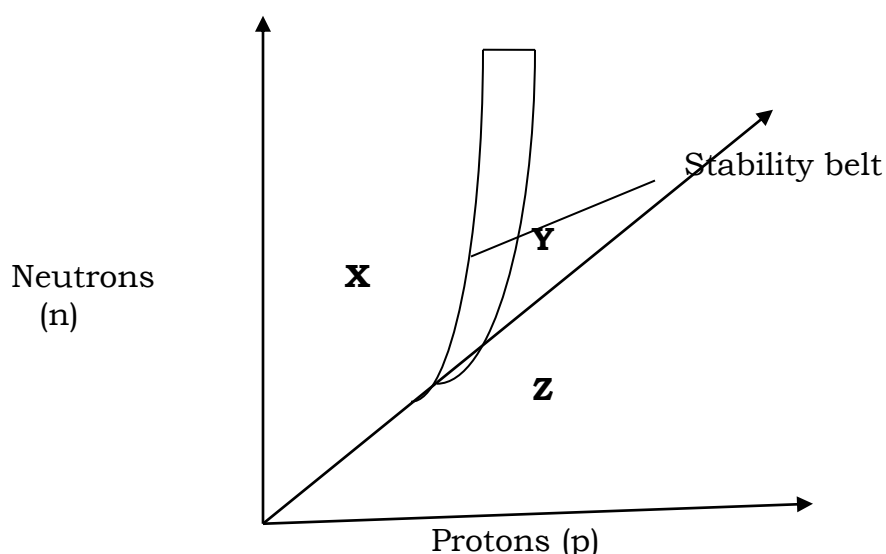
From the graph above all stable nuclides lie in the region which is shaded
Isotopes X, Y and X are unstable and they can become stable by approaching the stability bell. X has no excess neutrons with few protons. To approach the stability belt it reduces on the number of neutrons and excess on the no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

$$^{1}_{0}n \longrightarrow ^{1}_{1}H + ^{0}_{-1}e$$
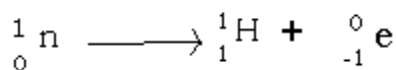
This reduces on the number of neutrons but increases the number of protons. The electron produced as a beta particle in a process called beta particle emission. Nuclide Y has an excess of protons and neutrons which combine to form alpha particles

$$2\left(^{1}_{1}H\right) + 2\left(^{1}_{0}n\right) \longrightarrow ^{4}_{2}He$$
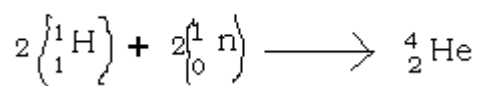
This reduces both protons and neutrons in alpha particles emitted. Z has an excess of neutrons and protons. To attain stability it reduces on the number of

protons in its nucleus but increasing the number of neutrons. It does this through capturing an electron and liberating a neutron.

$$_1^1 H + _{-1}^0 e \longrightarrow _1^0 n$$
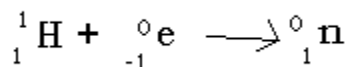
Laws of radioactivity.
1. Radioactive nuclides disintegrates spontaneously giving new and flesh element
2. The disintegration of an element is as a result of either emission of an alpha particle or Beta or Gamma rays.
3. The rate of disintegration of a nuclides not affected by physical factors e.g concentration, 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 $\propto$ un decayed atoms

$\frac{-dN}{dt} \propto Nt$ -------------(1)

$\frac{-dN}{dt} \propto Nt$ ------------(2)

Where x is decay constant

$-\int \frac{dN}{Nt} = xdt$

Integration

$-\int \frac{dN}{Nt} = x\int dt$

In Nt = λt + c-------------------(3)

If t = 0, λt = No = C

Substituting in equation (3) we get

In Ne = λE – in No

In Nt + No – λt

Therefore $(\frac{No}{Nt}) = \lambda t$---------------(3)

In term of logarithms to base ten

From in $(\frac{No}{Nt}) = \lambda t$

$(\frac{No}{Nt}) = e$

Taking log10 on either sides

Log 10 $(\frac{No}{Nt}) = Log_{10}^{ext}$

$log10 (\frac{No}{Nt}) = \lambda t \times \frac{1}{log\,10}$

$log10 (\frac{No}{Nt}) = \frac{\lambda t}{log^{10}}$

$Log_{10} \times log_{10} (\frac{No}{Nt}) = \lambda t$

$2.303 \, log_{10} (\frac{No}{Nt}) \, \lambda t$

If a graph of $\log_{10}\left(\frac{No}{Nt}\right)$ is plotted time, a straight from the origin is obtained with a positive gradient equal to $\frac{\lambda}{2.303}$ as shown below.

$\log_{10}\left(\frac{No}{Nt}\right)$

Slope $=\frac{\lambda}{2.303}$
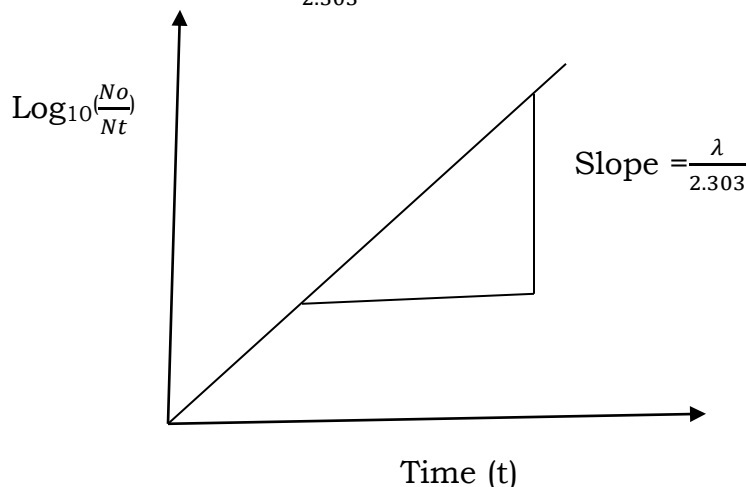
Time (t)

However when a graph of $\left(\frac{No}{Nt}\right)$ is plotted against time, a straight line graph from the origin but with a negative gradient is obtained as shown below

Time(s)

$\log_{10}\left(\frac{Nt}{N0}\right)$

Slope $= -\frac{\lambda}{2.303}$
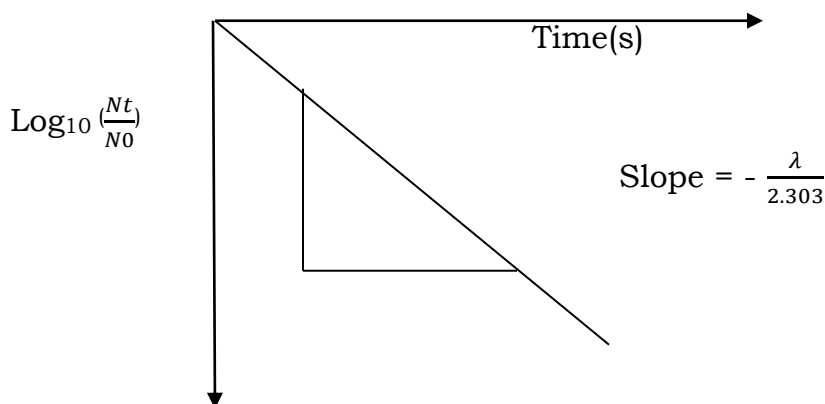
Deriving an expression for half **life.**
Half life is the time taken for half of the initial amount of a substance to disintegrate to and remains constant regardless of the initial amount.

From $\qquad$ In $\left(\frac{No}{Nt}\right) = \lambda t$

If $t = t\frac{1}{2}$, No $= \frac{1}{2}$ No

In $\left(\frac{No}{2No}\right) = \lambda t\frac{1}{2}$

In $\left(\frac{2\,No}{No}\right) = \lambda t\frac{1}{2}$

In $2 = \lambda t\frac{1}{2}$, $\qquad t\frac{1}{2} = \frac{0.693}{\lambda}$

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.

Initial concentration (mol/l) vs Time(s) — decay curve with markers at $\frac{No}{2}$, $\frac{No}{4}$ and $\frac{t}{2}$, $\frac{t}{4}$
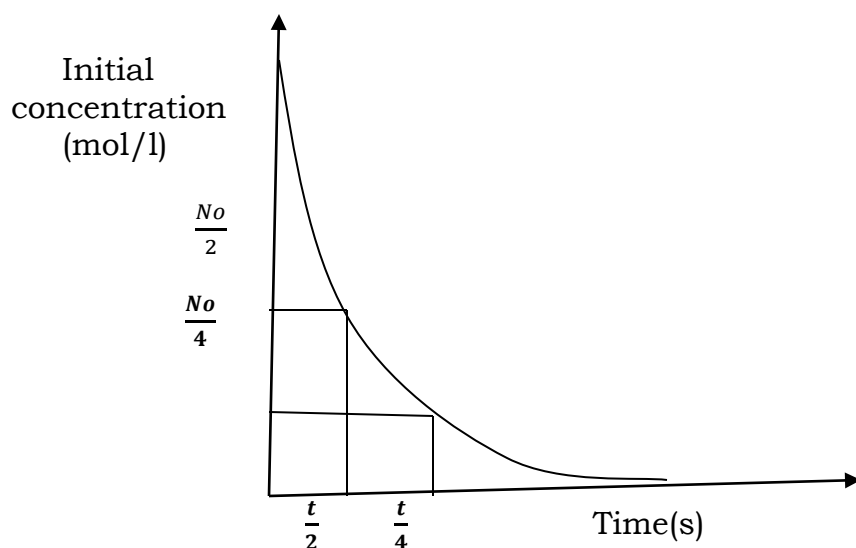
Examples.

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 years.

t=22880 years.

No =100%

Nt= ?

$$\frac{No}{Nt} = 2^{\left(\frac{t}{t\frac{1}{2}}\right)}$$

$$\frac{100}{Nt} = \frac{16}{1}$$

Nt = 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 4units and it is converted to another element of a lower atomic number by 2 units.
   - Beta particles.
   - **Effects;** the atomic number increases by 1unit 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 $^{234}_{91}Pa$ varies with time.

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

(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 in $\left(\frac{No}{Nt}\right) = \lambda t$

$in\left(\frac{8}{1}\right) = 0.0108\ t$

$in\ \frac{(8)}{0.0108} = \frac{0.0108t}{0.0108}$

$t = \left(\frac{2.0794}{0.0108}\right)$

$t = 192.54s$

(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 $\log_{10}\left(\frac{No}{Nt}\right)$ against t.

    Use it to determine.
(v) Decay constant of Y
(vi) Half life of Y

Solution

No	Nt	$\left(\frac{No}{Nt}\right)$	$\text{Log}_{10}\left(\frac{No}{Nt}\right)$	$\left(\frac{Nt}{No}\right)$	$\text{Log}_{10}\left(\frac{Nt}{No}\right)$	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) $t\frac{1}{2} = \frac{0.613}{\lambda}$

$\quad t\frac{1}{2} = \frac{0.693}{\lambda}$

$\quad \frac{64}{1} = \frac{0.693}{\lambda}$

$\quad \frac{64\lambda}{64} = \frac{0.693}{64}$

$\quad \lambda = 0.0108$

(iv) See on the graph.

(v) $t\frac{1}{2} = 168$

$\quad$ but $t\frac{1}{2} = \frac{1}{\lambda}$

$\quad 168 = \frac{0.693}{\lambda}$

$\quad \frac{168\lambda}{168} = \frac{0.693}{168}$

$\quad \lambda = 0.00413$

(vi) from $in\left(\frac{No}{Nt}\right) = \lambda t$

$\quad in\left(\frac{8}{1}\right) = 0.0413\ t$

$\quad in\ \frac{(8)}{0.0108} = \frac{0.0108t}{0.0108}$

$\quad t = \left(\frac{2.0794}{0.0108}\right)$

$\quad t = 192.54s.$

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.

   - $No= 1000g$, $Nt= 125g$, $t= 6minutes.$

     $In\left(\frac{No}{Nt}\right) = \lambda t.$

     $In\left(\frac{1000}{125}\right) =6\lambda.$

     $\lambda =in\left(\frac{1000}{125x\ 6}\right) =0.3466min^{-1}$

     $t\frac{1}{2} = \frac{in\ 2}{\lambda},\quad t\frac{1}{2} =\frac{in\ 2}{o.3466},\quad t\frac{1}{2} =2minutes.$

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

   Solution.

   - $\lambda = 1.356x10^{-11}\ s^{-1}$, 10% decayed and 90% remained.

     $In\left(\frac{N0}{Nt}\right) = \lambda t,\quad in\left(\frac{100}{90}\right) =1.356x10^{-11}$

$$t = in\left(\frac{100}{90}\right) \times \frac{1}{1.356x10^{11}} \text{ , } t=7.7699x10^9 s.$$

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

Solution

- No= 32g , Nt = 2g, $t_{\frac{1}{2}}$= 8days

$$\left(\frac{No}{Nt}\right) = 2\left(\frac{t}{t_{\frac{1}{2}}}\right), \quad \frac{32}{2} = 2\left(\frac{t}{8}\right)$$

Log 16 = $\frac{t}{8}$ log2, $\quad t = \frac{8log16}{log2}$, t=32days.

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.

$$3.303 \log_{10}\left(\frac{No}{Nt}\right) = \lambda t$$

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 14C 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 14C .How old is the mummy case if the half of 14 C if the half life of carbon -14 is 5600years.

$$\lambda = t \tfrac{1}{2} = \frac{1n^2}{\lambda}$$

$$\lambda = \frac{1n^2}{t\tfrac{1}{2}}$$

$$\lambda = \frac{0.69}{5600}$$

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

$$2.303 \log_{10}\frac{(No)}{Nt} = \lambda t$$

$$t = \frac{2.303log10\left(\frac{No}{Nt}\right)}{\lambda}$$

$$t = \frac{2.303log10\left(\frac{15}{9.5}\right)}{1.2378x10^{-4}}$$

$$t = 3690.75 years.$$

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

Solution.

No= 8.25min^{-1}g^{-1} , No = 15.3min^{-1}g

From $\lambda = \frac{in2}{t\frac{1}{2}}$

$\lambda = \frac{0.69}{5600} = 1.2378 \times 10^{-4}$.

$2.303 \log_{10} \frac{(No)}{Nt} = \lambda t$.

$t = \frac{2.303 \log 10 \left(\frac{15.3}{8.25}\right)}{1.2378 \times 10^{-4}}$

t= 2672years.

- **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 meal 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
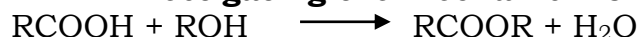
RCOOH + ROH $\longrightarrow$ RCOOR + H_2O
Acid   alcohol   Ester

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 H_2O molecule given out it's found to be not radioactive. This can now lead to a conclusion that O_2 comes from acid.

Investigation of Bio chemical reaction e.g photosynthesis

CO_2 + H_2O $\longrightarrow$ CH_2O + O_2
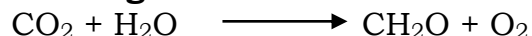
The O_2 of CO_2 is labeled radioactive O_2-18 and supplied to plants to carry out photosynthesis. The O_2 then given is then tested by radioactivity and its to be non radioactive. This leads to a conclusion that the O_2 evolved during photosynthesis is comes from water.

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 $10,000,000^0C$ which is enough H_2 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.

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{98}_{38}Sr + ^{138}_{54}Xe + 3\,^{1}_{0}n$$
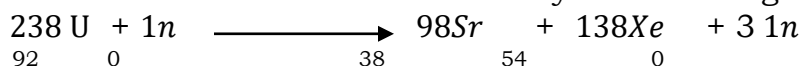
Uses of uranium.
- Uranium – 238 is used in atomic bombs.
- It is also used in nuclear reaction to produce thermal electricity.

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 = $h\nu$ where DE is change in energy, h- is constant = 6.626 x 10^8 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, 4 ....and 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 us 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 Bracket's series. This is shown on the diagram below;

The hydrogen spectrum can be represented as follows.

λ
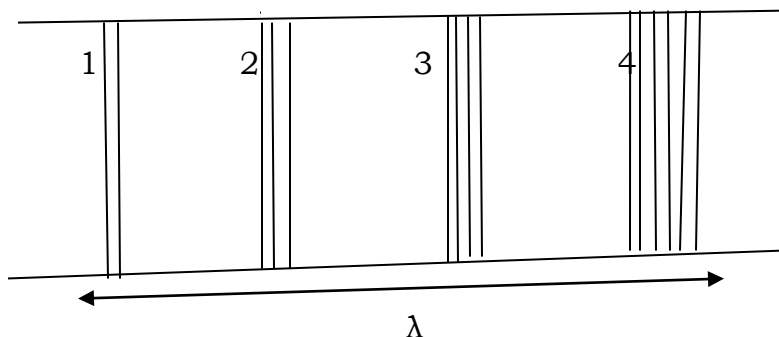
There are so many lines in the H_2 spectrum but the most important ones are from 1-4 which include lines in the Lyman. Balmer, Paschen and Brucket series. The lines get closer together as you move from the nucleus to decrease in the wave length of radiation emitted and eventually line emerge into a continuous spectrum. At this point the radiation emitted is in the invisible range and this one occurs at ionization when the electron is completed removed from on 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;

$\frac{1}{\lambda}$ - Rh $(\frac{1}{n1^2}$ - $\frac{1}{n2^2})$ where Rh is Rydberg's constant, n^1 and n^2 are the energy levels.

In the lyman series $n_1=1, n_2=2,3,4......$etc
In Balmer series $n_1 = 2$, $n_2 = 3, 4, 5..$etc
In Paschen $n_1 = 3$ $n_2 = 4, 5, 6............$etc

Examples.
1. Calculate the radiation emitted in Lyman's series if the electron turns from n=4, Rh = 1.097373 x 10m^{-1}

Solution

    From $n_1 = 1$, $n_2 = 4$

    $\frac{1}{\lambda}$ = Rh $(\frac{1}{n1^2}$ - $\frac{1}{n2^2})$

    $\frac{1}{\lambda}$ = 1.097373 x 10^7 $(\frac{1}{1^2}$ - $\frac{1}{4^2})$

    1.097373 x 10^7 $(1 - \frac{1}{4})$

    $\frac{1}{\lambda}$ = 1.097373 x 10^7 $(\frac{3}{4})$

    $\frac{1}{\lambda}$ = 1.097373 x 10^7 x 0.75

    $\frac{1}{\lambda}$ = 0.82302975 x 10^7

$$\lambda = \left(\frac{1}{0.82302975 \times 10^7}\right) \times 10^9 = 121.5nm.$$

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

Solution.

$$\frac{1}{\lambda} = Rh \left(\frac{1}{n2} - \frac{1}{n^2}\right).$$

$$\frac{1}{\lambda} = 109678\left(\frac{1}{2^2} - \frac{1}{3^2}\right).$$

$$\frac{1}{\lambda} = 109678 \times 0.138888888$$

$$\frac{1}{\lambda} = 15233.05556, \lambda = 6.565 \times 10^{-5} \times 10^9, = 65647nm.$$

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

E = $h\upsilon$. Where h= plank's constant, V – speed of light given by $V = \frac{c}{\lambda}$

$$\therefore E = \frac{hC}{\lambda}$$

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 $(E_1 - E_4) = \frac{hC}{\lambda}$.

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

Examples.

1. The diagram below represents some energy levels of the hydrogen spectrum.
   E/kj/mol^{-1}

```
   0    ——————————————————————————      n=∞
 -12    ——————————————————————————      n=4

 -146   ——————————————————————————      n=3
-1310   ——————————————————————————      n=2

-1810                                   n=1
        ——————————————————————————
```
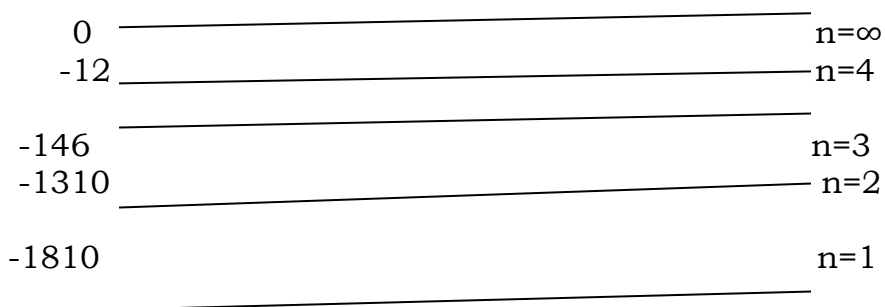
(a) If an electron is in the ground state, calculate the maximum of amount of energy for its maximum ionization.

Solution.

$E_1 = -1310$Kjmol^{-1}, $E_\infty = 0$kjmol^{-1}

$\Delta E = E_\infty - E_1$

= 0- -1310

= +1310kjmol^{-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 x 10^{-13}Kjs^{-1}.

Solution.

$E_3 - E_1 = h\upsilon$

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

$V = \dfrac{1165}{3.99 \times 10^{-13}}$

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

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

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

$\dfrac{1}{\lambda} = Rh\left(\dfrac{1}{n^2} - \dfrac{1}{n^2}\right).$

$\dfrac{1}{\lambda} = 1.097373 \times 10^7 \left(\dfrac{1}{1^2} - \dfrac{1}{5^2}\right).$

$\dfrac{1}{\lambda} = 1.097373 \times 10^7 \times 0.96$

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

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

$\dfrac{1}{\lambda} = Rh\left(\dfrac{1}{n^2} - \dfrac{1}{n^2}\right).$

$\dfrac{1}{\lambda} = 1.097373 \times 10^7 \left(\dfrac{1}{2^2} - \dfrac{1}{5^2}\right).$

$\dfrac{1}{\lambda} = 1.097373 \times 10^7 \times 0.21$

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

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

Solution.

   (i) $E = h\upsilon,\ \upsilon = \dfrac{c}{\lambda}\ ,\ E = \dfrac{hc}{\lambda}$

$E = \dfrac{3.99 \times 10^{-13} \times 3 \times 10^8}{9.49 \times 10^{-8}}$

$= 1261.33 \text{kjmol}^{-1}$

   (ii) $E = h\upsilon,\ \upsilon = \dfrac{c}{\lambda}\ ,\ E = \dfrac{hc}{\lambda}$

$E = \dfrac{3.99 \times 10^{-13} \times 3 \times 10^8}{4.34 \times 10^{-7}}$

$= 275.81 \text{kjmol}^{-1}$

RELATIVE ATOMIC MASS

Is the number of times an atom of an element is heavier than the mass of carbon 12 ($^{12}_6 C$).It can also be defined as a mass of 1 atom of an element divided by the $\dfrac{1}{12}th$ mass of 1 atom of ($^{12}_6 C$). 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 in 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

      M(g) + e ⟶ M⁺(g) +2e
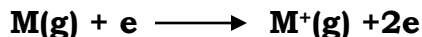
- The gaseous atoms are then accelerated by strong electric field at the same velocity. The ions then enter the magnetic field where various

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 $^{35}_{17}Cl$ and $^{37}_{17}Cl$ which are represented on the spectrum below;
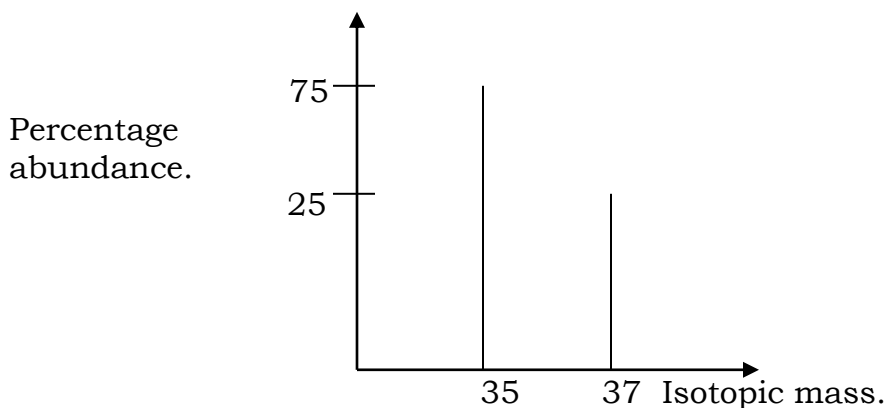
Calculating R.A.M from isotopes.

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

$$R.A.M = \sum \left(\frac{isotopic\ mass\ x\ percentage\ abundance}{100}\right)$$

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;

From RAM = $\sum \left(\frac{isotopic\ mass\ x\ percentage\ abundance}{100}\right)$, RAM = $\left(\frac{35\ x\ 75}{100}\right) + \left(\frac{35\ x\ 25}{100}\right)$

RAM = 35.5

Examples.

1. Calculate the RAM of lead from the spectrum;
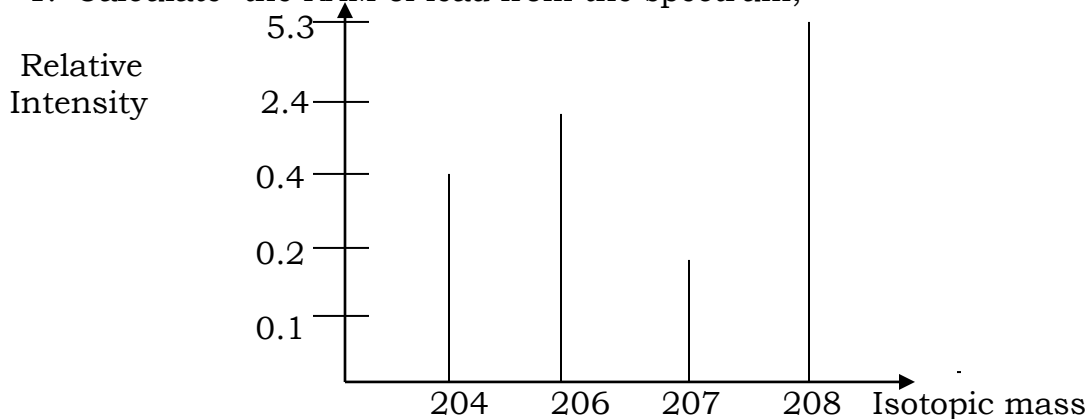
From RAM = $\sum \left(\frac{isotopic\ mass\ x\ percentage\ abundance}{100}\right)$

RAM $\left(\frac{0.4\ x\ 204}{8.3}\right) + \left(\frac{2.4\ x\ 206}{8.3}\right) + \left(\frac{0.2\ x\ 207}{8.3}\right) + \left(\frac{5.3\ x\ 208}{8.3}\right)$

RAM = 9.831 + 59.566 + 4.988 + 132.892

RAM = 207

2. A sample of Rubidium was introduced into a mass spectron and was found to give 2 isotopes whose masses are 54.999 and 86.9092. it was found that there was in ratio of 5.4: 2.1 respectively. Calculated the RAM.

Solution

84.9199 : 86.9092

5.2 : 2.1

Total ratio = 7.5

RAM = $\frac{5.4\ x\ 84.9199}{7.5} : \frac{2.1\ x\ 80.9092}{7.5}$

= 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) $\frac{70\ x\ 9}{16} + \frac{72\ x\ 6}{16} + \frac{74\ x\ 1}{1}$

   39.373 + 27 + 4.625 = 71

(b) RAM = $\frac{mass\ x\ \%\ abundance}{100}$

   Since Cl_2 is a diatonic = $\frac{71}{2}$ = 35.5

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

   $35.5 = \frac{35\ X}{100} + \frac{37\ (100-x)}{100}$

   $35.5 = \frac{35x}{100} + \frac{3700-37x}{100}$

   $35.5 = \frac{-2x+3700}{100}$

   $\frac{2x}{2} = \frac{150}{2}$

   ^{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 $\frac{1}{12}th$ of mass of 1 molecule or mole of carbon-12 ($^{12}_{6}C$). 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.

$V.D = \dfrac{mass\ of\ 1\ volume\ of\ a\ gas}{mass\ of\ 1\ volume\ of\ hydrogen}$

$V.D = \dfrac{mass\ of\ 1\ molecule\ of\ a\ gas}{mass\ of\ 1\ molecule\ of\ hydrogen}$

Since H_2 is a diatomic gas

$V.D = \dfrac{mass\ of\ 1\ molecule\ of\ a\ gas}{mass\ of\ 1\ molecule\ of\ hydrogen}$

But mass of 1 molecule of a gas is its RMM

$VD = \dfrac{RMM}{2}$

$RMM = 2VD$

Example.

1. Given the vapour density of a gas , its RMM can be calculated eg The mass of $257cm^3$ of a gas at 18^0C and $100400Pa$ pressure is $0.162g$. calculate the molar mass using its V.D.

From $\dfrac{V_1 P_1}{T_1} = \dfrac{V_2 P_2}{T_2}$

$\dfrac{267\ x\ 100400}{291} = \dfrac{760\ x\ V_2}{273}$

$V_2 = \dfrac{V_1 P_1 T_2}{T_1 P_2}$

$V_2 = \dfrac{267\ X\ 100400\ X\ 273}{101325\ X\ 291} = 248.2$

$Density = \dfrac{mass}{volume}$

$\dfrac{0.162}{248.2} = 6.53\ x\ 10^{-4} g/cm^3$

$Density\ of\ H_2 = \dfrac{mass}{volume}$

RMM of Hydrogen = 2

$\rho_{H_2}^{of} = \dfrac{2}{22400}$

$= 8.93\ x\ 10^{-5}$

$V.D = \dfrac{6.53\ x\ 10^4}{8.93\ x\ 10^5}$

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 it 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 Vcm^3 of contain is noted and the temperature and pressure at which this is does are also noted from the ideal gas equation

$Pv = nRT$

$n = \dfrac{m}{mr} = PV = \dfrac{m}{mr}RT$

but mass of a gas = (a – b)

where PV = $\frac{(a-b)}{mr}$RT

$\therefore$ Mr = $(\frac{a-b}{Pv})$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 Vcm^3.

Temperature of the jacket is TK.

Pressure of the system is p atmosphere.

From the ideal gas equation

Pv = nRT

N = $\frac{a}{mr}$

Pv = $\frac{a}{mr}$RT

Mr = $(\frac{a}{pv})$ RT.

Examples.

1. When 0.16g volatile was injected into gas syringe at 72^{0}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$745mm contain ($\frac{101231}{760}$ x 745)

= 99325.66mm

Volume = 61.5 x 10^{-6}m^3

$$\frac{0.16 \times 8.314 \times 345 \times 10^6}{99325.16 \times 61.5}$$

Mr = 75.

Method 2;

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \qquad V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}, \qquad V = \frac{745 \times 61.5 \times 273}{760 \times 345} = 47.7 cm^3$$

47.7cm³ of gas contain 0.16g.

22400cm³ of a gas will be $\left(\frac{0.16 \times 22400}{47.7}\right)g$

Mr =75.

2. A gas syringe contains 20.6cm³ of air at 45⁰C was injected with 0.24g of a volatile liquid . After vaporization the volume of was found to be 63.7cm³ at pressure of 1.0x10⁵pa.calculate the relative formula mass of volatile liquid.

Solution.

Volume of vapour of the liquid produced = 63.7- 20.6cm³.

=43.1cm³ or 43.1x10⁶m³

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

P= 1.01x10⁵pa, T= 273+ 48= 321K.

Mr $= \frac{mRT}{PV}$, $= \frac{0.246 \times 8.314 \times 321}{43.1 \times 10^{-6} \times I.01 \times 10^5} = 150.8g$.

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

Its state 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 $\propto 1/\sqrt{\rho_g}$ ------------------(1)

R $\propto 1/\sqrt{Rmm}$ ------------------(2)

R $= k/\sqrt{Rmm}$ ------------------(3)

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

R₁ $= k/\sqrt{Rmm_1}$ ------------------(4)

R₂ $= k/\sqrt{Rmm_2}$ ------------------(5)

$\frac{R_1}{R_2} = k/\sqrt{Rmm_1} \div k/\sqrt{Rmm_2}$

$\frac{R_1}{R_2} = \sqrt{\frac{Rmm_2}{Rmm_1}}$ 6

Examples.

1. It takes 2 minutes for 50 cm³ of helium to diffuse through a porous partition. How long will it take for the same volume of ammonia to diffuse?

Mr(NH₃) = 17

Mr (He) = 4

$R_{(He)} = (\frac{50}{2}) = 25cm^2 / min$, $R(NH_3) = (\frac{50}{t})$ cm^3 / min, $Mr_{(He)} = 4$, Mr. $NH_3 = 17$

From the equation, $(\frac{V(He)/t}{V(NH_3)/t}) = \sqrt{(\frac{Mr(NH3)}{Mr(He)}}$, $\;(\frac{50/2}{50/t}) = \sqrt{(\frac{17}{4})}$, $\;(\frac{25t}{50})2 = \sqrt{(\frac{17}{4})}$

$(\frac{t}{2})2 = \sqrt{(\frac{17}{4})}$, $\;t^2 = \sqrt{(\frac{4x17}{4})}$, t=4.123minutes.

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

Solution

$RO_2 = y$, $Rg = 4y$, $\;\frac{RO_2}{Rg} = \sqrt{\frac{Mrg}{MrO_2}}$, $\;(\frac{y}{4y}) = \sqrt{\frac{Mrg}{32}}$, $\;(¼)^2 = (\frac{Mrg}{32})$, $\;Mrg = 2$

3. 141.4cm² of an inert gas diffuse through porous plug in the same time as it takes 50cm³ of O_2 to diffuse through the same plug under identical conditions. Calculate the molar mass of inert gas.

Solution

$\frac{Rn}{RO_2} = \sqrt{\frac{Mr_{O2}}{Mr_n}}$, $\;(\frac{14.4}{50})2 = (\sqrt{\frac{Mrn}{32}})^2$, $\;(\frac{141.4}{50})2 = \frac{32}{Mrn}$, $\;\frac{7.998Mrn}{7.998} = \frac{32}{7.998}$, $\;Mr_n = 4.0$,

4. 6.3cm³ of X diffuses through a porous plug in 5minutes. If 7.4cm³ of oxygen diffuses through the same plug and same time. Calculate the molar mass of X.

Solution.

$\frac{Rx}{RO_2} = \sqrt{\frac{Mr_{O2}}{Mr_x}}$, $\;(\frac{6.3/5}{7.4/5})2 = (\sqrt{\frac{32}{Mrx}})2$, $\;(0.85135)^2 = \frac{32}{Mrx})$, $Mr_x = 44.2$

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 O_2 = 150cm

Vol of residue gas = 110cm³

Excess volume of O_2 = 30cm³

Vol of CO_2 = (110 – 30) = 80cm

Vol O_2 that reacted = (150 -30)

$C_xH_y + (x + \frac{y}{4}) O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$
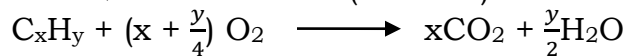
$\frac{20}{20}$ cm³ $\quad \frac{120}{20}$cm³ $\qquad \frac{80}{20}$cm³

1 : 6:4

X = 4

$$4 + \frac{y}{4} = 6$$
y =8
MF = C_4H_8
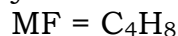
2. When a hydrocarbon (C_nH_m) was exploded with excess O_2, there was a contraction of $30cm^3$, when the mixture was cooled to room temperature. On heating with concentrated potassium hydroxide, there was further contraction to $20cm^3$. Determine value of n and m.

$$C_n + H_m + \frac{n+m}{4} O_2 \longrightarrow nCO_2 + \frac{m}{2}H_2O$$
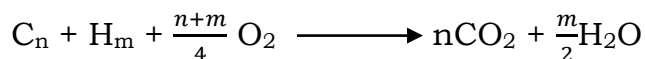
$\frac{10}{10}$ $\qquad$ $\frac{30}{10}$ $\qquad$ $\frac{20}{10}$

1 : 3 : 2

n=2, $\frac{n+m}{4}$ = 3

$\frac{2+m}{4}$ = $\frac{2}{1}$ + $\frac{m}{4}$ = 3,   8 + m = 12, M =4,   MF C_2H_4

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 fasting 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 = $(\frac{p^0 - p}{p^o})$

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

Therefore $(\frac{p^0 - p}{p^o}) = \frac{n_a}{n_a + n_b}$

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

Roult'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 $n_a <<<< n_b$

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

But na $= \frac{m_a}{mra}$, nb $= \frac{mass\ b}{mrb}$

$(\frac{p^0 - p}{p^o}) = (\frac{Ma}{mra} \times \frac{Mrb}{mb})$

$(\frac{p^0 - p)\ Mra - Mb}{p^o - p)mb} = \frac{Ma.Mrb.p^o}{(p^o - p)mb}$

Mra $= \frac{Ma - Mrb.p^o}{(p^o - p)mb}$

Conditions where Roault'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 $\frac{MsxMrb.p^o}{(p^o - p)mb}$

$\frac{4\ x\ 0.1554\ x\ 3167}{(3167 - 3154)100}$

Mrs = 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 9.42×10^4 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 0^0C and that of Ethanol is -120^0C, Ethanoic acid is 17^0C.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 0^0C. The difference between he 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.
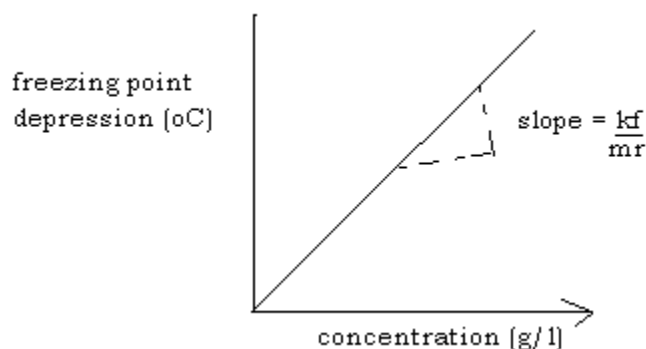
$Dt^0C \propto m$

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

$D + {}^0C \propto \dfrac{1}{mr}$

Where D- is the depression of freezing pt

K_f – is the cryoscopic constant

m-is the mass of solute dissolved

Mr. 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	Kf $^0Ckg^{-1}mole^{-1}$
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 $(\frac{a}{b} \times 1000)$g of a solute. Therefore from the expression

$Dt^0C = Kf\dfrac{m}{mr}$

M = repts $(\frac{a}{b} \times 1000)$

$Dt^0C = (\frac{kf\ a\ x\ 100}{mrb})$

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 tuble fitted with a stirrer and Beckman's thermometer
- The tube is placed in air jacket which is inturn 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 ^0C be the freezing pt of a solvent

t_2 ^0C be the freezing pt of a solution

let the RMM of solute be mr.

bg osf solvent dissolve ag of solute

1000g of solvent will dissolve $(\frac{a}{b}$ x 1000)g of solute

But depression of freezing pt = $(T_1 – T_2)^0C$ D + ^0C

D + ^0C in the D.F. Pt caused by $(\frac{a}{b}$ x 1000)^0C

Kf ^0C is D. freezing caused by $(\frac{a}{b}$ x 1000 x $\frac{kf}{Df})$

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 kf
- a g of Naphthalene will be $(\frac{a}{b} \times 1000 \times \frac{kf}{Dt})$
- kf is the d.f.pt caused by $(\frac{a}{b} \times 1000 \times \frac{kf}{Dt})$

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
Dt°C $\propto \frac{m}{mr}$
The RFM of the solute lowers since for it inversely proportional of f.pt
If the number of particles in the solution doubles, the elative M.Mass will become halfIf 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 0.78⁰C. Calculate the RFM of Benzene given that Kf for ethanoic acid is 3.9⁰Ckg

Solution.

- 22 g of ethanoic acid dissolve 0.055g of nitro benzene.
- 1000g of Nitrobenzene will be $(\frac{1000}{22}$ x0.55) =2.5g
- 0.78⁰C is the depression of point caused by 25g.
- 3.9⁰C is the depression of freezing point caused by $(\frac{25 \, x \, 3.9}{0.78})$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 -1.04⁰C at atmospheric pressure. Calculate the relative formular mass of X, kf of H_2O = 1.86⁰C kg/mol.

Solution.

- 30g of water dissolved 1.5g of x .
- 1000g of water dissolved by$(\frac{1.5}{30}$ x1000) =50g.
- 1.04⁰C is the depression of freezing point caused by 50g.
- 1.86⁰C is the depression caused by $(\frac{50 \, x \, 1.86}{1.04})$ =89.4

    RFM of X is 89.4

3. A solution containing 1.54g of Nepthalene in $(C_{10}H_8)$ in 18g of camphor froze at 148.3⁰C. the freezing point of camphor is 175⁰C. Calculate cryoscopic constant $(k_f)$of camphor.

Solution.

- Freezing point depression = (175-148.3)=26.7⁰C.
- 18g of camphor dissolve 1.54g of naphthalene.
- 1000g of camphor dissolve $(\frac{1.54 \, x \, 1000}{18})$g =85.56g.
- RFM of $C_{10}H_8$= 128
- 85.5g of naphthalene cause a freezing point depression of 26.7⁰C.
- 128g of naphthalene cause a freezing point depression of$(\frac{26.7 \, x \, 128}{85.56})$= 39.9⁰C.
- K_f of camphor is 39.9⁰C.

4.Asolution was prepared by dissolving 7.5g of propan 1,2,3 triol $(C_3H_8O_3)$ IN 200Gg at 25⁰C. calculate the freezing point of the solution at atmospheric pressure. $(K_f$ of water = 1.86⁰Ckg⁻¹mol⁻¹).

Solution.

- RFM of $C_3H_8O_3$ =92
- 200g of water dissolve 7.5g of propan 1,2,3 triol.
- 1000g of water dissolve $(\frac{7.5 \, x \, 1000}{200})$g.
- 92g of propan 1,2,3 triol cause a freezing point depression of water of 1.86⁰C.

- 37.5g of propan 1,2,3 triol causes a freezing point depression of $(\frac{7.5 \times 37.5}{92})$
$$= 0.748^0C.$$
- The freezing point of the solution $= (0-0.758) = -0.758^0C$

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 100^0C and that Ethanol is 78^0C.
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 (Dota t)
The Dt is proportional to amass of a non-volatile solution dissolved in the solute.
$$D + {}^0C \propto M \text{ -------------(i)}$$
Elevation of Boiling pt is also inversely proportional to the molar mass of a non volatile solute.
$$D + {}^0C \propto \frac{1}{mr} \text{.....................(ii)}$$
Combining the two equations and introducing a constant
$$D + {}^0C = K_b \frac{m}{mr} \text{-------------(iii)}$$
Where Dt – is the elevation of
K_b – Ebullic scopic constant
M – Mass of the solute dissolved in a solution
Mr- molar mass of E
Ebulliscopic 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 $(\frac{a}{b} \times 1000)$ of solution

Dt ^0C is the Elevation of boiling point caused by $((\frac{a}{b} \times 1000)g$

Kb is the elevation of boiling pt caused by $(\frac{a}{b} \times 1000 \times {}^{kb}/_{Dt})$

TMF of a solute $= (\frac{a}{b} \times 1000 \times {}^{kb}/_{Dt})$

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

$= \frac{A-B}{A} \propto \frac{n_1}{n_0+n_1}$

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 $\frac{AC}{CE} = \frac{AB}{CD}$

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

AC = Dt also AB = BC = Dt

$Dt = \frac{n_1}{n_0+n_1}$

But $n_1 = \frac{m_1}{mr1} \quad - \quad \frac{An_1}{n_0+n_1}$

$n_0 = \frac{m_1}{mr0}$

$Dt = A \left(\frac{m_1}{mr1}\right) \div \left(\frac{m_1}{mr1} + \frac{m_0}{mr0}\right)$

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

$Dt = A \left(\frac{m_1}{mr1} + \frac{m_0}{mr0}\right)$

$Dt = A \left(\frac{m_1}{mr1} \times \frac{m_0}{mr0}\right)$

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
Ethexyethane	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 $(\frac{b}{a} \times 1000)$

$(T_1 - T_0)$ is the elevation of B.p caused by $(\frac{b}{a} \times 1000 \times \frac{Kb}{T_1 - T_0})$

RFM of a solvent is $[\frac{1000b \times Kb}{(T_1 - T_0)a}]$

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 100.2^0C. calculate the molar mass of cadmium (ii) iodide given that K_b for water is $0.52mol^{-1} kg^{-1}$

Solution;
20g of water dissolves 2.8g of cadmium (ii) iodide.
1000g of water will dissolve $\underline{2.8 \times 1000}$
$\qquad\qquad\qquad\qquad\qquad\qquad 20$
0.2^0C is the elevation of boiling point caused by 140g of cadmium(ii) iodide.
0.52^0C is the elevation of boiling point caused by $\underline{140 \times 0.52}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 0.2$
$$\text{FRM of } CdI_2 = 364$$

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 aregion of their low concentration(I.efrom 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 cconnected to the pressure gauge and piston
- Osmosis is allowed to take place ie 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 droped
- 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.
$C \propto \pi$
$T \propto \pi$
$\pi \propto C$--------------(1)
$\pi \propto T$.................(2)
$\pi \propto CT$
$\pi = KCT$...............(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 $(\frac{1}{V})$
$C = \frac{1}{v}$
From equation -------(3)
$\pi = k\frac{1}{v}T$
$\pi = \frac{KT}{V}$
TV = KT-----------(4)
Since the solution behaves like an ideal gas, for I mole of the solute becomes
$\pi r = RT$
Where R=gas constant
If V is in M³, π in NM⁻²
T :n Kelvins
R = 8.314JK⁻¹mol⁻¹.
But if V is in dm⁻³(litres)
π is in atmosphere, T is in Kelvin
R = 0.8314 atm litres
$\pi r = RT$ 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 25⁰C, 19.15g sugar was dissolved in 1 dm² of solution. Determine the relative molecular mass of the polymer.
solution

T = 25 + 273 = 298K

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

Number of moles of sucrose = $(\frac{19.15}{342})$

= 0.056moles

From $\pi V = nRT$

$\pi = \frac{nRT}{V}$

$= \frac{0.56 \, x \, 8.314 \, x \, 298}{1 \, x \, 10.3}$

= $138744.032NM^{-2}$

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 25^0C 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 $100cm^2$ of solution caused by 1.35g of protein.

1216 pa is the osmotic pressure of the 22400cm of solution at 298 caused by $(\frac{1.35}{100}$ x 22400)g

Therefore 101321 is the osmotic pressure of $22400cm^3$ at 25^0C caused by $(\frac{1.35 \, x \, 22400}{100}$ x $\frac{101321}{1216}$ x $\frac{298}{273})$

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: $R \propto \frac{dc}{dt}$

$= R = \frac{kdc}{dt}$

Where R = rate

Dc= change in concentration

Dt = change in time

K = rate constant

Consider the equation of the reaction

A + B ⟶ P
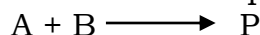
(reactants)   (product)

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

$R \propto \frac{dA}{dt}$

$= R = \frac{k-dA}{dt}$----------------------(1)

Or $R \propto \frac{dp}{dt}$

$= R = \frac{kdA}{dt}$----------------------(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 = $\frac{K-dA}{dt}$

But $\frac{-dA}{dt} \propto [A]$

Rate $\propto [A]$

Introducing a constant

Rate = K[A]--------------------------(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

A+B+C ⟶ p
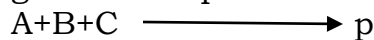
(reactants)   (product)

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 ½ .

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.
Rate = $K[A]^0 [B]^p [C]^q$
Therefore K has a definite value for a given reaction at a given temperature.
$$K = \frac{rate}{K[A]^0 [B]^p [C]^q}$$

Units for rate constant
Rate of reaction is measured in moles per cubic decimeter per second. ($moldm^{-3}S^{-1}$) or in moles per litre per second ($mol\ l^{-1}S^{-1}$)
Concentration of each of the reactants is measures in moles per cubic decimeter ($mol\ dm^{-3}$) or moles per litre
Therefore the units for rate

Constant $= \dfrac{rate}{[A]^0 [B]^p [C]^q}$

$$\frac{mol\ dm^{-3}s^{-1}}{(mol\ dm^{-3})^3}$$

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

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

Or $= \dfrac{mol\ L^{-1}S^{-1}}{(mol\ L^{-1})^3}$

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 [Ho---R---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.

Thus Rate = $[A]^x [B]^y$

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

A + B ⟶ P
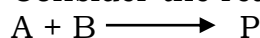
(reactants)   (product)

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.
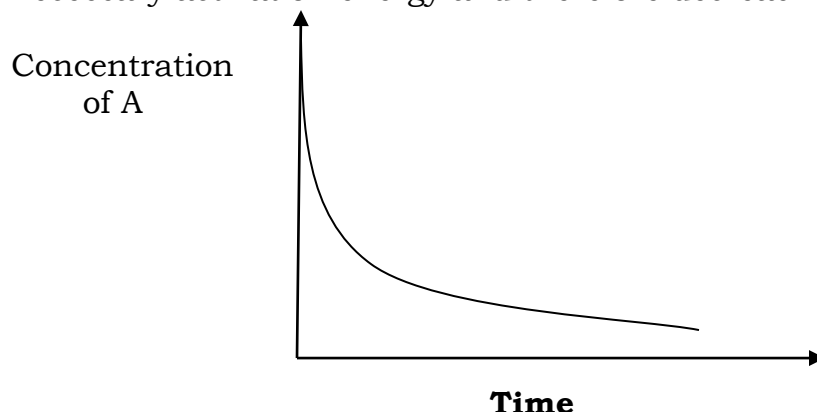
Effect of temperature on the rate of a reaction
Temperature mainly influences the rate of the reaction and the rate at which the reaction reaches an equilibrium or completion. The effect of temperature on the rate of reaction is based on two assumptions which include;
(i)The reacting molecules or particles 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 turns 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
$CH_3Cl + R – OH \longrightarrow CH_3\text{-}OH + R –Cl \qquad DH = -ve$
This reaction takes place in a single step mechanism and this referred to as bimolecular reaction. Thus $CH_3 – Cl + OH^- \longrightarrow CH_3\text{-}OH + Cl^-$
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

◄

Potential
Energy

[Cl-CH$_3$-OH]

Ea=activated energy.
ΔH=enthalpy change of reaction

CH$_3$Cl+OH⁻

E$_a$

ΔH

CH$_3$OH +Cl⁻

Reaction pathway
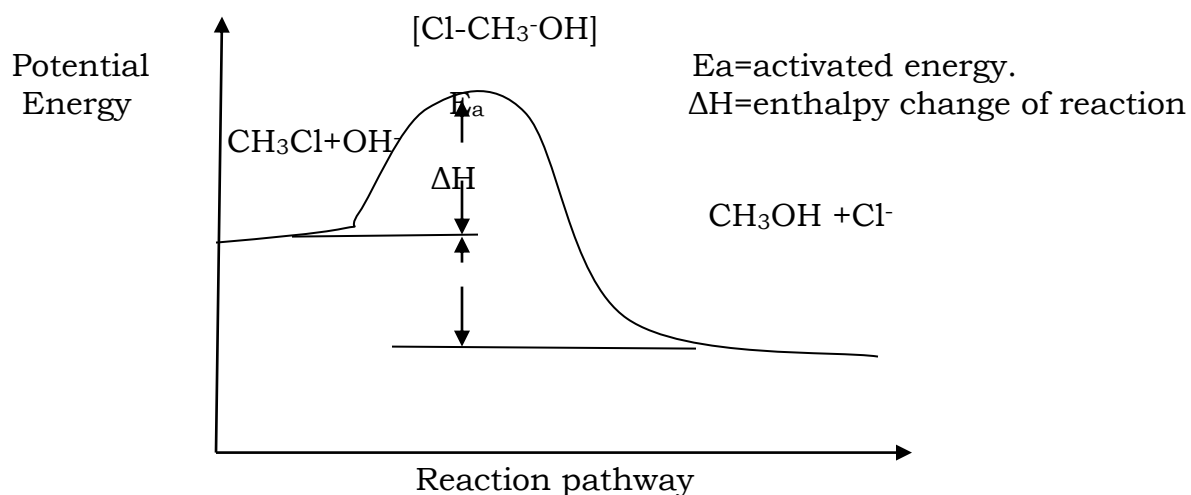
From the energy diagram above, the C–Cl bond is partially broken up in the activated complex as the C-OH bond is partially formed. The final products formed. The final products formed are CH$_3$OH and Cl⁻

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 firs activated complex (i) is formed in the first step and the second activated complex (ii) is also formed in the second step. Thus: R$_3$Br   R$_3^+$ + Br⁻

Then; R$_3^+$ + OH   ⟶   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.

Potential
Energy

[R$_3$—OH]

[R$_3$—Br]

Ea$_2$

Ea$_1$

R$_3$Br+OH⁻

ΔH

R$_3$OH +Br⁻

Reaction pathway.
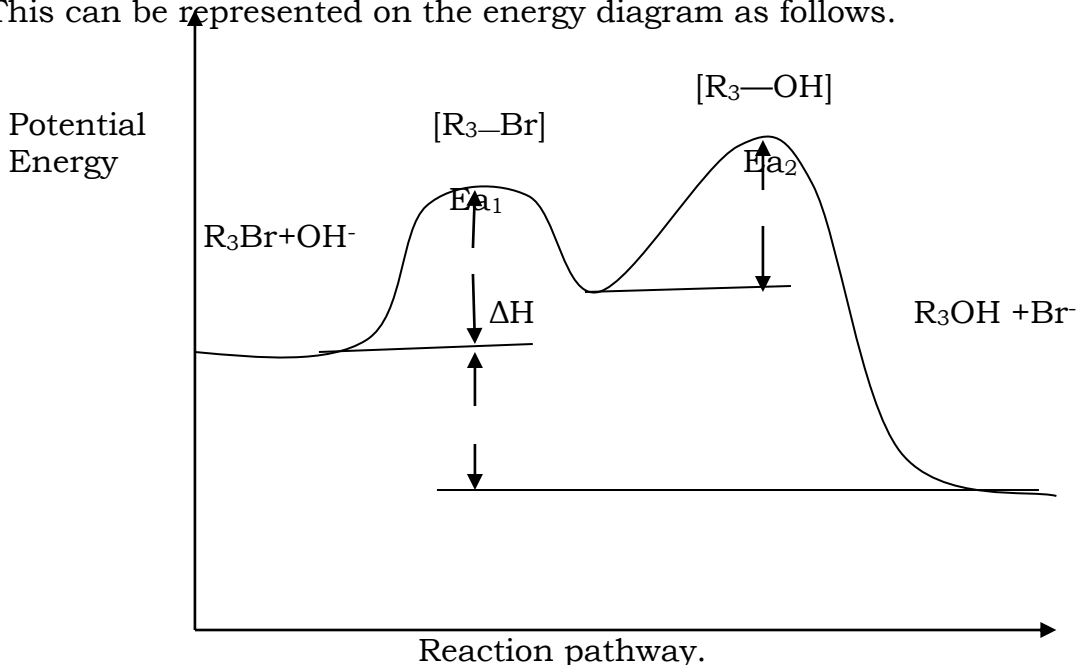
Where DH = Enthalpy change of the reaction
Ea$_1$ = First activation energy
Ea$_2$ = Second activation energy
Note: unimolecular reaction is common among tertiary alkyl halides especially when they undergo hydrolysis e.g 2bromo 2methyl propane [(CH$_3$)$_3$C-Br] under goes the following mechanism.

$$(CH_3)_3C\text{-Br} \xrightarrow{\text{slow}} (CH_3)_3 - C^+ + Br^-$$

Then $(CH_3)_3 - C^+ \longleftarrow OH^- \xrightarrow{\text{fast}} (CH_3)_3C - OH$
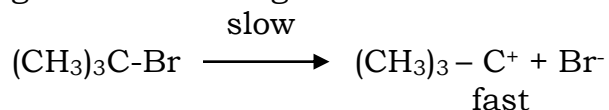
From the energy diagram above up in the first activated complex while C-OH bond is partially formed in the second activated complex. The final products formed are R$_3$OH and Br$^-$.

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

AB + X $\longrightarrow$ AX + B$^-$, DH = $^+$ve
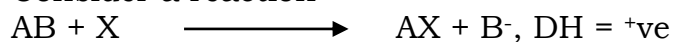
Suppose the reaction takes place in a single step mechanism, then it is also referred to as a bimolecular reaction since it involves one molecule in the rate determines step. It also involves the formation of a single activated complex from which the final products are formed. This is represented on 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)
Consider the equation of the reaction X Y + z $\longrightarrow$ X Z + Y$^-$ DH = +ve
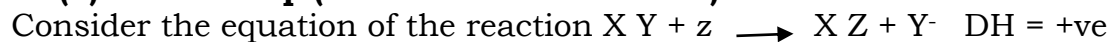
Suppose the reaction occurs in a double step mechanism, then it is referred as a unimolecular reaction since involves two molecules in the rate determining step.It also involves the formation of two activated complexes, one formed in the first step and the other of the second step. This can be represented 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(CH$_3$Cl)$^-$ (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(R$_3$-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, pallets, 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 – hived 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 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 react 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.
$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$
When powdered calcium carbonate is used, the reaction takes place more vigorously and reaches completion earlier than that of the un ground calcium carbonate. Smaller particles with large surface area also collide more frequently with the necessary energy hence react more quickly than the large lumps.
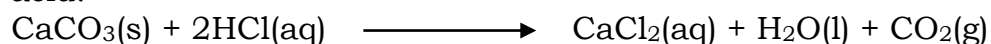
Effect of light on the rate of some reaction.

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

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.

$2H_2O_2 \xrightarrow{\text{light}} 2H_2O(l) + O_2$

$Cl_2(g) + H_2(g) \xrightarrow{\text{U.V light}} 2HCl(g)$

$Cl_2 \xrightarrow{\text{U.V light}} 2Cl$
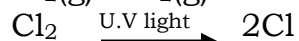
Light increases the number of effective collisions per unit rate thus increasing the rate of reaction.

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

$$-\frac{dx}{dx} \propto [X_2].$$

Introducing a constant,

$$\frac{-dx}{dt} = k0[x0] = k0 \dots\dots\dots\dots\dots\dots\dots\dots\dots 1$$

Where K_0 = rate constant.

Thus $\frac{-dx}{dt} = k_0$

By integrating, $\int d[x] = -k0 \int dt.$

Introducing natural log.

In $[X] = -K_0 t + C \dots\dots\dots\dots\dots\dots\dots\dots\dots 2$

Converting to log base 10.

$2.303 \log_{10} [x] = -k_0 t + C \dots\dots\dots\dots\dots\dots 3$

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

$2.303 \log_{10} [X_0] = - K_0 t + C.$

$\therefore C = 2.303 \log_{10}[X_0] \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4$

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

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

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

$2.303 \log_{10} \left(\frac{[X0] - [X0]}{2 \quad 1}\right) = - K_0 t_{1/2}.$

$2.303 \log_{10} \frac{1}{2}[X_0] = K_0 t_{1/2} \dots\dots\dots\dots\dots\dots\dots\dots 5$

$K_0 = 2.303 \log_{10} \dfrac{[X0]}{2t\frac{1}{2}}$ 6

$t_{\frac{1}{2}} = 2.303 \log_{10} \dfrac{[X0]}{2K0}$ 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;
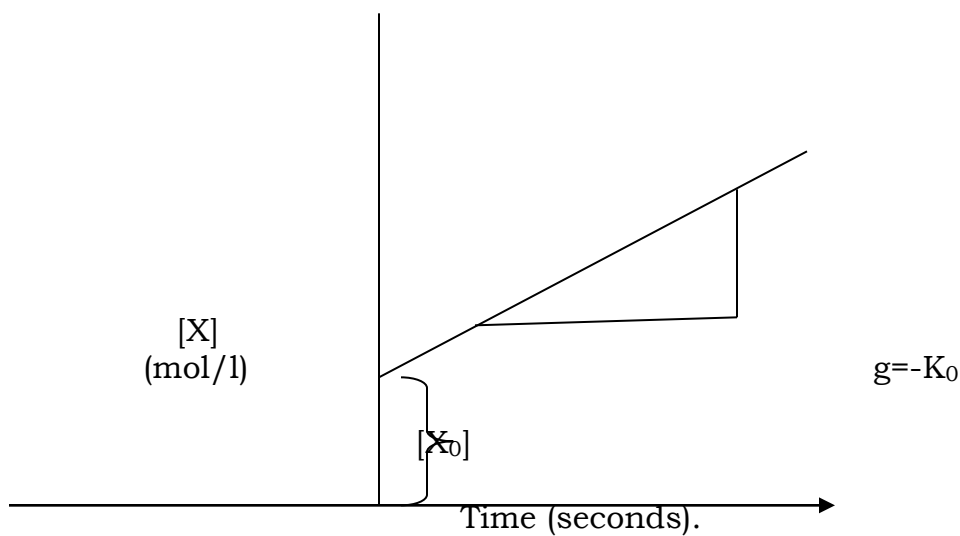
If a graph of $\frac{1}{t}$ against concentration is plotted, a straight line also obtained as follows;

Concentration(mol/l).
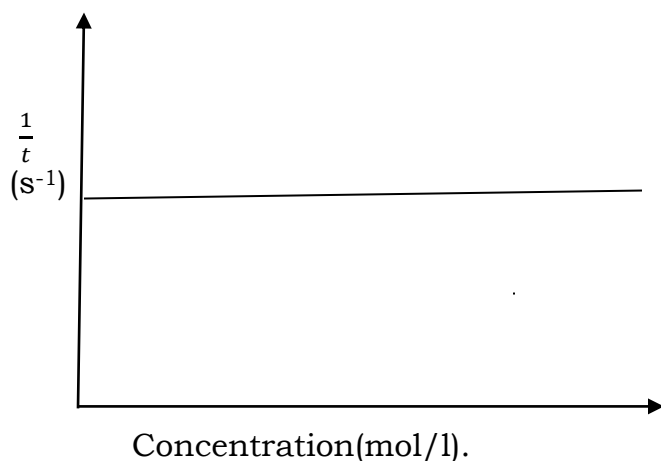
From the last graph above, the rate of the reaction does not depend on the concentration of the reactants.

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

$HCOOC_2H_5 \longrightarrow C_2H_4 + HCOOH$

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

Thus: $\frac{d[C_2H_4]}{dt}$ = K$_1$ (HCOOC$_2$H$_5$]

But rate $\propto \frac{d[C_2H_4]}{dt}$ $\therefore$rate = K$_1$ (HCOOC$_2$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;

A + B $\longrightarrow$ P
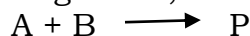
If C = change in concentration of A then the rate equation is given by;

Rate = K $\frac{-dc}{dt}$

But $\frac{-dc}{dt}$ = KC-----------------------(1)

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

The concentration of A at time (t) = (a-x)

Therefore C = (a-x)

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

Then $\frac{-d(a-x)}{dt}$ = K$_1$(a-x) -------------(2)

Then $\frac{dx}{dx}$ = K$_1$ (a-X)

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

$\frac{dx}{(a-x)}$--------------------(3)

By integration

$\int \frac{dx}{(a-x)}$ = K$_1 \int dt$

$\int (a-x)^{-1}$dx = k$_1 \int dt$

Introducing natural log

in(a-x) = K$_1$t + C

Since – in x = 2.303 log$_{10}$^{x}

Introducing log to base 10

$\therefore$ 2.303 log$_{10}$ (a-x) = K$_1$t + C …………………..(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 + 2.303log$_{10}$^{a}

2.303 log $_{10}$$^{(a-x)}$ – 2.303log$_{10}$^{a} = K$_1$t

$\frac{2.303 \, log_{10}(\frac{a}{a-x})}{2.303} = \frac{k_1 t}{2.303}$

Log$_{10}$ $(\frac{a}{a-x})$ = $\frac{k_1 t}{2.303}$……………………………… (5)

$\therefore$ log$_{10}$ $(\frac{a}{a-x})$ $\propto$ t

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

$$\log_{10}\left(\frac{a}{a-x}\right) \qquad s = \frac{K_1}{2.303}$$

time/sec
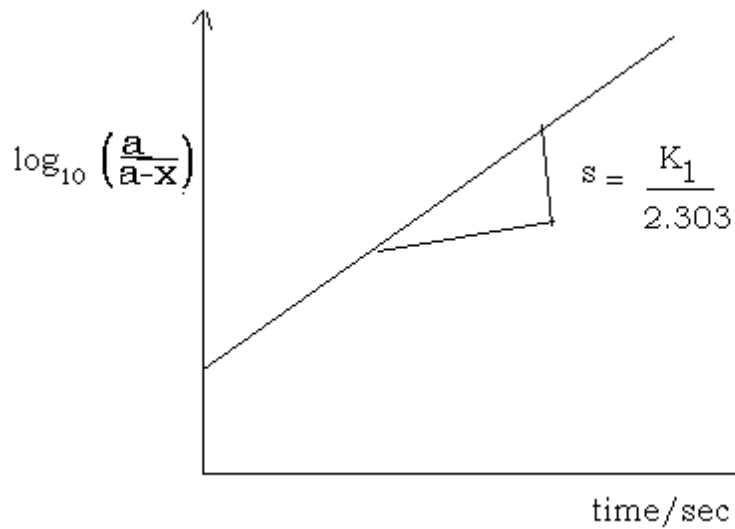
From equation (5), $\text{Log}_{10}a - \log_{10}(a-x) = \frac{K_1 t}{2.303}$, $\therefore \log_{10}(a-x) = -\frac{K_1 t}{2.303} + \log_{10}a$, where $\log_{10}a$ =constant.

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

$$\text{Log}_{10}(a-x) \qquad S = -\frac{-k_1}{2303}$$

Time/ s
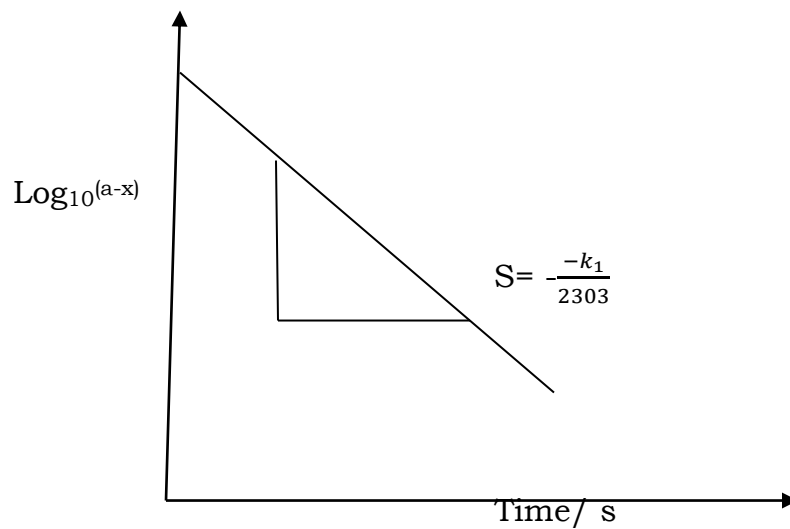
However if a graph of $\frac{1}{t}$ is plotted against concentration, a straight line graph which passes through the origin is obtained.

$$\frac{1}{t}/s^{-1}$$
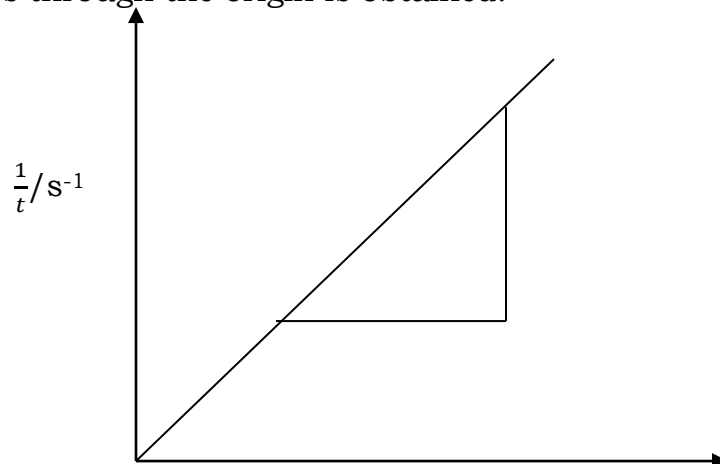
Concentration(mol/l).

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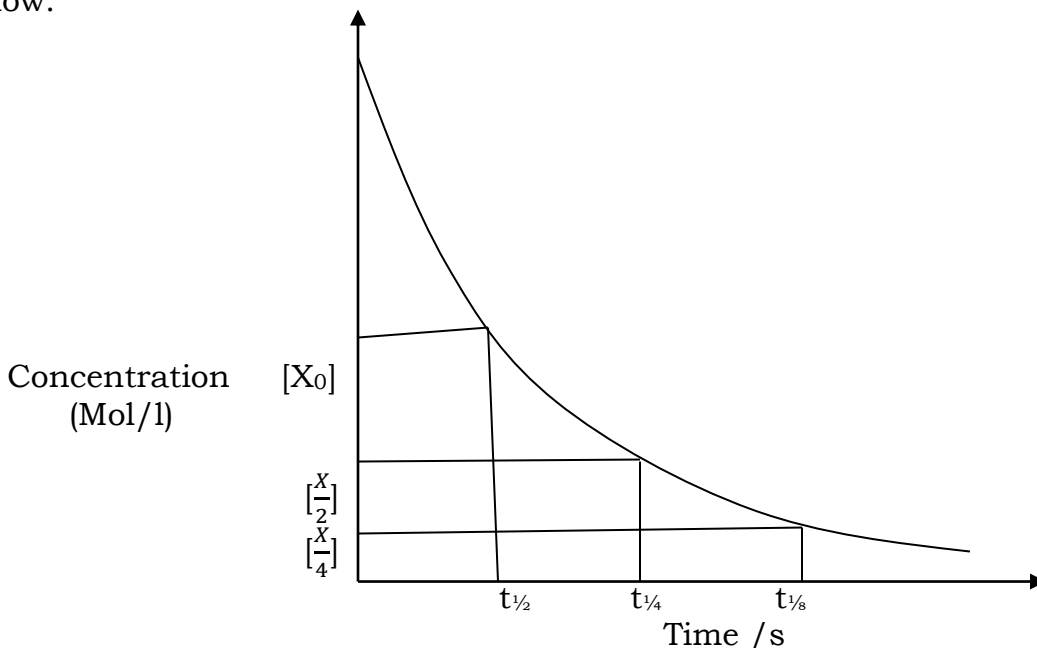
If the half life is constant that id $t_{1/2} = t_{1/4} = t_{1/8}$ etc, the order of the reaction is first order since the rate of the reaction is directly proportional to the concentration of the a single reactant.

Then rate $\propto$ [X],

$\therefore$ Rate $= K[X]$.

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

Rate $= \frac{dx}{dt}$, $\quad \frac{dx}{dt} = - K[X_O]$.................................1

Separating the variables and integrating, we get;

$\int \frac{dx}{x_o} = \int -Kt$...2

Introducing natural log

$In[X] = in-Kt$...3

Converting to log e, it gives;

$\log e \frac{x}{x_o} = \log e^{-Kt}$

Dividing through by log e, gives, $\frac{x}{x_o} = e^{-kt}$

63

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

$t = t_{\frac{1}{2}}$, $x = \frac{x_0}{2}$, $\quad \frac{x_0}{2} = x_0 e^{-Kt_{\frac{1}{2}}}$

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

$\therefore 2 = e^{kt_{\frac{1}{2}}}$

Reintroducing natural log.

$\ln 2 = \ln e^{Kt_{\frac{1}{2}}}$ 6

But $\ln e = 1$, $\ln 2 = kt_{\frac{1}{2}}$, also $\ln 2 = 0.69$.

$kt_{\frac{1}{2}} = 0.69$, $\quad t_{\frac{1}{2}} = \frac{0.69}{k}$ 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,

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
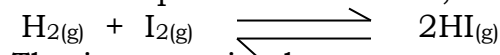
The increase in the concentration of the hydrogen iodide at any time is given by;

$\frac{d[HI]}{dt} = K_2 [H_2][I_2]$.

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.

$2HI_{g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$
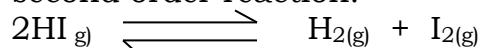
$\frac{d[H_2]}{dt} = K_2 [HI]^2$.

Also $\frac{d[I_2]}{dt} = K_2 [HI]^2$.

In general, consider the reaction;
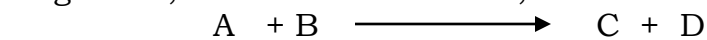
$\qquad\qquad A + B \longrightarrow C + D$

Initially; $\quad$ a $\quad$ a $\qquad\qquad$ 0 $\quad$ 0

At a time,t $\;$ (a-x) (x-a) $\qquad\quad$ x $\quad$ x

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 .

Thus; $\frac{dx}{dt} \propto (a-x)^2$,$\frac{dx}{dt} = k(a-x)^2$ 1

Separating variables; $\frac{dx}{(a-x)^2} = K_2\, dt$ 2

Integrating, $\int \frac{dx}{(a-x)^2} = K_2 \int dt$, $(a-x)^{-1} = K_2 t + C$ 3

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

When t=0, x=0, (a-x)=a $\therefore C = 2.303 \log 10 (\frac{1}{a})$ 5

Substituting equation 5 in equation 4, we get;

$2.303 \log 10 (\frac{1}{a-x}) = K_2 t + 2.303 \log 10 (\frac{1}{a})$ 6

$2.303 \log 10 (\frac{1}{a-x}) - 2.303 \log 10 (\frac{1}{a}) = K_2 t$

$2.303\log 10 \left(\frac{1}{a-x} - \frac{1}{a}\right) = K_2 t,\quad 2.303\log 10 \left[\frac{a-(a-x)}{a(a-x)}\right] = K_2 t$

$\therefore \log 10\left[\frac{x}{a(a-x)}\right] = \frac{K_2}{2.303} t$ 7

Hence, $\log 10\left[\frac{x}{a(a-x)}\right] \propto t,\ K_2 = 2.303\log 10\left[\frac{x}{a(a-x)t}\right]$ or $K_2 = \left[\frac{x}{a(a-x)t}\right]$.

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;

Consider the reaction; X+ Y $\longrightarrow$ p

Initially= $[x_0]$ 0
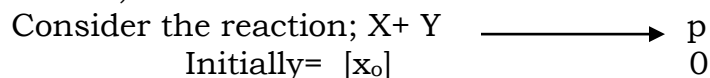
The rate of the reaction depends on the decrease in the concentration of the reactant (x) at agiven time.

Thus; $-\frac{dx}{dt} \propto [x]^2 ,\ -\frac{dx}{dt} = K_2[X_2]$...1

Separating variables; $-\frac{dx}{[x]^2} = K_2\ dt$....................................2

Integrating, $\int \frac{dx}{[x]^2} = K_2\int dt, [x]^{-1} = k_2 t + C$...........................3

Introducing natural log, $in\frac{1}{[x]} = K_2 t + C$...........................4

Converting to log base 10, $2.303\log 10\frac{1}{[x]} = K_2\ t + C$........5

When t=0, $[x]=[x_0]$, $\therefore c = 2.303\log 10\left[\frac{1}{x_{0;}}\right]$..........................6

Substituting equation 6 in equation in 5 gives;

$2.303\log 10\frac{1}{[x]} = k_2 t + 2.303\log 10\left[\frac{1}{x_0}\right]$...........................7

$2.303\log 10\frac{1}{[x]} - 2.303\log 10\left[\frac{1}{x_0}\right] = K_2 t$.

$2.303\log 10\left[\frac{1}{[x]} - \frac{1}{[x_0]}\right] = K_2 t,\ K_2 = 2.303\log 10\left[\frac{[x_0]-[x]}{[x][x_0]}\right]$ OR $K_2 = \left[\frac{[x_0]-[x]}{[x][x_0]t}\right.$.......8

Type equation here.When agraph of $\frac{1}{[x]}$ against t from equation is plotted, astraight line which does not pass through the origin is obtained as shown below;

$\frac{1}{[x]}$ (Mol/l)

s=K_2

$\frac{1}{[x_0]}$

Time /s
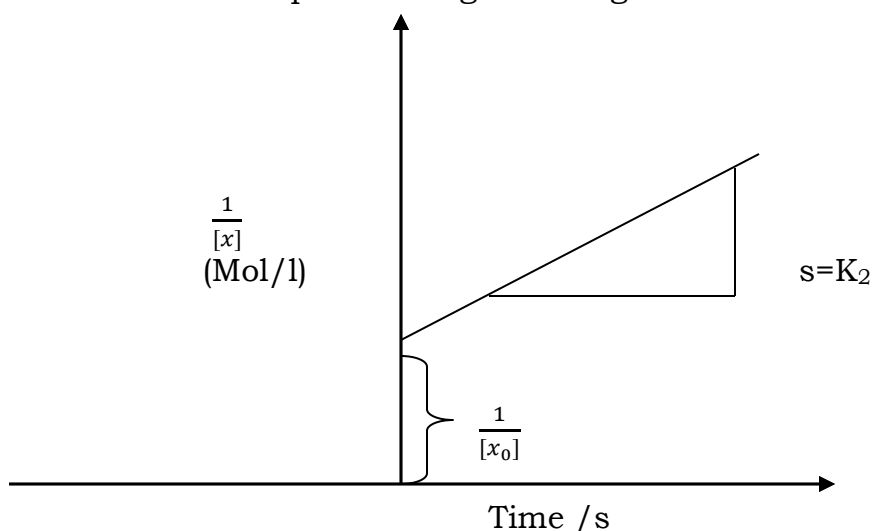
HAILF LIFE METHOD FOR SECOND ORDER REACTION.

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 nof the reactant.

if $[x] = [\frac{x_0}{2}]$, then t= $t_{½}$, $\frac{1}{[x]} = [\frac{1}{x_0/2}] = \frac{2}{[x_0]}$

From $\frac{1}{[x]} = K_2 t_{½} t \frac{1}{[x_0]}$..1

Substituting in equation 1; $\frac{2}{[x_0]} = K_2 t_{½} + \frac{1}{[x_0]}$, $\frac{2}{[x_0]} - \frac{1}{[x_0]} = K_2 t_{½}$,

$\frac{2[x_0]-[x_0]}{[x_0]^2} = K_2 t_{½}$

$\frac{x_0}{[x_0]^2} = K_2 t_{½}$, $\frac{1}{x_0} = K_2 t_{½}$.....................................2

$t_{½} = \frac{1}{[x_0]K_2}$ 3

OR $K_2 = \frac{1}{[X_0]t_{½}}$...4

Equation 3 above shows that the half life ($t_{½}$)of the second order reaction depends on the initial concentration of the reactants.

If agraph of $\frac{1}{t}$ is plotted against concentration, a curve is obtained as shown below;

Concentration(mol/l)
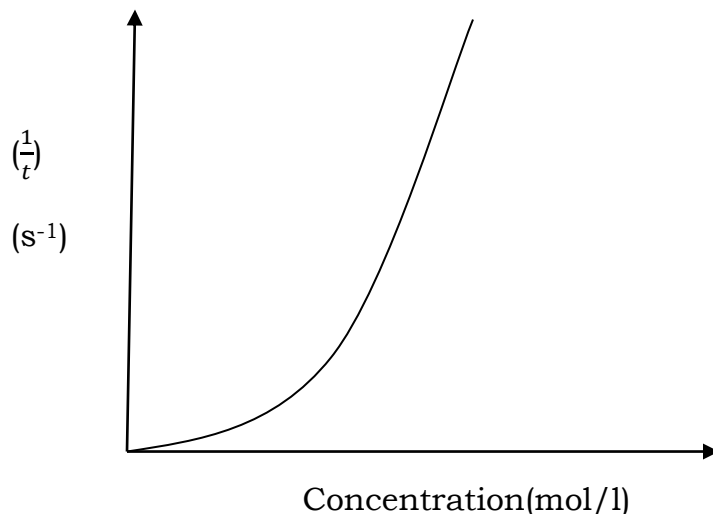
From the graph above, the rate of the reaction increases exponentially with increase in the concentration of the reactant.

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;

$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$
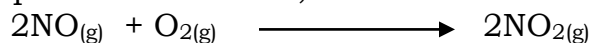
Initially   a   a   o
At time (t)(a-x)   (a-x)   x

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;

$\frac{d[NO_2]}{dt}$ = K₃[NO]²[O₂]

The above reaction is second order with respect to NO and first order with respect to O₂ .The overall order of the reaction is 3 i.e third order reaction.

But since $\frac{dx}{dt}$ ∝ (a- x)³ , $\frac{dx}{dt}$ =K₃(a-x)³ or $\frac{dx}{(a-x)^3}$= dt...............1

Integrating; ∫ $\frac{dx}{(a-x)^3}$ =K₃ ∫ dt, ∫$(a-x)^3$dx = K₃t +C

Introducting natural log.

in$\frac{1}{2(a-x)^2}$ = K₃t + C 2

Converting to base 10.

2.303log10($\frac{1}{2(a-x)^2}$ = K₃ + C..3

When t=0, x=0,then (a-x)² = (a-0)² =a².

C =2.303log10($\frac{1}{2a^2}$)..4

∴ 2.303log10($\frac{1}{2(a-x)^2}$) = K₃t + 2.303log($\frac{1}{2a^2}$)

2.303log10 ($\frac{1}{2(a-x)^2}$) - 2.303log($\frac{1}{2a^2}$)= K₃t.

2.303log10($\frac{1}{2(a-x)^2}$ -$\frac{1}{2a^2}$) = K₃t

2.303log10($\frac{2x^2}{4a^2(a-x)^2}$)= K₃t.

K₃ = 2.303log10($\frac{2x^2}{4a^2(a-x)^2t}$)..5

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

t = $\frac{3}{2Ka^2}$..6

thus t, is inversely proportional to the square of the initial concentration or a²t 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 ($CH_3COOC_2H_5$) 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.

$$CH_3CO_2C_2H_{5(l)} + H_2O_{(l)} \longrightarrow CH_3CO_2H_{(aq)} + C_2H_5OH_{(aq)}$$
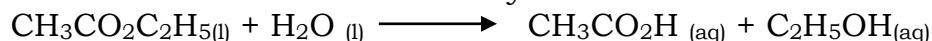
(ii)   Reactions between iodine and propanone (Acetone)

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + H^+ + I^-$$

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

$$2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$
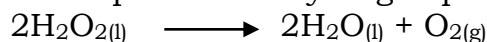
(iii)   The loss in mass of reaction mixture due to the loss of a gaseous product. For example in the reaction.

$$CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$
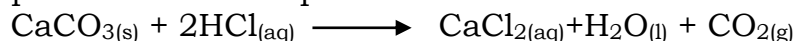
In this reaction, the mass of reaction mixture decreases as carbon dioxide evolves.

Loss in mass of mixture

Time/s
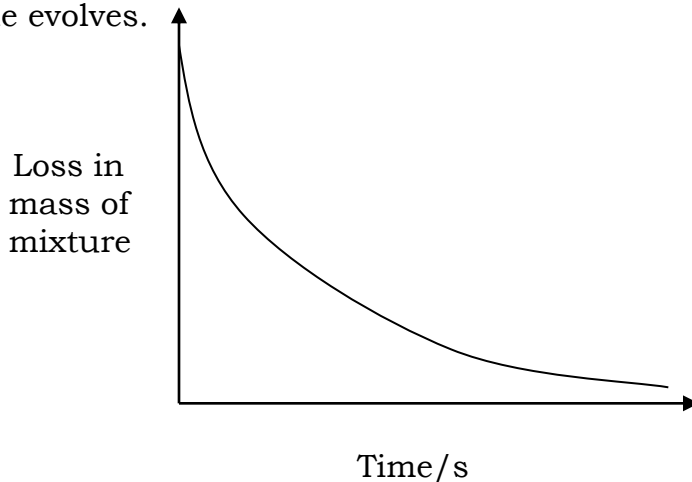
(iv)   The rate of change in concentration of a coloured reactant can be followed by colon meter. This translates the intensity of light transmitted by a coloured solution into an electrical measurement, by means of a light sensitive cell. Examples of reactions where this method is applied include the 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.

$$(CH_3)_3C\text{-}Br + H_2O \longrightarrow (CH_3)_3C\text{-}OH + H^+_{(aq)} + Br^-_{(aq)}$$
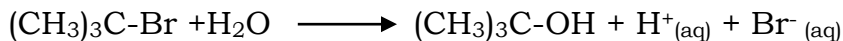
(d)Optical rotation/activities.

The ability of a certain substance to rotate the place 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.
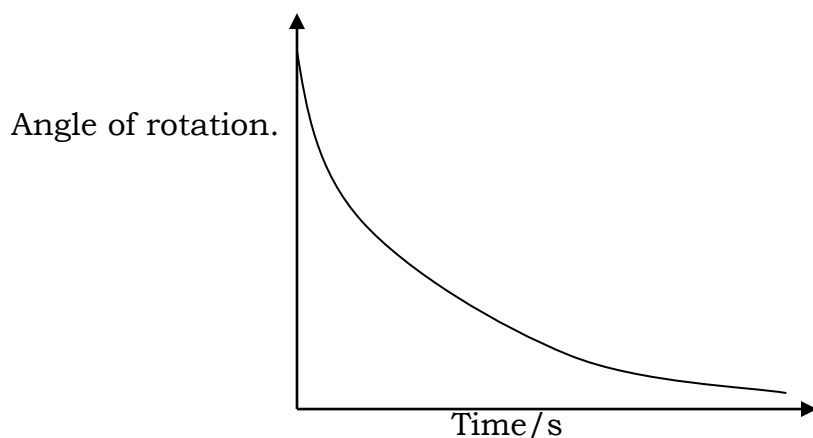
(e)The change in gas pressure

For example in the reaction;

$$2N_2O_5 \rightleftharpoons 2N_2O_4(g) + O_{2(g)}$$
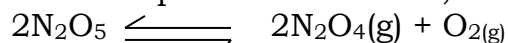
In the above reaction, if the volume is kept constant the increase in pressure can be followed and used as a parameter for determining the rate of decomposition of nitrogen pent oxide.

(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 $(CH_3CH = CH_2)$ (Br_2) where k=30 mol^{-1}l^{-1}s^{-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 = $[CH_3CH = CH_2]$ $[Br_2]$
                = 30.$(0.02)^2$
                = 0.012 mol l^{-3}S^{-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; $H_2O_{2(aq)} + 2H^+_{(aq)} + I^-_{(aq)} \longrightarrow 2H_2O_{(l)} + I_{2(aq)}$
The following experimental data were recorded

Experiment	Concentration			
	$[H_2O_2]$ (mol dm³)	$[I^-]$ (mol dm³)	$[H^+]$ (mol/dm³)	Rate (mol/dm³S⁻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 (H_2O_2) (I^-), Since H^+ is a catalyst

(ii) K = $\dfrac{Rate}{[H_2O_2][I^-)}$

Considering experiment [5]

K = $\dfrac{10.5 \, x \, 10^{-6}}{(0.03 \, x \, 0.02)}$ = 1.75 x 10⁻² mol⁻¹dm⁻³S⁻¹

K= $\dfrac{mol \, /dm^{-3}S^{-1}}{(\, mol \, /dm^3)^2}$ =mol⁻¹dm⁻³S⁻¹

(iii) Order of reaction with respect to H_2O_2
From experiment (1) and (2)

X log $(\frac{3.0 \, x \, 10^{-2}}{1.0 \, x10^{-2}}$) = log $(\frac{5.25 \, x \, 10^{-6}}{1.75 \, x10^{-6}})$

X log $(\frac{3.0}{1.1})$ = log $(\frac{5.25}{1.75})$

X log 3 = log 3

Log₃ˣ = log₃

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 $(\frac{2.0 \, x \, 10^{-2}}{1.0 \, x10^{-2}}$) = log $(\frac{10.5 \, x \, 10^{-6}}{5.25 \, x10^{-6}})$

y log $(\frac{2}{1})$ = log $(\frac{10.5}{5.25})$

y log2 = 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 x 10⁻⁵ mol l⁻¹S⁻¹.
   (a) Write down the rate equation.
   (b) Calculate
       (i)The rate constant

(ii)Its units
Solution

(a) Rate = $K(HI)^2$

(b) Rate constant = $\frac{Rate}{(HI)^2} = \frac{6.04 \times 10^{-5}}{(0.2)^2}$ = 1.51 x 10^{-3} mol l^{-1}S^{-1}

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

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

Rate = $K[A]^x [B]^y$

From experiments (i) and (2)

The order of reaction with respect to A

$X \log (\frac{1}{0.5}) = \log (\frac{8.0 \times 10^{-2}}{2.0 \times 10^{-2}})$

$X \log 2 = \log 4$

$\therefore x \log 2 = 2 \log 2$

$X = 2$

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

From experiments (2) and (3)

$Y \log (\frac{1}{0.5}) = \log (\frac{16.0 \times 10^{-2}}{8.0 \times 10^{-2}})$

$Y \log 2 = \log 2$

$Y = 1$

$\therefore$ 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 = $\frac{rate}{[A]^2 [B]}$

From experiment (1)

$K = \frac{2.0 \times 10^{-2}}{(0.5)^2 (0.5)}$

= 0.16 mol^{-2}dm^{-6}S^{-1}

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

A + B $\longrightarrow$ P
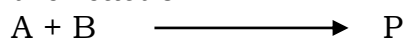
Experiment	[A] mol / 1 X10^{-3}	[B] mol / 1 X10^{-3}	Rate x 10^{-3} Mol / 1 S^{-1}
1	1.2	4.4	12.1
2	2.4	4.4	24.3
3	1.2	1.1	3.0

(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

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

X log $(\frac{2.4 \ x \ 10^{-3}}{1.2 \ x \ 10^{-3}})$ = log $(\frac{24.3x \ 10^{-3}}{12.1 \ x \ 10^{-3}})$

X log 2 = log 2

X = 1

The order of reaction with respect to a is 1

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

(b) K= $\frac{Rate}{[A][B]}$ = $\frac{3.0x10^{-3}}{(1.2x10^{-3})(1.1x10^{-3})}$ =2.273x10^3 mol/dm^{-3}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; $CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$

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.
 (i) The concentration of propanone is doubled but the concentration of iodine is kept constant
 (ii) The concentration of propanone and iodine are doubled
 (iii) The concentration of propanone is kept constant and that of iodine is doubled.
 (iv) The concentration of propane halved and that of iodine is kept constant

Solution

(a) Rate = K [CH_3COCH_3] [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 [CH_3COCH_3] [I_2]^0
 Assuming K =1
 Rate = [2]^1[1]^0 = 2
 (ii) Rate = K [CH_3COCH_3] [I_2]^0
 = [2] [1]^0 = (2 x 1)= 2

If K = 1

(iii) Rate = $K[CH_3COCH_3] [I_2]^0$

    =[2] [1]^0

    = 1

(iv) Rate = $K[CH_3COCH_3] [I_2]^0$

    If K = 1

    Rate = $(\frac{1}{2}) (1)^0$

    Rate = ½

    = ½

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.

　X $_{(g)}$ + 2Y$_{(g)}$ ⟶ XY$_{2(g)}$
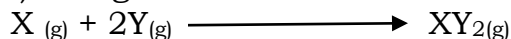
Experiments were performed at 400k in order to determine the order of this reaction and the following results were obtained.

Experiment	Concentration of X [mol/l]	Concentration of Y [mol/l]	Rate [mol/dm³s⁻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)

　　　$Xlog(\frac{0.2}{0.1}) = log(\frac{2.0x10^{-4}}{2.0x10^{-4}})$, xlog2= log2, 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)

　　　$Y log (\frac{0.2}{0.1}) = log (\frac{4.0x10^{-4}}{1.0x10^{-4}})$, Y log2 = log4, Ylog2 = 2log2, Y=2

　　　Rate =$K[x][Y]^2$

　　　(iii) Rate = $[X][Y]^2$

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

$$3A + B \longrightarrow 2p$$
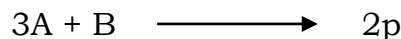
Exp't No.	[A] (mol dm^{-3})	[B] (mol dm^{-3})	Initial rate (mol dm^{-3})
1	0.20	0.20	1.2 x 10^{-8}
2	0.20	0.60	1.2 x 10^{-8}
3	0.40	0.60	4.8 x 10^{-8}

(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 rection with A, because when the concentration of A is doubled the initial rate is multiplied by 4.
i.e $2^x = 4$, $2^x = 2^2$, x = 2.
Proof;
Expt2; 1.2 x 10^{-8} = K $[0.2]^x[0.6]^y$
Expt3; = 4.8 x 10^{-8} = K$[0.4]^x[0.6]^y$
Dividing 3 by 2.

$$\text{Log}[\frac{4.8 \ x \ 10^{-8}}{1.2 \ x \ 10^{-8}}] = \log[\frac{(0.4)^x}{(0.2)^x}]$$

$$\text{Log}4 = x\log(\frac{0.4}{0.2}), \ 2^2 = 2^x, \ X = 2.$$

(ii) Zero order with B, because when the concentration of B is trippled the initial rate remained constant (multiplied by 1)
$3^y = 1$, $3^y = 3^0$, y = 0
Proof;
Expt1; 1.2 x 10^{-8} = K$(0.2)^x(0.2)^y$
Expt2; 1.2 x 10^{-8} = K $(0.2)^x(0.6)^y$
Dividing 2 by1,

$$\text{Log}[\frac{1.2 \ x \ 10^{-8}}{1.2 \ x \ 10^{-8}}] = \log[\frac{(0.6)^y}{(0.2)^y}]$$

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

(b) Over all order = 2+0 = 2.
(c) Rate = K $[A]^x [B]^y$
   Rate = K$[A]^2[B]^0$
   Rate = K $[A]^2$
(d) Rate constant
   1.2 x 10^{-8} = K$(0.2)^2$

$$K = [\frac{1.2 \ x \ 10^{-8}}{(0.2)^2}] \ [\frac{mol \ dm^{-3}}{mol^2 dm^{-6}}]$$

K= 3 x10^{-7} mol^{-1}dm^3

9. The following results were obtained in a study of a reaction between peroxide sulphate ($S_2O_8^{2-}$) and iodide ions

$$S_2O_8^{2-}(aq) + 2I(aq) \longrightarrow 2S_2O_4^{2-}(aq)$$
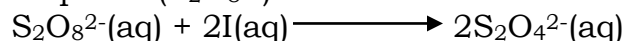
Expt No	$[S_2O_3^{2-}]$ (moldm^{-3})	$[I^-]$ (moldm^{-3})	Initial rate (moldm^{-3}S^{-1})
1	0.024	0.12	9.6 x 10^{-6}
2	0.048	0.12	1.92 x 10^{-5}
3	0.048	0.06	9.6 x 10^{-6}

(a) Determine the order of reaction with respect to
   (i) $S_3O_8^{2-}$ 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) Rate = $K(S_2O_8^{2-})^x (I^-)^y$
       Consider; Expt1; $9.6 \times 10^{-6} = K(0.024)^x(0.12)^y$.
            Expt2; $1.92 \times 10^5 = K(0.048)^x(0.12)^y$.
       Dividing 2by1,
       $Log[\frac{1.92x10^{-5}}{9.6 \ x \ 10^{-6}}] = log[\frac{(0.048)^x}{(0.024)^x}]$
       $2 = 2^x, 2 = 2^x, X = 1$
       The reaction is of first order with respect with $S_2O_8^{2-}$ ion
   (ii) Rate = $K(S_2O_8^{2-})^x (I^-)^y$
       Expt2; $1.92 \times 10^{-5} = K(0.48)^x(0.12)^y$
       Expt3; $9.6 \times 10^{-6} = K(0.48)^x(0.06)^y$
       Dividing 3 by2,
       $Log[\frac{9.6x10^{-6}}{1.92 \ x \ 10^{-5}}] = log[\frac{(0.06)^y}{(0.12)^y}]$
       $(½) = (½)^y, Y = 1$
       The order of reaction with respect to I^-ions is one.
   (b) Over all order = 1 + 1 = 2
   (c) Rate equation;
       Rate = $K[S_2O_8^{2-}]^1[I^-]^1$
       Rate = $K[S_2O_8^{2-})[I^-]$
   (d) Rate constant;
     For expt $9.6 \times 10^{-6} = K(0.024) (0.12)$
     $K = \frac{9.6x \ 10^{-6}}{(0.024)(0.12)}$, K=3.33 x 10^{-3} mol^{-1}dm^{3}S^{-1}

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

Expt	[A] (moldm^{-3})	[B] (moldm^{-2})	[C] (moldm^{-3})	Initial rate (moldM^{3}S^{-1})
1	0.10	0.20	0.20	8.0 x 10^{-5}
2	0.10	0.05	0.20	2.0 x 10^{-5}
3	0.05	0.10	0.20	2.0 x 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 respectC.

(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 x 10^{-5} = K(0.1)^x(0.20)^y(0.20)^z

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

Dividing 1 by 2

$$\text{Log} \left[\frac{8.0 \times 10^{-5}}{2.0 \times 10^{-5}}\right] = \log \left(\frac{0.10}{0.10}\right)^x \left(\frac{0.20}{0.05}\right)^y \left(\frac{0.20}{0.20}\right)^z$$

Log4= ylog4, y=1.

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

Consider;

Expts1; 8.0x10^{-5} = K(0.1)^x(0.2)^y(0.2)^z

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

$$\text{Log} \left[\frac{2.0 \times 10^{-5}}{2.0 \times 10^{-5}}\right] = \log \left(\frac{0.10}{0.05}\right)^x \left(\frac{0.05}{0.1}\right)^y \left(\frac{0.20}{0.20}\right)^z$$

1 = 2$^{(x-y)}$, 0 = x – y but y= 1, X = 1

The Order of reaction with respect to A is one.

From, X + y+z = 4, 1+1+z = 4, ∴ Z = 2

The Order of reaction with respect to C is two.

(b) Consider;

Expt3; 2.0 x 10^{-5} = K(0.05)^x(0.10)^y(0.20)^z

Expt4; A = K(0.10)^x(0.10)^y(0.10)^z

$$\text{Log } \left[\frac{2.0\ x\ 10^{-5}}{a}\right] = \log\left(\frac{0.05}{0.1}\right)^x \left(\frac{0.10}{0.10}\right)^y \left(\frac{0.2}{0.1}\right)^z$$

$$\left[\frac{2.0\ x\ 10^{-5}}{a}\right] = 2^{-x}\ 2^z, \text{ but } x = 1 \text{ and } z = 2, \left[\frac{2.0\ x\ 10^{-5}}{a}\right] = 2^{-1}.2^2$$

$$= 2.0\ x\ 10^{-5} = 2a, \quad a = 1.0\ x\ 10^{-5}$$

(c) $8.0\ x\ 10^{-5} = K(0.10)^1(0.20)^1(0.20)^2$

$$K = \frac{8.0\ x\ 10^{-5}}{(0.10)(0.20)(0.20)^2} \quad \frac{mol\ dm^{-3}}{mol^4\ dm^{-2}}$$

$K = 0.1\ mol^3 dm^9 S^{-1}$

(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.

$[CH_3CHO]$ (mol/dm^3)	$[CH_3CH_2]^2$	Initial rate (moldm^{-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	9.35x 10^{-3}

(a)Plot a suitable graph of initial rate against $[CH_3CHO]$ 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 ti gives an exponential curve showing that the initial increases exponentially with increases in concentration of CH_3CHO.

Slope = K, K = Slope = $\left(\frac{85-15}{0.51-0.24}\right)$ x 10^{-4} = 0.0259 S^{-1}

(b) Rate equation; Rate = $K[CH_3CHO]^2$

(c) $1.5\ x\ 10^{-3} = K(0.20)^2$, K = $\frac{1.5\ x\ 10^{-3}}{0.20^2}$, K= 0.0375 mol^{-1}dm^{3}S$^-$

12. The kinetic data for the reaction P⟶products

Time (min)	0	5	10	20	30
[P] (moldm^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 2nd $t_{1/2}$ =2 x 1st $t_{1/2}$, it is a 2nd order reaction.

Rate = $K(P)^x$

At t = 5

Rate = $\frac{1}{5}$ = 0.5 at t=20 rate 0.05

Expt 1 0.2 = $k(0.0133)^x$-------------R_1

Expt 2 0.05 = $K(0.069)^x$------------R_2

$$\frac{R_1}{R_2} = \frac{0.2}{0.05} = \frac{K(0.0133)^x}{K(0.069)^x}$$

b. 1st t $\frac{1}{2}$ = 10

2nd t $\frac{1}{2}$ = 31

2nd t $\frac{1}{2}$ - 1st t $\frac{1}{2}$ = 31-10 = 21

Since 2nd t $\frac{1}{2}$ $\cong$ 2x 1st t $\frac{1}{2}$ it is second order reaction

C. Rate at [P] = 0.0069

$$= \frac{QR}{PR}$$
$$= \frac{0.0076-0.006}{25-16.5}$$
= 1.882 x 10^{-4}

Rate at [P] = 0.014

$$= \frac{BA}{CA}$$
$$= \frac{0.016-0.0118}{0.5-4-5}$$
= 1.882 x 10^{-4}

Expt1 1.882 x 10^{-4} = $K(0.00069)^x$

Expt2 2.1 x 10^{-3} = $K(0.014)^x$

$$\frac{R_1}{R_2} = \frac{02.1 \; x \; 10^3}{1.882 \; x \; 10^{-4}} = \left(\frac{0.014}{0.0069}\right)^x$$

11.1111   2.02899^x

Log11.1111 = x log2.02899

X = $\frac{\log 11.1111}{\log 2.02899}$

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.
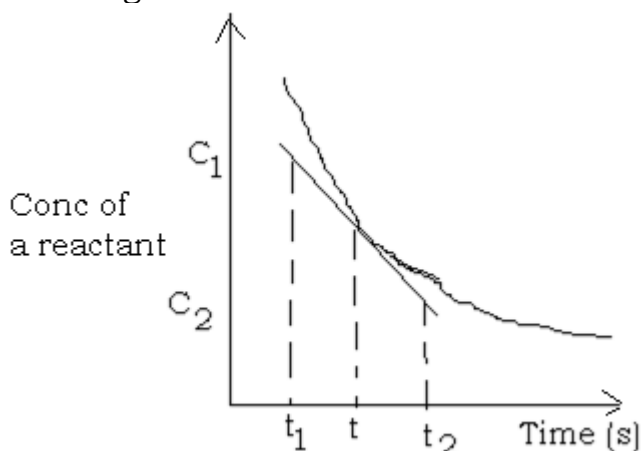
Gradient = Rate at time t

$$T = \frac{\square\square}{\square\square}$$

$$= \frac{\square_1\square_2}{\square_1\square_2}$$

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.
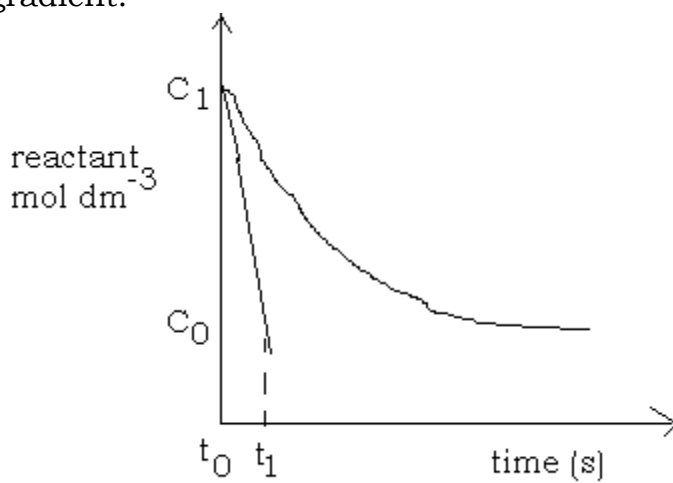
Gradient = initial rate

$$= \frac{\square_1 \square_0}{\square_1 \square_0}$$

In this case the gradient has a negative value because the reactants are decreasing with time.

Gradient = initial rate

$$= \frac{\square_1 \square_0}{\square_1 \square_0}$$
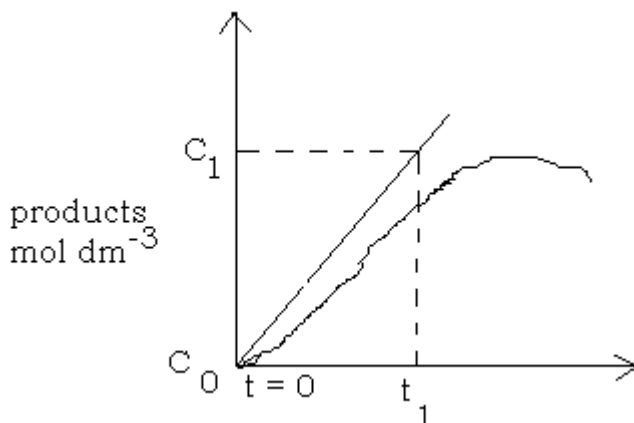
The initial fuse is very useful in determining the order of reaction because its always the highest as its obtained from the steepest part of the tangent.

The initial rate is always high because the reactants are still in very conc.

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 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

A + B $\longrightarrow$ products
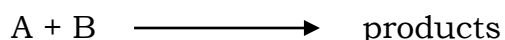
Rate of reaction $\propto [A]^m[B]^n$

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

[HCl] = 1 R_1

[HCl] = 2 R_2

$Mg(s) + 2HCl (aq) \longrightarrow MgCl_2(g) + H_2(g)$
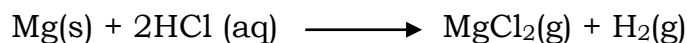
If $R_2 = R_1$ then the order of reaction with HCl is zero. Rate = $K(HCl)^0$

If $R_2 = 2R_1$ then the order of reaction is one (1st order) with HCl.

Rate = $K [HCl]^1$

If $R_2 = 4R_1$ then the order of reaction is two (2nd order) with to the conc of HCl

Rate = $K[HCl]^2$.

If $R_1 = R_2$

$R_1 = K[1]^x$

$R_2 = K[2]^x$

$\frac{R_2}{R_2} = \frac{K[2]^x}{K\ 1^x}$, $1 = 2^x$, $2^0 = 2^x$, X = 0

If $R_2 = 2R_1$, $\frac{R_2}{R_2} = \frac{K[2]^x}{K\ 1^x}$, $\frac{2R_2}{R_1} = 2x$, $2 = 2x$, X=1, Order of reaction is 1.

If $R_2 = 4R_1$, $\frac{R_1}{R_1} = \frac{K[2]^x}{K\ [1]^x}$, $\frac{4R_2}{R_1} = \frac{K[2]^x}{K\ [1]^x}$, $2^2 = 2^x$, 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 Rate = $k\ [A]^2[B]^1$

What will happen to the rate if the concentration of both reactants is doubled.

Expt 1 = $R = K(x)^2 \ X\ y^1$

$R_2 = K(2x)^2 = (2y)$

$R_1 = Kxy$

$$R_2 = K4x^2 2y; \; 8Kx^2 2y; \; \frac{R_2}{R_1} = \frac{8kx^2 y}{kx^2 y}$$

$$\frac{R_2}{R_1} = 8; \; R_2 = 8R$$

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 pulled 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 Rate = $K(A)^0$ (Zero order reaction)
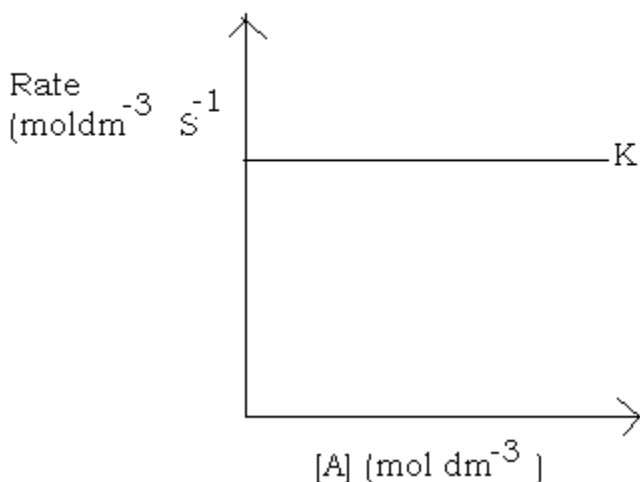
Rate = K(A) (1st order reaction)

$$\text{Slope} = \frac{\Delta rate}{\Delta [H]} = K$$
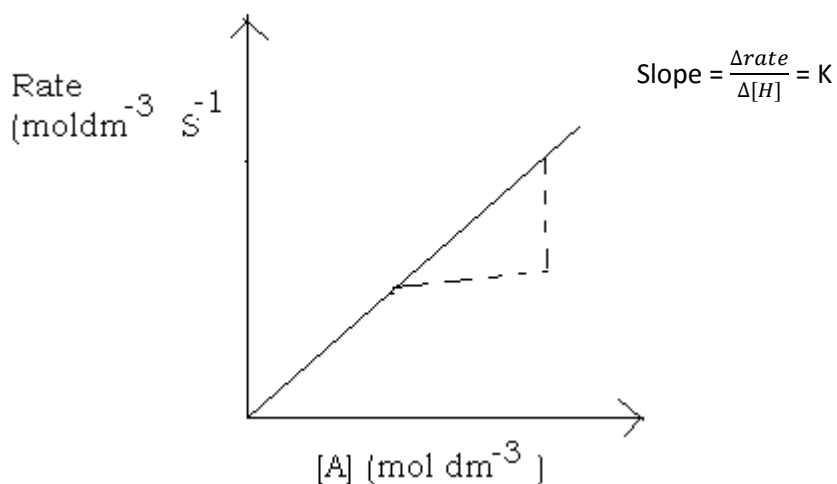
Rate = $K[A]^2$ (2nd order reaction)
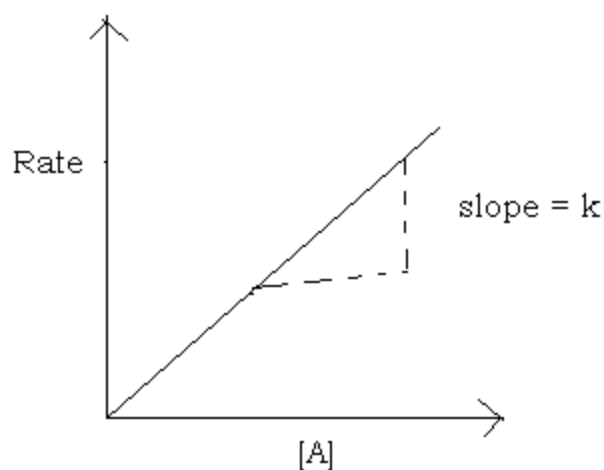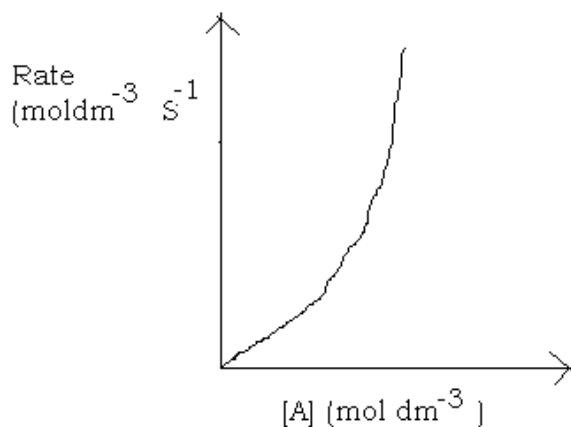
Half life of first order reaction

Half life is the time taken for the conc is a reactant to decrease to half its original value

If [A] = Co and $[A]_t$ = Ct

At t = t ½ , Ct ½ = ½ Co

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

Conc $(moldm^{-3})$

$\frac{1}{2}Co$

$\frac{1}{4}Co$ $\leftarrow t\frac{1}{2} \rightarrow \leftarrow t\frac{1}{2} \rightarrow$

T1   T2   time (s)
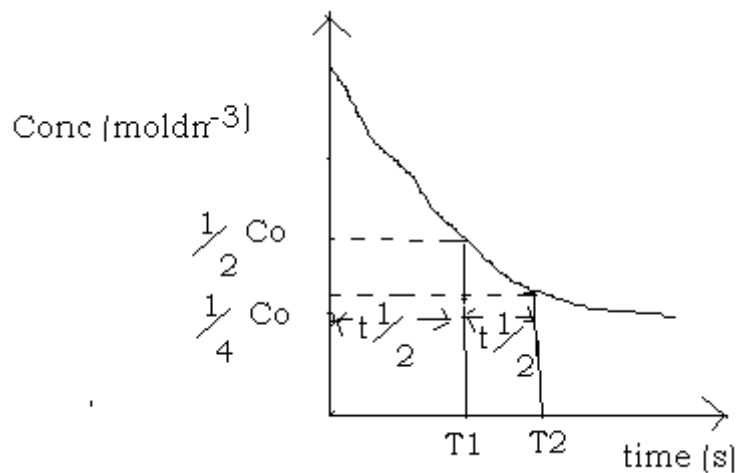
1st t ½ = T

2nd t ½ = (T$_2$- T$_1$)

1st order reaction

1st t ½ = 2nd t ½

For 2nd order reaction

$\frac{1}{2}Co$

$\frac{1}{4}Co$ $\leftarrow 1^{st}t\frac{1}{2} \rightarrow \leftarrow 2^{nd}t\frac{1}{2} \rightarrow$

T1   T2   time (s)
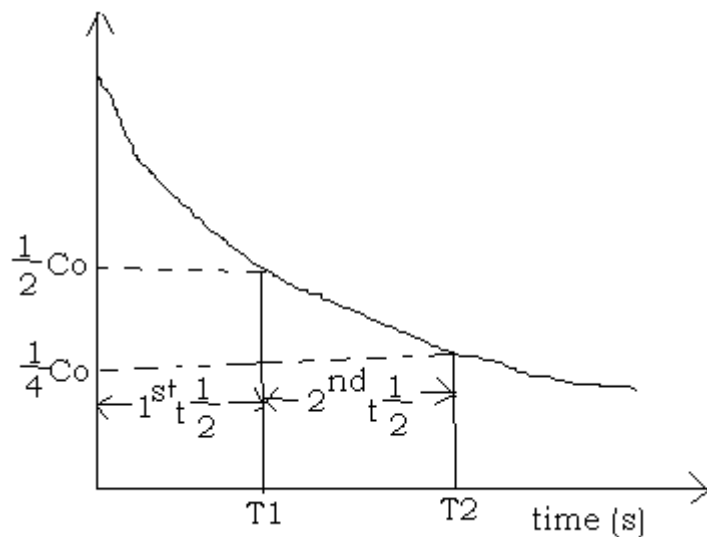
1st t ½ = T$_1$
2nd t ½ = T$_2$- T$_1$
For 2nd order reaction
The tangent of the curve at any point gives us that rate of reaction at that time.
When the rates at different points are compared with their corresponding conc,
the order of reaction can be determined.

Integrated rate equation for first order reaction
Given the reaction
A $\longrightarrow$ products
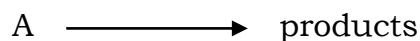
Rate $= \frac{-d[A]}{dt} = k[A]$

If $[A]_{t=o} = a_o$ moldm^{-3} and at time t, x moldm^{-3} of A has reacted, therefore amount of A remaining in the reaction mixture at time t.

$[A]_t = a_o - x$

Rate $= \frac{-d[A]t}{dt} = \frac{dx}{dt} = k[A]_t$

$\frac{dx}{dt} = K[H]_6$

$\frac{dx}{dt} = K(a_o\text{-}x)$

$\frac{dx}{K(a_o-x)} = kdt$

Taking intergrals on both sides

$\int(\frac{1}{a_0-x})dx = K \int dt$

- In $(a_o\text{-}x) = kt + e$

Initially at 6 = 0, x = 0

- In $(a_o\text{-}x) = K(0) + C$
- In $Cl_0 = C$
- In $(Cl_0\text{-}x) = kt - InCl_0$

Collecting like terms

-In $(a_v - x) + InCl_o = Kt$

$In(\frac{a_v}{a_0-x}) = kt$

Or

-kt $= In(a_o\text{-}x) - Ina_v$

-kt $= In(\frac{a_0-x}{a_v})$

$In(\frac{a_0-x}{a_v}) = $ -kt

Interms of logarithm to base ten

In $= log_e$

$Log_e (\frac{a_v}{a_0-x}) = kt$

$(\frac{a_v}{a_0-x}) = e^{kt}$

$Log_{10} (\frac{a_v}{a_0-x}) = kt \, log_{iv}^e$

$Log_{10} (\frac{a_v}{a_0-x}) = \frac{kt}{log_e^{10}}$

log_e^{10} x $log_{10}(\frac{a_v}{a_0-x}) = kt$

2.303 $log_{10}(\frac{a_0}{a_0-x}) = kt$

Or 2.303 $log(\frac{a_v}{a_0-x}) = $ -kt

Deriving an expression for the half life

At half life (t ½)^x = ½ av

$2.303\log_{10}(\frac{a_0}{a_0-x}) = kt$

$2.303 \log 10 (\frac{a_v}{a_0-\frac{1}{2}av}) = kt$

$2.303\log 10 (\frac{a_v}{\frac{1}{2}a})= kt_{\frac{1}{2}}$

$2.303\log_{10}^2 = kt_{\frac{1}{2}}$

$2.303 \times 0.3010 = kt_{\frac{1}{2}}$

$kt_{\frac{1}{2}}=0.693$

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

   a. Derive the expression for the half life for a first order reaction. $2.303\log(\frac{a_0}{a_0-x_1})= kt$, where a_v is the initial concentration of the reactant and (a_0-x) is the concentration at time t.

   b. The half life of a first order reaction is 100g

   c. Calculate the rate constant

   d. Determine the percentage of the reactant that reacted after 250s

a. $2.303\log_{10}(\frac{a_0}{a_0-x}) = kt$

at t = t ½

x = ½ a$_0$

$2.303\log_{10}(\frac{a_v}{a_0-\frac{1}{2}av})= kt_{\frac{1}{2}}$

$2.303\log 10 (\frac{a_v}{\frac{1}{2}a_0})= kt_{\frac{1}{2}}$

$2.303\log_{10}^{(2)} = kt_{\frac{1}{2}}$

$0.6931 = kt_{\frac{1}{2}}, t_{\frac{1}{2}} = \frac{0.6931}{k}$

b. $t_{\frac{1}{2}}$ = 100s

(i) $kt_{\frac{1}{2}}=0.0931$

$K= \frac{0.6931}{t_{\frac{1}{2}}}$

$K = \frac{0.6931}{100}$

K = 6.931 x 10^{-3}S^{-1}

(ii) t=250s

$2.303\log_{10}\left(\frac{a_0}{a_0-x}\right) = kt$

$2.303\log_{10}\left(\frac{100}{100-x}\right) \; 6.931 \times 10^{-3} \times 250$

$\text{Log}\left(\frac{100}{100-x}\right) = \frac{6.931 \times 10^{-3} x250}{2.303}$

$\text{Log}\left(\frac{100}{100-x}\right) = \log\frac{6.931 \times 10^{-3} x250}{2.303}$

$\frac{100}{100-x} = 5.6544$

$565.44 - 5.6544x = 100$

$465.44 = 5.6544x$

$X = 82.3\%$

The percentage that reacted is 82.3%

Graphic representation integrated rate equation for first order reaction

From $2.303\log_{10}\left(\frac{a_0}{a_0-x}\right) = kt$

Or $2.303\log\left(\frac{a_v}{a_0-x}\right) = -kt$

A plot of $2.303\log\left(\frac{a_0}{a_0-x}\right)$ against t gives a straight line with a positive gradient (slope) which is equal to $\frac{k}{2.303}$
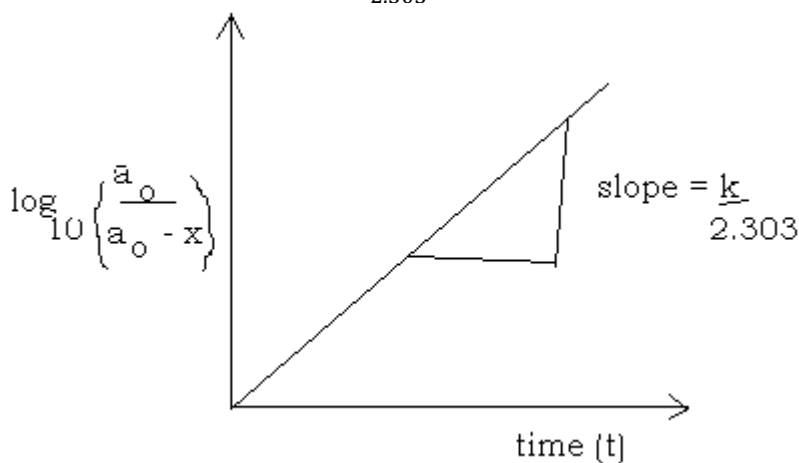
The table below shows the results for the reaction A ⟶ Products

Time (min)	0	9	18	27	40	54	72	105
[A]$_t$ (moldm³)	0.106	0.096	0.086	0.077	0.065	0.054	0.043	0.030

    a. Plot a graph of $\log_{10}[A]_t$ against time
    b. Use your graph to determine the order of reaction with respect to A
    c. The rate constant for the reaction and state its units

Time (min)	0	9	18	27	40	54	72	105
[A]$_t$ (moldm³)	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 – products
The data in the table below was obtained for the reaction A $\longrightarrow$ 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

    a. Plot a graph of log$_{10}$(A) against time
    b. From graph determine the order of reaction
    c. Calculate
    i) The rate constant for the reaction
    ii) The half life of the reaction

1st order reaction

Slope $= \dfrac{-0.1-0.83}{C-0.2}$

$= -1.2586 = -0.1259$

Slope $= \dfrac{-k}{2.303}$

-0.1259 x 2.303

K = 0.2899hr^{-1}

$t_{\frac{1}{2}} = \dfrac{0.693}{k}$

$t_{\frac{1}{2}} = \dfrac{0.693}{0.2899}$

$t_{\frac{1}{2}} = 2.3905$hrs

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 catalised by dilute sulphuric acid.
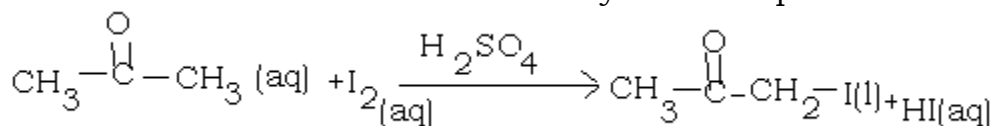
Known concentration of propanone, iodine in potassium iodide and dilute sulphuric acid are prepared and brought to a required temperature in other most at bath.
The conc of propanone is higher than that of iodine.
Known volumes of propanone and iodines are mixed in a beaker or conical flask.
A known 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 thiiosulphate.

Iodine reacts with sodium thiosulphale according to the following equation.

$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2J^-(aq) + S_4O_6^{2-}(aq)$
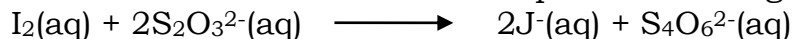
The experiment is repeated with out stopping the stop clock at half minute intervals for 5 mins.

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
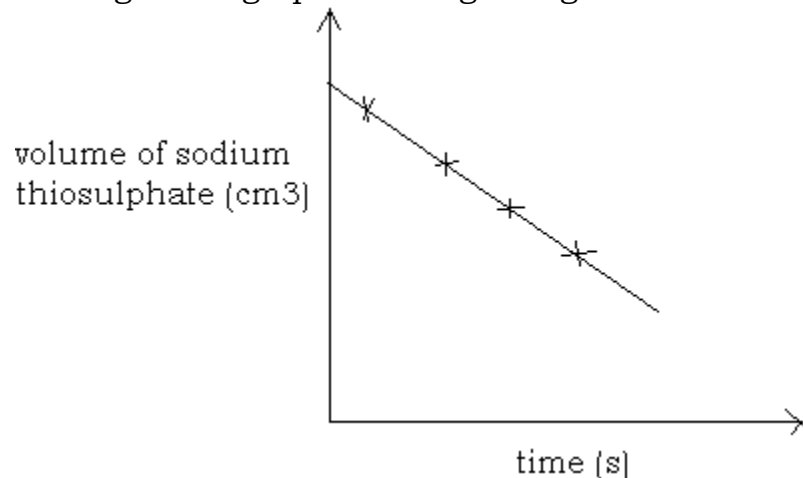
This shows that the conc of iodine is decreasing at a constant rate and therefore the order of reaction with respect sodine is Zero

Rate = $k[I_2]^0$

The slope of the graph gives the rate constant

2. First order reaction

Experiment to show that catalystic decomposition of hydrogen peroxide is first order.

Hydrogen peroxide decomposes according to the following equation

$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$
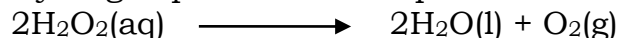
- A known volume of standard hydrogen peroxide solution is transferred into a cornical flask.
- A fixed volume of iron (iii) chloride solution is added which is followed by an equation volume of sodium hydroxide solution and the stop clock is simultaneous by started.
- The mixture is allowed to stand at the room temperature (iii) catalyzes the mixtures 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 micture is titrated against a standard solution of potassium permanganet and the volume of potassium per managete is noted.

The produce is repeated at several time intervals

A graph of volume of potassium manganate (vii) against time is plotted.

The graph is an exponentral curve with contant half lives implying that the reaction is first order.

A graph of log10 volume of potassium manganate (vii) against a straight line graph of negative gradient is obtained showing that the reaction as first order.
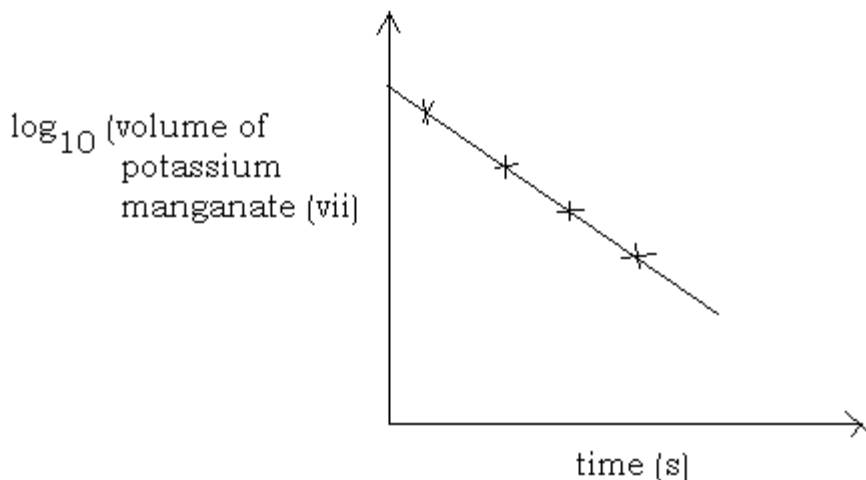
Experiment to show that the order of reaction between sodium thiosulphate and hydrochloric acid is the with thiosulphate ions.
The reaction between sodium thiosulphate solution and dilute hydrochloric acid produces a yellow ppt of sulphur according to the equation.
$S_2O_3^{2-}(aq) + 2H^+(aq)$ $SO_2(aq) + S(s) + H_2O (l)$

- 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 occassionary
- The time taken fo the ppt of sulphur to block from new to cross or dot is noted
- Concentration of hydrochloric acid is kept constant buigher than that of sodium thiosulphid.
- 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 / obsecure from view a big cross/dot noted at each new conc.

A graph of $\frac{1}{t}$ against conc of sodium thio suplphate 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 reactions is first order with respect to sodium thiosulphate.

Note: $\frac{1}{t}$ = rate of reaction

slope = rate constant
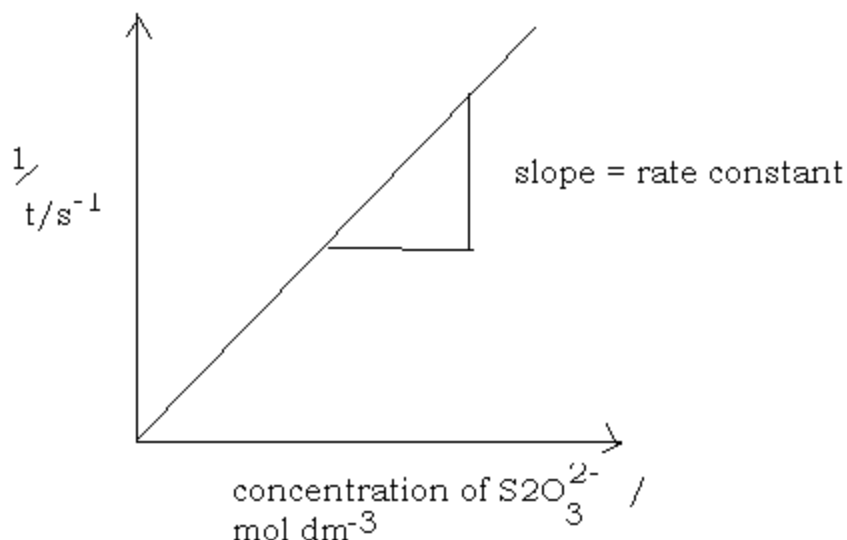
Rate K = k[S$_2$O$_3{}^{2-}$]

Slope = $\frac{D\ Rate}{D\ [S_2O_3^{2-}]}$ = K

50cm³ of 0.15 sodium thiosulphate solution and 5 cm³ of 2.0M 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 wit 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$_3$ (cm³)	Volume of water (cm³)	Conc of Na$_2$S$_2$O$_3$ (mol dm^{-3})	Time taken for the cross to be obsecured (s)	Rate of reaction $\frac{1}{t}$
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

   a. Complete the table above
   b. Plot the graph of rate against concentration of sodium thiosulphate
   c. Use the graph to determine
   i.   The order of reaction with respect to sodium thiosulphate
   ii.   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 equation.*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.

$$A + B \rightleftharpoons C + D$$
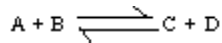
At equation the rate of formation of C and D (rate of formation of products) is equal to the rate of formation of reactant ie A and B. The rate of reaction can be defined as the decrease in the conc of the reactants per unit time or the increase in the conc of the products per unit time. Eg when steam 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.

$$Fe(s) + H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$
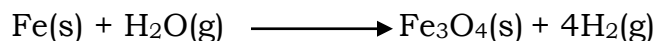
The direction of the reaction depends on the conditions available. If hydrogen gas is removed as soon as it is formed, then the reaction will proceed kin the forward direction. But if steam is constantly removed from the reaction mixture, the reaction will proceed in the back ward direction and with 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 equiliblium, 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, *Kc or Kp. Kc* is equilibrium constant for a reversible reaction in terms of molar concentrations. *Kp* is equation constant for the reversible reaction in terms of partial pressure

$$aA + bB \longrightarrow cC + dD$$
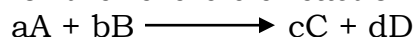
$$Kc = \frac{[C]^c \ [D]^d}{[A]^a \ [B]^b}$$

$$Kp = \frac{Pc^c \ Dd^d}{PA^a \ PB^b}$$

Kp is for only those reactions involving gases

Kc is for reactions both in gaseous state and liquid state

It is noted that the conc of the solid is taken as unity

Ie $[Fe] = [Fe_3O_4] = 1$

$\quad P_{Fe} = P_{Fe_2O_4} = 1$

Write the expression for Kc or Kp for the following reactions

    a. $N_2(g) + 3H_2(g) \qquad\qquad\qquad 2NH_3(g)$

$Kc = \dfrac{(NH_3)^2}{[N]^1[N_2]^3} \quad Kp \dfrac{P^2NH_3}{PN_2O - P^3N_2} \quad$ units $\dfrac{mol^{-2}dm^6}{-atm}$

Calculations of Kc and Kp

In a reaction of the type $\quad A+B \rightleftharpoons C+D \quad$ if a mole of A and b moles of B where initially present in a volume of Volm^3. At equation and at a given temperature x mole at A and x moles of B have reacted to form x mole of C and x moles of D. the KC and Kp can be calculated as follows.

$A+B \rightleftharpoons C+D$
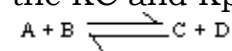
Initial moles

a   b   0:0

Reacting

Moles

x   x   x: x

Equilibrium

moles

a-x   b-x   x :x

Equilibrium

ancentrations

$\dfrac{a-k}{v} \quad \dfrac{D-x}{v} \qquad\qquad \dfrac{x}{v} \quad \dfrac{x}{v}$

$Kc = \dfrac{[c]\,[D]}{[c]\,[d]} = \dfrac{[c]\,[D]}{[A]\,[B]}$

$Kc = \dfrac{x}{v} : \dfrac{x}{v}$

$\dfrac{A-x}{v} \quad - \dfrac{b-x}{v}$

$Kp = \dfrac{P_cP_D}{P_AP_B}$

Partial pressure = mole gration x total pressure

Total number of moles of equation

9a − x0 + (b − x) + x + x

Let P_T be the total pressure of the gaseous mixture

$P_A = \left(\dfrac{a-x}{a+b}\right) P_T$

$D_B = \left(\dfrac{b-x}{a+b}\right) P_T$

$D_c = \left(\dfrac{x}{a+b}\right)P_T$

$Pd = (\frac{x}{a+Tb})P_T$

Therefore $KP = (\frac{x}{a+b})P_T \qquad (\frac{x}{a+b})P_T$

$$(\frac{a-x}{a+b})P_T \qquad (\frac{b-x}{a+b})P_T$$

$$\frac{x^2}{(a-x)(b-x)}$$

Phosphorns (V) Chloride dissolute at higher temperature and pressure according to the equation

PCl$_5$(g)   PCl$_3$(g) + Cl$_2$(g)

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

Kc for the equation [P=31, Cl = 355]

R.F.M of PCl$_5$ = 31 + 35.5 x 5 = 208.5

R.F.M of PCl$_3$ = 31 + 3 x 5 = 131.5

R.F.M of PCl$_2$ = 35.5 x 2 = 71

No. of moles of PCl$_5$ = $\frac{84.3}{208.5}$ = 0.4

No. of moles of PCl$_2$ = $\frac{11.1}{71}$ = 0.156

PCl$_5$ (s)	PCl$_3$(g)	Cl$_2$(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	$\frac{0.244}{9.23}$	$\frac{0.156}{9.23}$	$\frac{0.156}{9.23}$

$Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

$= [\frac{\frac{0.156}{9.23} \quad \frac{0.156}{9.23}}{\frac{0.244}{9.23}}$

= 0.0108 mol dm^{-3}

Partial pressures

Total moles = 0.244 + 0.156 + 0.156 = 0.556

PCl$_2$ $= \frac{0.156}{0.556}$ x 280 = 70.14

PpCl$_3$ $= \frac{0.156}{0.556}$ x 280 = 70.14

PpCl$_5$ $= \frac{0.244}{0.556}$ x 230 = 109.71

$$Kp = \frac{PpCl_3 \; PCl_3}{PpCl_5} = \frac{70.14 \; x \; 70.4}{109.71}$$

= 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.
   a. Calculate the equation constant Kc for the reaction at the temperature
   b. Calculate the mass of ethyl ethanoate that would be formed when 90g of ethanoic acid were heated with 93g of ethanol at that tempe.

R.F.M of CH_3CH_2CH = 2 x 12 + 16 + 6 = 40
R.F.M of CH_3COOH = 2 x 12 + 4 +16 + 2 = 60
R.F.M of H_2O = 18

$CH_3COOH(l) + CH_3CH_2OH(l)$ ⇌ $CH_3CH_2OCH_2CH_3(l) + H_2O(l)$

Initially	$\frac{60}{60}:1$	$\frac{40}{40}:1$	0	0
Reacting moles	x	x	x	x
Equation moles	1-x	1-x	x	x
But $x=\frac{12}{18}=6.67$	1-0.67	1-0.67	0.67	0.67
	0.33	0.33	0.67	0.67
Equation conc	$\frac{0.33}{V}$	$\frac{0.33}{V}$	$\frac{0.67}{V}$	$\frac{0.67}{V}$

$$Kc = \frac{[CH_2CH_2OCH_2CH_3][H_2O]}{[CH_2COOH][CH_3CH_2OH)}$$

$$Kc = \frac{[0.67][0.67]x\frac{1}{V}}{[0.33][0.33] \; x\frac{1}{V}}$$

Kc = 4.1221

Nitrogen and hydrogen are mixed in a molar ratio 1:3. At equation at 600⁰C and 10 atm, the percentage of ammonia in the mixture of gases is15%. Calculate the value of the equilibrium constant Kp for the reaction at 600⁰C

$N_2(g) + 3H_2(g)$ ⇌ $2NH_3(g)$

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 = $\frac{2a}{4-2a}$ x 100 = 15

a = 0.26

Mole fraction $\frac{0.74}{3.48}$ $\frac{2.22}{3.48}$ $\frac{0.52}{3.48}$

Partial pressure of $N_2.PN_2 = \frac{0.74}{3.48}$ PT

$= \frac{0.74}{3.48}$ x 10

$= \frac{7.4}{3.48}$

Partial pressure of H_2, $PH_2 = \frac{2.22}{3.45}$ x 10 $= \frac{2.22}{3.48}$

Partial pressure of NH_3, $PNH_3 = \frac{0.52}{3.48} \times 10$

$$= \frac{0.52}{3.48}$$

$Kp = \frac{P^2NH_3}{PN_2 x P^3N_2} = \frac{(\frac{5.2}{3.48})^2}{(\frac{2.4}{3.48})-(\frac{22.2}{3.48})^5}$

$= 0.1646$ atm^{-2}

3. A mixture of 3 moles of hydrogen and 1mole of Nitrogen is allowed to reach equation at a pressure of $5 \times 10^6 NM^{-M}$. The composition of the gaseous mixture is then 8%NH_3 23%N_2, 69%H_2 by Volume calculate Kp.

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 cm of the standard alkali for neutralization. Find the value of Kc for the estenfication 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 Kp under these conditions.

6. hydrogen and iodine react to form hydrogen iodide according to the following equation.

$H_2(g) + I_2(g) \qquad 2HI(g)$

  (i)   Write the expression for the equilibrium constant Kc for the reaction

  (ii)   1 mole of hydrogen and $\frac{1}{3}$ mole of Iodine were heated together at 450^{0}C until equation was attained. Calculate the number of moles of hydrogen iodide present in the equilibrium mixture at 450^{0}C [The equilibrium constant Kc for the reaction between H_2 and I_2 is 50].

(b) Briefly explain how the conc of I_2 in the equation mixture can be determined.

Experiment to determine the equilibrium constant for the etherification 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^{0}C. After some hrs at this temperature the acid and the alcohol will have reacted to form the equation mixture. The tube is the cooked and the amount of acid it contains if found by titration with standard acid alkali.

If there are x moles of acid present at equation it follows that (a-x) moles at acid have been converted into easter and water. Since 1 mole at ester and 1 mole of water were formed from 1 mole of acid, there must be (a –x) moles of at ester and of water present in the equation mixture (a-x) moles of alcohol must have been used up so that the amount of alcohol present at equation will be [b-(a-x)] moles.

For a scaled tube of volume V litres equation concentration in mole pe litre would be as follows.

Acid $\frac{x}{V}$ Ester $\frac{a-x}{V}$

Alcohol $\frac{b-(a-x)}{V}$ water $\frac{a-x}{V}$

The equation constant will be given by

$$Kc = \frac{\left(\frac{a-x}{V}\right) - \left(\frac{a-x}{V}\right)}{\left(\frac{x}{V}\right)\left(\frac{b-(a-x)}{V}\right)} = \frac{(\square-\square)^2}{\square[\square-(\square-\square 0]}$$

Factors affecting equilibrium reactions

The concentration – catalyst

Temperature

Pressure

Concentration

The effect of conc of the equation of reaction was predicted by lechateliers principle which states that if one of the external factors affecting the system in equation is altered, then the system tends to react in such away as to minimize any changes resulting from the alteration of external factors.

Effect of conc does not change the equation constant but it affects the equation position ie the reaction may tend to go to the forward or may take the backward reaction

eg A + B   C + D

$$Kc = \frac{[\square][\square]}{[\square][\square]}$$

If the concentration of A is increased by adding more A kin the reaction mixture at equation, 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 Kc constant provided other conditions such as tempt. And pressure are kept constant.

If the conc of C is increased by adding it from out the reaction mixture at equation the equation 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 Kc constant.

Similarly, if the conc Dc is reduced by constantly removing it from the reaction mixture the position of equation will shift to the right ie the forward reaction will be favoured ie more A and B will read to replace C. this is done to keep Kc constant.

In the contact process where SO_2 and O_2 react to form SO_3.

$$2SO_2(g) + O_2(g) \qquad 2SO_3(g)$$

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 10^0C rise in temperature. This is because the reactant

molecules gain enough Ke and collide more frequently and this result 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.

$Log\ k \propto \frac{\square\square}{\square}$ (Exothermic reaction)

$Log\ \frac{1}{4} \propto \frac{\square\square}{\square}$ (Endothermic reaction)

Where K = equation constant

DH = Enthalpy of reaction
T = absolute temperature (k)
For exothermic reactions where DH is negative, increase in temperature decreases the Kc 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 reactiin and the equation constant increases because the concentration of the products increases while the conc of the reactants decreases.
$H_2(g) + I_2(g) \longrightarrow 2HI(g)$ DH = + 11.5KJMol^{-1}
The above reaction is an endothermic reaction. When the temperature is increases, more H_2 and I_2 will combine to form HI and therefore Kc or K_p will increase. But when the temperature is lowered, the equation position will shift to the left HI will disocrate to form H_2 gas and I_2 molecules and Kc will decrease.
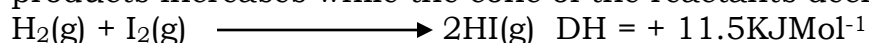
Effect of pressure on equilibrium reactions.

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 doesnot 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.

$2SO_2(g) + O_2(g) \longrightarrow SO_3(g)$ (Volume decrease)---------1

$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$ (volume increase)---------2

$2HI(g) \longrightarrow H_2(g) + I_2(g)$ (no volume change)----------3

$N_2 + 3H_2(g) \longrightarrow 2NH_3(g)$ (volume decrease)------------4
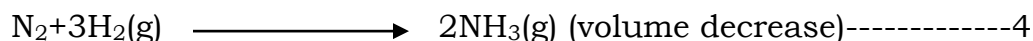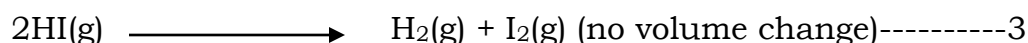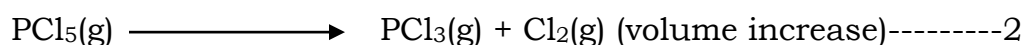
In reaction 1 the forward reaction proceeds with decrease in volume. The gaseous reactants occupy 3 volumes and the products occupy 2 volumes.

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 Kp or Kc 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.

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $DH^2r = -92KJmol^{-1}$.
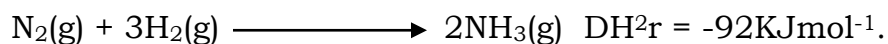
The forward reaction proceeds with decrease in volume therefore high pressure favour the forward reaction. Maintaining high pressure is quite expensive.A rational pressure of 500 atm can be used for optimum yield at ammonia.Also the reaction proceeds with evolution of heat on exothermic reaction. Therefore 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 500^0C 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.
$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2)(l) DH = -900KJmol^{-1}$.
In this reaction, there is a small increase in volume. I t would be expected that low pressure will be used. Therefore 9 atms are used for the optimum yield of
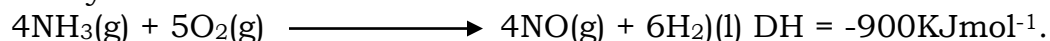
No. temp between 600-9000℃ are used for the reaction with platimum rhodium as a catalyst.

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}.

$NO(g) + O_2(g) \longrightarrow NO_2(g)$
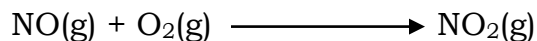
- Nitric acid is used in the manufacturer of
  - Dyes
  - Explosives
  - Fertilizers

Nitric acid can react with copper in two ways.

When concentrated

$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + NO_2(g)$

When dilute

$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$
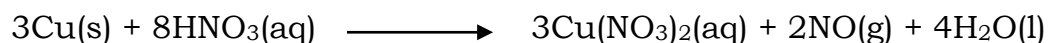
It can react with sulphur to form sulphuric acid

$S(s) + 6HNO_3(aq) \longrightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$

3. Contact process

In contact process SO_2 react with O_2 to form SO_3. The reaction proceed with decrease in volume and heat is evolved.

$2SO_4(g) + O_2(g) \qquad\qquad 2SO_3(g)$ DH = -188KJmol^{-1}.

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.

$SO_3(g) + H_2SO_4(l) \longrightarrow H_2S_2O_4(l)$
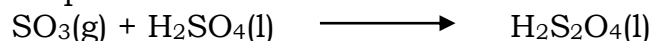
Oleum is diluted with a particular amount of water to obtain 98% w/w sulphuric acid with a density of 1.8gcm^{-3}.

$H_2S_2O_2(l) + H_2O(l) \longrightarrow 2H_2S_2O_4(l)$
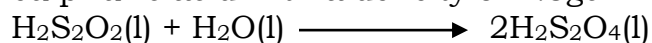
Sulphuric acid is used in the manufacturer of superphosphates which are fertilizers.

Liquid system (homogeneous)

Consider a reaction

$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$
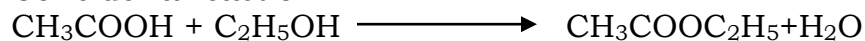
Suppose that a mole of ethanoic and are mixed with b mole of ethanol and total volume of the mixture is V/m^3.

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.

$$CH_3COOH + C_2H_5OH \qquad CH_3COOC_2H_5 + H_2O$$

Initially	a	b	O	O
At eq $\equiv$ m	(a-x)	(b-x)	x	x
	$(\frac{a-x}{V})$	$(\frac{b-x}{V})$	$(\frac{x}{v})$	$(\frac{x}{v})$
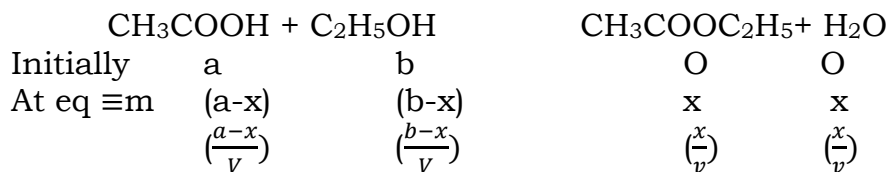
By the law of mass action the equilibrium constant K_c is given by

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$\frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{((a-x)/v)\,((b-x)/V)}$$

$$K_c = \frac{(x^2/v^2)}{\frac{(a-x)(b-x)}{v^2}}$$

$$= \frac{\frac{x^2}{V^2}.V^2}{(a-x)(b-x)}$$

$$K_C = \frac{X^2}{(a-x)(b-x)}$$

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 $C_2H_5OH = \frac{8.28}{46} = 0.18$

No of moles of $CH_3COOH = \frac{60}{60} = 1$

Remaining moles $= \frac{49.74}{60} = 0.829$

Moles that reacted = (1-0.829)

X = 0.171

From $K_c = \frac{(X)^2}{(a-x)(b-x)} = \frac{(0.171)^2}{0.829(0.18-0.17)}$

$K_c = \frac{0.029241}{0.007461}$

GASEOUS EQUILIBRIUM (HOMOGENEOUS)

Consider a reaction

$$2HI(g) \qquad\qquad H_2(g) + I_2(g)$$

Suppose we start with a mole of hydrogen iodide and at equilibrium x mole have dissociated.

Since 1 mole of HI on dissolution finishes ½ mole of hydrogen and ½ mole of iodine vapour, there we have

$$2HI \qquad\qquad H_2(g) + I_2(g)$$

At eq $\equiv$m $\quad$ (a-x) $\qquad\qquad \dfrac{x}{2} \qquad \dfrac{x}{2}$

Total number of moles

$= a - x + \dfrac{x}{2} + \dfrac{x}{2}$

$\dfrac{a-x}{1} + \dfrac{x}{2} + \dfrac{x}{2} = \dfrac{2(a-x)+x+x}{2}$

$= \dfrac{2a-2x+2x}{2}$

= a moles

Partial pressure = mole fraction x total pressure

Ie $P^0 = X^0 P$

$P^0(H_I) = \left(\dfrac{a-x}{a}\right) p$

$P^0(H_2) = \left(\dfrac{x/2}{a}\right) p$

$= \left(\dfrac{x/2}{a}\right) p$

Therefore $Kp = \dfrac{\left(\frac{x}{2}\right)x\ (\frac{x}{2}/a)P^2}{\left(\frac{a-x}{a}\right)^2 P^2}$

$= \dfrac{\left(\frac{x^2}{4}\right)/a^2}{\left(\frac{a-x}{a}\right)^2} = \dfrac{\frac{x^2}{4}/a^2}{(a-x)^2/a^2}$

$= \dfrac{\left(\frac{x^2}{4}\right)a^2}{a^2(a-x)^2} = \dfrac{x^2}{4} \div \dfrac{(a-x)^2}{1}$

$$\dfrac{x^2}{4} \ X \ \dfrac{1}{(a-x)^2}$$

$\left(\dfrac{x^2}{4}\right)/(a-x)^2 = \dfrac{x^2}{4(a-x)^2}$

$Kp = \dfrac{x^2}{4(a-x)^2}$

From an opposite direction by heating hydrogen and iodine together

$$I_2 + H_2 \qquad\qquad\qquad 2HI$$
$$\dfrac{(a-x)}{v} \quad \dfrac{(b-x)}{v} \qquad\qquad \dfrac{(2x)}{v}$$

If we start with a mole of iodine and b moles of hydrogen in the total volume of V (mm^2) and if at equilibrium x moles of hydrogen n and iodine have disappeared the concentrations of the substance present at ....above since the volume remains constant.

Then by law of mass action

$K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

$$= \frac{\frac{4x^2}{v^2}}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}$$

$$\frac{\frac{4x^2}{v^2} \times v^2}{(a-x)(b-x)}$$

$K_c = \frac{4x^2}{(a-x)(b-x)}$

K_p calculation of K_p

At eq $\equiv$m (a-x) mole of I_2 and (b-x) of H_2 together 2x of HI

Total number of moles = (9-x) + (b-x) + 2x

$$= a-x + b - x + 2x$$

$$= (a+b)$$

$P_1^0 H_2 = \left(\frac{b-x}{a+b}\right) P$

$P_2^0 I_2 = \left(\frac{a-x}{a+b}\right) P$

$P_3^0 HI = \left(\frac{a-x}{a+b}\right) P$

$K_p = \frac{(P_3^0)^2}{P_1^0 P_2^0} = \frac{\left[\left(\frac{2x}{a+b}\right)P\right]^2}{\left[\left(\frac{a-x}{a+b}\right)P\right]\left[\left(\frac{b-x}{a+b}\right)P\right]}$

$$= \frac{\frac{4x^2}{(a+b)^2}}{\frac{(a-x)(b-x)}{(a+b)^2}} = \frac{\frac{4x^2}{(a+b)^2}(a+b)^2}{(a-x)(b-x)}$$

$K_p = \frac{4x^2}{(a-x)(b-x)}$

K_c in terms of degree of dissociation.

Consider the reaction
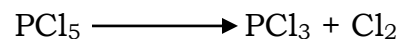
$PCl_5 \longrightarrow PCl_3 + Cl_2$

Initially 1   0   0

$\propto$- Degree of dissociation

V- Volume at eq $\equiv$m   (1-$\propto$) $\propto$ $\propto$

Considering a certain volume V

$\left(\frac{1-\propto}{v}\right)$ $\left(\frac{\propto}{v}\right)$ $\left(\frac{\propto}{v}\right)$

From the law of mass action

$Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

$K_c = \frac{(\propto/v)(\propto/V)}{(1-\propto)/v}$

$$= \frac{(\propto^2/v^2 \times V^1)}{(1-\propto)}$$

$$K_c = \frac{\propto^2}{V(1-\propto)}$$

In moles per metre

For Kp in terms of degree of dissociation $\propto$ and total pressure, P at eq≡m is as follows;

Total number of moles = $(1-x) + \propto + \propto$

$= 1-\propto + 2\propto$

$= 1 + \propto$

Therefore

$P_1^0 (PCl_5) = (\frac{1-\propto}{1+\propto})P$

$P_2^0 (Cl_3) \equiv P^0(Cl_2)$ and given as below

$= (\frac{1-\propto}{1+\propto})P$

$Kp = \frac{(P_2^0)^2}{P_1^0} = \frac{(\frac{\propto}{1+\propto})^2 P^2}{(\frac{1-\propto}{1+\propto})P}$

$Kp = \frac{\frac{\propto^2}{1+\propto} \cdot p}{1-\propto}$

$Kp = \frac{\propto^2 . P}{(1-\propto) + (1+\propto)}$

$Kp = \frac{\propto^2 P}{(1-\propto)^2}$

6. Dissociation of Dinitrogen tetraoxide

$N_2O_4 \longrightarrow 2NO_2$
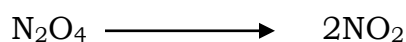
Initially there is 1 mole of N_2O_4

$\propto$ = degree of dissociation

$$N_2O_4 \longrightarrow 2NO_2$$
$$1 \qquad\qquad\qquad O$$
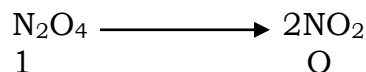
At eq ≡m $1-\propto$ $2\propto$

Consider a given volume, V we get

$\frac{1-\propto}{v}$ $\frac{2\propto}{v}$

$K_c = \frac{[NO_2]^2}{[N_2O_4]}$

$= \frac{(\frac{2\propto}{v})^2}{(\frac{1-\propto}{v})} =$

$K_c = \frac{4x^2}{v(1-\propto)}$

7. Combination of Nitrogen and hydrogen.

1 mole of nitrogen combines with 3 moles of hydrogen as shown the equation below.

$N_2 + 3H_2(g) \longrightarrow 2NH_3(g)$
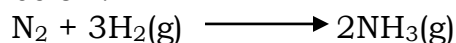
eq ≡m $\quad\quad \frac{1-x}{v} \quad\quad 3\left(\frac{1-x}{v}\right) \quad\quad \frac{2x}{v}$

From the law of mass action

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{1-x}{v}\right)\left(\frac{3-3x}{v}\right)^3}$$

$$K_c = \frac{\frac{4x^2}{v^2} \times v^{4-2}}{(1-x)3^2(1-x)^2(1-x)}$$

$$Kc = \frac{4x^2v^2}{(1-x)9(1-x)^2.(1-x)}$$

$$Kc = \frac{4x^2v^2}{9(1-x)^{2+2}}$$

$$Kc = \frac{4x^2v^2}{9(1-x)^4}$$

But since $(3-x)^2 = (3-3x)^2.(3-3x)$

$$= 3(1-x)^2.3(1-x)$$

$$= 3^2(1-x)^2(1-x)$$

For Kp; total number of moles = 1-x + 3-3x + 2x = 4-2x

$$P^0(NH_3) = \left(\frac{2x}{4-2x}\right)P$$

$$P^0N_2 = \left(\frac{1-x}{4-2x}\right)P$$

$$P^0H_2 = \left(\frac{3-x}{4-2x}\right)P$$

$$Kp = \frac{P^0(NH_3)}{P^0(N_2).(P^0H_2)}$$

$$Kp = \frac{\left(\frac{2x}{4-2x}\right)^2 P^2}{\left(\frac{1-x}{4-2x}\right)^p\left(\frac{3-3x}{4-2x}\right)^3 P^3}$$

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

aA(g) + bB(g) $\quad\quad\quad\quad\quad\quad$ cC(g) + dD(g)

rate of forward non Rp $\propto [A]^a [B]^b$

rate of backward non Rb $\propto [C]^c [D]^d$

$R_f = K_1[A]^a [B]^b$ $Rb = K_2[C]^c[D]^d$

At eqb m Rf = Rb

$K_1[A]^a [B]^b$ $Rb = K_2[C]^c[D]^d$

$K_1 = K_2 \frac{[C]^c.[D]^d}{[A]^a.[B]^b}$ $\frac{K1}{K2} = \frac{[C]^c.[D]^d}{[A]^a.[B]^b}$

The ratio $\frac{k_1}{k_2}$ gives the equilibrium constant Kc 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 stoictriometic equation at constant temps.

$Kc = \frac{[products]^n}{[reactant]^m}$ are powers to which the reactants and the products are raised in the stoichio metry of the equation.

Acid consider the etherification reaction

$CH_3COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3COOCH_2CH(l) + H_2)(l)$
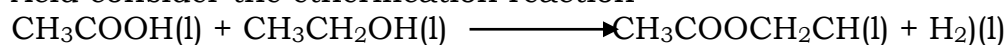
$Kc = \frac{[CH_3COOCH_2CH_3].[H_2O]}{[CH_3COOH].[CH_3COOH]}$

Experimental determination of Kc.

The value of Kc for the above equation system can be experimentally determined. In this investigation known moles of ethanol and ethonoic acid or mixed in a closed container and the container is left to stand in an 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 phenolphithalein 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.

$CH_3COOH (aq) + NaOH(aq) \longrightarrow CH_3OONa(aq) + H_2O(l)$
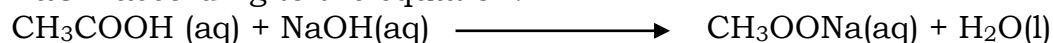
The concentration of ethanoic acid that has reacted can be computed and since 1 mole of ethanoic acid of Ethanol acid reacts with 1 mole Alcoholl (Ethanol) then the moles of ethanol reacted can be determined. Again 1 mole of ethamoic acid reacts to give 1 mole of the eater and 1 mole of water then the 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 dm^3

Moles of ethanoic acid reacted be X moles

	$CH_3COOH(l)$ +	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH(l)$ +	H_2 (l)
Initial	a moles	b moles	0	0
Let x moles	-x moles	-xmoles	+xmoles	+xmoles
Of the acid				
React				

Moles at Eqb m	(a-x)moles	(b-x)moles	x moles	x moles
Conc (moldm⁻³)	$(\frac{a-x}{v})$	$(\frac{b-x}{v})$	$(\frac{x}{v})$	$(\frac{x}{v})$

$$Kc = \frac{[CH_3COOCH_2CH_3].[H_2O]}{[CH_3COOH].[CH_3COOH]}$$

$$Kc = \frac{(\frac{x}{v})(\frac{x}{v})}{(\frac{a-x}{v})(\frac{b-x}{v})}$$

$$= \frac{x^2}{(a-x)(b-x)}$$

Examples.

1. Stoichiometric moles of ethanoic acid and ethanol were introduced in a 1L vessel and cooked at 298 K. the non was allowed to attain eqn m. Al eqb m 0.2 moles of the ester were formed. Calculate the value of Kc at tms temperature.

$$CH_3COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3COOCH_2CH(l) + H_2 (l)$$

Initial	1 moles	1 moles	0	0
if x moles reacted at Eqbm	-x	-x	+x	+x
Conc (moldm⁻³)	$(\frac{1-x}{1})$	$(\frac{1-x}{1})$	$(\frac{x}{1})$	$(\frac{x}{1})$

$$Kc = \frac{[CH_3COOCH_2CH_3].[H_2O]}{[CH_3COOH].[CH_3COOH]}$$

$$Kc = \frac{x.x}{(1-x)(1-x)}$$

$$= \frac{0.2 \times 0.2}{(1-0.2)(1-0.2)}$$

$$= 0.0625$$

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 eqb m. the vessel was found to contain 0.2 moles of ethanoic acid (a) Calc the value of Kc at this temp (b) if stoichiometric moles of acid and Alkolol were used instead at the same temperature and the reaction allowed to attain eqbm. Calculate the eqb m moles of all the participating species.

$$CH_3COOH(l) + CH_3CH_2OH(l) \qquad CH_3COOCH_2CH(l) + H_2 (l)$$

Initial	0.4 moles	0.6 moles	0	0
if x moles reacted at Eqbm	-x	-x	+x	+x
Conc (moldm⁻³)	$(\frac{0.4-x}{1})$	$(\frac{0.6-x}{1})$	$(\frac{x}{1})$	$(\frac{x}{1})$

But at Eqbm moles of ethanoic acid are 0.2 moles

Therefore (0.4-x) = 0.2

X = 0.2

$Kc = \dfrac{[CH_3COOCH_2CH_3].[H_2O]}{[CH_3COOH].[CH_3COOH]}$

$= \dfrac{x.x}{(0.4-x)(0.4-x)}$

$= \dfrac{0.2 \times 0.2}{(0.4-0.2)(0.6-0.2)}$

= 0.5

(b)   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)	(1-x)	x	x
Conc (moldm^{-3})	$(\frac{1-x}{1})$	$(\frac{1-x}{1})$	$(\frac{x}{1})$	$(\frac{x}{1})$

$Kc = \dfrac{[CH_3COOCH_2CH_3].[H_2O]}{[CH_3COOH].[CH_3COOH]}$

$= \dfrac{x^2}{(1-x)(1-x)}$

$0.5 = \dfrac{x^2}{(1-x)(1-x)}$

$X^2 = 0.5[(1-x)(1-x)]$

$X^2 = 0.5(1-2x + x^2)$

$X^2 = 0.5 - x + 0.5x^2$

$0.5x^2 = 0.5 - x$

$ax^2 + bx + C = 0$

$0.5x^2 + x - 0.5 = 0$

$X = \dfrac{-b\pm\sqrt{b^2-4ac}}{2a}$

$X = 0.1414$

$= 0.414$

$X -2.4$

Eqbm moles

     i.   CH$_3$COOH = (1-0.414) = 0.586moles

     ii.   CH$_3$CH$_2$OH = (1-0.414) = 0.586moles

     iii.   CH$_3$COOCH$_2$CH$_3$ = 0.414 = 0.414moles

     iv.   H$_2$O   = 0.414 = 0.414 moles

When 1 mole of Ethamoic acid is maintained at 25^{0}C which 1 mole of ethanol in a 1 L vessel and the reaction allowed to attain eqbm, $^1/_3$ of ethanoic acid remained when eqbm is attained. How much would have remained if $^3/_4$ of ethanol had been used instead of 1 mole of the same 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	-x	-x	+x	+x
at Eqbm	(1-x)	(1-x)	x	x
Conc (moldm^{-3})	$(\frac{1-x}{1})$	$(\frac{1-x}{1})$	$(\frac{x}{1})$	$(\frac{x}{1})$

But at eqbn $^1/_3$ of ethanoic acid remained

$(1-x) = 1/3 \quad x = 2/3$

$Kc = \dfrac{[CH_3COOCH_2CH_3].[H_2O]}{[CH_3COOH].[CH_3COOH]} = \dfrac{x^2}{(1-x)(1-x)}$

$= \dfrac{\left(\frac{2}{3}\right)^2}{\left(1-\frac{2}{3}\right)\left(1-\frac{2}{3}\right)} = \dfrac{\left(\frac{2}{3}\right)^2}{\left(\frac{1}{3}\right)^2}$

$= 4.0$

If $\frac{3}{4}$ of Ethanol had been used instead

	CH₃COOH(l) + CH₃CH₂OH(l)		CH₃COOCH₂CH(l) + H₂ (l)	
	$CH_3COOH(l)$ +	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH(l)$ +	$H_2 (l)$
Initial	1 moles	1 moles	0	0
if x moles reacted	-x	-x	+x	+x
at Eqbm	(1-x)	$(\frac{3}{4}$-x)	x	x
Conc (moldm⁻³)	$(\frac{1-x}{1})$	$(\frac{\frac{3}{4}-x}{1})$	$(\frac{x}{1})$	$(\frac{x}{1})$

$Kc = \dfrac{x^2}{(1-x)\left(\frac{3}{4}-x\right)} \qquad 4 = \dfrac{x^2}{(1-x)\left(\frac{3}{4}-x\right)}$
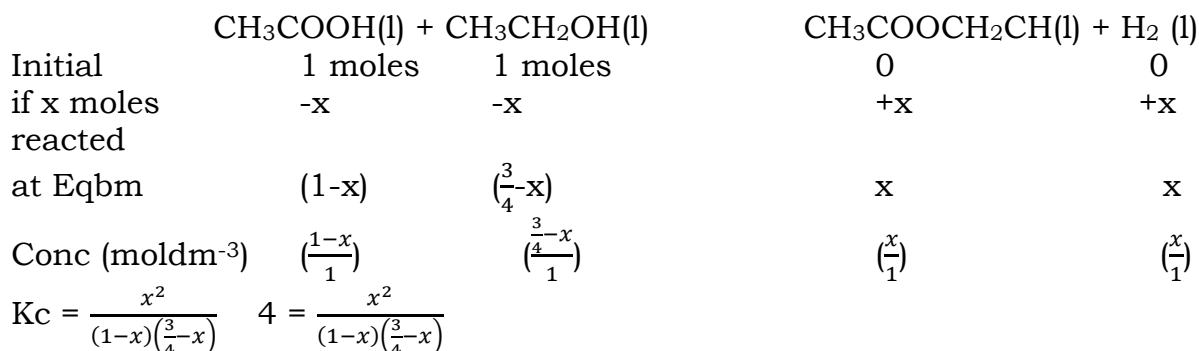
$X^2 = 4\left(\frac{3}{4}\text{-x} - \frac{3}{4}\text{x} + x^2\right)$

$X^2 = 4\left(\frac{3}{4}-\frac{7}{4}\text{x} + vx^2\right)$

$X^2 = 3\text{-}7x + 4x^2$

$-3x^2 + 7x + 3 = 0$

$3x^2\text{-}7x + 3 = 0$

$Ax^2 + bx + c = 0$

$X = 0.57$

The amount of Ethanoic acid that remained was (1-0.57)

= 0.43

Consider the eqbm

2HI(g) $\qquad\qquad$ H₂(g) + I₂(g)
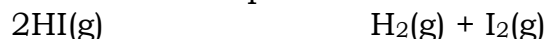
Involving the dissociation of HI. The conc expression for eqbm constant Kc = $\dfrac{[H_2]\,[I_2]}{[HI]^2}$. The value of the eqbm constant Kc can be determined experimentally. Known moles of HI are put in a sealed bulb known volume with is introduced into an incubator 400K. the non is given ample time to reach and one eqbm is attained the bulb is ...cooled to room temperature and broken KI(aq) solution. The Iodine liberated is ....which standard solution of Na₂S₂O₃ (sodium sulpate) using starch indicator at the ... and the moles of iodine formed at between can be calculated. Iodine reacts with Na₂S₂O₃

I₂(aa) + 2S₂O₃²⁻(aq) $\longrightarrow$ 2I⁻(aa) + S₄O₆²⁻
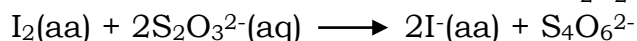
Treatment of results
Let moles of hydrogen iodide used be a moles
Moles of iodide formed be X moles
Moles of HI reacted will be 2 x (according to the equaton)
Volume of the vessel = vdm^3
$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
1.54g of HI when heated in a $600cm^3$ were heated in a $600cm^3$ bulb at 530^0C. when equilibrium was attained the bulb was rapidly cooled to room temperature and broken under KI solution. The iodine armed from the decomposition required $67cm^3$ of 0.1 sodium theosulphate for complete reaction. Calculate the no. of moles of HI present initially
(H= 1, I= 127)
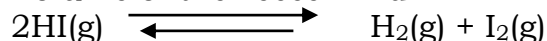
   iii) The value of Kc at this temperature
Molar mass of HI = (1+127) = 128g
Moles of HI = $(\frac{1.54}{128})$ = 0.012 moles
$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
$$I_2(aa) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aa) + S_4O_6^{2-}$$
Moles of $S_4O_6^{2-}$ used = $(\frac{0.1}{1000}$ x 67) moles
2 moles of $S_4O_6^{2-}$ react with 1 mole of I_2 (aa) 6.7 x 10^{-1} moles of $S_4O_6^{2-}$(aq) will react with $\frac{6.7 \ x \ 10^{-3}}{2}$
= (3.35 x 10^{-3})
Moles of I_2 present at eqbm = 3.35 x 10^{-3} moles
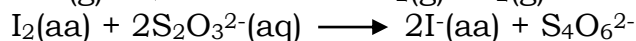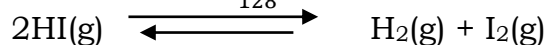
	2HI(aq)	H_2(g) + I_2(aq)	
Initial	0.012 moles	O	O
Of x reaction	-2x	+x	+x
At eqbm	(0.012-2x)	x	x

But at equilibrium moles of I_2 = 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 $(\frac{5.3 \ x10^{-3}x100}{600})$
Molarity = 8.83 x 10^{-3}M

Molar concentration of I_2 at equilibrium = $(\frac{3.35 \ x10^{-3}x100}{600})$
= 5.583 x 10^{-3}M

Molar conc of H_2 at equilibrium $(\frac{3.35 \ x10^{-3}x100}{600})$
= 5.583 x 10^{-3}M

   (i)   Kc = $\frac{[H_2][I_2]}{[HI]}$

   = $\frac{(5.583 \ x \ 10^{-3})^1 \ (5.183 \ x \ 10^{-3})^1}{(8.83 \ x \ 10^{-3})^2}$

      0.4
Consider an industrial important reaction
$$N_2(g) + 3H_2(g) \qquad 2NH_3(g)$$

Initially	1mole	3 moles	0
At eqbm	-x	-3x	+2x
Concn. In mol/L	$(\frac{1-x}{V})$	$(\frac{3-3x}{V})$	$(\frac{2x}{v})$

$$Kc = \frac{[NH_3]^2}{[N_2]^1 [H_2]^3}$$

$$= \frac{(\frac{2x}{v})^2}{(\frac{1-x}{v})(\frac{3-3x}{v})^3}$$

Stoichiometric moles of H_2 and N_2 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 N_2 and H_2
    (ii)   The value of Kc at this temperature and state its units

Solution

	$N_2(g) + 3H_2(g)$		$2NH_3(g)$
Initially	1mole	3 moles	0
If reacted	-x	-3x	+2x
At eqbm	(1-x)	3-3x)	2x
Concn. In mol/L	$(\frac{1-x}{V})$	$(\frac{3-3x}{V})$	$(\frac{2x}{v})$

But at equilibrium of NH_3 = 0.8 moles
2x = 0.8   x = 0.4 moles
Equilibrium moles of N_2 = (1-0.4)
                   = 0.6 moles
Equilibrium moles of H_2 = (3-x)
                   = (3-x 0.4)
                   = 1.8 moles

$$Kc = \frac{[NH_3]^2}{[N_2]^1 [H_2]^3}$$

$$\frac{(0.8)^2}{(0.6)(2.6)^3}$$

$$\frac{(moldm^{-3})}{(moldm^{-3})^1 (moldm^{-3})^3}$$

$Mol^{-2}dm^6$

Qn. Nitrogen monoxide combines with oxygen to form nitrogen dioxide according to equilibrium.

$$2NO(g) + O_2(g) \qquad 2NO_2(g)$$

    i)   Write an expression for the equation constant Kc
    ii)   3 moles of NO and 1.5 moles of O_2 were put into a vessel which was heated to 400^0C when equilibrium was attained, the vessel was found to contain 0.5 moles of O_2. Calculate the value of Kc at this temp and state the units
    iii)   When temperature was raised to 500^0C, the mixture above was found to contain 25% of the initial ND at equilibrium.
Calculate the value of Kc at this temperature.
    (i) $\frac{[NO_3]}{[NO][O_2]}$

(ii) $2NO(g) + O_2(g)$ $2NO_2(g)$

Initially   3mole   1.5 moles   0

If reacted   -2x   -x   2x

At eqbm   (3-2x)   (1.5-3x)   2x

But at equilibrium O_2 = 0.5 moles

    1.5   − x = 0.5

    X = 1.0 moles

Equilibrium moles of NO(g) = (3-2x1) = 1 moles

Equilibrium moles of $NO_2(g)$ = 2 x 1 = 2 moles

$Kc = \dfrac{[NO_3]^2}{[NO]^2 [O_2]}$

$\dfrac{(2)^2}{[1]^2(0.5)}$ $\dfrac{mol^2}{mol^2 mol}$

8mol^{-1}

iii) Raising temperature to 500^{0}C, the vessel contained 25% of the initial NO(g)

The vessel contained $\dfrac{25}{100}$ x 3

0.75 moles

(3-2x) = 0.75

X = 1.125 moles

New equilibrium moles of NO(g) = 0.75 moles

$O_2(g)$ = (1.5 x 1.125) = 0.375 moles

NO_2 = 2x1.125 = 2.25 moles

$Kc = \dfrac{(2.25)^2}{[0.75]^2(0.575)}$ $\dfrac{mol^2}{mol^3}$

    iv)   If the temperature is raised to 600k. the vessel was young to contain 30% of the initial oxygen. Calculate the value of Kc at the temperature.

The vessel contains $\dfrac{30}{100}$ x 1.5 = 0.45 moles

(1.5 − x) = 0.45

X = 1.05 moles

New equilibrium of NO_2 = 2x = 2x1.05 = 2.1

O_2 = (1.5 − 1.05) = 0.45

NO = (3-2 x 1.05) = 0.9

$Kc = \dfrac{(2.1)^2}{[0.45]^2(0.9)^2}$ = $\dfrac{mol^2}{mol^3}$

Kc = 12.10mol^{-1}

For an industrially important reaction

$2SO_2(g) + O_2(g)$ $2SO_3(g)$

If stoichometric moles were used and the reaction gives time to attain equilibrium then

                  $2SO_2(g) + O_2(g)$ $2SO_3(g)$

Initially   2moles   1moles   0

If reacted   -2x   -x   +2x

At eqbm   (2-2x)   (1-x)   2x

Concn. In moldm^{-3} $\left(\dfrac{2-2x}{V}\right)$ $\left(\dfrac{1-x}{V}\right)$ $\left(\dfrac{2x}{v}\right)$

Ex3. 3 moles of SO_2 were mixed with 2 moles of O_2 in a one litre vessel which was tightly corcked and the mixture allowed to attain equilibrium at 400k. When 20% of the initial sulphurdioxide. Calc the values of Kc at this temperature.

$$2SO_2(g) + O_2(g) \qquad\qquad 2SO_3(g)$$

Initially	3moles	2moles	0
If reacted	-2x	-x	+2x
At eqbm	(3-2x)	(2-x)	2x

By 20% change = $\frac{20}{100}$ x 3 = 0.6moles

SO_2 3-2x = 0.6

X = 0.7 moles   1.2 = x

SO_3 2x = 2 x 1.2   x = 2.4 moles

O_2 (1-0.7) = 0.3

$Kc = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

$20 mol^{-1}dm^3 = \frac{(2.4)^2}{[0.8]^2(0.8)} = \frac{mol^2}{mol^3}$

18.15 $mol^{-1}dm^3$

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.

   a. Write an equilibrium for the decomposition of SO_3
   b. 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 $O_2(g)$ and 0.7 moles of SO_3^{2-}. Where introduced into the vessel in an at look. Calc the value of Kc.

$Kc = \frac{[SO_2]^2[O_2]^1}{[SO_2]^2}$

Initially	1moles	0	0
If reacted	-2x	+2x	+x
At eqbm	(1-2x)	(2x)	x
Concn. In moldm^{-3}	$(\frac{1-2x}{1})$	$(\frac{2x}{1})$	$(\frac{x}{1})$

1-2x = 0.35

X = 0.325 moles

Concn. Of SO_2 = 2 x 0.325 = 0.65 moles

O_2 = x

$Kc = \frac{(0.65)^2(0.325)}{(0.325)^2}$

= 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.

$$2SO_3(g) \longrightarrow 2SO_2(g) + O_2(g)$$
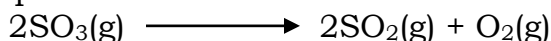
If the vessel of equilibrium contains 20% of SO_3 then the equilibrium moles of SO_3 which is 0.2.

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% SO_2 at equilibrium then this is its mole fraction.

If stoichiometric moles of SO_3 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 SO_3

$$\frac{20}{100} = \frac{2-2x}{2+x}$$

$$0.2 = \left(\frac{2-2x}{2+x}\right)$$

$$0.4 + 0.2x = 2-2x$$

$$\frac{-1.6}{-2-2} = \frac{-2.2x}{-2.2}$$

$$X = 0.75$$

$$X = 0.73$$

Qn : Phosphorous pentachloride dissociates according to the equation

$PCl_5(g)$ $PCl_3(g) + Cl_2$

1 tonne of PCl_5 when heated in a 2 dm^3 vessel at 100k. at equilibrium the vessel was found to chlorine. Chlorine 25% Calculate the value of V at their temperature.

	$PCl_5(g)$	$PCl_3(g)$	+	Cl_2O
Initially	1mole	0		0
If reacted	-x	+x		+x
At eqbm	1-x	x		x

Total equilibrium moles = (1-x + x+x)

                       (1+x)

At equilibrium $\frac{25}{100} = \frac{x}{1+x}$

$X= 0.25 + 0.25x$

$0.75x = 0.25$

$X = 0.33$ moles

$$Kc = \frac{[PCl_3]^1 \, [Cl_2]^1}{[PCl_5]}$$

$$Kc = \frac{\frac{0.33}{2} \cdot \frac{0.33}{2}}{\frac{0.66}{2}}$$

Equilibrium containing

$PCl_5 = (\frac{1-0.33}{2}) = 0.335$ $Kc = 0.0825$

$PCl_3 = (\frac{0-33}{2}) = 0.165$ $Kc = 0.08$

$Cl_2 = (\frac{0.33}{2}) = 0.165$

Question5. 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 Kc of this temperature.

	$N_2(g)$ + $3H_2(g)$		$2NH_3(g)$
Initially x	1 mole	3 moles	O
Equilibrium 1-x	(3-3x)		2x

Total number of moles = (1-x) + (3-3x) + (2x) = (4-2x)
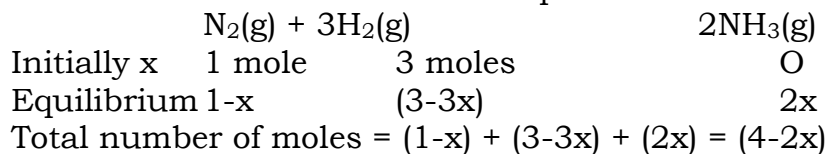
$\frac{80}{100} = \frac{2x}{4-2x}$

0.3 (4-2x) = 2x

X = 0.888

Conc of N_2 is $\frac{1-0.888}{2}$ = 0.05 moles

Moldm⁻³

H_2 is $\frac{3-3(0.888)}{2}$ = 0.168 moles

NH_3 is 2 x 0.888 = 1776 moles

$Kc = \frac{[HN_3]^2}{[N_2]^2 [H_2]^3}$

$Kc = \frac{[1.776]^2}{(0.05)(0.168)^3}$

Kc = 1995.6

Kc = 13303.4

Note: This value of Kc may have or not have units. If the change is stoichiometric number of moles on the product and reactant side is Zero then Kc has no units eg

$H_2(g)$ + $I_2(g)$ $2HI(g)$
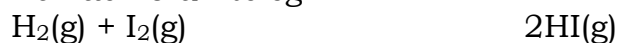
$Kc = \frac{[HI]^2}{[H_2][I_2]}$ hence has no units

If the change is stoichiometric number of moles is greater or less than zero, then Kc has units eg

$N_2(g)$ + $3H_3(g)$ $2NH_3(g)$

$Kc = \frac{[HH_3]^2}{[N_2][H_2]^3}$ $\frac{(moldm^{-3})^2}{(moldm^{-3})(moldm^{-3})^3}$

(ii) The equilibrium rule only applies to system which have attained equilibrium

(iii) The Kc value remains constant provided temperature remains constant

(iv) The value of Kc shows the extent of chemical reaction. A high value of Kc indicates a high proportion of products to reactants and a small value of Kc shares a small proportion of products compared to reactants.

EQUILIBRIUM CONSTANT (K_p) AND PARTIAL PRESSURES.

The equilibrium constant Kp is only applicable to gaseous systems of equilibrium and is expressed in terms of partial pressures

Consider a reaction

$$N_2O_4(g) \longrightarrow 2NO_2(g)$$
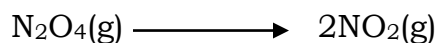
$Kp \dfrac{(PNO_2)^2}{PN_2O_4}$ where P is partial pressure of the gas similarly

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$
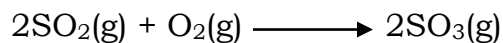
$Kp \dfrac{(PSO_3)^2}{(PSO_2)^2.PO_2}$

Relationship between Kp and Kc

Consider a reaction

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$
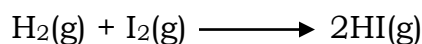
$Kp = \dfrac{P^2 HI}{PH_2.PI_2}$

From ideal gas equation PV = n\rt

Or $P = \dfrac{n}{v}RT$

But $\dfrac{n}{v}$ is conmc of the gas if V is in dm^3 $\dfrac{mol}{dm^3}$ therefore p =[gas] RT in a closed container of volume $volm^3$, the value os P is equal to the partial pressure of a particular gas ie

P gas = [gas] RT

Partial pressure of HI = [HI] RT
Partial pressure I_2 = $[I_2]$ RT
Partial pressure of H_2 = $[H_2]$ RT
Example: show the relationship between Kp and Kc for the following equilibrium system
    (i) $N_3(g) + 3H_2(g)$ $2NH_3(g)$
    (ii) $2SO_3(g)$ $2SO_2(g)+ O_2(g)$
Solution
$KP = \dfrac{p^2 NH_3}{PN_2.PH_2^3}$
But $PNH_3 = [NH_3]RT$
$PN_2 = [N_2]RT$
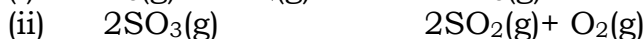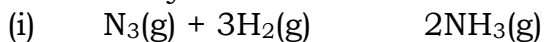
$PH_2 = [H_2]$ RT

$Kp = \dfrac{([NH_3]-RT)^2}{[N_2]RT([H_2]RT)^3}$

$= \dfrac{[NH_3]^2.(RT)^R}{N2]^3(RT)^2}$

$Kp = Kc(RT)^{-2}$

$Kp = \dfrac{(P^2SO_2.PO_2}{P^2SO_3}$

But $PSO_2 = [SO_2]\,RT$

$PO_2 = [O_2]\,RT$

$PSO_3 = [SO_3]\,RT$

$KP = \dfrac{([SO_2]RT)^2.[O_2]RT}{([SO_3])(RT])^2}$

$KP = \dfrac{[SO_2]^2.(RT)^2[O_2]RT}{[SO_3]^2(RT])^2}$

$Kp = KcRT$
In general
$Kp = Kc(RT)^n$
Where n = (stoichiometric moles on product side)- (stoichiometric moles on reactant side)
Eg dor the reaction
2NO(g) + O$_2$(g)   2NO$_2$(g)
$Kp = Kc(RT)^{-1}$
Similary for the reaction
PCl(s)   PCl$_3$(g) + Cl$_2$(g)
$Kp = Kc(RT)^{-1}$
Example
At 700k, the equilibrium constant for the reaction
2SO$_3$(g)   2SO$_2$(g) + O$_2$(g) is 1.8 Pa
Calculate the value of Kc at the same temperature and comment of extent of the forward reaction.
Solution
$Kp = Kc(RT)^{-1}$
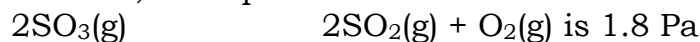
$Kc = \dfrac{Kp}{RT} = \dfrac{1.8NM^{=2}}{8.314 \; x \; 700NMOP^{-1}K^{-1}K}$

$= 3.093 \; x \; 10^{-4} \; molm^{-3} \; x \; 10^{-3}$

$= 3.093 \; x \; 10^{-7} moldm^{-3}$

From PV = nRT

$R = \dfrac{PV}{nT} = \dfrac{Nm^{-2}m^3}{mole \; K}$
= Nmmol
The volume of KC is very small showing that the reaction lies more on the left ie 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 pressure ie $PT = P_1 + P_2 + P_3$

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 ie

Partial pressure = mole fraction of the gas x total pressure

Or $P_2 = X_i.PT$

Where P_i = partial pressure of gas z

X_i = mole fraction of gas z

PT = total pressure of the system

If the moles of the gases are $n_1 n_2$ and n_3 then mole fraction of gas $1 = \dfrac{n_1}{n_1 n_2 n_3}$

Consider the gaseous system

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
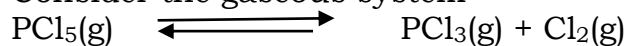
Initially	1	0	0
X	-x	+x	+x
Eqbm	(1-x)	x	x

Total eqbm moles = (1-x) + x + x
= (1+x) moles

$P_{PCl5} = X_{PCl5}\ PT$

$= \left(\dfrac{(1-x)}{(1+x)}\right) PT$

$P_{Cl2} = X_{Cl2}.\ PT$

$= \left(\dfrac{x}{1+x}\right) PT$

$Kp = \dfrac{P_{pcl3}.P_{Cl2}}{P_{pcl5}}$

$$\dfrac{\left(\dfrac{x}{1+x}\right).PT\left(\dfrac{x}{1+x}\right)PT}{\left(\dfrac{1-x}{1+x}\right).PT}$$

$$\dfrac{(\dfrac{x}{1+x})^2 PT}{\dfrac{(1-x)}{(1+x)}}$$

Stoichiometric moles of N_2 and H_2 were reacted at 50 atmp 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 N_2
(ii) The value of the equilibrium constant and state its units
Solution
a(i) $N_2(g) + 3H_2(g) \qquad\qquad 2NH_3(g)$

$Kp = \frac{p^2 NH_3}{P_{N_2} P^3 H_2}$

(b) $N_2(g) + 3H_2(g)$ $2NH_3(g)$

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

2 x = 0.8, X = 0.4 moles

Equilibrium moles of (i) N_2 = (1-x) = 1.0.4
                             = 0.6 moles

H_2 = (3-3x) = (3-3x 0.4)

= 0.8

Total equilibrium moles = (0.8 + 0.6 + 1.8)

= 3.2 moles

Using $P_2 = X_1 P_T$

$PNH_3 = (\frac{0.8}{3.2}) \times 50 = 12.5$

$PNH_3 = (\frac{0.6}{3.2} \times 50) = 9.38$ atms

$PH_2 = (\frac{1.8}{3.2} \times 50) = 28.13$ atms

$Kp = \frac{(12.5)^2}{9.38 \; x \; (28.13)^3}$

7.484×10^{-4} atm^{-2}

3.4 moles of SO_3 were decomposed at 600k in a 50dm^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 Kp at this temperature and use it to deduce the value of Kc.

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 2 x = 0.06

X = 0.03 moles

Equilibrium concentration

(i) $SO_3 = \frac{(3.4 - 2 \; x \; 0.03)}{50}$ = 0.0668 m

(ii) $SO_2 = \frac{0.06}{50}$ = 1.2 x 10^{-3}m

(iii) $O_2 = \frac{0.03}{50}$ = 6 x 10^{-4}m

Total equilibrium concentration = $(\frac{3.4 + 0.03}{50})$ = 0.0686m

$Kp = \frac{P^2 SO_2 . PO_2}{P^2 SO_3}$

$= \frac{(\frac{1.2 \; x \; 10^{-3}}{0.0686} x \; 120)^2 \; (\frac{6.0 \; x \; 10^{-4}}{0.0686} x \; 120)}{(\frac{0.0668}{0.0686} x 120)^2}$

= 3.39 x 10^{-4} atms

Kp = Kc$(RT)^1$

Kc = $\frac{Kp}{RT}$

= 6.89 x 10^{-6} moldm^{-3}

Qn. Stoichometric 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

$N_2(g)$ + $H_2(g)$ $2NH_2(g)$
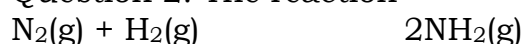
(i) Calculate the % of NH_3 in equilibrium mixture formed at 400k and 3.0 x 10^7 Pa pressure. When gaseous H_2 and N_2 are mixed kin the ratio 3:1 and 61% of N_2 has been converted to ammonia at equilibrium.

(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 gase remaining was in a) 0.58, 0.33, 0.15, 0.07 moles respectively. Calculate the average value of the equilibrium constant fro the etherification reaction.

$CH_3OOOH(l)$ + $CH_3CH_2OH(l)$ $\longrightarrow$ $CH_3COOCH_2CH_3(l)$ + $H_2O(l)$
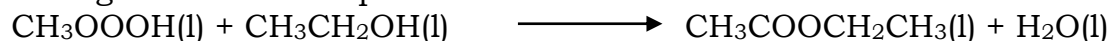
Question 2: calculate the amount of ethylethanoate ($CH_3COOCH_2CH_3$)formed when 1 mole of ethanoic acid and 3 moles of ethanol are allowed to come to equilibrium. The value of the equilibrium constant is 4.

Question 3: A mixture of iron and steam is allowed to come to equilibrium at 600^0C. The equilibrium pressures of hydrogen and steam are 3.2 Kpa and 2.4 Kpa. Calculate the equilibrium constant Kp for the reaction.

$3Fe(s)$ + $4H_2O(g)$ $H_2(g)$ + $Fe_2O_4(s)$

Question 3: The equilibrium constant for the reaction

CO + $H_2O(g)$ $CO_2(g)$ + $H_2(g)$ is 40
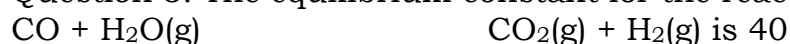
If 1 mole of carbonmonoxide and 1 mole of water are allowed to come to equilibrium. What function of CO will remain? What fraction would remain. If 2 moles of CO were used instead of 1 mole.

Solution

    (i)   The equation

$CH_3OOOH(l)$ + $CH_3CH_2OH(l)$ $\longrightarrow$ $CH_3COOCH_2CH_3(l)$ + $H_2O(l)$

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

$$Kc = \frac{[CH_3COOCH_3].[H_2O]}{[CH_3COOH].[CH_3CH_2OH]}$$

$$\frac{[0.42].[0.42]}{[0.58].[0.08]}$$

$$= \frac{0.1764}{0.0464}$$

Kc = 38

b) At equilibrium

The acid = (1-x)

Ethamol = (1-x)

Ester = x

Water = x

But 0.33 = (1-x)

0.33-1 = -x

-0.67 = -x

X = 0.67

Equilibrium moles of Acid = (1-x) = 1-0.067 = 0.33 moles

Ethamol (1-x) = 1-0.67 = 0.33 moles

Ester = x = 0.67 moles

Water = x = 0.67 moles

$$Kc = \frac{[0.67].[0.67]}{[0.330.[0.33]}$$

$$\frac{0.4489}{0.1089}$$

Kc= 4.12

(c) At equilibrium

The Acid = (1-x)

Ethamol = (2 –x)

Ester = x

Water = x

But 0.15 = 1-x

0.15-1 = -1

-0.85 = -x

X = 0.85

Equilibrium moles of

Acid = (1-x) = 1-0.93 = 0.07moles

Ethamol = (4-x) = 4-0.93 = 3.07 moles

Ester = x = 0.93 moles

Water = x = 0.93 moles

$$Kc = \frac{[0.93]^2}{[0.07][3.07]}$$

Kc = 4.02

$$\text{Average value of Kc} = \frac{3.8+4.12+4.188+4.02}{4}$$

Average Kc = 4.032

Question. 2

$CH_3OOOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3COOCH_2CH_3(l) + H_2O(l)$

$Kc = \dfrac{[CH_3COOCH_3].[H_2O]}{[CH_3COOH].[CH_3CH_2OH]}$

1mole	3moles	0 moles	0 moles
-x moles	-x moles	+x moles	+x moles
(1-x)	(3-x)moles	x	x
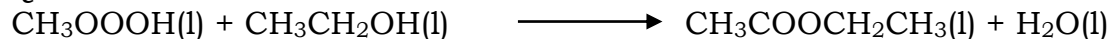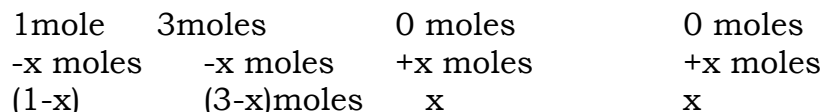
But Kc = 4

$4 = \dfrac{[x].[x]}{[1-x].[3-x]}$

$4 = \dfrac{x^2}{3-4x+x^3}$

$X^2 = 4(3-4x+x^2)$

$X^2 = 12-16x + 4x^2$

$0 = 12-16x + 4x^2-x^2$

$0 = 12-16x + 3x^2$

$3x^2 - 16x + 12 = 0$

X = 4.43 or x = 0.9

X = 0.9

The amount of Ethyl ethanoate formed is0.9 moles

Question. Stoichiometric moles of sulphur dioxide and oxygen were heated in a 1L vessel at 400k and 2 atms. When equilibrium was attained the vessel was found to contain 20% SO_3. Calculate

   i.   The equilibrium moles of the participating species

   ii.   The value of equilibrium constant at the is temperature.

Solution

	$2SO_2(g)$	+	O_2	$2SO_3(g)$
Initially	2moles		1mole	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 $\dfrac{20}{100} = \dfrac{2x}{(3-x)}$

$\dfrac{1}{5} = \dfrac{2x}{3-x}$

3-x = 10x

$\dfrac{3}{11} = \dfrac{nx}{n}$

$X = \dfrac{3}{11}$

Equilibrium moles of SO_2 = (2-2x)

= 2-2$(\frac{8}{11})$ = $\frac{16}{11}$ moles

Equilibrium moles of C_2 = 1-x =1-$\frac{3}{11}$

= $\frac{8}{11}$ moles

Equilibrium of SO_3 = 2 x $\frac{3}{11}$ = $\frac{6}{11}$ moles

  (ii) $KP = \frac{P^2SO_3}{P^2SO_2.PO_2}$

Total equation moles = 3-x = 3-$\frac{3}{11}$ = $\frac{30}{11}$

HETEROGENEOUS EQUILIBRIUM

These are equilibrium system 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 $CaCO_3$.

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
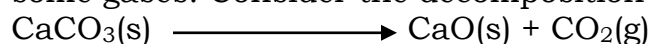
The expression for Kp is expected to be

Solid don't exert in partial pressure and at equilibrium they affect on the magnitude of Kp isn't significant.

Therefore its only CO_2 that affects the value of Kp so the x – pression of Kp is written as

$Kp = P_{CO2}(g)$

Eg A mixture of iron and steam is allowed to come to equilibrium at 600°C. the equilibrium pressures of Hydrogen and sterm are 3.2 Kpa and 2.4 Kpa. Calculate the equilibrium constant Kp for the iron.

$2Fe(s) + 4H_2O(g) \quad Fe_3O_4(s) + 4H_2(g)$
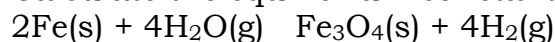
$Kp = \frac{P^4H_2}{P^4H_2O} = \frac{(3.2)^4}{(2.4)^4} = 3.16$

For the equilibrium reaction

aA + bB   cC + dD

write an expression for Kp and Kc if

    i.   All A, B, C and D are gases

$Kp = \frac{P^cC.P^dD}{P^aA.P^bB}$

    ii.   All are liquids

$Kc = \frac{[C]^c.[D]^d}{[A]^a.[B]^b}$

If A, C, D are solid but B is n gas

$Kp = \frac{1}{P^bB}$

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 ends on exorthemic in the forward solution. Consider a highly exthonermic reaction leading to formation of ammonia in the herber process.
$N_2(g) + 3H_2(g) \qquad\qquad 2NH_3(g)$ DH^2 = -92Kjmol^{-1}
Since the forward reaction is exothermic it is favoured by low temps. Lowering the temperature of the above system increases the eqb m position from the left to the right more of H_2 combines with N_2 forming ammonia.
An increase in the conc of Ammonia at eqbm causes an increase in the magnitude of the eqbm constant (kp/Kc).
An increase in temp of the above system shifts the equation position from right to left increasing the equation yield of ammonia but increasing the eqb m concs of N_2 and H_2. The effect of this is a lowered value of the equation constant
For a highly endothermic reaction
$H_2(g) + I_2(g) \xrightarrow{\hspace{2cm}} 2HI(g)$ DH^2 = -92Kjmol^{-1}
The forward non is favoured by high temperature since it is endo thermic therefore an increase in forming HI. This increases the equilibrium yield of hydrogen iodide and shifts the equilibrium position maginutude of the value of the equilibrium constant.
Increase in temperature for the above shifts the equilibrium position from right to left since the back and reaction is exo thermic and is favoured by ow temps. This increases the equilibrium conc of HI and hence the ma... of the equilibrium constant increases. (Kc/Kp).
The effect of temperature on any equilibrium system has been explained by Leclateliers principle which states that for any system that has attained equilibrium when subjected to a change equilibrium, the system adjusts itself to a new equilibrium stage so as to oppose the sand change.

The effect of pressure
The effect of pressure depends on the stoichiometry of the non ie
    a) Reactions where there is no change on the stoichometric moles on the left and right eg
$H_2(g) + I_2(g) \xrightarrow{\hspace{2cm}} 2HI(g)$
The 2 volumes o 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
$2SO_3(g) \xrightarrow{\hspace{2cm}} 2SO_2(g) + O_2(g)$
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 interms of Lectate principle ie for a system at equilibrium when subjected to a change in pressure it lands. To oppose the sand change by adjusting to a new equation stage increase in pressure makes the many volumes get over crowded and to over come the over crowdness they react to form the few. There is no effect on the value of the equilibrium constant.
Reactions with proceed by increase in no. of molecules.
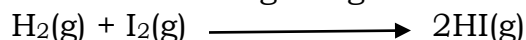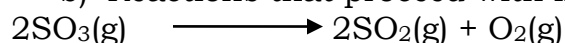
$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
4 volumes   2 volumes
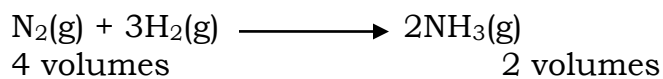
An increase in pressure shifts the equilibrium position from left to right since there are more molecules on the left compared to the right. More of N_2 and H_2 combine to form ammonia according to lectatelers principle but there is no effect on the value of Kc. An increase in pressure shifts the equilibrium position from right to left because the backward position from right to left because the backward non 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 non 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 is proceed by increase in no. of volumes are favoured by increase in the volume of the container eg

$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$
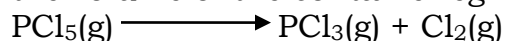
Since the forward reaction proceeds by increase in no. of volume. Increase in volume of the container shifts the equilibrium position from the left to the right.

Reactions to proceed by increase in the number of molecules of volumes are favoured by increase in the volume of the container eg

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
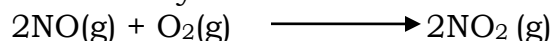
Since the forward non proceeds by increase in no of molecules/volumes. It is favoured by increase in the volume of the container which causes the equilibrium position to shift from left to right without change in the magnitude of the equilibrium position to shift from left to right without change in 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

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
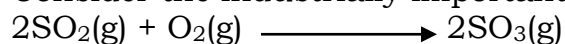
Withdrawal of some of the SO_3 from the above equilibrium disturbs the equilibrium and to restore the equilibrium of O_2 and SO_2.

The presence and absence of a catalyst has of the equilibrium yield but its presence does it kin 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 (Kc).

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 Kc or Kg 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 mert gas

Eg Neleon, 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 equation constant. For reactions where there is….And the value of the equilibrium constant. If reaction where were is change in stoichometric number of moles.

$$N_2(s) + 3H_2(g) \longrightarrow 2NH_3(g)$$
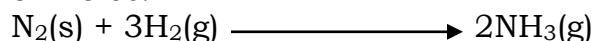
The effect of the inert gas depends on pressure and of the system. At constant pressure, when an inert gas such He, Ne, Argon is introduced into the system. The inert gas reduces the partial pressure of which individual gases in order to be accommodated at a constant pressure.

This causes adilutes effect shifting the equilibrium position in the direction leading to arriation of more volumes. Therefore in the herber process introducing heriem at a constant pressure the ammonia dissociates to form N_2 and H_2 shifting the equation position from right to left. No effect on the value of the equilibrium constant Kc or Kp.

Adding the inert gas at constant vol, has no effect on both position of equilibrium and the value of the equilibrium constant. Since the inert gas doesnot appear in expression for Kc or Kp.

Application of equilibrium system in industrial processes.

1.In the constant process for the manufacture of H_2SO_4.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \ \Delta H^2= -188 \ kjmol^{-1}$$
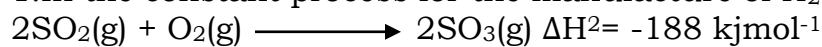
Equilibrium yield of SO_3 is increasedby low temperatures since the forward reaction is exothermic and is favoured by low temperatures accordingly lechate principle. However, although low temperature make the reaction thermodynamically stable in ward direction. The reaction becomes kinetically very slow. So a temperature of 450^0C is used to speed up the rate of attainment of equilibrium.

    i.   Increasing conce of SO_2 or O_2 but excess O_2 is preferred since it is readily available from air

    ii.   Increasing the conc of SO_3 by constantly removing it as soon as it is made. This shifts the equilibrium from left to right.

    iii.   High pressure/low volume since the forward reaction proceeds by increase in the number of molecules or volume. It is favoured by high pressure

iv.   Using a catalyst (vanadisum penta oxide V_2SO_5 in has no effect pm the equilibrium sp a lot of SO_3 is made in a shorter time then in the absence of the catalyst.

v.   The above equilibrium is important in the industrial manufacturer of sulphuric acid (H_2SO_4).

$SO_3(g) + H_2O_4(l) \longrightarrow H_2S_2O_7(l)$

$H_2S_2O_7 + H_2O(l) \longrightarrow 2H_2SO_4(l)$
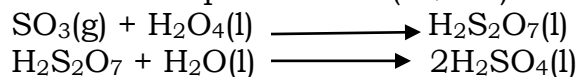
The SO_3 formed in dissolved in conc sulphuric acid forming Oleam which is late hydrolyzed which is about 98% acid.

It is possible to make sulphuric acid by directly dissolving SO_3 in water according of the equation.

$SO_3(g) + H_2SO_4 \longrightarrow H_2SO_4(l)$
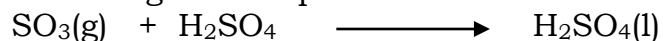
But the reaction is highly exothermic and occurs violently so it cant be controlled.

2. In the Herber process for the manufacturer of ammonia

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \Delta H -92Kj mol^{-1}$
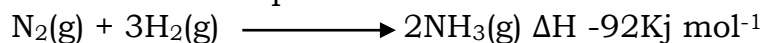
The equilibrium yield of ammonia is increased by using low temperatures, high pressure, employing a catalyst, adding excess nitrogen and hydrogen and continuously removing ammonia as soon as it is made. Like in the contact process low temperature makes the reaction kinetically very slow to increase the rate of the non a temp of a bout 550^0 is used.

High pressure is requires and usually a pressure of 2-5 atmospheres is used by 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 herber process is used in the catalytic manufacturer of nitric acid.

$2NH_3(g) + \frac{5}{2}O_2 \longrightarrow 2NO(g) + 3H_2O(g)$

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

$2NO_2(g) + H_2O(l) + \frac{1}{2}O_2 \quad 2HNO_3(l)$
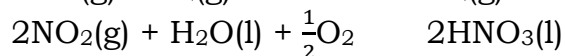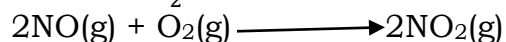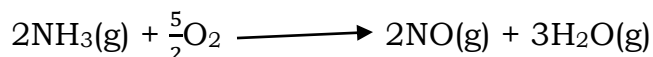
The reactions involve an initial catalystic oxidation of Ammonia using heated plantinum catalyst to term Nitrogen monoxide which is oxidized by air to NO_2, NO_2 is dissolved in water in presence of O_2 to nitric acid which is about 70% acid.

IONIC EQUILIBRIUM

This is an equilibrium established between the ions and the undissolved molecules of either a weak electrolyte or a solid of a spongly soluble salt.

Consider a weak electrolyte AB which weakly ionizes in solution according to the equation.

$AB(aq) \longrightarrow A^+(aq) + B^+(aq)$

The extent to which AB has ionized is called the degree of ionization and is given the symbol $(\propto)$

$AB(aq) \longrightarrow A^+(aq) + B^-(aq)$

Initially   1   0   0

After ionization $1-\propto$ $+\propto$ $+\propto$

Concn at equbm $c(1-\alpha)$ $C\alpha$ $C\alpha$

By law of Mass action

Keqbm = $\frac{[A^+].[B^-]}{[AB]}$

K equilibrium = $\frac{C\alpha.C\alpha}{C(1-\alpha)}$

$\frac{C^2\alpha^2}{C(1-\alpha)}$

Maximum ionization for a weak electrolyte occurs at O concn (zero) or infinite dilution. At α is maximum and for a weak electrolyte even at infinite dilution the value of α is small such that 1-x $\approx$1. This is called the Ostwald's dilition law which states that At infinite dilution weak electrolytes give the max ionization and the extent of ionization is low even at infinite filution. From Ostwald's dilution law

K equilibrium = $C\alpha^2$

$\alpha = \sqrt{\frac{\alpha equilibrium}{C}}$

The above expression is applicable to weak acids that ionize in a single step. For acids that ionize sulphuric such as carbonic acid. The expression takes a different form ie

$H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$ Ka_1

$HCO_3^-(aq) \longrightarrow H^+(aq) + HCO_3^{2-}(aq)$ Ka_2

Overall $H_2CO_3(aq)$ $2H^+ + CO_3^{2-}(aq)$ Ka

Initially   1   0   0

After ionization $1-\alpha$ 2α α

Concn at equbm $c(1-\alpha)$ $2C\alpha$ $C\alpha$
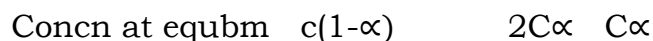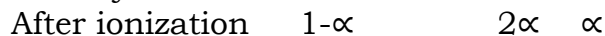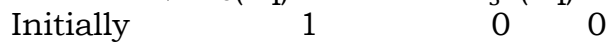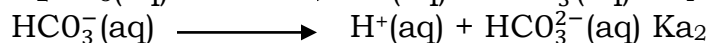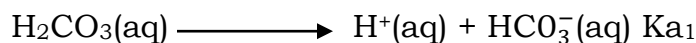
By law of mass action

Ka = $\frac{[H^+]^2.[CO_3^{2-}]}{[H_2CO_3]}$

$\frac{(2C\alpha)^2.c\alpha}{c(1-\alpha)}$

But $1-\alpha \approx 1$

Ka = $4C^2\alpha^3$

$\alpha = \sqrt[3]{\frac{K_a}{4C^2}}$

Note: The value of Ka_1 is greater than Ka_2 because it is easier to remove a proton from a molecular acid than removing it from the ionized acid HCO_3^- because afterremoval of the 1st proton the negative charge attained strongly attract the remaining proton. Therefore the increased electrostatic attraction between negative charge and the proton reduced the ionization of the acid lowering the value of Ka_2.

Consider a weak base that only slightly ionizes

                    $BOH(aq) \longrightarrow B^+(aq) + OH(aq)$

Initially   1   0   0

At eqbm $1-\alpha$ α α
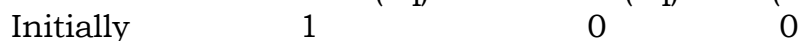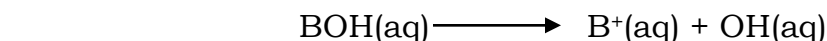
Concn at equbm $c(1-\alpha)$ $C\alpha$ $C\alpha$

By law of mass action

$Kc = \dfrac{[B^+].[OH]}{[BOH]}$

$\dfrac{C\alpha.C\alpha}{C(1-\alpha)}$, $Kc = \dfrac{C\alpha^2}{(1-\alpha)}$, But $1-\alpha \approx 1$, $Kc = C\alpha^2$, $\alpha = \sqrt{\dfrac{Kc}{C}}$

But for weak bases the constant is given as Kb.

$\alpha = \sqrt{\dfrac{Kc}{C}}$

Where Kb is the base ionization constant

Examples

1. Calculate the degree of ionization of a 0.1 m solution of ethanoic acid Ka = 1.8×10^{-3}

Solution

	$CH_3COOH(aq)$		$CH_3COO^-(aq) + H^+(aq)$
Initially	1mole	0	0
At eqbm	$(1-\alpha)$	α	α
Concn at equbm	$c(1-\alpha)$	$C\alpha$	$C\alpha$

$Ka = \dfrac{[CH_3COO^-].[H^+]}{[CH_3COOH]}$

$\dfrac{C\alpha.C\alpha}{C(1-\alpha)}$

$= \dfrac{C\alpha^2}{(1-\alpha)}$
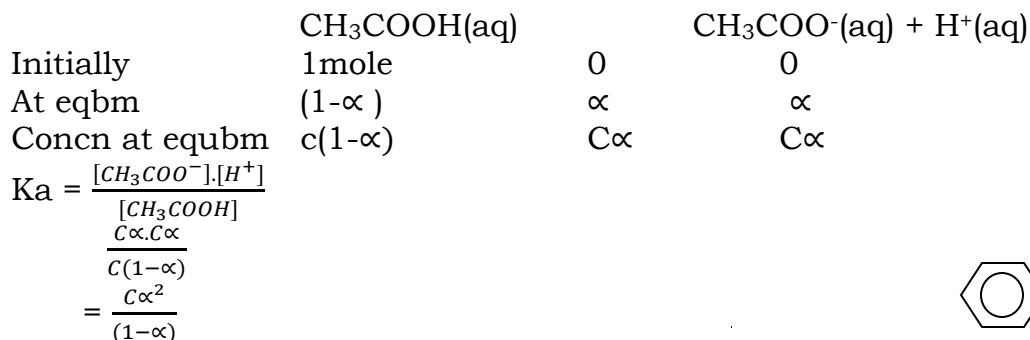
But $1-\alpha \approx 1$

$Ka = C\alpha^2$

$\alpha = \sqrt{\dfrac{Ka}{C}}$

2. Benzoic Acid is 0.2% ionized at 25^0C calculate the acid ionization constant for a 0.1 m solution of Benzoic acid at this temperature.

Initially	1mole		0	0
At eqbm	$(1-\alpha)$		α	α
Concn at eqbm	$c(1-\alpha)$	$C\alpha$	$C\alpha$	

By law of mass action

$\dfrac{C\alpha.C\alpha}{C(1-\alpha)}$

$= \dfrac{C\alpha^2}{1-\alpha}$

But $\alpha = \dfrac{0.2}{100}$
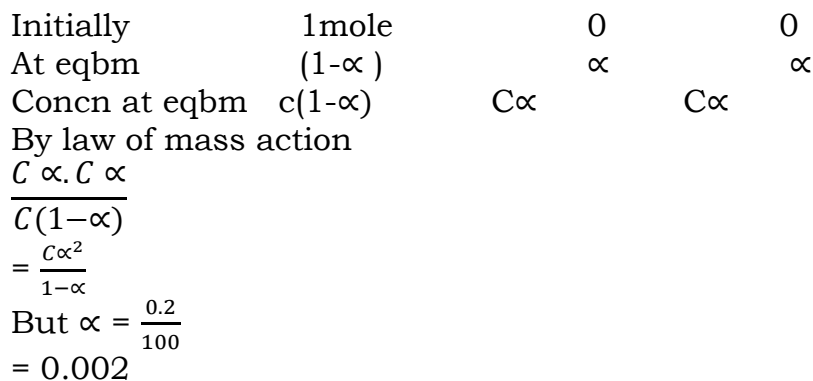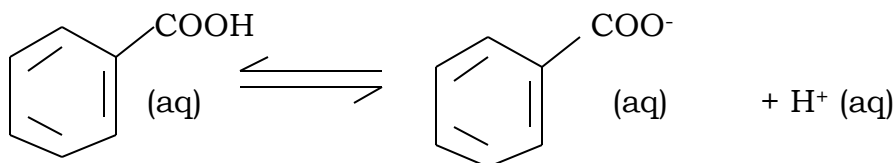
$= 0.002$

$Ka = \frac{0.1\ (0.002)^2}{1-0.002}$

$Ka = 4 \times 10^{-7}$

4.008×10^{-7}

3. (a) Calculate the degree of ionization of a 1M solution of ammonia at 25°C
(Kb for ammonia = 1.75 x 10⁻⁵moldm⁻³)
(b) Determine the molar concentration of the hydrogen ions in the solution of ammonia in (a) above

Solution

$$NH_4OH(aq) \longrightarrow NH_4^+ (aq) + OH^- (aq)$$

Initially   1mole   0   0

At eq≡m $(1-\alpha)$ α α

Concn at eqm $c(1-\alpha)$ $C\alpha$ $C\alpha$

By law of mass action
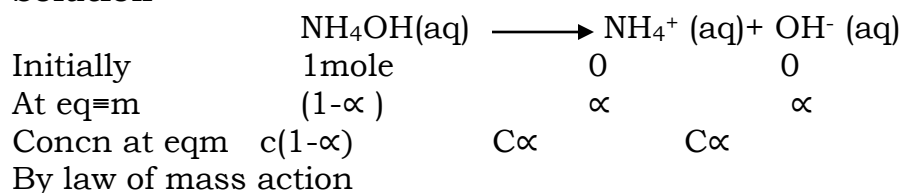
$Kb = \frac{[NH_4^+].[OH^-]}{[NH_4OH]}$

$Kb = \frac{C\alpha.C\alpha}{C(1-\alpha)}$

$\frac{C^2 \alpha^2}{c(1-\alpha)}$

$Kb = C\alpha^2$

When $1-\alpha \approx 1$

$\alpha = \sqrt{\frac{Kb}{C}} = \sqrt{\frac{1.75\ x\ 10^{-5}}{1}}$

$\alpha = 4.18 \times 10^{-3}$

(b) $[O^-H] = C\alpha$

$= 1 \times 4.183 \times 10^{-3}$

$= 4.183 \times 10^{-3} moldm^{-3}$

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

$NH_4OH(aq)$ $NH_4^+ (aq) + O^-H(aq)$

1mole   0   0

$(1-\alpha)$ α α

$c(1-\alpha)$ $C\alpha$ $C\alpha$
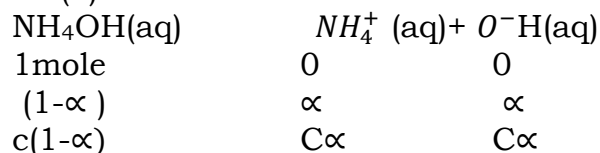
$Kb = \frac{[NH_4^+].[O^-H]}{[NH_4OH]}$

$Kb = \frac{C\alpha.C\alpha}{C(1-\alpha)}$

$Kb = C\alpha^2$

When $1-\alpha \approx 1$

But $\alpha = \frac{4}{100} = 0.04$

$Kb = 0.04^2 \times 0.1$

$Kb = 1.6 \times 10^{-4}$

$[OH] = C\alpha$

$= 0.1 \times 0.04$

= 4×10^{-3} moldm-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   HA(aq) H$^+$(aq) + A$^-$(aq)

Other examples

Conjugate acid	Protton	conjugate Base
HCl	H$^+$	Cl$^-$
HNO$_3$	H$^+$	NO$_3^-$
CH$_3$COOH	H$^+$	CH$_3$COO$^-$

A base which it gains the proton from a minute and is therefore called configurate base eg the base B (aa)

B$^-$(aa)   +   H$^+$(aq)   BH

[conjugate base]   [Base]   [conjugate acid]

Other examples

Conjugate acid	Proton	conjugate Base
NH$_3$	H$^+$	NH_4^+
CH$_3$NH$_2$	H$^+$	$CH_3^+NH_3$
H$_2$O	H$^+$	H$_3$O$^+$

Acids and Bases are therefore conjugate pairs and a conjugate pair defers by a proton lewis defines an acid as a zone pair of electrons acceptor while a base as a zone pair donor.

Consider the base ammonia

      NH$_3$ +   H$^+$ $\longrightarrow$ NH$_4$$^+$

(Lone pair donor)(lone pair acceptor)

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 eg all organic acids. These differences apply to a work and strong base only that the base releases hydroxide law in solution. According to Bronsted and ca... strength of an acid is measured so the ease which 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 eg Ethanoic acid is a weaker acid in water but a stronger acid in ammonia ie

CH$_3$COOH(aa) + H$_2$O(l) $\longrightarrow$ CH$_3$COō + H$_3$O$^+$(aa)

CH$_3$COOH(aa) + NH$_3$(aa) $\longrightarrow$ CH$_3$COō + NH$_4$(aa)

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 eg HCl is a weaker acid than HBromic acid and hydro iodo acid. Down the gap the atomic radius of the Halogens increases this makes the bond weaker and the halogen can easily release a proton in solution therefore HI cydro iodo acid is the strongest acid followed by HBr and HCl is the weakest.

Nature of the attached gap of the acid eg

If the group is electron which ....the strength of he acid is high but if the gap is electron donating the strength of acid reduces. The methyl gap in ethanaic acid is electron donating. Bond and making it deferent to release a proton. The

phenyl $\left[\bigcirc - CH_2 \overset{O}{\underset{\|}{C}} - OH \right]$ and chloride gaps $\left[ClCH_2 \overset{O}{\underset{\|}{C}} - OH \right]$ are electron with drawing 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)

H – NH₂   CH₃ ⟶ NH₂

Increased electron density

$\bigcirc \overset{\longleftarrow NH_2}{}$

The benzene ring is electron with drawing reducing the electron density on the amine gap electron the lone pair of electrons unavailable for accepting a proton.

Note: An increase in the number of electron donates gaps increases the basic strength.

A
$CH_3 \longrightarrow \overset{..}{N}H_2$

B
$CH_3 \longrightarrow NH$
          $\underset{CH_3}{\overset{\uparrow}{|}}$

C
$CH_3 \longrightarrow N \overset{\nearrow CH_3}{\underset{\searrow CH_3}{}}$

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 group increase the electron density around the Nitrogen atom but they mask the proton from accessing the ione pair of electrons. This is called sterric hindrance.

The strength of an acid or base is determined from the value of the dissociation or ionization constant, Kb or Ka. The greater the value the stronger the acid or base.

Acid	Ka/moldm⁻³
$H - \overset{O}{\underset{\|}{C}} - OH$	2.0×10^{-4}
$CH_3 - \overset{O}{\underset{\|}{C}} - OH$	1.8×10^{-5}

Cl - CH$_2$ - C(=O) - OH

1.6 X 10^{-3}

(phenyl) - CH$_2$ - C(=O) - OH

1.8 X 10^{-3}

Chloro ethanoic acid and phenyl ethanol acid are the spongest acids because of the negative inductive effect of the attached gap. Ethanoic acid is the weakest acid because of the positive inductive effect of the methyl gap.

Amino benzene is the weakest base and has the lowest value of Kb because of the phenyl gap is electron with drawing. Amino methane (or methylamine) is the strongest base with the highest value of Kb because the methyl gap is electron bonding.

Ionic product of water

$H_2O(l) \longrightarrow H^+(a) + \bar{o}H(aq)$

OR $H_2O(l) + H_2O(l) \longrightarrow H_3O^+(aa) + \bar{o}H(aq)$

K equilibrium = $\frac{[H^+].[\bar{o}H]}{[H_2O]}$ or K equilibrium $\frac{[H_3O][\bar{o}H]}{[H_2O]^2}$

K eqbm [H_2O] = [H^+] . [OH] = Kw = [H^+].[$\bar{o}H$]

In pure water at 25^{0}C   [H^+] = 1.0 x 10^{-7}

[OH$^-$] = 1.0 x 10^{-7}

Kw = 1.0 x 10^{-7} x 1.0 x 10^{-7}
Kw = 1.0 x 10^{-14} mol^{2}dm^{-6}

Water is a weak electrolyte is weakly ionizes as above. The ionic product of water is defined as the product of the concentration of hydrogen ions or hydroxomim ions and hydroxide ions in pure water at 25^{0}C.

Note: Kw remains constant at constant temperature and is assigned a value of 1.0 x 10^{-14} mol^{2}dm^{-6} at 25 favours the backward reaction reducing the concentration of hydrogen and hydroxide ions hence lowering the value of Kw.

Temp/^{0}C	18	25	40	70
Kw/mol^{2}dm^{-6}	0.01 x 10^{-14}	1.0 x 10^{-14}	2.92 x 10^{-1}	16.9 x 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 logarithsm to base ten. It is the negative logarithsm to base 10 of molar hydrogen ion concentration.*

PH = –log10$^{[H+]}$

This eliminates very small fraction of hydrogen ions in solution. For pure water, the hydrogen ions has a concentration of 1.0 x 10^{-7} and therefore the P.H of pure water PH = - log (1.0 x 10^{-7}). For acidic solutions the PH is less than 7 eg 0.00/m solution of HCl

HCl (aq) $\longrightarrow$ H$^+$(aa) + Cl$^-$(aa)
0.01   0.001
pH = -log$_{10}$[H$^+$]
    = -log$_{10}$ [H$^+$]
    = 3.0
For alkaline solutions , the P.H is greater than seven for example for a solution containing 0.01m NaOH [ōH] = 0.01
But from Kw = [H$^+$] . [ōH]

$$[H^+]= \frac{Kw}{[\bar{o}H]} = \frac{1.0 \times 10^{-14}}{0.01}$$

= 1.0 x 10^{-12}
p.H = -log [H$^+$]
= log (1.0 x 10^{-12}]
= 12
Relationship between pH and poH
poH is the negative to base ten of molar hydrogen ion concentration
poH = - log$_{10}$[ōH]
for pure water the hydroxide concentration is 1.0 x 10^{-7}
poH = - log (1.0 x 10^{-7}]
= 7.0
pH and poH are related by the ionic product of water ie
Kw = [H$^+$] . [ōH]
Introducing –log$_{10}$
-log$_{10}$ Kw = -log$_{10}$[H$^+$] + -log$_{10}$[ōH]
Log$_{10}$(1.0 x 10^{-14}) = -log$_{10}$(1.0 x 10^{-7}) + -log(1.0 x 10^{-7})
14 = 7+7
14 = 14
And therefore
PKw = pH + poH
14 = pH + 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$_2$SO$_4$
Solution
H$_2$SO$_4$(aa) $\longrightarrow$ 2H$^+$(aa) + SO$_4^{2-}$ (aa)
0.01   0.01 x 2
[H$^+$] = 0.02m
pH = -log$_{10}$[H$^+$]
=log$_{10}$ (0.02)
= 1.7
Calculate the pH of a 0.01m solution of nitric acid solution
HNO$_3$(aa) $\longrightarrow$ H$^+$(aa) + NO$_3^-$(aa)
0.01   0.01
[H$^+$] = 0.01m
pH   = -log [0.001]

= -log [0.01]
= 20

b) Strong bases

Solution

Calculate the P.H of a 0.1m solution of NaOH

$NaOH(aq) \longrightarrow Na^+(aa) + \bar{o}H(aq)$

But we know that $Kw = [H^+] . [\bar{o}H]$

$[H^+] = \dfrac{Kw}{[\bar{o}H]} = \dfrac{1.0 \times 10^{-14}}{0.1}$

$[H^+] = 1.0 \times 10^{-13}$

$pH = -\log_{10}(1.0 \times 10^{-13})$

= 3

Alternatively

Since $[OH] = 0.1$

$pOH = -\log_{10}[\bar{o}H]$

$= -\log_{10}$

= 1

But Ph + poH = 14

Ph = 14 – 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.

Moles of HCl = $(\dfrac{0.1 \times 5}{1000})$ = 1.5 x 10⁻³

Moles of NaOH = $\dfrac{0.1 \times 20}{1000}$ = 2.0 x 10⁻³

Moles of excess NaOH = (2.0 x 10⁻³ – 1.5 x 10⁻³)

= 0.5 x 10⁻³

Total volume = 20 + 15 = 35cm³

35cm³ contain 0.5 x 10⁻³ moles of NaOH

1000cm³ of solution contain $(\dfrac{0.5 \times 10^{-3} \times 1000}{3})$ moles of NaOH

= 0.014M

$NaOH(aa) \qquad\qquad Na^+(aa) + \bar{o}H(aa)$

0.014   0.014

$[H^+] = \dfrac{Kw}{\bar{o}H} = \dfrac{1.0 \times 10^{-14}}{0.014}$

= 7.143 x 10⁻¹³

$pH = -\log_{10}[H^+]$

= -log [7.143 x 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

$2NaOH(aa) + H_2SO_4(aa) \longrightarrow Na_2SO_4(aa) + 2H_2O(l)$

Moles of sodium used = $(\dfrac{0.1}{1000} \times 20)$ moles

2 moles of NaOH react with 1 mole of H_2SO_4

Moles of NaOH reacted = ½ $(\frac{0.1 \times 20}{1000})$

1.0×10^{-3} moles

Initial moles of H_2SO_4 = $(\frac{0.1}{1000} \times 80)$

= 8.0×10^{-3} moles (moles supplied)

Excess moles of H_2SO_4 = 8.0×10^{-3}

= 7.0×10^{-3} moles

Initial vol = 20 + 80 = 100cm³

Molar concentration of excess H_2SO_4 = $(7.0 \times 10 = 3 \times \frac{1000}{100})$

= 0.07m

H_2SO_4(aa) $\longrightarrow$ $2H^+$(aa) $+SO_4^{2-}$ (aa)

0.07   0.07 x 2

$[H^+]$ = 0.14m

pH = $-\log_{10}[H^+]$

= $-\log_{10}$ (0.14)

= 0.8539

Calculate the pH of a solution by mixing 25cm³ of 0.2m NaOH with 10cm³ of 0.1 m H_2SO_4

Solution

2NaOH(aa) + H_2SO_4 $\longrightarrow$ Na_2SO_4 + $2H_2O$(l)

Moles of sulphuric acid

Used = $(\frac{0.1}{1000} \times 10)$

= 1×10^{-3} moles

But

1 mole of H_2SO_4 reacts with 2 moles of NaOH (1 x 10⁻³) moles of H_2SO_4 react with $1 \times 10^{-3} \times 2$

1×10^{-3} moles

Initial moles = $(\frac{0.2}{1000} \times 25)$ moles = 5×10^{-3} moles

Excess moles of base

= $(5 \times 10^{-3} - 2 \times 10^{-3})$ moles

= 3×10^{-3} moles

Concentration of the base

$(3 \times 10^{-3} \times {}^{1000}/_{35})$m = 0.0857m

NaOH $\longrightarrow$ Na^+ + ōH

0.0857   0.0857

$[H^+] = \frac{Kw}{[ōH]}$

$[H^+] = \frac{1.0 \times 10^{-4}}{0.0857}$

= 1.6686×10^{-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 (Kw = 1.0 x 10^{-14})

Solution

pH = -log$_{10}$[H$^+$]

9.6 = -log[H$^+$]

[H$^+$] = 2.5 x 10^{-10}

[H$^+$] = 10 x 10^{-14}

$[H^+] = \frac{Kw}{[\bar{o}H]}$

$[\bar{o}H] = \frac{1.0 \, x \, 10^{-14}}{2.5 \, x \, 10^{-10}}$

$\bar{o}H$ = 4 x10^{-5}moles

$Mg(OH)_2 \longrightarrow Mg^{2+} + 2\bar{o}H$

2moles of hydroxide ions are released for 1 mole of Mg^{2+}.

4 x 10^{-5} moles of ($\bar{o}H$) ions react with $\frac{1 \, x \, 4 \, x \, 10^{-5}}{2}$

= 2.0 x 10^{-5}M

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 CH$_3$COOH. This partially ionizes according to the equation

CH$_3$COOH(aq)   CH$_3$CO$\bar{O}$(aa) + H$^+$(aa)

By law of mass action

$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

Assumptions

At eqbm [CH$_3$CO$\bar{O}$] = [H$^+$]

$Ka = \frac{[H^+][H^+]}{[CH_3COOH]}$

$= \frac{[H^+]}{[CH_3COOH]}$

$[H^+] = \sqrt{Ka[CH_3COOH]}$

pH = -log [H$^+$]

$pH = -log_{10}\sqrt{Ka[CH_3COOH]}$

Ex 1.

Calculate the pH of a 0.1 mole ethamoic acid at 25^{0}C (Ka for CH$_3$COOH at 25^{0}C is 1.8 x 10^{-5} moldm^{-3})

Solution

$CH_3COOH(aa) \quad CH_3CO\bar{O}(aa) + H^+(aa)$

$Ka = \dfrac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

Assumptions

At eqbm $[CH_3CO\bar{O}] = [H^+]$

$Ka = \dfrac{[H^+]}{[CH_3COOH]}$

$[H^+] = \sqrt{Ka[CH_3COOH]}$

$\qquad = \sqrt{1.8 \times 10^{-5} \times 0.1}$

$\qquad = 1.34 \times 10^{-3}$

$pH = -\log [H^+]$
$\qquad = -\log_{10} (1.34 \times 10^{-3})$
$\qquad = 2.872$

Question. 0.1m solution of methanoic acid has a P.H of 2.4 at 25⁰C. calculate the value of the ionization constant at this temperature.

Solution

$HCOOH(aa) \qquad\qquad HCO\bar{O}(aa) + H^+$

$Ka = \dfrac{[HCO\bar{O}].[H^+]}{[HCOOH]}$

At equilibrium $[HCO\bar{O}] = [H^+]$

$Ka = \dfrac{[H^+]^2}{[HCOOH]}$

But from $-\log_{10} [H^+]^- = 2.4$

$\log_{10}[H^+]^{-1} = 2.4$

$10^{2.4} = \dfrac{1}{[H^+]}$

$[H^+] = 3.0 \times 10^{-3}M$

$Ka = \dfrac{[3.9 \times 10^{-3}]^2}{0.1}$

$= 1.58 \times 10^{-4} moldm^{-3}$

A 0.01m solution of chloromethamoic Acid is 18% ionized. Calculate

    i)   The ionization constant of the acid at the same temperature

    ii)   The pH of the acid

Solution

$ClCOOH(aa) \qquad\qquad ClCO\bar{O}(aa) + H^+(aa)$

Initially   1   0   0

At equilibrium $(1-\alpha)$ α α

$Ka = \dfrac{[HCO\bar{O}].[H^+]}{[ClCOOH]} = \dfrac{C\alpha^2}{1-\alpha}$

$Ka = \frac{0.01 \, x \, (0.18)^2}{1-0.18} = 3.95 \times 10^{-4}$

pH from $Ka = \frac{[HCO\bar{O}].[H^+]}{[ClCOOH]}$

at equilibrium $(ClCO\bar{O}) = [H^+]$

$Ka = \frac{[H^+]^2}{[ClCOOH]}$

$[H^+] = \sqrt{Ka \, [ClCOOH]}$

$\quad = \sqrt{3.95 \, x \, 10^{-5} x 0.07}$

$= 1.987 \times 10^{-3}$

But

$pH = -\log_{10}[H^+]$

$= -\log_{10} (1.987 \times 10^3]$

$= 2.7$

For weak bases eg Ammonia, they ionizes as follows

$NH_3(aa) + H_2O(l) \qquad\qquad NH_4^+(aq) + \bar{O}H(aa)$

By law of mass action

$Kb = \frac{[NH_4^+].[\bar{O}H]}{[NH_3]}$

Note: water is in large excess so its concentration remains constant

At equilibrium $= \frac{[H^+]^2}{[NH_3]}$

$[\bar{O}H] = \sqrt{Kb[NH_3]}$

$[H^+] = \frac{Kw}{[\bar{O}H]}$

$= \frac{Kw}{\sqrt{Kb[NH_3]}}$

Calculate the pH of a 0.1M solution of Ammonia at 25^0C $(Kb(NH_3) = 1.75 \times 10^{-5}$ moldm^{-3} at 23^0C.

Solution

$NH_3(aa) + H_2O(aa) \qquad\qquad NH_4^+(aa) + \bar{O}H$

$Kb = \frac{[NH_4^+].[\bar{O}H]}{[NH_3]}$

At equilibrium $[NH_4^+] = [\bar{O}H]$

$Kb = \frac{[\bar{O}H]^2}{[NH_3]}$

$[\bar{O}H] = \sqrt{Kb[NH_3]}$

$= 1.75 \times 0.1 = 1.32 \times 10^{-3}M$

From $Kw = [H^+] . [\bar{O}H]$

$[H^+] = \frac{Kw}{[\bar{O}H]} = \frac{1.0 \, x \, 10^{-14}}{1.32 \, x \, 10^{-3}} = 7.58 \times 10^{-12}$

$pH = -\log_{10} [H^+]$

$= -\log_{10}(7.5 \times 10^{-12})$

$= 11.12$

Exercise

Qn 1: The pH of a 0.1m propanoic Acid is 3.8 at 25^0C
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 dimethylaine has a pH of 10.2 at 25^0C. calculation
    i.   The base dissociation constant (Kb)
    ii.   The degree of ionization of the base at the same temperature (Kw at $25^0C = 1.0 \times 10^{-14}$)
Qn 3. Calculate the pH of a solution made by mixing $35cm^3$ of 0.1m H_2SO_4 with $15cm^3$ of 0.1M KOH
Qn 4: $25cm^3$ 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 ($CH_3NH_3NO_3^-$) 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 denied 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
$CH_3CO\bar{O}(aq) + H_2O(l)$ $CH_3COOH(aa) + \bar{O}H(aa)$
Since it is the anion that undergoes hydrolysis. This is called anionic hydrolysis. From the above equation an expression from or the hydrolysis Kl can be written
$KL = \frac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$
The following assumptions are made when writing the above expression
    i.   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.
    ii.   Sodium ethamoate is a strong salt and fully dissociates according to the equation.

$CH_3COO^-Na^+(aa) \longrightarrow CH_3COO^-(aa) + Na^+(aa)$

Since 1 mole of $CH_3COO^-Na^+$ releases 1 mole of ethanoate items, then

$[CH_3COO^-Na^+] = [CH_3CO\bar{o}]$

At equilibrium assumed that

$[CH_3COOH] = [\bar{O}H]$

So the expression for KL can be written as

$KL = \dfrac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$

Example

Sodium ethamoate undergoes hydrolysis when dissolved in water

i.   Write an equation for the hydrolysis reaction

$CH_3CO\bar{O}(aa) + H_2O(l) \rightleftharpoons CH_3COOH + \bar{O}H$

ii.   Write an expression for the hydrolysis constant

$KL = \dfrac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$

iii.   Calculate the pH of the solution made by dissolving 8.4g of the sopt in 1 L of water (Kw = 1.0 x 10^{-14}, KL = 5.5 x 10^{-10}

Qn. Sodium propanoate ($CH_3CH_2COO^-Na^+$) undergoes hydrolysis.

i.   Write equations for the hydrolysis reactions of constant of sodium proponoate.

ii.   Write the expression for the hydrolysis constant of sodium propanoate

iii.   The P.H of a 0.1M solution of sodium propanate is 8.9. calculate the hydrolysis constant for the salt (Kw = 1.0 x 10^{-14}mol^{2}dm^{-6})

Solution

(i) $CH_3CH_2COO^-Na^+(aq) + H_2O \qquad CH_3CH_2COOH(aq) + \bar{O}H(aq)$

(ii) $KL = \dfrac{[CH_3CH_2COOH].[\bar{o}H]}{[CH_3CH_2CO\bar{O}]}$

At equilibrium $[CH_3CH_2COOH] = [\bar{O}H]$

$KL = \dfrac{[\bar{O}H]^2}{[CH_3CH_2CO\bar{O}]}$

From pH = -log [H$^+$]

8.9 = -log$_{10}$[H$^-$]

$10^{89} = \dfrac{1}{[H^+]}$

$[\bar{O}H] = \dfrac{Kw}{[H^+]} = \dfrac{1.0\ x\ 10^{-14}}{1.26\ x\ 10^{-9}}$

$KL = \dfrac{(7.9\ x\ 10^{-6})}{0.1}$

= 6.299 x 10^{-14}M

Degree of salt hydrolysis

Since water is a weak electrolyte is only slightly ionizes releasing very few H$^+$ then can be abstracted. Therefore much of the salt remains unhydrated. The extent of hydrolysis can be calculate. Consider the hydrolysis of sodium Benzoate

$C_6H_5CO\bar{O}(aq) + H_2O \longrightarrow C_6H_5COOH(aq) + OH$

$\quad 1 \qquad\qquad\qquad\qquad\qquad\qquad 0 \qquad\qquad\quad 0$

$C(1-\alpha) \qquad\qquad\qquad\qquad\qquad\qquad C\alpha \qquad\qquad C\alpha$

$KL = \dfrac{[C_6H_5COOH].[\bar{O}H]}{[C_6H_5CO\bar{O}H]} = \dfrac{C\alpha^2}{1-\alpha}$

Since the extent of hydrolysis is very small

$1-\alpha \approx 1$

$KL = C\alpha^2$

$\alpha = \sqrt{\dfrac{KL}{C}}$

Example a 0.01m solution of sodium benzoate undergoes hydrolysis
  i. Calculate the degree of hydrolysis
  ii. Calculate the pH of the resultant solution ($Kl = 5.0 \times 10^{-10}$)

Solution

$C_6H_5CO\bar{O}(aq) + H_2)(l) \quad C_6H_5COOH(aq) + \bar{O}H(q)$

The degree of hydrolysis is α

$Kl = C\alpha^2$

$\alpha = \dfrac{Kl}{C} = \sqrt{\dfrac{5.0 \times 10^{-10}}{0.01}}$

$\alpha = 2.24 \times 10^{-4}$

Phenyl amine [benzene ring]$-NH_2$

[benzene ring]$-NH_2$ + HCl(aq) $\longrightarrow$ [benzene ring]$-NH_3\,Cl^-$
$\qquad$ (aq)

The salt formed is phenyl amine hydrochloride. The salt undergoes hydrolysis

[benzene ring]$-NH_2$ + HCl(aq) $\rightleftharpoons$ [benzene ring]$-NH_3\dfrac{Cl^-}{(aq)} + H^+$
$\qquad$ (aq)

$H_2O(l) \qquad\qquad\qquad H^+(aq) + \bar{O}H(aq)$

Phenyl ammonium removes OH from the water equilibrium which becomes disturbed and to restore the ionic equilibrium of water more water molecules ionuise leaving an excess of hydrogen ions in solution making the resultant solution acidic.

Note: during catiome 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

$NH_4^+ + H_2O(l) \qquad\qquad NH_3(aq) + H_3O^+(aq)$

Calculate the mass of phynyl amine HCl that should be added to 1 litre of H_2O to form a solution of PH 5.2 ($Kl = 6.0 \times 10^{-5}M$.

The solution formed undergoes hydrolysis.

[benzene ring]$-\overset{+}{N}H_2$ + HCl(aq) $\longrightarrow$ [benzene ring]$-\overset{+}{N}H_3\,Cl^-$
$\qquad$ (aq)

$$C_6H_5\text{-}\overset{+}{N}H_3\,(aq) + H_2O\,(l) \rightleftharpoons C_6H_5\text{-}NH_2 + H_3\overset{+}{O}\,(aq)$$

$$KL = \frac{[C_6H_5\text{-}NH_2]\cdot[H_3\overset{+}{O}]}{[C_6H_5\text{-}\overset{+}{N}H_3]}$$

$pH = -\log_{10}[H_3O^+]$

$5.2 = \log_{10}[H_3O^+]$

$10^{5.2} = \dfrac{1}{[H_3O^+]}$

$H_3O^+ = 6.3 \times 10^{-6}$ M

Assumption at equilibrium

$$[C_6H_5\text{-}NH_2] = [H_3\overset{+}{O}]$$

$$KL = \frac{[H_3\overset{+}{O}]^2}{[C_6H_5\text{-}\overset{+}{N}H_3]}$$

$$6 \times 10^{-5} = \frac{(6.3 \times 10^{-6})^2}{[C_6H_5\text{-}\overset{+}{N}H_3]}$$

$$[C_6H_5\text{-}\overset{+}{N}H_3] = 6.6 \times 10^{-7}$$

$$[C_6H_5\text{-}\overset{+}{N}H_3] = [C_6H_5\text{-}\overset{+}{N}H_3\,Cl^-]$$

Molar mass of $C_6H_5NH_3Cl^-$

$= (12 \times 6) (1 \times 8) + (1 \times 14) + (1 \times 35.5)$

$= 129.5$ g/mol

Mass of salt

$= 6.6 \times 10^{-7} \times 129.5$

$8.5 \times 10^{-5} gl^{-1}$

Question: Phenyl ammonia nitrate undergoes hydrolysis

a(i) Write equation for the hydrolysis of the salt

(ii) Write the expression for the hydrolysis constant

(b) a 0.01m solution of phenyl ammonium nitrate has a pH of 3.2. calculate

(i) the hydrolysis constant

(ii) The degree of hydrolysis

(iii) The mass of the salt that should be added to the litre of water to increase the pH by 2 units.

Solution

$KL = \dfrac{[C_6H_5NH_2].[H_3O]}{[C_6H_5NH_3]}$

From pH $= -\log_{10}[H^+]$

$3.2 = -\log_{10}[H^+]$

$10^{3.2} = \dfrac{1}{[H^+]}$

$[H^+] = 6.3 \times 10^{-4}$ M

Assumption

$[C_6H_5NH_2] = [H_3O^+]$

$KL = \dfrac{[H_3O^+)^2}{[C_6H_5NH_3]}$

$= 3.98 \times 10^{-5}$M

(ii) $\propto = \sqrt{\dfrac{Kl}{C}}$

$= \sqrt{\dfrac{3.98 \times 10^{-5}}{0.01}} = 0.0631$

(iii) New pH of solution

= 3.212 = 5

$10^{5.2} = \dfrac{1}{[H_3O^+]}$

$[H_3O^+] = 6.31 \times 10^{-6}M$

$KL = \dfrac{[H_3O^+]}{[C_6H_5NH_3]}$

$[C_6H_5N^+H_3] = 1.0 \times 10^{-6}M$

$[C_6H_5N^+H_3] = [[C_6H_5N^+H_3\ NO_3]$

Molar mass of $C_6H_5N^+H_3NO_3^-$

= (12 x 6) + (1x8) + (14x2) + (16 x 3)

= 156 ≈ x156

Mas of salt = 1.0 x 10^{-6} x 156

1.56 x 10^{-4}g/l

Relationship between Ka, Kw and KL

Consider the ionization of weak ethanoic acid

CH$_3$COOH   CH$_3$COŌ(aq) + H$^+$(aq)

$Ka = \dfrac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$...(1)

Consider also the hydrolysis of sodium ethanoate (CH$_3$CHOŌNa$^+$)

CH$_3$COŌ(aq) + H$_2$O(l)   CH$_3$COOH + ŌH(aq)

$Kh = \dfrac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$...(2)

Consider also the ionization of water

H$_2$O(l)   H$^+$(aq) + ŌH(aq)...................(3)

Kw = [H$^+$] [ŌH]

Dividing 3 by 1

$$\frac{Kw}{Ka} = \frac{[H^+].[\bar{O}H]}{\frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}} = \frac{[H^+].[\bar{O}H]x\,[CH_3COOH]}{[CH_3CO\bar{O}].[H^+]}$$

$$= \frac{[\bar{O}H].[CH_3COOH]}{[CH_3CO\bar{O}]}$$

$$\frac{Kw}{Ka} = Kh$$

Relationship between Kh, Kw and Kb

Consider the ionization of a weak base e.g ammonia

NH$_3$(aq) + H$_2$O(l)   N$^+$H$_4$(aq) + $\bar{O}$H(aq)

$$Kb = \frac{[N^+H_3].[\bar{O}H]}{[NH_3]}$$

Consider also the hydrolysis of ammonium chloride

NH_4^+(aq) + H$_2$O(l)   NH$_3$(aq) + H$_3$O$^+$

$$Kh = \frac{[NH_3].[H_3O^+]}{[NH_4]}$$

Consider the self ionization of water

H$_2$O(l) + H$_2$O(l)   H$_3$O$^+$(aq) + $\bar{O}$H(aq)

$$\frac{Kw}{kb} = \frac{[H_3O^+].[\bar{O}H]x\,[NH_3]}{[NH_4^+].[\bar{O}H]}$$

$$\frac{Kw}{Ka} = Kh$$

Qn: Phenyl ammonium chloride undergoes hydrolysis. Calculate the pH of a 0.1 M solution of phenyl ammonium chlorine (Kb for phenyl amine is 1.7 x 10^{-5} mold m^{-3})

Solution

$$KL = \frac{\left[\text{◯-}NH_2\right] \cdot \left[H_3\overset{+}{O}\right]}{\left[\text{◯-}\overset{+}{N}H_3\right]}$$

At equilibrium

$$\left[\text{◯-}NH_2\right] = \left[H_3\overset{+}{O}\right]$$

$$KL = \frac{\left[H_3\overset{+}{O}\right]^2}{\left[\text{◯-}\overset{+}{N}H_3\right]}$$

But $KL = \dfrac{Kw}{Kb} = \dfrac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}}$

$5.88 \times 10^{-10} = \dfrac{[H_3O^+]^2}{0.1}$

$[H_2O^+] = \sqrt{0.1 \times 5.88 \times 10^{-10}}$

$= 7.67 \times 10^{-6}$

$pH = -\log(7.67 \times 10^{-6})$

$= 5.12$

Qn: Calculate the mass of sodium ethanoate that should be added to 1 litre of water to make a solution of pH 8.9 (Ka for ethanoic acid is 1.8×10^{-5})

Solution

$CH_3CO\bar{O}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + \bar{O}H(aq)$

$Kh = \dfrac{[CH_3COOH].[\bar{O}H]}{[CH_3CO\bar{O}]}$

At equilibrium. $(CH_3COOH) = [\bar{O}H]$

$KL = \dfrac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$

But $pH + poH = 14$

$poH = 14 - pH$

(14-8.9) = 5.1

poH = $\log_{10}[\bar{O}H]$

5.1 = $-\log_{10}[\bar{O}H]$

$[\bar{O}H] = \frac{1}{10^{5.1}}$ = 7.94 x 10^{-6}M

Substituting in the expression

5.56 x 10^{10} = $\frac{(7.94 \, x \, 10^{-6})^2}{(CH_3CO\bar{O})}$

$[CH_3CO\bar{O}]$ = 0.11M

$[CH_3CO\bar{O}]$ = $[CH_3CO\bar{O}Na^+]$

RFM of $CH_3CO\bar{O}Na^+$

= (12 x 2) + (3) + (16x2) + (23) = 82

Mass of $CH_3CO\bar{O}Na^+$

= 82 x 0.11

= 9.02gl^{-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 densed from a strong base. Eg

A basic buffer is made up of a weak base and its soft 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 CH$_3$COŌNa$^+$ / CH$_3$COOH buffer solution. The acid is weakly ionized.

CH$_3$COOH $\qquad$ CH$_3$COŌ(aa) + H$^+$(aq)

The salt is fully dissociated

CH$_3$COŌNa$^+$(aq) $\qquad$ CH$_3$COŌ(aq) + Na$^+$

(Excess)

The buffer contains a large excess of an ionized molecules of the acid (CH$_3$COOH) 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 ethamate ions forming molecules of Ethanoic acid. Therefore the pH does not change.

CH$_3$COŌ(aa) + H$^+$(aq) $\qquad$ CH$_3$COOH(a)

On addition of a small amount of the base in form of hydroxide ions (ŌH) they have removed by reacting with molecules of ethanoic acid

CH$_2$COOH(aq) + ŌH(aq) $\qquad$ CH$_3$COŌ(aq) + H$_2$O(l)

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.

$\qquad$ b) Basic buffer

Consider a buffer NH$_3$/NH$_4$Cl buffer ammonia is a weak base and only slightly ionized.

NH$_3$+ H$_2$O $\qquad\qquad$ NH_4^+ + ŌH(aq)

Ammonia chloride is a strong salt and fully dissociated.

NH_4^+Cl(aq) $\longrightarrow$ NH_4^+(aw) + Cl$^-$

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.

NH$_3$(aa) + H$^+$(aa) $\qquad$ NH_4^+

Addition of a small amount of the base in form of (ŌH) they are removed by ammoniam ions so the pH doesn't change.

NH_4^+(aa) + OH(aa) $\longrightarrow$ NH$_4$OH(aa)

The effectiveness of a basic buffer therefore depends on the presence of a large number of ammoniam ions to buffer the hydroxide ions.

Calculating the pH of buffer solution consider the acidic buffer CH$_3$COŌNa$^+$/CH$_3$COOH

CH$_3$COŌNa$^+$(aq) $\longrightarrow$ CH$_3$COŌH(aq) + Na$^+$(aq)

CH$_3$COOH(aa) $\qquad$ CH$_3$COŌ(aa) + H$^+$

Ka = $\frac{[salt]}{[acid]}$

NH$_4$Cl(aa) $\longrightarrow$ NH_4^+(aa) + Cl$^-$(aa)

NH$_3$(aq) + H$_2$O $\qquad$ NH_4^+(aq) + ŌH(aa)

Kb = $\frac{[NH_4^+].[ŌH]}{[NH_3]}$

[ŌH] = Kb$\frac{[NH_3]}{[NH_4^+]}$

Assumptions

$[NH_4^+]$ = [salt]

$[NH_3]$ = [base]

Question. Calculate the pH of a solution made by mixing 0.5M of (CH_3COOH) with o.5M of sodium Ethanoate.

Ka = (CH_3COOH) = 1.8 x 10^{-5})

Solution

$CH_3COOH \qquad\qquad CH_3CO\bar{O}(aq) + H^+(aa)$

$CH_3CO\bar{O}Na^+ \longrightarrow CH_3CO\bar{O}(aq) + Na^+(aq)$

$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

$[H^+] = Ka \frac{[CH_3COOH]}{[CH_3CO\bar{O}]}$

$= Ka \frac{[acid]}{[salt]}$

1.8 x 10^{-5}

pH = -log(1.8 x 10^{-5}0

pH = 4.74

question 1: Calculate the pH of a solution made by mixing 25cm^3 of 0.1M ethanoic acid with 10cm^3 of 0.1M sodium hydroxide

Ka = (CH_3COOH) = (1.8 x 10^{-5})

Question 2. Calculate the pH of a solution made by mixing 6gl^{-1} of CH_3COOH = 8.2gl^{-1} of $CH_3CO\bar{O}Na^+$ (Ka = 1.8 x 10^{-5} moldm^{-3})

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Vol of excess acid = (25 – 10)

= 15cm^3

1000cm of excess acid contain 0.1 mole

15cm^3 of excess and contain $(\frac{0.1\ x\ 15}{100})$

35cm^3 of mixture contain $(\frac{0.1\ x\ 15}{100})$ moles

1000cm^3 of mixture contain $(\frac{0.1\ x\ 15\ x\ 1000}{1000\ x\ 35})$

= 0.0429M

1 mole of NaOH = 1mole of CH_3COONa

Moles of NaOH = $(\frac{0.1\ x\ 10}{1000})$ moles

35cm^2 of mixture contain $(\frac{0.1\ x\ 10}{1000})$

$1000cm^2$ of mixture contain $(\frac{0.1 \times 10 \times 100}{1000 \times 35})$

= 0.0286M

$pH = Pka + Log_{10} \frac{[salt]}{[Acids]}$

$= 4.74 + \log_{10} (\frac{0.0286}{0.0429}) = 4.57$

Calculate the pH of a solution made by mixing $50cm^3$ of 0.1M ethanoic acid with 0.1 mole of 50cm of sodium ethanoate. (Ka CH_3COOH = 1.8 x 10^{-5})

Question. Calculate the pH of a solution made by mixing $100cm^3$ of 0.1M ethanoic acid with $20cm^3$ of 0.1 M NaOH solution. (CH_3COOH) = 1.0 x 10^{-5})

$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3CO\bar{O}Na^+(aa) + H_2O(a)$

The salt formed and the excess acid constitute a buffer solution

Moles of NaOH used = $(\frac{0.1}{100} \times 20)$ moles

Moles of CH_3COOH used = $(\frac{0.1}{100} \times 20)$ moles

Moles of excess acid

$= (\frac{0.1 \times 100}{1000}) - (\frac{0.1}{1000} \times 20)$

= 0.01 – 0.002

= 0.008 moles

1 mole of NaOH reacts with 1 mole of ethanoic acid to form 1 mole of $CH_3CO\bar{O}Na^+$

Moles of $CH_3CO\bar{O}Na^+$

Formed = $(\frac{0.1}{100} \times 20)$

= o.002 moles

Total volumes of solution

= 100 + 20 = 120 cm^3

Molar concn of salt

$= 0.002 + \frac{100}{120}$

= 0.0167M

Molar concn of excess acid

$$= 0.008 \times \frac{2000}{120}$$

$$= 0.067M$$

Question: Calculate the pH of a solution by mixing 50cm^3 of 0.1M hydrochloric acid with 50cm3 of 0.2M aqueous ammonia Kb (NH$_3$) = 1.75 x 10^{-5}moldm^{-3}

Solution

NH$_3$(aq) + HCl(aa)   NH$_4$Cl(aq) + H$_2$O(l)

The salt formed and the excess ammonia constitute a buffer solution

Moles of HCl used   Moles of NH$_3$ used

$$= \frac{0.1}{1000} \times 50 \qquad\qquad (\frac{0.2}{1000} \times 50)$$

Excess moles of NH$_3$

$$= (\frac{0.2}{1000} \times 50)-(\frac{0.1}{1000} \times 50)$$

$$= (\frac{0.1}{1000} \times 50)$$

1mole of HCl reacts with the ammonia to give

1 mole of the salt

Moles of salt formed $= \frac{0.1}{1000} \times 50$

Total number = 50750 = 100cm^3

Molar concentration of excess

$$NH_3 = \frac{0.1}{1000} \times 50 \times \frac{1000}{100}$$

Molar concentration of salt formed

$$= \frac{0.1}{1000} \times 50 \times \frac{1000}{100}$$

NH$_4$Cl(aa) $\longrightarrow$ NH_4^+(aa) + Cl$^-$

NH$_3$(aa) + H$_2$O(l) NH_4^+(aa) + ŌH(aa)

$$Kb = \frac{[NH_4^+].[\bar{O}H]}{[NH_3]}$$
$$[\bar{O}H] = Kb\frac{[NH_3]}{[NH_4^+]}$$

$1.75 \times 10^{-5} \times \frac{0.05}{0.05}$

$[\bar{O}H] = 1.75 \times 10^{-5}$

$pOH = -\log_{10}[\bar{O}H]$

$= -\log_{10}[1.75 \times 10^{-5})$

$pOH = 4.757$

$14 = pH + pOH$

$pH = 14 - 4.57$

$= 9.24$

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

$(Ka(CH_3COOH = 1.8 \times 10^{-5})$

Solution

Before the titration, pH is determined by 0.1M CH_3COOH

$CH_3COOH(aa)$ $CH_3CO\bar{O}(aa) + H^+$

$Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

At equilibrium $= [CH_3CO\bar{O}] = [H^+]$

$Ka = \frac{[H^+]^2}{[CH_3COOH]}$

$[H^+] = \sqrt{Ka[CH_3COOH]}$

$= \sqrt{1.8 \times 10^{-5} \times 0.1}$

$[H^+] = 1.34 \times 10^{-3}$

$pH = -\log_{10}[H]$

$= -\log_{10}[1.3 \times 10^{-3}]$

$= 2.873$

At half neutralization

CH₃COOH(aa) + NaOH(aa) $\longrightarrow$ CH₃COŌNa⁺ + H₂O

At half neutralization

½ [Acid] has reacted to form the salt

[Acid] = ½ (0.1) = 0.05

[Salt] = ½ (0.1) = 0.05

Therefore at half neutralization

[Acid] = [Base]

CH₃COOH(aa) $\longrightarrow$ CH₃COŌ(aa) + H⁺

CH₃COOH(aa)   CH₃COŌ(aa) + H⁺(aa)

$Ka = \dfrac{[CH_3COŌ].[H^+]}{[CH_3COOH]}$

$[H^+] = Ka\ \dfrac{[Acid]}{[salt]}$

$[H^+] = Ka$

$[H^+] = 1.8 \times 10^{-5}$

$pH = -log_{10}[H^+]$

$= log_{10}(1.8 \times 10^{-5})$

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

CH₃COŌ(aa) + H₂O(l)   CH₃COOH(aa) + ŌH(aa)

But $KL = \dfrac{Kw}{Ka} = \dfrac{1.0\ x\ 10^{-14}}{1.8\ x\ 10^{-5}}$

At eqbm (CH₃COOH] = [ŌH]

$Km = \dfrac{[ŌH]^2}{[CH_3COŌ]}$

$5.56 \times 10^{-10} = \frac{[\bar{O}H]^2}{[0.1]}$

$[OH] = \sqrt{5.5 \times 10^{-1}}$

$pOH = -\log_{10} 7.4565 \times 10^{-6}$

5.13

$14 = pH + poH$

$pH = 8.87$

excess NaOH = (0.2 − 0.1) = 0.1M

[NaOH) for neutralization 0.1M

Twice as much = 0.1 x 2 = 0.2 m

Excess (NaOH) in solution = (0.1 x 0.1)

= 0.1M

0.1M NaOH is responsible for the pH

$NaOH(aa) \longrightarrow Na^+(aa) + \bar{O}H(aa)$

0.1   0.1

$[\bar{O}H]$ = 0.1M

$pOH = -\log(0.1)$

= 1.0

pH = 14-1

= 13

$25cm^3$ 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.

$(Kb(NH_3) = 1.75 \times 10^{-5})$.

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(Ka = (CH_3COOH) = 1.8×10^{-5})

Solution

$CH_3CO\bar{O}H(aq) \longrightarrow CH_3CO\bar{O}(aa) + Na^+(aa)$

$CH_3COOH(aa) \qquad CHCO\bar{O}(aa) + H^+(aa)$

$Ka = Ka = \dfrac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

$[H^+] = \dfrac{Ka[CH_3COOH]}{[CH_3CO\bar{O}]}$

$[H^+] = Ka \dfrac{[Acid]}{[salt]}$

But pH = $-\log_{10}[H^+]$ = 5.56

$[H^+]$ = 2.75 x 10^{-6}M

$2.75 \times 10^{-6} = \dfrac{1.8 \times 10^{-5} \times 0.1}{[salt]}$

[salt] = 0.65M

RFM of $CH_3CO\bar{O}Na^+$

=(12x2) + (3) + (16 x 2) + 23 = 82

Mass of salt = 0.65 x 82 = 53.3g/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 $CH_3CO\bar{O}Na^+$.

$CH_3COOH(aa) \qquad CH_3CO\bar{O}(aa)+ H^+(aq)$

$CH_3CO\bar{O}Na^+(aa) \longrightarrow CH_3CO\bar{O}(aa) + Na^+(aq)$

(a) Addition of a small amount of acid (H$^+$ ion]. The H$^+$ ions react with the ethanoate ions forming ethanoic molecules.

$CHCO\bar{O}(aa) + H^+(aa) \qquad CH_3COOH(aa)$

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 0.01MHCl is added to a litre of the solution.

Solution

$CH_3CO\bar{O}Na^+(aa) \longrightarrow CH_3CO\bar{O}(aa) + Na^+(aq)$

$CH_3COOH(aa) \qquad\qquad CH_3CO\bar{O}(aa) + H^+(aq)$

$Ka = Ka = \dfrac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

$[H^+] = Ka \dfrac{[Acid]}{[salt]}$

$[H^+] = 1.8 \times 10^{-5} \times \dfrac{0.5}{0.5}$

$pH = 4.74$

So pH changes by 0.01moles (very effective buffer)

Addition of a small amount of 0.01MHCl. The H^+ ions are buffered by the $CH_3CO\bar{O}$ ions

$CH_3CO\bar{O}(aa) + H^+(aq) \longrightarrow CH_3COOH$

This increases the $[CH_3COOH]$ by 0.01M

A new $[CH_3CO\bar{o}]$

= 0.5 + 0.01

= 0.51M

It decreases the $[CH_3CO\bar{o}]$ by 0.01M

A new [salt] = 0.5 – 0.01

= 0.49

$[H^+] = Ka \dfrac{[Acid]}{[salt]}$

$[H^+] = 1.8 \times 10^{-5} \times \dfrac{0.51}{0.49}$

$pH = 4.73$

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 $\bar{O}H$ ions react with the molecules of ethamoic acid.

$$CH_3COOH + \bar{O}H(aa) \longrightarrow CH_3CO\bar{O}(aa) + H_2O(l)$$

This decrease the $[CH_3COOH]$ but increases the $[CH_3CO\bar{O}]$ 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 $[H^+]$ 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

HPL(aa) $H^+ + PL^-$(aa)

The uncaused molecules of the indicator are colourless while the ionized are red (pink) in acidic solution the concn of $[H^+]$ is high and the ionized molecule shifting the equilibrium from right to left and the indicator appears colours.

In Alkaline medium, the $[\bar{O}H]$ is high which react with the hydrogen ions forming white 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

Me(aa) + H^+(aa) HM_e^+(aq)

Molecules Me are yellow but when they ionized by abstracting a proton they appear orange. In acidic medium the high concn of $[H^+]$ combine with methyl orange molecules, forming the ionized indicator shifting the equilibrium from left to night and the indicator appears orange in acidic medium.

In alkaline medium, the high $[\bar{O}H]$ react with the H^+ shifting the equilibrium from right to the left and the indicator appears yellow in alkaline medium

Indicator constant (Kin)

Consider the indicator which is a weak acid

HIn H^+(aa) + In(aa)

$$Kin = \frac{[H^+].[I_n^-]}{[HIn]}$$

Or $[H^+] = \frac{KIn.[HIn]}{[I_n^-]}$

The intermediate colour between the acidic and alkaline colour exists when

[HIn] = [In]
$[H^+]$ = Kin
Indicator has its KIn eg for phenolphthalein it is 7.0×10^{-10}

$[H^+]$ = Kin = 7.0×10^{-10}

And pH = $-\log_{10}[H^+]$

= $-\log10(7.0 \times 10^{-10})$

= 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 the they cant detect this end point. So a range of pH = ±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 kin the pH of the resultant solution at the end point of the titration eg for a titration of a strong acid which 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 $\bar{O}H$ are immediately neutralized forming water.

$$HCl \longrightarrow H^+ + Cl^-$$

H^+ in excess

$$H^+ + \bar{O}H \longrightarrow H_2O(l)$$

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 Vcm^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 (pH =7) because the salt formed (NaCl0 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 (NaOH / CH₃COOH)

Initially the pH is high because NaOH is a strong base and fully dissociates in solution releasing many ($\bar{O}H$] which are responsible for the high pH along AB the pH decreases gradually because the $\bar{O}H$ are still in excess, so any added H^+ from the acid are neutralized immediately at point B all the $\bar{O}H$ 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.

$CH_3COOH + NaOH \qquad\qquad CH_3CO\bar{O}Na^+(aa) + H_2(l)$

$CH_3CO\bar{O} + H_2O \longrightarrow CH_3COOH + \bar{O}H$

This releases $\bar{O}H$ in solution giving a pH greater that 7. The gradual decrease in pH along CD is because is because of the excess acid added and the buffering action of the thamoic acid and sodium ethanone.

3. Strong acid against weak base eg (HCl / NH₃OH)

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 ($\bar{O}H$) 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 intergoes hydrolysis releasing

$NH_4^+ + H_2O \qquad\qquad NH_3(aa) + H_3O^+$

The gradual increase in pH along CD is because of the excess base added and the buffering act ion 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 cant be followed using an acid base inductor.

Titration of Na_2CO_3 with HCl

But Na_2CO_3(aa) undergoes stepwise neutralization

$$Na_2CO_3(aq) + HCl(aq) \longrightarrow NaHCO_3(aa) + NaCl(aa)$$

Sodium carbonate undergoes step wise neutralization 1st it is half neutralized to $NaHCO_3$ and their neutralized to NaCl.

The gradual increase in pH along AB is because of the half neutralization of Neutralisation of Na_2CO_3 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 HCO_3^- undergo hydrolysis releasing hydroxide ions in solution

$$HCO_3(aa) + H_2O \qquad\qquad H_2CO_3(aa) + \bar{O}H(aa)$$

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) nbecause 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 phenolpthlein inductor 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 moldm^{-3}		Initial rate moldm^{-3}S^{-1}
	A	B	
1	1.0 x 10^{-4}	2.0 x 10^{-4}	1.8 x 10^{-5}
2	2.0 x 10^{-4}	2.0 x 10^{-4}	1.8 x 10^{-5}
3	3.0 x 10^{-4}	8.0 x 10^{-4}	7.2 x 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] = 0.1M

$$[B] = 0.2 \text{ M}$$

A Using experiments 1&2

$$\left(\frac{2.0 \ x \ 10^{-4}}{1.0 \ x \ 10^{-4}}\right) = \left(\frac{2.0 \ x \ 10^{-5}}{1.0 \ x \ 10^{-5}}\right)$$

$= 4y \qquad = 4^1 \ \ y = 1$

    (b) & C done

Question: Calculate the relative molecular mass of a solution of 2% glucose ($C_6H_{12}O_6$) (but solution 100.12^{0}C). boiling point constant for water is 0.52^{0}C mol^{-1}kg^{-1}

Moles of solvent = 98g

Mass of solute = 2g

98g of water dissolved 2g of glucose

100g of water dissolved $\frac{2x1000}{98}$

Dt = (100.12 − 100) = 0.12^{0}C

0.12 is elevation caused by 20.4g

0.52 is elevated caused by $\frac{0.52 \ x \ 20.4}{0.12}$

Question: Silver oxalate is a sparing 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 75^0C (Ksp is 1.10×10^{-10})

$Ag_2C_2O_4$ $2Ag^+(aq) + C_2O_4^{2-}$

$Ksp = [Ag^+]^2 [C_2O_4]^{-2}$

Question: Determine the phosphorous chloride bond energy in phosphorus penta chloride given the thermochemicle data

- Enthalpy of motion of phosphorus penta chloride is $-84Kjmol^-$
- Atomization energy of Chlorine atoms $O + 121 \ Kjmol^{-1}$
- atomization energy of phosphorous atoms $+200kjmol^{-1}$

Solution

¼ $P_4(g)$ + $\frac{5}{2}Cl_2(g)$————————→ $PCl_5(s)$

+200   5(+121)   B.E

P(g)   Cl(g)

$B.E = (-84) - ([5 \times +12]) + +200)$

$= -84$

$B.E = -84 - 805$

$= - 889Kjmol^{-1}$

$\frac{889}{5} = 177.8$

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. $Ba+$ and Ca^{2+}
ii. SO_3^{2-} and SO_4^{2-}
iii. NO_3^{2-} and NO_4^{2-}
iv. I^- and Cl^-
v. $C_2O_4^{2-}$ and CO_3^{2-}
vi. CrO_4^{2-} and $Cr_2O_7^2$
vii. Mg^2 and Ca^{2+}
viii. CO_3^{2-} and HCO_3
ix. $C_2O_4^2$ and $CH_3CO\bar{O}$
x. SO_3^{2-} 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 SO_3^{2-} turns from orange to green solution with SO_4^{2-} 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

$$CH_3COOH9aq) \qquad CH_3CO\bar{O}(aq) + H^+$$

Initially	1mole	0	0
If $\propto$ is degree	$-\propto$	$+\propto$	$+\propto$
Of ionization			
At eqbm	$(1-\propto)$	$\propto$	$\propto$
Conc	$c(1-\propto)$	$C \propto$	$C \propto$

$Ka = \dfrac{[CH_3CO\bar{O}][H^+]}{[CH_3COOH]} = \dfrac{c\propto^2}{(1-\propto)}$

Assumption

Calculate pH of 0.1M of ethanoic acid (Ka og acid = 10×10^{-5}M

$$CH_3COOH(aq) \qquad CH_2CO\bar{O}(aq) + H^+(aq)$$

$Ka = \dfrac{[CH_3CO\bar{O}][H^+]}{[CH_3COOH]}$

Assumption at equilibrium $[CH_3CO\bar{O}] = [H^+]$

$Ka = \dfrac{[H^+]}{[CH_2COOH]}$

$[H^+]^2 = Ka(CH_3COOH)$

$= \sqrt{1.0 \times 10^{-5} \times 0.1}$

$[H^+] = 1.0 \times 10^{-6}$M

pH = -log[H⁺]

= -log 1.0×10^{-6}

=6

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

From $CH_3CH_2COOH(aq) \qquad CH_3CH_2CO\bar{O}(aq) + H^+$

Assumption at equilibrium $[CH_3CO\bar{O}] = [H^+]$

$$Ka = \frac{[H^+]^2}{[CH_3CH_2COOH]}$$

From pH = -log[H$^+$]

[H$^+$] = 1 x 10^{-4}

$$Ka = \frac{[1 \times 10^{-4}]^2}{0.05}$$

2.0 x 10^{-7}

$$\alpha = \sqrt{\frac{2.0 \times 10^{-7}}{0.05}} \quad = \quad \text{From } ka = c\alpha^2$$

α = 2.0 x 10^{-3}

$$Ka = Ka = \frac{[1 \times 10^{-4}]^2}{0.05}$$

2.0 x 10^{-7}

2. 0.01 solution of dimethyl amine is 2% ionized. Calculate
i. the base dissociation constant
ii. the pH of the solution

CH$_3$NCH$_3$ + H$_2$O   CH$_3$(NH$_2$)CH$_3$ + ŌH

  1   0   0

C(1-α)   c(α)   c(α)

$Kb = \dfrac{c\alpha^2}{(1-\alpha)}$ but $\alpha = \dfrac{2}{100}$ = 0.02

$= \dfrac{0.01 \times (0.02)^2}{1-0.02}$

Kb = 4.08 x 10^{-6}moldm^3

$Kb = \dfrac{[(CH_3)_2NH_2][\bar{O}H]}{([CH_3)_2NH]}$

At equilibrium [(CH$_3$)$_2$NH] = [ŌH]

$Kb = \dfrac{[\bar{O}H]^2}{[(CH_3)_2NH)}$

$[\bar{O}H] = \sqrt{kb\,[(CH_3)_2NH)}$

$= \sqrt{4.08 \times 10^{-6} \times 0.01}$

= 2.0 x 10^{-4} moldm^{-3}

But $[H^+] = \dfrac{kw}{[\bar{O}H]}$

$= \dfrac{1.0 \times 10^{-14}}{2.0 \times 10^{-4}}$

= 5.0 x 10^{-11}M

pH = -log [H$^+$]

= -log 5.0 x 10^{-11}

= 10.30

pH = 10.30

calculate the pH of a solution made by mixing 20cm^3 of 0.1M HCl with 30cm^3 of 0.2M NaOH.

Solution

Acid

100cm^3 of solution contain 0.1 moles of HCl

20cm^3 of solution will contain ($\frac{0.1}{100}$ x 20)

= 2.0 x 10^{-3} moles of HCl

Base

100cm^3 of solution contain 0.2 moles of NaOH

30cm^3 of solution will contain ($\frac{0.2}{100}$ x 30)

= 6.0 x 10^{-3} moles of NaOH

Excess moles of NaOH = (6.0 x 10^{-3} – 2.0 x 10^{-3})

4 x 10^{-3} moles of NaOH

50cm^3 of solution contain 4 x 10^{-3} moles of NaOH

1000cm^3 of solution will contain $\frac{x\ 10^{-3}}{50}$ x 100

= 0.08M NaOH

pH = p^{KW} – p^k[OH]

= 14- -log 0.08

14 + log 0.8

12.9

pH = 12.9

calculate the pH of a solution made by mixing 20cm^3 of 0.1M KOH with 50cm^3 H$_2$SO$_4$

H$_2$SO$_4$(aq) + 2KOH(aq) $\longrightarrow$ K$_2$SO$_4$(aq) + H$_2$O(l)

[KOH] reacted = [$\frac{0.1}{1000}$ x 20 x $\frac{1000}{70}$]

2moles of KOH react with 1mole of H$_2$SO$_4$

0.029 moles of KOH will react with ($\frac{1}{2}$ x 69)M

= 0.0145M of H$_2$SO$_4$

[H$_2$SO$_4$] used = $\frac{0.2}{1000}$ x 50 x $\frac{1000}{70}$

= 0.143M

Excess [H$_2$SO$_4$] = 0.143 – 0.0145

= 0.143M

H$_2$SO$_4$(aq) 2H$^+$(aq) + SO_4^{2-}

0.1285   (0.1285 x 2)

        0.251

pH = -log[H$^+$]

= -log 0.257

= 0.59

= 0.6

0.1M CH_3COOH was titrated with NaOH using prenolpthaleine 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 (Ka CH_3COOH =1.0x10^{-3}M)

Solution

(i) From the equation

$CH_3COOH \qquad\qquad CH_3CO\bar{O} + H^+$

$Ka = \frac{[CH_3CO\bar{O}][H^+]}{[CH_3COOH]}$

at equilibrium $[CH_3CO\bar{O}] = [H^+]$

$Ka = \frac{[H^+]}{[CH_2COOH]}$

$[H^+]^2 = \sqrt{Ka(CH_3COOH)}$

$= \sqrt{1.0 \times 10^{-5} \times 0.1}$

$[H^+] = 1.0 \times 10^{-3}$M

$pH = -log[H^+]$

$= -log(1 \times 10^{-3})$

$pH = 3$

(ii) At half neutralization ; $[CH_3CO\bar{O}] = [CH_3COOH]$

Then from, $Ka = \frac{[CH_3CO\bar{O}].[H^+]}{[CH_3COOH]}$

$Ka = [H^+]$

$[H^+] = 1.0 \times 10^{-5}$

$pH = -log[H^+]$

$= -log\ 1 \times 10^{-5}$

pH = 5

$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3CO\bar{O}Na^+ + H_2O(l)$

At the end point, the contains the salt formed from a neutralization which undergoes hydrolysis.

$CH_3CO\bar{O}(aq] + H_2O(l) \qquad\qquad CH_3COOH(aq) + \bar{O}H$

$Kl = \frac{[CH_3COOH][\bar{O}H]}{[CH_3CO\bar{O}]}$

At eqbm $[CH_3COOH] = [\bar{O}H]$

1 mole of the acid reacts to give 1 mole of the salt

Conc of salt = 0.1M

Again

$KL = \frac{Kw}{Ka}$

$= \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}}$

1.0×10^{-9}M

$1.0 \times 10^{-9} = \frac{[\bar{O}H]^2}{0.1}$

$[\bar{O}H] = \sqrt{0.1 \times 1.0 \times 10^{-9}}$

$= 1.0 \times 10^{-5}$M

pH = $P^{kw} - P^k[OH]$

= 14- -log1.0 x 10^{-5}

=9

pH =9

calculate the pH of a solution made by mixing 80cm^3 of 0.1M ethanoic with 20cm^3 of 0.1M NaOH (Ka(CH$_3$COOH) = 1.0 x 10^{-50})

solution

CH$_3$COOH(aq) + NaOH(aq) $\longrightarrow$ CH$_3$COŌNa$^+$ + H$_2$O(l)

The excess CH$_3$COOH and the salt constitutes a buffer solution

[NaOH] = $\frac{0.1}{1000}$ x 20 x $\frac{1000}{100}$

0.02M

But 1 mole of NaOH is completely neutralized to form 1 mole of CH$_3$COŌNa$^+$

[CH$_3$COŌNa$^+$] = 0.02M

[CH$_3$COOH] used = ($\frac{0.1}{1000}$ x 80 x $\frac{1000}{100}$)

Excess [CH$_3$COOH] = 0.08 – 0.02

=0.06M

CH$_3$COŌNa$^+$ $\longrightarrow$ CH$_3$COŌ(aq) + Na$^+$(aq)

CH$_3$COOH(aq) $\longrightarrow$ CH$_3$COŌ(aq) + H$^+$(aq)

Ka = $\frac{[CH_3COŌ].[H^+]}{[CH_3COOH]}$

Assumption: all CH$_3$COŌ are derived from the salt

[H$^+$] = $\frac{Ka[CH_3COOH]}{[CH_3COŌ]}$ = $\frac{1.0 \, x \, 10^{-5}x0.06}{0.02}$

3.0 x 10^{-5}

[H$^+$] = 3.0 x 10^{-5}

pH = -log[H$^+$]

= -log 3.0 x 10^{-5}

= 4.52

pH = 4.52

Calculate the change in pH that occurs when 2cm^3 of 0.1M HCl were added to the above mixture.

Solution

Added H$^+$ions are buffered by the ethanaote ions

CH$_3$COŌ(aq) + H$^+$(aq) $\longrightarrow$ CH$_3$COOH

This increase [CH$_3$COOH] but decreases [CH$_3$COŌ]

Total vol of solution = 102cm^3

[H$^+$] added = $\frac{0.1}{1000}$ x 2 x $\frac{1000}{102}$

= 1.96 x 10^3 M

New [CH$_3$COOH] =(0.06 + 1.96 x 10^{-3}) M

= 6.2 x 10^{-2}M

New [CH$_3$COŌ] = 0.02-1.96 x 10^{-3}

= 1.80 x 10^{-2}M

[H$^+$] = $\frac{Ka [CH_3COOH]}{[CH_3COŌ]}$

$$= \frac{1.0 \times 10^{-5} \times 6.20 \times 10^{-2}}{[CH_3CO\bar{O}}$$

$[H^+]$ = 3.44 x 10^{-5}

pH = 4.46

change in pH

= 4.52 – 4.46

= 6.0 x 10^{-2}

0.06

30cm^3 of 0.1M Solution of ammonia was titrated with hydrochloric acid. At the end point, 5cm^3 of acid had been added. Calculate the pH of the resultant solution (Ka for NH$_3$ is 1.5 x 10^{-5} moldm^{-2})

Solution

NH$_3$OH(aq) + HCl(aq) $\longrightarrow$ NH$_4$Cl(aq) + H$_2$O

1mole of NH$_4$OH reacts with 1 mole of NH$_4$Cl

[NH$_4$OH] = [NH$_4$Cl]

NH$_4$Cl(aq) $\longrightarrow$ NH_4^+(aq) + Cl$^-$(aq)

H$_2$O(l) + NH_4^+(aq) $\longrightarrow$ NH$_3$(aq) + H$_3$O$^+$

$KL = \frac{[NH_3][H_3^+O]}{[NH_4^+]}$

[NH$_3$] = [H_3^+O]

$KL = \frac{[H_3^+O]^2}{[NH_4^+]}$ but KL = $\frac{kw}{kb}$

$[H_3^+O] = \sqrt{\frac{kw}{kb} NH_4^+}$

pH = -log ($\sqrt{\frac{kw}{kb}} NH_4^+$

= -log$\sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}} \times 8.57 \times 10^{-2}$

pH = 5.16

Salt hydrolysis

This is a reaction of salt with water in which the ions equilibrium of water is duturbed resulting into an acid or alkaline solution

Salt derived from a weak acid and a strong base eg RCO$\bar{O}$Na$^+$

RCO$\bar{O}$Na$^+$(aq) $\longrightarrow$ RCO$\bar{O}$(aq) + Na$^+$(aq)

H$_2$O(s)   H$^+$(aq) + $\bar{O}$H(aq)

Simply

H$_2$SO(l) + RCO$\bar{O}$(aq) $\longrightarrow$ RCOOH(aq) + $\bar{O}$H(aq)

This is called ionic hydrolysis

Salt derived from a strong acid and a weak base eg RNH$_3$Cl$^-$

NH$_4$Cl $\longrightarrow$ NH$_4$ + Cl$^-$

H$_2$O(l)   H$^+$(aq) + $\bar{O}$H

Or simply

NH_4^+(aq) + H$_2$O   NH$_4$OH(aq) + H$^+$

NH_4^+(aq) + H$_2$O(l)   NH$_3$(aq) + H_3^+O

This is called cationic hydrolysis

Example

Calculate the pH of a solution ethanoate made by dissolving 8.4g of the salt in laite of water (for sodium ethanoate = 5.5 x 10^-10 M)

Solution

RFM of $CH_3CO\bar{O}Na^+$ = $(12 \times 2) + (16 \times 2) + (1 \times 3) + (23 \times 1)$

=82

Conc of $CH_3CO\bar{O}Na^+$ = $\frac{8.4}{8.2}$ = 0.102M

$CH_3CO\bar{O} + H_2O(l) \qquad CH_3COOH + \bar{O}H$

$KL = \frac{[CH_3CO\bar{O}H][\bar{O}H]}{[CH_3CO\bar{O}]}$

At equilibrium

$[CH_3COOH] = [\bar{O}H]$

$KL = \frac{[\bar{O}H]^2}{[CH_3CO\bar{O}]}$

$KL = \frac{[\bar{O}H]^2}{0.102}$

$[\bar{O}H] = \sqrt{kh(0.102)}$

$= \sqrt{5.5 \times 10^{-10} \times 0.102}$

$[\bar{O}H] = 7.48999 \times 10^{-6}$

$[H^+] = \frac{kw}{[OH]}$

$= \frac{1 \times 10^{-14}}{7.48999 \times 10^{-9}}$

$[H^+] = 1.335 \times 10^{-9}$M

Example 2

Sodium proponoate hydrolyses in water

    i.   Write equation for the hydrolysis
    ii.   Give expression for hydrolysis constant KL
    iii.   If a pH of 0.1M acqueous solution of sodium propanoate is 8.9. calculate the value of KL

$CH_3CH_2CO\bar{O}(aq) + H_2O(l) \qquad CH_3CH_2COOH(aq) + \bar{O}H(aq)$

$Kh = \frac{[CH_3CH_2COOH][\bar{O}H]}{[CH_3CH_2CO\bar{O}]}$

pH = 8.9

$8.9 = log[H^+]$

$Log[H^+]^{-1} = 8.9$

$[H^+]^{-1} = \frac{1}{10^{8.9}}$

1.26×10^{-9}

At equilibrium $[CH_3CH_2COOH) = [\bar{O}H]$

$Kh = \dfrac{[\bar{O}H]^2}{[CH_3CH_2COO]}$

$[\bar{O}H] = \dfrac{kw}{[H^+]}$

$= \dfrac{1.0 \times 10^{-14}}{71.26 \times 10^{-9}}$

7.9365×10^{-6}

$Kh = \dfrac{(7.9365 \times 10^{-6})^2}{0.1}$

Example 3

Calculate the mass of pheny amyl hydrogenchlokride that should be added to 1 litre of water to form a solution of pH 5.2 (kh = 6.0×10^{-5} moldm^{-3}]

Solution

$C_6H_5NH_3(aq) + H_2O(l)$ $C_6H_5NH_2(aq) + H_3O^+(aq)$

$Kh = \dfrac{[C_6H_5NH_2].[H_3O^+]}{[C_6H_5NH_3]}$

$Kh = \dfrac{[H_3O^+]^2}{[C_6H_5NH_3]}$

$6.0 \times 10^{-5} = \dfrac{(\frac{1}{10^{32}})^2}{[C_6H_5NH_3]}$

$[C_6H_5NH_3] = 6.6 \times 10^{-7}$M

From 1 mole of $[C_6H_5NH_3]$ reacts with 1 mole of $C_6H_5NH_3Cl$-

$[C_6H_5NH_3cl-] = 6.6 \times 10^{-1}$ M

RFM of $C_6H_5NH_3cl- = (12 \times 6) + (1 \times 6) + (14 \times 1) + (35.5 \times 1)$

$= 127.5$

Mass $= RFM \times [C_6H_5NH_3cl-]$

$= 127.5 \times 6.6 \times 10^{-7}$

$= 7.65 \times 10^{-5}$

Degree of hydrolysis of a salt

Eg $NH_4^+(aq)$

$NH_4^+(aq) + H_2O(l)$ $NH_3(aq) + H_3O^+(aq)$

Before hydrolysis   1mole   0   0

If $\propto$ has hydrolysed   1-$\propto$ $\propto$ $\propto$

$Kh = \dfrac{C\propto^2}{1-\propto}$

A 0.01 M solution of bodsom benzoate undergoes hydrolysis

Calculate

  i.   The degree of hydrolysis of the salt
  ii.   The pH of the solution (Kh = 5.0×10^{-10})

A solution of 0.01M sodium ethanoate is 2% dyctrolysed. Calculate

  i.   The hydrolysis constant
  ii.   The pH of the solution

Solution

$Kl = \dfrac{C\propto^2}{1-\propto}$ but 1-$\propto \approx 1$

$\propto^2 = \dfrac{Kh}{C}$ $\propto \sqrt{\dfrac{5 \times 10^{-10}}{0.01}} = 2.236 \times 10^{-4}$

Calculate the pH of 0.01M solution of ammonium chloride ($Kh = 6.84 \times 10^{-8}$)

$[\bar{O}H) = \sqrt{khc}$

$= \sqrt{6.34 \times 10^{-8} \times 0.1}$

$= 7.96 \times 10^5$

$[H^+] = \frac{kw}{[\bar{O}H]}$

$= \frac{1 \times 10^{-14}}{7.96 \times 10^5}$

$= 1.2559 \times 10^{-10}$

pH $= -\log(1.2559 \times 10^{-10})$

$= 9.9$

Examples of salts that hydrolyse

$AlCl_3$

$FeCl_3$

$CrCl_3$

$BeCl_2$

Solution

No.1

$[\bar{O}H] = 2.236 \times 10^{-6}$

$[H^+] = \frac{kw}{[\bar{O}H]}$

$= (\frac{1 \times 10^{-14}}{2.236 \times 10^{-6}})$

$[H^+] = 4.472 \times 10^{-9}$

pH $= -\log [4.472 \times 10^{-9}$

$= 8.35$

(ii) pH

$[\bar{O}H] = \frac{\sqrt{khc}}{\sqrt{4.0816 \times 10^{-6} \times 0.01}}$

$= 2.02 \times 10^{-4}$

$[H^+] = \frac{kw}{[\bar{O}H]}$

$= (\frac{1 \times 10^{-14}}{22.02 \times 10^{-4}})$

$= 4.949 \times 10^{-11}$

pH $= -\log [4.9498 \times 10^{-11}]$

$= 10.31$

SOLUBILITY PRODUCT CONCEPT

Applicable to sparingly soluble salts ie a salt that slightly dissolves in water forming ions which remain in equilibrium with undissolved sold 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 stachometric equation at a constant temperature.

Example calculate the solubility of $BaSO_4$ in
    i.   Water
    ii.   0.1M sodium sulphate (Ksp $BaSO_4$ at $25^0c = 1.0 \times 10^{-10}$)

Calculate the amount of the $BaSO_4$ which was precitated as a result of dissolving barium sulphate in 0.1M sodium sulphate

$BaSO_4(s)$ $\qquad$ $Ba^{2+}(aq) + SO_4^{2-}$

Let solubility of $BaSO_4$ be 5 moldm^{-3}

$[Ba^{2+}] = 5$

$[SO_4^{2-}] = 5$

$Ksp = [Ba^{2+}] [SO_4^{2-}]$

$1.0 \times 10^{-10} = 5.5$

$S = \sqrt{1.0 \times 10^{-10}}$

$= 1 \times 10^{-5}M$

$Na_2SO_4(aq) \longrightarrow 2Na^{2+}(aq) + SO_4^{2-}(aq)$

Let the new solubility be s^1moldm^3

$[SO_4^{2-}] = [0.1 + S^1]$ moldm^{-3}

$[Ba^{2+}] = S^1$

But $0.1 >>> S^1$ such that $0.1 + S^1 = 0.1$

1.0 x ....

$S^1 = 1 \times 10^{-1}$ M

Moles precipitated $[1.0 \times 10^{-5} - 1.0 \times 10^{-9})$

Mass precipitated

$Ba - RFM = 233$

$(1.0 \times 10^{-5} - 1.0 \times 10^{-9})$ 233

2.33×10^{-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 (ksp for CaF_2 = 4.0 x 10^{-11}, Ka for Hf = 5.6 x 10^{-4}M)

Solution

$CaF_2(l)$ $\qquad$ $Ca^{2+}(aq) + 2F^-(aq)$

Let the solubility in water be s moldm^3

$[Ca^{2+}] = s$ $\quad$ $[F] = 2s$

$Ksp = [Ca^{2+}] [F^-]^2$

$4.0 \times 10^{-11} = s(2s)^2$

$S^3 = \dfrac{4.0 \times 10^{-11}}{4}$

$S = \sqrt[3]{\dfrac{4.0 \times 10^{-11}}{4}}$

$= 2.15 \times 10^{-4}M$

Let the solubility of CaF_2 in 0.01m NaF be a moldm^{-3}

$NaF(aq) \longrightarrow Na^+(aq) + F^-(aq)$

$CaF_2(s)$ $\quad$ $Ca^{2+}(aq) + 2F^-(m)$

$[Ca^{2+}] = a$ moldm^3

$[F^-] = 22$ (a + 0.01 moldm^{-3}

But $0.01 >>> a$

$[F^-] = 0.01 \times 2$

$4.0 \times 10^{-11} = 0.0001$ a

= 4.0 x 10^{-7} M

HF(aq) H^+(aq) + F^-(aq)

$Ka = \frac{[H^+][F^-]}{[H^+]}$

$[H^+] = [F^-]$

Ka 5.6 x $10^{-4} = \frac{[F^-]^2}{0.1}$

$[F\} = \sqrt{0.1 \; x \; 5.6 \; x \; 10^{-4}}$

= 1.4833 x 10^{-3}

Let new solubility be y

CaF_2 Ca^{2+}(aq) + $2F^-$(aq)

2y + 7.4833 x $10^{-3} \approx$ 7.4833 x 10^3

Ksp = $[Ca^{2+}]$ $[F^-]$

4 x 10^{-11} a 7.4833 x 10^{-3}

$A = \frac{4 \; x \; 10^{-11}}{7.4833 \; x \; 10}$

      5.345 x 10^{-9}M

write the expression for the solubility product of iron (ii) hydroxide and give the units.

Ksp = $[Fe^{2+}]$ $[\bar{O}H]^2$

If the ksp of $Fe(OH)_2$ at 25^0c is 6.6 x 10^{-15}, calculate the solubility in $mold^{-1}$ of $Fe(OH)_2$ first in pure water then in 1.0M ammonia (Kb Ammonia = 1.8 x 10^{-5}M)

In water let the solubility be s $moldm^8$

$Fe(OH)_2$(s) Fe^{2+}(aq) + $2\bar{O}H$(aq)

Ksp = $[Fe^{2+}]$. [OH]

6.6 x 10^{-15} = s(2s)^2

$S = \sqrt[3]{\frac{6.6 \; x \; 10^{-15}}{4}}$

1.1817 x 10^{-5} $moldm^{-3}$

Ammonia ionizes in solution according to the equation

NH4OH(aq) NH_4^+(aq) + $\bar{O}H$(aq)

$Kb = \frac{[NH_4^+][\bar{O}H]}{[NH_4OH]}$ at equilibrium

1.8 x $10^{-5} = \frac{[\bar{O}H]^2}{1.0}$

$[\bar{O}H] = \sqrt{1.8 \; x \; 10^{-5} \; x \; 1.0}$

= 4.24 x 10^{-3} M

Let the solubility of $Fe(OH)_2$ in 1M NH_3 be a $moldm^3$

$Fe(OH)_2$(s) Fe^{2+}(aq) + $2\bar{O}H$(aq)

a   a   (29 + 4.24 x 10^{-3})

but 2a <<<<4.24 x 10^{-3}

such that 2a + 4.24 x $10^{-3} \approx$ 4.24 x 10^{-2} M

ksp = $[Fe^{2+}]$ $[\bar{O}H]^2$

6.6 x 10^{15} = a.(4 x 4.24 x 10^{-3})

$a = \frac{6.6 \; x \; 10^{15}}{4 \; x \; 4.24 \; x 10^{-3}}$

= 3.67 x 10^{-10}M

b) The Ksp of barium sulphate and strontrum sulphate are 1.1×10^{10} and 2.8×10^{-7} mol^2dm^{-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 strantion ions in solution because barium sulphate has a lower solubility product hence a low solubility and its ksp is easily exceeded.

Calculate the concentration of $BaSO_4$ in a solution which is saturated with both barium sulphate and throntion sulphate.

Solution

$BaSO_4(s) \qquad\qquad Ba^{2+}(aq) + SO_4^{2-}(aq)$ ksp = 1.1×10^{-10}

$S_rSO_4(s) \qquad\qquad S_r^{2+}(aq) + SO_4^{2-}(aq)$ ksp = 2.8×10^{-7}

Assumption

In a saturated solution of the two salts, the common ion comes from only the more soluble salt, so the sulphate are from $SrSO_4$

$SrSO_4(s) \qquad\qquad Sr^{2+}(aq) + SO_4^{2-}$

0.01 $\qquad\qquad$ 0.01

$Ksp = [Sr^{2+}] [SO_4^{2-}]$

$[SO_4^{2-}] = \frac{ksp}{[Sr^{2+}]}$

$= \frac{2.8 \times 10^{-5}}{0.01}$

$= 2.8 \times 10^{-5}$

Barium sulphate

$Ksp - [Ba^{2+}] [SO_4^{2-}]$

$1.10 \times 10^{-10} = [Ba^{2+}] = 2.5 \times 10^{-5}M$

$[Ba^{2+}] = \frac{1.1 \times 10^{-10}}{2.5 \times 10^5}$

$[Ba^{2+}] = 3.93 \times 10^{-6}M$

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 phenophalein indicator.

The volume of the acid need to reach end point is noted.

Treatment of results

Let concn of acid be x $moldm^{-2}$

Volume of acid to reach and point is noted

Treatment of results

Let concentration of acid be x $moldm^3$

Volume of acid needed to reach end be V_1 cm^3

Volume of saturated solution pipette be V_2 cm^3

Moles of acid used = $(\frac{x}{100}$ x $V_1)$

From the equation

$\bar{O}H(aq) + HCl(aq) \longrightarrow Cl^-(aq) + H_2O(aq)$

Moles of $\bar{O}H$ that reacted = $(\frac{x}{100}$ x $V_1)$moles

V_2 cm^3 of solution contain $(\frac{xV_1}{1000})$ moles of $\bar{O}H$ ions

1000cm^3 of solution $(\frac{xV_1}{1000}$ x $\frac{1000}{V_2})$ moles of $\bar{O}H$ ions.

From the equation

$Ca(OH)_2 \qquad\qquad 2\bar{O}H(aq) + Ca^{2+}(aq)$

1 mole of $Ca(OH)_2$ releases 2 moles of $(\bar{O}H)$ ions

$[\bar{O}H] = (\frac{xV_1}{1000}$ x $\frac{1000}{V_2})$ x 2

For every of $\bar{O}H$ released 1 mole of Ca^{2+} is released

$[Ca^{2+}] = \frac{1}{2} [\bar{O}H]$

$= (\frac{xV_1}{1000}$ x $\frac{1000}{V_2})$ x 2 x $\frac{1}{2}$

$= (\frac{xV_1}{1000}$ x $\frac{1000}{V_2})$

What is meant by the term common ion effect?

This is the precipitation of a sparing soluble salt from its saturated solution by introducing a soluble salt containing one of the of the saturated springly soluble salt.

Calcium iodate, $Ca(IO_3)_2$ is sparingly soluble in water

Write

The equation for the solubility of calcium iodate in water.

$Ca(IO_3)_2 \qquad\qquad Ca^{2+}(aq) + 2IO_3^-(aq)$

An expression for the solubility product, ksp of calcium iodate

$Ksp = [Ca^{2+}] . [IO_3^-]^2$

If the solubility product of calcium iodate at 25^{0}C is 1.95 x 10^{-3}. Calculate the solubility in moles per litre at 25^{0}C of calcium iodate in.

Water

$Ksp = 1.95$ x 10^{-4}moldm^{-3}

Let the solubility of $Ca(IO_3)_2$ in water be $\propto$

$Ksp = (\propto) (2\propto)^2$

1.95 x 10^{-4} M $= 4\propto^3$

$\propto = \sqrt[3]{\frac{1.95 \, x \, 10^{-4}}{1}}$

$\propto = 3.653$ x 10^{-2}M

The solubility is 3.633 x 10^2 M

A 0.01 M solution of sodium iodate

$NaIO_3 \quad Na^+(q) + IO_3^-(aq)$

0.1   0.1

Let the new solubility be $\propto$

$Ca(IO_3)_2 \qquad Ca^{2+}(aq) + 2SO_3(aq)$

$\qquad\qquad\qquad\qquad \propto + 0.1$

But 25 <<<<0.1

$2\alpha + 0.1 = 0.1$

$Ksp = \alpha(0.1)^2$

$\alpha = \dfrac{1.95 \; x \; 10^{-4}}{(0.1)^2}$

$V = 1.95 \; x \; 10^{-2}$

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 moldm^{-3} of methanoic acid is 1% ionized.

Calculate

The pH of methanoic and solution

Let the degree of ionization be x

$$HCOOH \qquad\qquad HCO\bar{O} + H^+$$
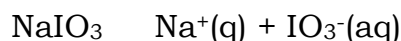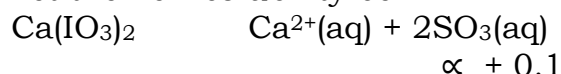
1	0	0
$1-\alpha$	α	α
$C(1-\alpha)$	$C\alpha$	$C\alpha$

$Ka = \dfrac{[HCO\bar{O}]\;[H^+]}{[HCOOH]}$

$Ka = \dfrac{Cx\;.\alpha C}{C\;(1-\alpha)}$

But $1-\alpha$

$Ka = \alpha^2 C$ but $\alpha = 0.01$

$(1-\alpha) = 1-0.01$

$= 0.99$

$Ka = (0.01)^2 \; 0.001$

$Ka \; 1 \; x \; 10^{-7} \; moldm^3$

$Ka = \dfrac{[HCO\bar{O}]\;[H^+]}{[HCOOH]}$ but $[HCO\bar{O}] = [H^+]$

$[H^+] = \sqrt{[HCOOH].Ka}$

$[H^+] = \sqrt{0.001 \; x \; 1 \; x \; 10^{-7}}$

$= 1 \; x \; 10^{-5} \; moldm$

$pH = -\log [H^+]$

$= -\log(1 \; x \; 10^{-5})$

$= 5$

$pH = 5$

(ii) The acid dissociation constant Ka for methanoil acid

$Ka = \alpha^2 C$

$Ka = (0.01)^2 \; x \; 0.001$

$1 \; x \; 10^{-1} \; mold \; m^3$

Calcium fluoride is a sparingly soluble salt in water

(a) Write an equation for the solubility of calcium fluoride

$CaF_2(s) \qquad\qquad Ca^{2+}(aq) + 2F^-$

(b) Expression for the solubility product ksp of calcium include. Let the solubility be k

$Ksp = [Ca^{2+}]\;[F^-]^2$

Calculate the solubility for calcium fluoride in a solution containing $0.35mol^{-1}$ of fluoride ions at 25^0C. (Ksp = 1 x 10^{-10} at 25^0C)

Let the solubility be y

$CaF_2(s)$ $\qquad\qquad\qquad$ $Ca^{2+}(aq) + 2F^-$

But 2y + 0.35 $\approx$ 0.35

Because 2y <<<< 0.35

$Ksp = y \times (0.35)^2$

$1.7 \times 10^{-10} = y \times (0.35)^2$

$y = \dfrac{1.7 \times 10^{-10}}{(0.35)^2}$

= 1.3878×10^{-9} 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

$CH_3NH_2(aq) + H_2O(aq)$ $\qquad\qquad$ $CH_3NH_2(aq) + \bar{O}H(aq)$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ H $^|$

An expression for the base dissociation constant Kb for methyl amine

Let it be the degree of ionization

$\qquad\qquad\qquad$ $CH_3NH_2(aq) + H_2O(aq)$ $\qquad\qquad\qquad$ $CH_3NH_3(aq) + \bar{O}H(aq)$

Initially: $\qquad$ c(1-$\propto$) $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\propto$ $\qquad\qquad$ $\propto$
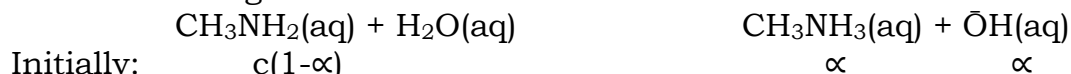
$Kb = \dfrac{[CH_3NH_3][\bar{O}H]}{[CH_3NH_3]}$

$\dfrac{c \propto . \propto C}{c(1-\propto)}$

$Kb = \dfrac{C\propto^2}{1}$

$Kb = C\propto^2$

(b) The hydrogen ion concentration of a 1M methylamine solution is 2.5×10^{-13} mol l^{-1}. Calculate kb for methylamine.

$\qquad$ $[CH_3NH_2] = 1.0M$

$\qquad$ $[H^+] = 2.5 \times 10^{-13}M$

$\qquad$ $Kb = \dfrac{[CH_3NH_3][\bar{O}H]}{[CH_3NH_3]}$ but $[CH_3NH_3] = [\bar{O}H]$

$\qquad$ $Kb = \dfrac{[\bar{O}H]^2}{[CH_3NH_2]}$

$\qquad$ But kw = $[\bar{O}H]$ $[H^+]$

$\qquad$ $[\bar{O}H] = \dfrac{Kw}{[H^+]}$

$\qquad$ $= \dfrac{1 \times 10^{-14}}{25 \times 10^{-13}}$

$\qquad$ $[OH) = 4.0 \times 10^{-2}$ M

$\qquad$ $Kb = \dfrac{[\bar{O}H]^2}{[CH_3NH_2]}$

$\qquad$ $\dfrac{(4 \times 10^{-2})^2}{10}$

$\qquad$ $Kb = 1.6 \times 10^{-3}$ mol^2l^{-2}

5. The solubility products of lead (ii) chloride is $1.6 \times 10^{-3}l^{-3}$ at 25^0C

(a) Write an expression for the solubility products of lead(ii) chloride

$Ksp = [Pb^{2+}].[Cl-]^2$

(b)(i) The concentration of the chloride ion in mol l^{-1} in a saturated solution of lead (ii) chloride at 25^{0}C

Let the solubility be x

$Ksp - [x] . [2x]^2$

$1.6 \times 10^{-5} = 4x^3$

$x = \sqrt{\dfrac{1.6 \times 10^5}{4}}$

$1.5874 \times 10^2 mol\ l^{-1}$

The concentration of chloride ions = 1.5874 x 10^{2}mol l^{-1}

The solubility lead (ii) chloride in grams per litre at 25^{0}C ions litre contains 1.5874 x 10^2 moles

RFM of pbCl$_2$

207 + (35.5 × 2)

218

One litre contains $1.5874 \times 10^{-2} \times 278$

$= 4.413gl^{-1}$

(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 lachatelier'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 x 10^{-6}moldm^{-3} of aluminium hydroxide completely ionizes in water (Kw = 1 x 10^{-14})

(i)Write equation for the reaction of aluminium hydroxide

(ii)Calculate the pH of the resultant solution.

Solution.

(i) $Al(OH)_3 \longrightarrow Al^{3+}(aq) + 3\bar{O}H(aq)$

(ii)2.3 x 10^{-6}moldm^3 2.3 x 10^{-6}moldm^3
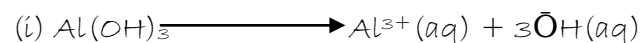
$Kw = [H^+] [\bar{O}H]$

$[H^+] = \dfrac{kw}{[\bar{O}H]}$

$= \dfrac{1 \times 10^{-14}}{2.2 \times 10^{-14}}$ $= 4.3 \times 10^{-9}$

$pH = -log (4.35 \times 10^{-9})$

$= 8.36$

PHASE EQUILIBRIA

Apure 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 rending 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-

Vapourequibliuria 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 spaces 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 animal species eg Water system which can be.

   iii)   The phase system eg liquid vapour equilibrium
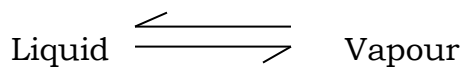
Liquid $\rightleftharpoons$ Vapour

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 0 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 a long 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 ie the temperature beyond which the vapour can not be condensed by just applying pressure.

Which the system at any one phase egMis 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 vapourie no change in phase occurs until the pressure on OB is reached at which pressure, the vapour states to change into

a liquid (condensation) and the two (liquid and vapour) remain in remain equilibrium at this pressure.

Further increase in pressure beyond curve OB compresses the remaining vapour causing a further decrease in volume until all is aliquid as phase O

When phased O is subjected to a decrease in temperature at constant pressure the liquid continues to loose but with out change in phase until curve OC is recharged 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) Thee phase diagram of carbon dioxide (CO_2)

Diagram;

Point A is the triple point of CO_2 ie 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 ie the temperature beyond which CO_2 can not be liquefied no mater the applied pressure.

Curve AO represents the solid-vapour equilibrium or vopour 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 ie,

 (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 with out a change in phase. However further heating of the solid makes it liquefied at its melting point when a long curve AB. occurs At this point the solid remains in equilibrium with the a liquid.

Further heating of the solid turns every thing into a liquid when the liquid is heated consciously 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 deceasing its pressure causing an increase in its volume and it change into a vapourie it sublimes. If the pressure of the liquid is decreased, the liquid change to a vopour.

3. **Three phase diagram of sulphur.**

   Diagram;

Sulphur has two allotropsie Rhombic and monoclinic sulphur which are stable over different temperatures. The transition temperature of 96^0C determines which allotrop is stable at what temperature Rhornbic is stable at temperatureless than 96^0C but monoclinic is stable At temperature greater than 96%. Point C is called the triple point of sulphur where all the three phases can exist.

Point D is called the intical point of sulphur. When any of the phase is subjected to change in temperature of pressure it will disappear and another dominates.

When Rhombic Suphur is heated no change in phase occur but expands causing an increase in volume. This continues until curve EF is reached. When rhombic sulphur starts Liquifying at its mp. The solid remain in ………either 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 number 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 presents
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 change to point B

b) Solution

i) The temperature and pressure beyond which the vapour can not be liquefied no matter the apllied 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 suphur.

When the curve EF is reached, rhombic sulphur turns into monoclinic sulphur and the two remain in equilibrium at the transition temperature (96^0C). Further decrease in pressure with sight increase in temperature all rhombic sulphur turns into monoclinic sulphur is reduced it nattiness 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 vopour and the solid remains in equilibrium with the vapour at a given temperature and pressure.

Further decrease in pressure with sight income in temperature all solid monoclinic turna into sulphurvapour.

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 solifies 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 0^0C because the presence of Nacl in

the solution depresses the freezing point of water. Similarly when a merely saturated solution of sodium chloride is cooleds, crystals of sodium chloride form at a temperature lower than the true freezing point of Nacl becauseH_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 0^0C 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 <u>constant pressure</u> solidifies at a <u>constant temperature</u> to give ales erogenous solid of the same composition. The temperature at which an eutectic mixture solidifies is called an <u>eutectic temperature.</u> It is defined as then constant temperature is oil 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 holeogenous 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 fractuations in atmosphere pressure.

    ii.   They can be separated by physical means yet ......can 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 ofNaCl of composition about 55% sodium chloride is cooled from a temperature above 30^0C, 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 unitl 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 nepthane 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 napthane 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 reacted 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 nepthatene and Benzene solidifies out as constant temperature forming an eutectic mixture and this continues unitl 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
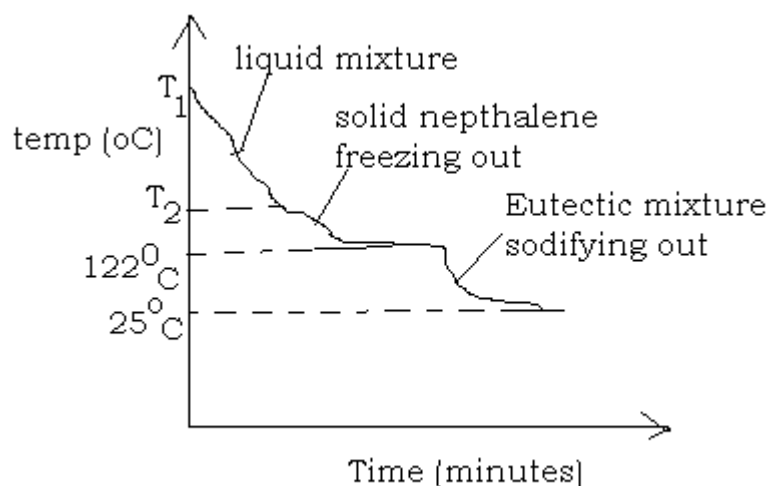
Qn: Explain what is meant by the term Eutectic mixture

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^{0}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^{0}C is cooled to room temperature.

(c) If the mixture of 400^{0}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^{0}C and 271^{0}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 (^{0}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^{0}C was gradually cooled.

The graph curve is V. shaped.

Pure bismuth has a high freezing point of 271^0C but the freezing point lowers along AE due to increase in the mount of cadmium which acts 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 1 from 350 ^{0}C until a temperature lower than 271^0C at point X along curve AE. At this point pure bismuth starts solidifying out and remains in equilibrium with the liquid mixture. At 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.

E_1- 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 avapour 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 the liquid-vapour equilibrium.
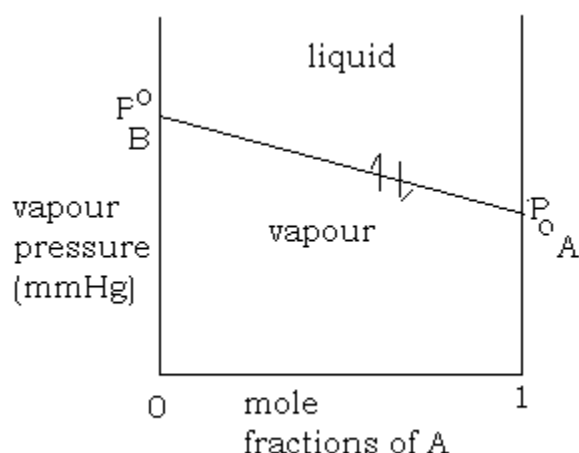
B is more volatile and in its pure form it exacts a high vapour pressure compound to A which is les volatile.
An increase in the Amount of A in the mixture causes a decrease in the vopour pressure of B until a point is reached when it is only pure A that is expecting ap a vapour pressure which is less than that of pure B.

Binary ideal solution and Renault's law
For binary ideal solution , Result's law is obeyed exactly the law state the partial vapour pressure of a component per an idea solution is equal to the saturated vapour pressure of a pure component at that temperature multi plied by the mole fraction of a component in the liquid mixture ie
P1 = Xipi   where Pi = Partial vapour pressure of component
In the liquid mixture   Pi =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

vapourabove 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.

$P_A = X_A P_A$ & $P_B = X_B P^0_B$

X_A = mole fraction of A

X_B = mole fraction of b

P^0_A & P^0_B = Vapour pressures of pure A and B at a particular temperature.

But mole fraction of a component

$X_A = \dfrac{\text{no of moles of A}}{\text{Total no of moles in the mixture}}$

$X_B = \dfrac{\text{no of moles of B}}{\text{Total no of moles in the mixture}}$

If n $_A$&n$_B$are the moles of A & B respectively in the liquid mixture.

Then $X_A = \underline{n_A}$ & $X_o = \underline{n_B}$

$n_A + n_B n_A + n_B$

The total vapour pressure above the boiling liquid is given as

$P_1 = P_A + P_B$

OR

$P_T = X_A P^0_A + X_B P^0_B$

But for ideal solution

$X_A + X_B = 1$

OR

$X_A + X_B = 100$

$P_1 =$

$X_A = (1-X_B) + A_B P^0_B$

OR

$P_r = P^0_A (100 - X_B) + X A_B P^0_B$

The magnitude of P_A and P_B above the boiling liquid depends on the mole of the components A and B respecting ie

$P_A \times X_A$ & $P_B \times X_B$

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: $P^0{}_A > P^0{}_B$ 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 al B above the liquid mixture at a given temperature.

The above phase diagram is only true for a binary ideal solution.

An ideal solutions 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

At88°C thevapour pressures of benzene and toluene are 935 and 378 mmHg respecting. 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

$X_B = \dfrac{2}{(1+2)} = \dfrac{2}{3}$

$X_T = \dfrac{1}{3}$

$P_B = X_{Ben} \ P_B$

$\dfrac{2}{3}$x 935

= 623.3

$P_T = X_T \times P_T^o$

$= \dfrac{1}{3}$ (373)

= 126

P 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 20^0C. Calculate the vapour pressure of the mixture containing 0.5 mole of each liquid at 20^0C

Solution

P_A^0 $\quad\quad\quad$ $A_A = (\frac{0.5}{0.5\ x\ 0.5}) = 0.5$

P_B^0 $\quad\quad\quad$ $X_B = (\frac{0.5}{0.5\ x\ 0.5})$ $\quad = \quad 0.5$

Moles of A = 0.5 Moles

Moles of B = 0.5 moles

$P_A = X_A P_A^0$

$\quad$ =B $\quad$ = 0.5Mole

$P_A = X_A P_A^0$

= (0.5 x 10)

= $5KNM^{-2}$

$P_B = X_B P_B^0$

0.5 x 2.92 KNM-2

$\quad\quad$ **=146**

P Total = P_A + P_B

$\quad$ = 1.46 + 5

6.46 KNM^{-2}

Calculate the vapour pressure of the solution containing 50g of heptanes and 35g of octane at 200C (the vapour pressure of heptanes and octane at 200C are 473.2 Pa and 139.8 Pa respectively

Solution

RFM of Heptane (C_7H_{10}) = (12 x 7) + (1 x 16)

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ = 100

Moles of heptanes = $(\frac{50}{100})$

$\quad$ = 0.5 moles

Moles of actare

RFM of actare (C_8H_{18})

Moles = $\frac{38}{114}$

= $\frac{1}{3}$

Total moles = $\frac{1}{2} + \frac{1}{3} = \frac{5}{6}$ in mixture

X neptane = $(\frac{\frac{1}{2}}{\frac{5}{6}})$

= $\frac{6}{10}$

X actare = $\frac{\frac{1}{3}}{\frac{5}{6}}$)

$= \frac{6}{15}$

$P_H = X_H.P_H^0$

$= (\frac{6}{10} \times 473.2)$

= 283.92 Pa

$P_0 = X_0 P_O^0$

= 5592Pa

Vapour pressure of solution

$P_1 = P_0 + P_H$

55.92 + 283.92

= 339.84Pa

Note

For a binery ideal liquid mixture made of two components A and B, it follows that the forces of attraction between the molecules of A (Cohensive forces) and those of molecule by B (Cohensive 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 (Cohensive forces) are equal in magnitude and kind to the intermolecules forces of attraction between unlike molecules (adhensive forces).

Ideal miscible liquid mixture, are rare and many immisable 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

a. An ideal solution is one that obeys Roult's law through out its composition. The solution is formed with no volume change and temperature change. Such a solution the cohensive forces between the molecules ofcomponents are equal in magnitude and kind to the adhensive forces between the molecules of the components in the mixture.

b. For solutions that do not obey Roult's law or non ideal solutions. The forces of attraction in mixture between the molecules (cohensive 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 composit ion 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.biling 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 Roult's law for ideal solutions

(b) A mixture of liquids A and B obeys roult's law the vapour pressures of A and B are 380, and 445mmHg respectively at 20^0C.

 (i) Calculate the composition fot he vapour containing equal moles of each component in the liquid mixture at 20^0C.

(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 = ½

       X_B= ½

       $P_{A=}X_A P_B^0$ P_B= $X_B P_B^0$

       = ½ x 380   ½ x 445

= 190mmHg   = 222.5mmHg

$P_T = P_A + P_B$

= (190 + 222.5)mmHg

= 412.5mmHg

$Y_A = \frac{190}{412.5} \times 100$ $Y_B = \frac{222.5}{412.5} \times 100$

= 46%   =54%

B is more volatile because it is more richer in vapour phase.

Qn: Two components A and B form an ideal solution. At 50⁰C 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

$X_A = 0.4$

$X_B = 0.6$ (1-04)

$P_A = X_A P_A^0$ = (0.4 x 200)

             = 80mmHg

$P_A = X_B P_B^0$ = (0.6 x 640)

             = 384mmHg

$P_T = P_A + P_B$

= (80 + 384)mmHg

= 464mmHg

$Y_A = \frac{80}{464} \times 100$

= 17%

$Y_B = \frac{354}{469} \times 100$

= 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

$X_A = 0.17$

$X_B = 0.83$

$P_A = X_A P_A^0$ = (0.17 x 200)

             = 34mmHg

$P_B = X_B P_B^0$ = (0.83 x 640)

      = 531.2mmHg

$P_T = P_A + P_B = 565.2$

$Y_A = \frac{34}{565.2} \times 100$

= 6%

$Y_B = \frac{531.2}{565.2} \times 100$

= 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 anmnd 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 gives a vapour riches in Y and X because Y is more volatile. This leaves the residue in the flask riches 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 compositin 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 consting of gas beads which increase the surface area even which the vapour condenses and seperates out the various components condenses around the glass beads but it is revolatilised by the upcoming vapourand is led into the liebig. Condenser where it is cooled and obtained in the pure term as a distillate. The vapour due to the drip 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 20^0C
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 Roult's law (ideal behavior)

Deviations a rise 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 roult's law such liquid mixtures form non ideal solution.

If the forces of attraction between like molecules in the mixture (cohensive forces) are stronger than the forces of attraction between unlike molecules (adhesive forces) then the liquid mixture is said to deviate positively from Rout'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 Roult'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 spare 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 devate 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 adhensive forces are stronger than the cohesive forces. The net effect is allowed 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 fromRoult's law, there is a decrease in volume in temperature ie heat is given cut 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 Roult'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 Roult's law.

Positive deviation	Negative deviation
Cohessive 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 Roult's law	The mixture has a lower V.P than expected from Roult'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 Roult'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^{0}C)
Shows negative deviation from Roult'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 Roult's law

Solution
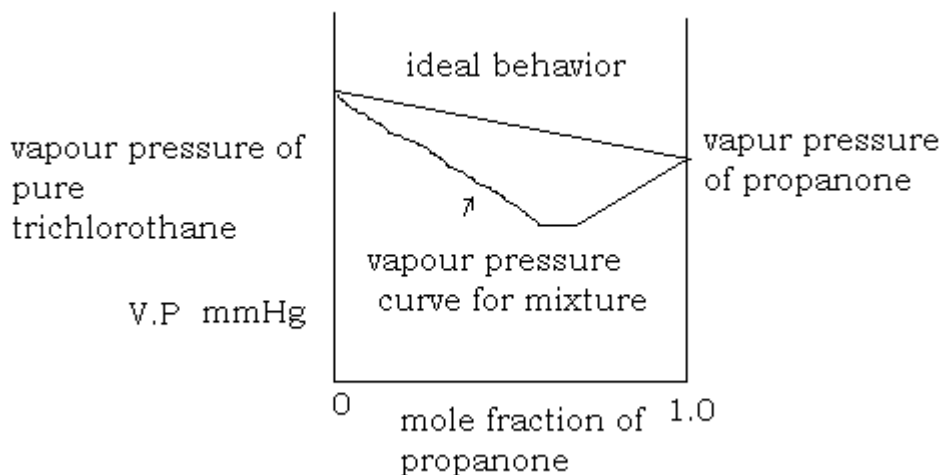
Explanation

The curve of the mixture lies below the line 4 ideal behavior. For Roult'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 propanane are weaker than the forces of attraction between molecules of chloroquine and propanone. Molecules of chlorophones associates via weaker vander wall forces similarly molecules of chloroform and propanate 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
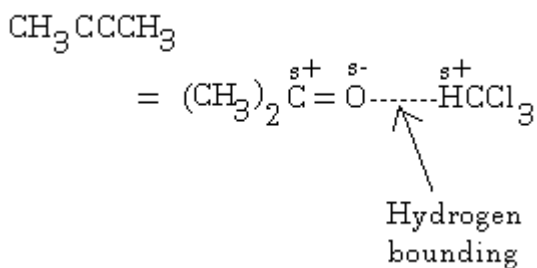
Qn: A mixture of ethanol (Bpt-78^{0}C) and water (Bpt – 100^{0}C) deviates positively from Roult's law

(i)   Draw the vapour pressure composition diagram for the mixture in relation to Roult's law

(ii)   Explain the shape of the curve for the vapour pressure of the mixture in relation to Roult's law.
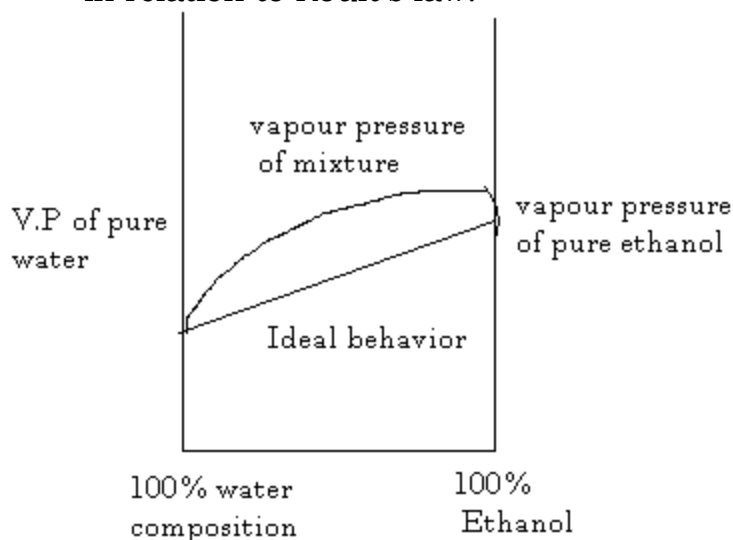
The curve for the mixture is above the curve for ideal behavior. For Roults law to be true, cohesive forces must be similar to adhesive forces

The adhesive forces between molecules of water that 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 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 molecules of pure water and those in molecules of pure ethanol hence the escaping tendency of molecules of each component is increased in presence of molecules of the other leading to an increase in vapour pressure of the mixture.

Liquid mixture that deviates from Routt's law other positively or negatively can not 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 Roult's law

The composition x corresponds to the composition with the least or weakest intermolecular forces of attraction.

On the vapour pressure composition diagram shows a maximum and on the boiling point comp diagram 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 ateotropic

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 technicque of a teotropic 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 past because 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 his fractionally distilled, the ateotropic mixture X collects as a distillate leaving the residue in flask as pure A.

If a liquid mixture of composition 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 ateoctrope 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.
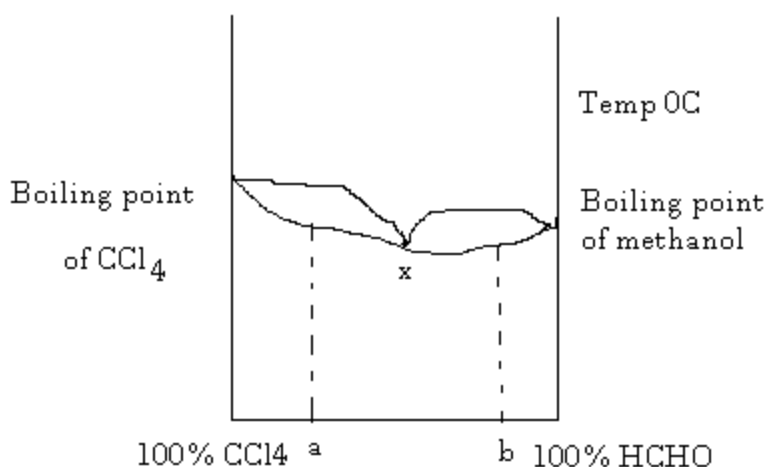
If a liquid mixture a is fractionally distilled, it boils to give a vapour which is richer in the Ateotropic mixture leaving the residue in the richer in carbon tetrachloride cooling this vapour procedures a liquid mixture of the same composition which when heated produces a vapour richer in the a teotropic 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 ateotropic 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 distilled as the ateotrope.

Note: Molecules of carbon tetrachloride associate via weak vandarwaal forces similarly molecules of methanol associate via weak vandarwaal forces. When mixed the molecules of carbon tetrachloride associates via much weaker vandar-waal-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 vandar – waal 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 vandar-waal forces due to the high molecular mass so the boiling point is higher than that of the a teotropic 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 than the molecules of pure carbon tetrachloride. The decrease in boiling pt continues a liquid mixture of composition x which has the weakness vandar – waal forces and the lowest boiling pt is attained.

Boiling point composition diagram for a liquid mixture that deviates negatively from Raoul's law.

When a liquid mixture that deviates negatively from Roult's law is fractionally distilled, the distilled 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 a zoetrope 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

It a liquid mixture of composition is fractionally distilled at its Bpt while the residue in the flask is the azeotropic mixture containing 40% A and 50% B. 70%A and 30%B.

If a liquid mixture of composition b is distilled fractionally pure B is obtained as the distillate at the Bpf leaving the residue in the flask as the a zoetrope 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 resuls 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 xeotropic 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 zoetrope 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 110^0C.
   (ii)   Sketch a labeled diagram of the boiling point composition for HCl and water system (Boiling pt of water is 100^0C
   (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 ($\frac{20}{100}$ x 1.18)

= 0.236gcm^{-3}

Mass of acid in gl^{-1}

1cm^3 of acid contain 0.236g

1000cm^3 of acid contain $\frac{0.236}{1}$ x 1000

= 236gl^{-1}

RFM od HCl

(1 x 1) + (35.5 x 1)

= 36.3

Majority of original acid

$=\frac{conc\ (gl^{-1})}{RFM}$

$=\frac{236}{36.5}$

= 647M

647 moles are contained in 1000cm^3 of acid

2 moles are contained in

$\frac{1000 x 2}{6.47}$

= 309.1 cm^3

So to prepare 2M solution of hydrochloric acid measure 309.1cm^3 of he 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 soilid is dissolved in methanol the Bpt is raided

    d.   The following data were obtained for a mixture cychexane (Bpt = 81^{0}C) in methanol (Bpt = 65^{0}C)

Bpt (^{0}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 Roult's law

Use your graph to obtain the composition of the a zeotrop and explain why it can not nbe 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.

$$CaO(s) + H_2(l) \longrightarrow Ca(OH)_2(aq)$$
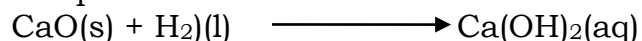
Distillation using a third component

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 100^0C while phenyl Amine boils at 184^0C at 760mmHg. A mixture of phynyl Amine and water boils at 98^0C 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 a ………technique 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 condence 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.

warm water out

cold water

substance A

water

heat

heat

water

heat
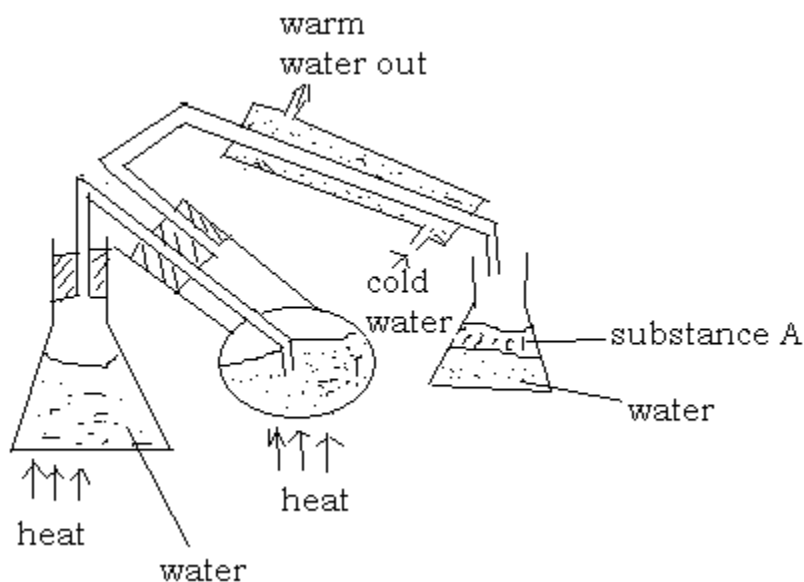
Composition of distillate

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 $= \dfrac{VP\ of\ substance\ x\ RMM\ of\ substance}{VP\ of\ water\ x\ Rmm\ of\ water}$

The mass of the substance can be expressed in gas asa 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 extert a reasonable vapour pressure at a given temperature.

The impurities must e non volatile this ensures that they are not part of the distillate.

Examples

Compound x was steam distilled at 80^0C and 760mmHg the distillate was found to contain 9m0% by mass of X (VP of H_2O at 80^0C = 240). Calculate the formular mass of X

$\dfrac{mass\ of\ sub}{mass\ of\ H_2O} = \dfrac{VP\ of\ substance\ x\ RMM\ of\ substance}{VP\ of\ water\ x\ Rmm\ of\ water}$

$$\frac{90}{(100-90)}$$

For the mixture to boil

$P_A + P_w$ = 760mmHg

P_A = (760 – 240)

$$\frac{90}{(100-90)} = \frac{(760-240)x\ molar\ mass\ of\ x}{240\ x\ 18}$$

Molar mass of X = $\frac{240\ x\ 18x9}{(760-240)}$

= 74.8g

When asp y was distilled at standard atmospheric pressure and 96^{0}C, The VP of the H_2O at this temperature was 730mmHg and the distillate contained 74% water. Calculate the molar mass of y.

Solution

$$\frac{mass\ of\ y}{mass\ of\ H_2O} = \frac{VP\ of\ y\ x\ RMM\ of\ y}{VP\ of\ H_2O\ x\ Rmm\ of H_2O}$$

RMM of y = $\frac{mass\ of\ y\ x\ V.P\ of\ H_2O\ x\ RMM\ of\ H_2O}{VP\ of\ y\ and\ RMM\ of\ H_2O}$

Qn: Amino hydroxyl benzene is usually contaminated with some impurities to remove the impulties it was steam distilled at 96^{0}C and standard atmospheric pressure. At this temp, the VP of water was 654mmHg. Calculate the percentage composition of the distillate.

Solution

RFM of H_2O = 18

= (12 x 6) + (1x7) + (10x1) = 109

Vapour of 2-nitro phenol = (760 – 654)

106mmHg

$$\frac{mass\ of\ sub}{mass\ of H_2O} = \frac{V.P\ of\ substance\ x\ RMM\ of\ substance}{VP\ of\ H_2O\ x\ RMM\ of H_2O}$$

$$= \frac{106\ x\ 109}{654\ x\ 18}$$

$$\frac{mass\ of\ sub}{mass\ of\ H_2O} = \frac{0.981}{1}$$

% of substance = $\frac{0.981}{1.981}$ x 100

= 49.5%

Total mass = 0.981 + 1

= 1.981

% of water = $\frac{1}{1.981}$ = 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 93^0C and 750mmHg the distillate contained 55% of y by mass. Calculate the relative molecular mass of y (the partial vapour pressure water at 95^0C is 65.4mmH)
Let the total mass of the distillate be x

$$\frac{0.55\,x}{0.45x} = \frac{(RMM)x\,(750-654)}{654\,x\,18}$$

$$\frac{654\,x\,18\,x\,0.55}{740-654\,x\,0.45}$$

= 149.875
184
The relative molecular mass of y is 149900
= 149.9g

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 Rem of CO_2 (12x2) + (16 x 2) = 44

$\frac{y}{2}$-1 Composition of carbon = $\frac{2}{18}$ x 15.78

Y = 2 RFM of H_2O = (1x1) + (16x) = 18

C_3 composition of hydrogen = $\frac{2}{18}$ x 538 = 0.598

No of moles:	carbon	Hydrogen
	$\frac{4.306}{12}$	$\frac{0.598}{1}$

$$\frac{0.3586}{0.3586} \qquad \frac{0.598}{0.3586}$$

1:1.7   x3

3:3

X was steam distilled at 80^0C and 760mmHg and the distillate was found to contain 90.8% by mass of X (The vapour pressure of water at 80^0C is 240mmHg).

Calculate the formula mass of x

$$\frac{mass\ of\ x}{mass\ of\ H_2O} = \frac{RMM\ opf\ x \times V.P\ of\ x}{Rmm\ of\ H_2O \times V.P\ of\ H_2O}$$

$$\frac{90.8}{9.2} = \frac{(Rmm)_x \times (760-240)}{18 \times 240}$$

$$(Rmm)_x = \frac{90.8 \times 18 \times 240}{[9.2 \times (760-240]}$$

= 81.993

≈ 82

The formualr mass of X is 82

Reduce the formula of X

$(C_3H_5)_x = 82$

$[(12 \times 3) + (1\times5)]_x = 82$

$41x = 82$

$(C_3H_5)_2$

$= C_6H_{10}$

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/^0C	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 o 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 container 1.6g of water and 1.1g of x

Calculate the relative molecular mass of X using the informationfrom the graphs you have drawn.

Explain the principle of separating of mixture by stream 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.

Vapour pressure of $X = 12K.pa$

Vapour pressure of $H_2O = 88.5k.pa$

Mass of $x = 1.1 g$

Mass of $H_2O = 1.6g$

$$\frac{moles\ of\ water\ in\ distillate}{moles\ of\ X\ in\ distillate} = \frac{vapour\ pressure\ of\ water}{vapour\ pressure\ of\ X}$$

$$\frac{\frac{MH_2O}{RFM}}{\frac{Mx}{Mr.x}} = \frac{V.P\ H_2O}{VP\ of\ x}$$

$$\frac{M_{H20}}{Mr_{H20}} \times \frac{Mrx}{Mx} = \frac{V.PH2O}{(V.P)_x}$$

$$\frac{M_{H20}}{Mr_x} = (V.P)H_2O$$

$$\frac{1.1\ x\ 88.5\ x\ 18}{1.6\ x\ 12}$$

$Mr. = 91.27$

The three component system;

Distribution / partion of a solute between two immiscible solvents.
This is a case of three component system if a solute (solid of 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 on equilibrium is established. At equilibrium, the ratio of the conc of the solute in is solvent to the conc of a solute in another solvent in 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 equilibrium whether solute is soluble both solvents at a given temperature.
Suppose a solute x is shaken with a mixture of two immiscible solvent A and B at a given temperature, then at equilibrium.

$\frac{concn\ of\ X\ in\ A}{concn\ of\ X\ in\ B}$ = constant

OR $\frac{concentration\ of\ x\ in\ A}{concentration\ of\ x\ in\ B}$ x K_D

The partition coefficient K_D is derived from the partition law which *states that when a solute a solute miscible in two immiscible solvent in the same system is shaken in a constant ratio at constant temperature when equilibrium is attained.*
The pattion law has some initations
i). Temperature must be kept constant.
ii). The solute must be soluble in both solvent.
iii) The solute must not dissociate rassonate in either solvent it should remain

in the same molecular state
(iv)The should not react with either solvent
(v) The solvents must be immiscible
(v)The solution used must be fairly dilute i.e solute should not saturate either solvents.

Determination of K_D between solvent

Determination of KD of Ammonia between water and trichloromethane

Procedure;
- A given volume of a standard solution of Ammonia is shaken with a given solume of a mixture of water and trichloromethane in a stopper separating funnel at a given temperature for about 15minutes. This ensures that equilibrium is attained.
- The mixture allowed to stand to let the layers separate out. Equal volume of either layer are pipped and separately titrated with a standard solution of HCl using phenolphthaline indicator Ammona reacts with HCl according to the equation
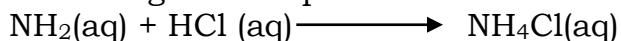
  NH$_2$(aq) + HCl (aq) $\longrightarrow$ NH$_4$Cl(aq)
- The volume of HCl required to react end point is noted and theconcn of ammonia in either layer can be calculated. The value of KD is obtained from the expression.

  KD = $\dfrac{[NH_3]in\ water}{[NH_3]in\ trichromethane}$
- 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$_2$O are reduced in a separating refunnel. 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 pipeted and titrated separately with standard solution of sodium hydroxide using phenolpthalern as the indicator.
- Ethanoic acid reacts with sodium hydroxide according to the equation.
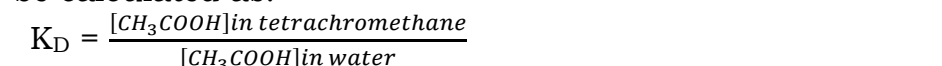
  CH$_3$COŌH(eq) + NaOH(aq) $\longrightarrow$ CH$_3$COŌNa$^+$(aq) + H$_2$O(l)
- The volume ofsodium hydroxide required to reach end point for the separate layers is noted and the concn of ethanoic acid in either layer is then determined from which the partition coefficient of ethanoic acid can be calculated as.

  K$_D$ = $\dfrac{[CH_3COOH]in\ tetrachromethane}{[CH_3COOH]in\ water}$

- Ethanoic acid is much more soluble in tetrachlorimethane than water and theKD 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 pippeted kin separate conical flask and separately titrated with a standard solution of sodium thiosulpate 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
$$I_2(aq) + 2S_2S_2O_3^{2-}{}_{(aq)} \longrightarrow 2I^-(aq) + S_4O_6^{2-}{}_{(aq)}$$

Note: Iodide is acovalent solute, non-polar with limited interaction between its molecules andwater so it has avery law solubility in water.

APPLICATIONS OF PARTITION LAW; The main applications include;
(i) Solvent attraction.
(ii) Determination of formula of complexes.
(iii) Chromotograpy.

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 acqueous 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. 100cm^3 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 other (the KD of Z ether and water is 5)

Solution
$$KD = \frac{conc\ of\ Z\ in\ other}{conc\ of\ Z\ in\ acqueos\ (water)}$$

$$5 = \frac{\frac{a}{100}}{\frac{30-a}{100}}$$

150-5a-a

$a = \dfrac{160}{6}$

= 20g

The mass extracted by 100Cm^3 of t is 20g

Using the two 50cm^3 portion of ether

First portion

Let b the mass extracted by the first portion of 5cm^3

The mass of a remaining acqueos layer is (30-b)g

$K_D = \dfrac{conc\ of\ z\ in\ ether}{concn\ of\ z\ in\ water}$

$S = \dfrac{\frac{b}{50}}{\frac{30-b}{100}}$

$S = \dfrac{2b}{30-b}$

150-5b = 2b

$b = \dfrac{150}{7}$

2143g

Mass remaining in acqueos layer = (30 – 2143)

8.57g

$KD = \dfrac{concn\ of\ z\ in\ ether}{concn\ of\ z\ in\ water}$

$S = \dfrac{\frac{c}{30}}{\frac{8.57-c}{100}}$

$S = \dfrac{2c}{8.57-c}$

2c = 5 x 8.57. 5c

7c = 40.85

C = 6.12g

= 27.55g

2. 100cm^3 of an acqueous solution containing 20g of w was shaken once with 50cm^3 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 25cm^2 of ether.

Solution

Let the mass of w extracted by 50cm^3 of ether be xg

Mass of w remaining in water = (20 – x)g

$KD = \dfrac{concn\ of\ w\ in\ ether}{concn\ of\ w\ in\ water}$

$S = \dfrac{\frac{x}{50}}{\frac{20-x}{100}}$

$4 = \dfrac{2x}{20-x}$

80 – 4-x = 2x

X = 13.3g

First partition

Let the mass of w extracted by the first 26cm^3 portion be y

Mass of w remaining (20-y)

$$KD = \frac{\frac{y}{25}}{\frac{20-x}{100}}$$

$80 - 4y = 4y$

$$Y = \frac{80}{8}$$

$Y = 10g$

Mass remaining in acqueous layer = (20-10)

= 10g

2nd portion

Let z be the mass of w extracted by the second portion. Then mass of w remaining in acqueous layer = (10-z)

$$y = \frac{\frac{z}{25}}{\frac{10-z}{100}}$$

$$y = \frac{4z}{10-z}$$

$40 - 4z = 4z$

$$z = \frac{40}{8}$$

z=5g

total mass extracted by using portions

= (5 + 10)₂

= 15g

3.100cm³ of an acqueos 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 acqueous layer required 127.5cm³ of the acid while 25cm3 of the chloroform layer required 5cm² of the same acid, calculate the value of K_D for the distribution of ammonia between chloroform and water

Solution

$NH_3(aq) + HCl (aq) \longrightarrow NH_4Cl(aq)$
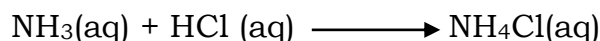
Organic layer

1000cm³ of solution contain 0.1 moles of HCl

5 cm³ of solution contain $(\frac{0.1 \, x \, 5}{1000})$ moles of HCl

Moles of ammonia reacted $(\frac{0.1 \, x \, 5}{1000})$ moles

25cm² of solution contain $(\frac{0.1 \, x \, 5}{1000})$ moles of ammonia

1000cm³ of solution contain $\frac{0.1 \, x \, 5}{1000}$ x $\frac{1000}{25}$

= 2 x 10⁻²M

Aqueous layer

1000cm³ of solution contain 0.1 moles of HCl

827.5cm³ of solution contain $(\frac{0.1}{1000}$ x 127.5) moles of HCl

1 mole of HCl reacts with 1 moles of NH₃

Moles of NH₃ reacted

$= (\frac{0.1 \, x \, 127.5}{1000})$moles

$25cm^3$ of solution contain$(\frac{0.1\,x\,127.5}{1000})$moles of NH_3

$1000cm^3$ of solution contain $(\frac{0.1\,x\,127.5}{1000}\,x\,\frac{1000}{25})$moles

$= 51 \times 10^2 M$

$K_D = \frac{[NH_3]in\,CHCl3}{[NH_2]in\,H_2O}$

$K_D = \frac{2\,x\,10^{-2}}{5.1\,x\,10^{-1}}$

$KD = 0.04$

4. $50cm^3$ of 1.5M ammonia solution were shaken with $50cm^3$ of trichloromethene in a separating funnel. After the layers had settled, 20 cm of the chloroform layer were pippeted and titrated with 0.05m HCl. If 23Ml of the acid were required for neutralization, calculate the value of KD of Ammonia between water and chloroform at that temperature.

Solution

$1000cm^3$ of solution contain 0.05 moles of HCl

$23cm^3$ of solution contain $(\frac{0.05}{1000}$ x 23) moles of HCl

1 mole of HCl reacts with 1 mole of NH_3

Moles of NH_3 reacted

$= (\frac{0.05\,x\,23}{1000})$

$20cm^3$ of solution contain $(\frac{0.05\,x\,23}{1000})$moles of NH_3

$1000cm^3$ of solution contain $(\frac{0.05\,x\,23}{1000})$ x $\frac{1000}{20}$

$= 0.0575M$

Conc NH_3 remaining in acqueous solution layer

$= (1.5-0.0575)$

$= 1.4425M$

$K_D = \frac{[NH_3]in\,H_2O}{[NH_2]in\,CHCl3}$

$= \frac{1.4425}{0.0575}$

$= 251$

5. $50cm^3$ of an acqueous 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 seperate out. $20cm^3$ of each layer were pipeted and titrated separately against a 0.05M sodium thiosulphate solution using starch indicator.

The organic layer required $47.50cm^3$ while the acqueous layer required $7.2cm^3$ of the same solution of sodium thiosulphate. Calculate the value of K_D of I_2 between the organic layer and the acqueous layer.

Solution

Equation

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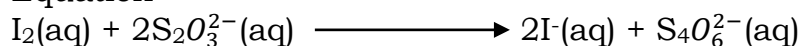
Organic layer

$1000cm^3$ of solution contain 0.05moles of $S_2O_3^{2-}{}_{(aq)}$

$47.5cm^3$ of solution contain $\frac{0.05}{1000}$ x 475 moles of $S_2O_3^{2-}{}_{(aq)}$

$(\frac{0.05}{1000}$ x 47.5) moles of $S_2O_3^{2-}$ react with ½ $(\frac{0.05}{1000}$ x 475) moles I_2

20cm³ of solution contain ½ $(\frac{0.05 \; x \; 475}{1000})$ moles of I_2

1000cm³ of solution contain $(\frac{1}{2}$ x $\frac{0.05 \; x \; 475}{1000}$ x $\frac{1000}{25})$moles of I_2

= 0.0475M

Aqueous layer

1000cm³ of solution contains 0.05moles of $S_2O_3^{2-}$

75cm³ of solution contain $(\frac{0.05 \; x \; 75}{1000})$ moles of $S_2O_3^{2-}$

2 moles of $S_2O_3^{2-}$ react with 1 moles of I_2(aq)

$(\frac{0.05 \; x \; 7.5}{1000})$ moles of $S_2O_3^{2-}$ will read with $\frac{1}{2}$ $(\frac{0.05 \; x \; 75}{1000})$ moles of I_2

1000cm³ of solution will contain (½ x $\frac{0.05 \; x \; 75}{1000}$ x $\frac{1000}{25})$ moles of I_2

$K_D = \frac{[I_2]in \; CCl_4}{[H_2] \; in \; H_2O} \frac{0.0475}{7.5 \; x \; 10^{-3}}$

= 6.3

2.Determination of formula of complex ions

Eg the number of ligands in the complex $(Cu(NH_4)_2]^{2+}$. The partition law can be used to determine the formular of the complex ion, found in one of the layers ie acqueous 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.

Cu^{2+}(q) + nNH_3(aq) $[Cu(NH_3)_n]^{2+}$

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 phenolpthalan indicator.

The concn of ammonia is ether layer is then determined free and ammonia complexed.
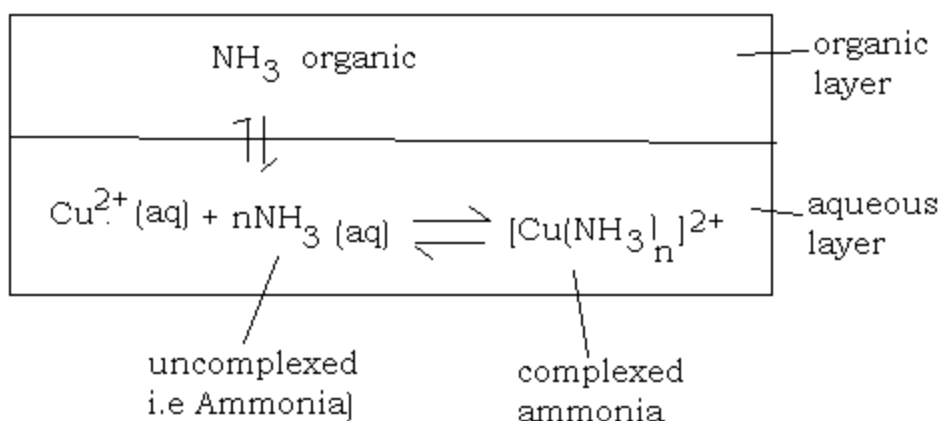
From the partition coefficient of ammonia between water and acquoeys layer can be determined

$$K_D = \frac{concn\ of\ free\ NH_3\ in\ aq.layer}{[NH_3]organic}$$

In the acqueous

$[NH_3]_{total} = [NH_3]_{free} + complex\ [NH_3]_{free}$

$[NH_3]_{(aq)}\ complexed = [NH_{3\ total}] - [NH_3]_{free}$

Knowing the total concn of Ammonia in the acqueous and Ammonia concn free in the acqueous layer, the concentration of complexed Ammoia can be determined.

$[NH_3]_{(aq)}\ complexed = [NH_3]_{total} - K_D\ (NH_3)organic$

By company the concn of Cu^{2+} ions and complexed Ammonia in theaqueous layer, the formula of the complex formed between Cu^{2+} ions and Ammonia is obtained ie.

$[Cu^{2+}], [NH_3]_{fixed} = 1.n$

Question: Excess NH_3 was shaken with an acqueous 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 acqueous layer to form the complex $[Cu(NH_3)_n]^{2+}$
At equilibrium the concn of Ammonia in the trichloromethane and the aqueous layer were 0.021 and 0.725 mol l^{-1} respectively. (The partion coefficient of CHCl$_2$ between water and trichloromethane is 25cm^3.
Calculate
    (i)   The concn of free Ammonia in the aqueous layer
    (ii)   Theconcn of Ammonia that formed the complex with Cu^{2+} ions
    (iii)   The values of n in thecomplex and write the formula of the complex.
Solution
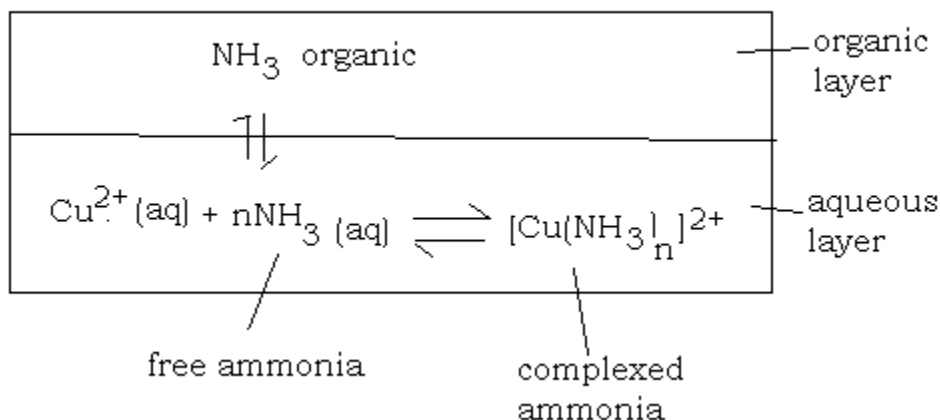
$K_D = \dfrac{[NH_3](aq) free}{[NH_3] organic}$

$25 = \dfrac{[NH_3] of\ free}{0.021}$

$[NH_3]free = 25 \times 0.021$

$= 0.525m$

Concentration of $[NH_3]$ complexed

$= [NH_3]_{total} - [NH_3]_{free}$

Volume of n

$[Cu^{2+}](aq) : [NH_3]_{fixed}$

$\dfrac{0.05}{0.05} : \dfrac{0.7}{0.05}$

n=40

n = 40

Alternatively, the value of m in the formula of the complex $[Cu(NH_3)_2]^{2+}$ can be obtained from the graph

From $[NH_3](aq)total = [NH_3]free + [NH_3](aq)$ fixed

But $[NH_3](aq)\ free = K_D[NH_3]$ organic

Substituting for $[NH_3]aq\ free$

We get

$[NH_3](aq)\ total = K_D[NH_3]$ organic + $[NH_3](aq)$ fixed

$y= Mx + C$

A plot of $[NH_3]aq$ total against $[NH_3]$ organic gives a straight line graph with Kd as the gradient and $[NH_3]aq$ fixed as the intercept on the y-axis
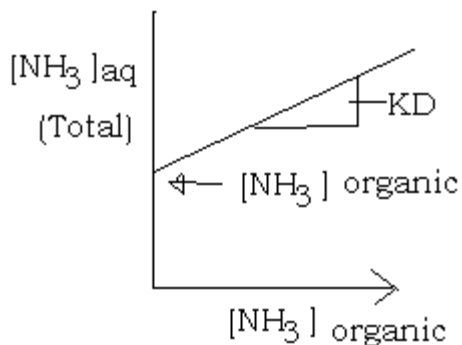
The concn of fixed Ammonia is obtained as the intercept for which the value of n can be obtained using the ratio Cu^{2+} $[NH_3]_{fixed}$ = 1:n

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 $CHCl_2$	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 he 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

Pippeted 10ml 0.5M HCl Vol required = 16.5cm

Organic layer

Pipeted

2cm³   0.05M HCl vol required 10.2cm³

Organic layer

1000cm³ of solution 0.05moles of HCl

10.2cm³ of solution contain ($\frac{0.05}{1000}$ x 10.2) moles of HCl

$NH_3(aq) + HCl\ (aq) \longrightarrow NH_4Cl(aq)$
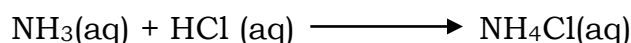
1 mole of NH_3 reacts with 1 mole of HCl

Moles of NH_3 reacted = ($\frac{0.03}{1000}$ x 10.2) moles

20cm³ of solution contain ($\frac{0.03}{1000}$ x 10.2) moles

1000cm³ of solution contain ($\frac{0.05}{1000}$ x 10.2 x $\frac{1000}{20}$) 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 ($\frac{0.5}{1000}$ x 16.5) moles ofHCl

$NH_3(aq) + HCl\ (aq) \longrightarrow NH_4Cl(aq)$
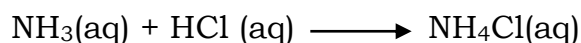
1 mole of HCl reacts with 1 mole of NH_3

Moles of NH_3 reacted ($\frac{0.5}{1000}$ x 16.5) moles

10cm³ of solution contain ($\frac{0.5}{1000}$ x 16.5) moles of NH_3

1000cm³ of solution contain ($\frac{0.5}{1000}$ x 16.5 x $\frac{1000}{10}$)

= 0.825M

But from $K_D = \frac{[NH_3](aq)free}{[NH_3]organic}$

$[NH_3]$free = K_D x $[NH_3](aq)$ organic

= (25 x 0.025)

= 0.652

$[NH_3]_{(aq)}$ complexed = $[NH_3]_{aq}$ total – $[NH_3]_{aq}$ free

= 0.825 – 0.625

= 0.2M

From the equation leading to the formation of the complex

$Cu^{2+}(aq) + nNH_3(aq) \qquad Cu(NH_3)_n^{2+}$
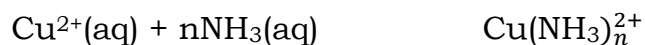
$1000cm^3$ of solution contain 0.1 moles of Cu^{2+} ions

$25cm^3$ of solution contain $(\frac{0.1}{1000}$ x 25) moles of Cu^{2+} ions

$50cm^3$ of solution contain $(\frac{0.1 \, x \, 25}{1000})$ moles of Cu^{2+} ions

$1000cm^3$ of solution contain $(\frac{0.1 \, x \, 25}{1000} \, x \, \frac{1000}{50})$ moles of Cu^{2+} ions

= 0.05M

$[Cu^{2+}]$: $[NH_3]$ complex

$\frac{0.05}{0.05}$ $\qquad$ $\frac{0.2}{0.05}$

1 : 4

The formular is $Cu(NH_3)_4^{2+}$

Determination of the equilibrium constant Kc

Partition can be used to investigate an equilibrium in acqueous 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.

$I_2(aq) + I^-(aq) \qquad I_3^-$
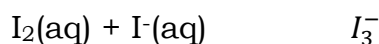
Only the covalent iodine molecules I_2 will dissolve in the organic solvent. If an acqueous solution of Iodine in Iodide ions is shaken with an organic solvent such as carbonisulphade. The equillibria below are established.
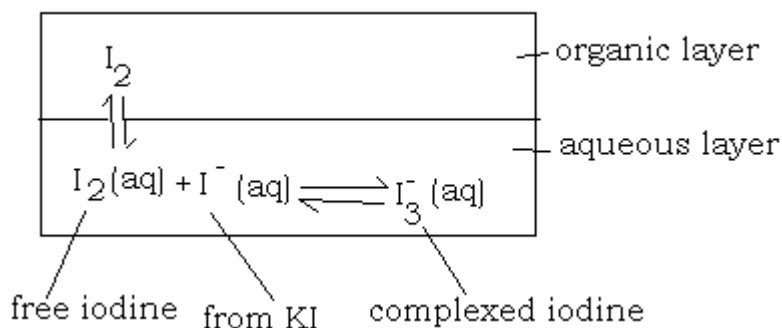
A sample from the organic layer is pippeted and titrated with standard sodium thiosulphate using starch indicator.

The concentration of Iodide in the organic layer can be determined. Eqn for reaction between iodine and sodium thiosulphate $(S_2O_6^{2-})_{(aq)}$

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

Knowing the concn of I_2 in the organic layer, the concn of free iodine in the acqueous layer can be obtained from the expression.

$K_D = \frac{[I_2]org}{[I_2]aq\ free}$

$[I_2](aq)\ free = \frac{[I_2]organic}{K_D}$

The value of K_D is obtained from the data on K_D values at a particular temperature.

Another sample of the aqueous layer is pippeted and titrated with standard sodium thiosulphate $(2S_2O_3^{2-})$ using starch indicator this gives the concentration of Iodine in the acqueous layer which includes the free iodine and the complexed Todine. The complexed iodine

$[I_3^-]$ is obtaind by subtracting the fire iodine from the total iodine

$[I_2^-] = [I_2]aq\ total - [I_2]aq\ free$

The concentration of iodide ions is obtained by subtracting

$[I_2]_{aq}$ from the original Iodide ions

Example: Iodine is dissolved in water containing 0.16M potassium iodkide and the solution is shaken tetra cloromethane. The concentration of iodine in the aqueous layer was found to to be 0.08M and that in the organic layer 0.1M. the partion coefficientfor Iodine between tetrachloromethane and water is 85. Calculate the equilibrium constant for the reaction.

$\qquad I_2(aq) + I^-(aq) \qquad\qquad I_3^-$
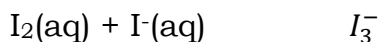
Solution

$[I_2]$ in $CCl_4 = 0.1M$
$K_D = \frac{[I_2]org}{[I_2]aq\ free}$
$[I_2]free = \frac{0.1}{85}$
$[I_2]aq = 0.08M$
$[I_3^-]_{(aq)} = [I_2]aq\ Total - [I_2]_{aq}\ free$

$= 0.08 - 1.176 \times 10^{-3}$

$= 0.0788$

Initial [I⁻] = 0.16M

[I⁻] reacted = 0.0788

[I⁻] at equilibrium = (0.16 − 0.0788)

= 0.0812M

$K_D = \dfrac{[I_3^-]}{[I_2][I^-]}$

$= \dfrac{0.0788}{(1.176\ x\ 10^3)(0.0812)}$

= 825.21mol⁻¹dm³

1. X is 12.0 times more soluble in trichloromethane that water. What mass of X will be extracted from 1.00dm³ an acqueous solution containing 25.0g by shaking with 100cm³ of trichloromethane.

2. The partition coefficient of y between ethaxyethane (ether) and water is 80. If 200cm³ of an acqueous solution containing 5g of y is shaken with 50cm³ of ethaxyethane. 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 50cm³ in volume and contains 4.00g of Z. the acqueous layer is 250cm² in volume and contains 1.00g of z. what is the partition coefficient of Z between ethaxyethane and water. (20.0)

500cm³ of aqueous solution of concentration 0.120 moldm³ is shaken with 50.0cm³ 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 (0.0154mol)

The distribution coefficient of A between ethaxyethane and water is 90. An acqueous solution of A with a volume of 500cm³ contains 5.00g. what mas of A will be extracted by

    i.   100cm³ of ethoxyethane and
    ii.   Two successive portions of 50.0cm³ of ethoxyethane

An organic acid is allowed to reach an equilibrium in a separating funnel containing 50cm³ of ethoxyethane and 500cm³ of water. On titration, 25.0 cm³ of the ethoxyethane layer required 22.5cm³ of 1.00moldm⁻² sodium hydroxide. Solution and 25.00m of the aqueous layer required 9.0cm³ of 0.0100 moldm⁻³ Sodium hydroxide solution. Calculate the partition coefficient for the acid between ethoxyethane and water.

7. A small amount of Iodide is shaken in a separating funnel containing 50.0cm³ of tetrachloromethane and 500cm³ of water. On titration 25cm³ of an

aqueous layer required 6.7cm³ of a 0.0550 moldm⁻³. Solution of sodium thiosulphate 250cm³ of the organic solvent require 27.2cm³ of 1.15moldm⁻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 4g in 12cm³ of y by extracting it with
    a. 12cm³ of x
    b. Three successive portions of 4cm³ of x

9. The partion of T between ethoxyethane and water at room temperature with 100cm³ of ethoxyethane at room temperature. What mass of T will be present in the ethoxyethane layer.
(b) What would be the totalmass of T extracted if the ethoxy...were used in the separate 50cm³ portions, instead of the single 100cm³ portion.

Solution

$K_D = 12 = \dfrac{}{[x]in\ H2O}$

Let mass of x extracted be Z

$12 = \dfrac{\frac{z}{100}}{\frac{25-z}{100}}$

$12 = \dfrac{z}{100} \cdot \dfrac{1000}{25-z}$

$12 = \dfrac{10z}{25-z}$

$22z = 300$

$t = \dfrac{300}{22}$

$z = 13.6g$

$KD = 80 = \dfrac{[y]ether}{[y]H2O}$

Let mass of y extracted from solution be x

$80 = \dfrac{\frac{x}{50}}{\frac{5-x}{100}}$

$80 = \dfrac{x}{50} \cdot \dfrac{1000}{5-x}$

$50(5-x) = 4x$

$400 = 84x$

$X = 4.76$

$KD = \dfrac{[z]ethoxyethane}{[z]\ in\ H2O}$

$\dfrac{mass\ of\ z\ in\ ether/volume\ of\ ethoxyethane}{mass\ of\ z\ in\ H_2O/volume\ of\ H_2O}$

$K_D = \dfrac{\frac{y}{50}}{\frac{1}{250}}$

$K_D = \dfrac{y}{50} \text{ x } 250$

$K_D = 20.0$

No. 5 Let mass of A extracted be x

$$90 = \frac{\frac{x}{100}}{\frac{5-x}{200}}$$

$$90 = \frac{x}{100} \times \frac{500}{5-x}$$

$$90 = \frac{5}{5-x}$$

95x = 90 x 5

X = 4.74g

Mass of A extracted by 100cm^3 of Ether is 4.74g

Let the mass extracted by first portion be x

$$90 = \frac{X1}{50} \times \frac{500}{5-x1}$$

$$90 = \frac{10x_1}{5-x_1}$$

X_1 = 4.5g

Mass of A remaining in aqueous solution = 5.45

=0.5

X_2 be mass extracted by second portion

$$90 = \frac{y}{50}$$

$$90 = \frac{x_2}{50} \times \frac{500}{0.5-x_2}$$

45 = 100x$_2$

X_2 = 0.45

Total mass extracted = 0.457 + 45

= 4.95g

Acqueous layer

100cm^3 of solution contain 1 mole of NaOH

22.5cm^3 of solution contain $(\frac{1}{1000}$ x 22.5) moles

Mole 1:1

25cm^3 of solution contain $(\frac{1}{1000}$ x 22.5) moles of organic acid

1000cm of solution contain $(\frac{1}{1000}$ x 22.5 x $\frac{1000}{25})$

= 0.9M

Acqueous layer

1000cm^3 of solution contain oil of NaOH

9cm^3 of solution contain $(\frac{0.1}{1000}$ x 0.9) moles of NaOH

1 mole of NaOH reacts with 1 mole of organic acid

23cm^3 of solution contain $(\frac{0.1}{1000}$ x 0.9) moles of organic acid

1000cm^3 of solution contain $(\frac{0.1}{1000}$ x 0.9 x $\frac{1000}{25})$

= 0.036M

$$K_D = \frac{[organic\ acid]organic\ layer}{[organic\ acid]in\ acqueous\ layer}$$

$$K_D = \frac{0.9}{0.036}$$

K_D = 25

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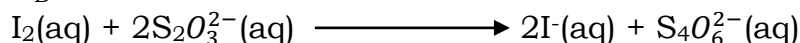
Acqueous layer

$1000 cm^2$ of solution contain 0.0550 moles of $S_2O_3^{2-}$

$6.7 cm^3$ of solution contain $(\frac{0.055}{1000} \times 6.7)$ moles of $S_2O_3^{2-}$

1 mole of iodine reacts with 2 moles of $S_2O_3^{2-}$

$(\frac{0.055}{1000} \times 6.7)$ moles of $S_2O_3^{2-}$ react with $(\frac{1}{2} \times \frac{0.055}{1000} \times 6.7)$

$25 cm^3$ of solution contain ($\frac{1}{2} \times \frac{0.055}{1000} \times 6.7 \times \frac{1000}{25}$)

$= 7.37 \times 10^{-3} M$

Acqueous layer

$1000 cm^3$ of solution contain 1.15 moles of $S_2O_3^{2-}$

$27.2 cm^3$ of solution contain $(\frac{1.15}{1000} \times 27.2)$ moles of $S_2O_3^{2-}$

1 mole of Iodine reacts with 2 moles of $S_2O_3^{2-}$

Moles of iodine reacted $= \frac{1}{2} (\frac{1.15}{1000} \times 27.2)$ moles

$25 cm^3$ of solution contain ($\frac{1}{2} \times \frac{1.15}{1000} \times 27.2$) moles of I_2

$1000 cm^3$ of solution contain ($\frac{1}{2} \times \frac{1.15}{1000} \times 27.2 \times \frac{1000}{25}$) moles of I_2

$= 0.6256$

$K_D = \frac{[I_2]H_2O}{[I_2]organic\ layer}$

$\frac{737 \times 10^{-2}}{0.6256}$

$= 1.18 \times 10^2$

$K_D = \frac{[A]x}{[A]y}$

The mass of A that form a solution of 4g is $12 cm^3$ of y be E

$3 = \frac{\frac{z}{12}}{\frac{4-z}{12}}$

$3 = \frac{z}{12} - \frac{12}{4-z}$

$12 - 3t = t$

$4z = 12$

$Z = 3y$

The mass that would form a solution of 9g

Let the extraction of first portion be x

$3 = \frac{\frac{x_1}{4}}{\frac{4-x_1}{12}}$

$3 = \frac{x_1}{4} - \frac{12}{4-z}$

$12 - 3x_1 = 3x_1$

$X_1 = 2$

Mass of remaining 4-2

$= 2$

Mass extracted by 2nd portion X_2

$3 = \frac{x_2}{y} - \frac{2-x_2}{12}$

$3 = \frac{x_2}{4} \cdot \frac{12}{2-x_2}$

$6 - 3x_2 = 3x_2$

$X_2 = 1$

Mass of y remaining = 2-1

= 1

Let mass extracted of 3rd portion be x_2

$3 = \dfrac{\frac{x_3}{4}}{1-x_3}$

$3 = \dfrac{23^{\frac{12}{3}}}{4} \cdot \dfrac{12}{1-x_3}$

$3-3x_3 = 3x_3$

$6x_3 = 3$

$X_3 = 0.5$

Total mass extracted = $x_1 + x_2 + x_3$

2+1+0.3

3.5g

$K_D = 19 = \dfrac{[I]ether}{[I]H2O}$

Let mass extracted by Ether be K

$19 = \dfrac{\frac{k}{100}}{\frac{5-k}{100}}$

$\dfrac{k}{100} \cdot \dfrac{100}{5-k} = 19$

19 (5-k) = k

20K = 95

K = 4.75g

Mass extracted = 4.75g

First portion

Let mass extracted be K_1

$19 = \dfrac{k_1}{50} \cdot \dfrac{100}{5-k1}$

$95-19k_1 = K_1$

Mass of I remaining in H_2O = 5.452

= 0.45

Mass extracted by 2d portion be K_2

$19 = \dfrac{k_2}{50} \cdot \dfrac{100}{0.48-k2}$

$19 (0.48 - K_2) = 2K_2$

$\dfrac{21k_2}{21} = \dfrac{9}{21}$

$K_2 = 0.43$

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 loosing an electron, an atom gains a positive charge and becomes an ion.

The two appositively charged cation and anion attract each other with a very strong electron static forces thus ionic compounds have very high melting points.

Eg include Na^+Cl^- $Mg^{2+}Cl^-$, $Zn^{2+}O^{2-}$

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 distotation of the electron cloud of an anion is called polarization

Properties of covalent bonds

1. They are normally liquid or grass in room temperature
2. They have low boiling point and melting point
3. They are insoluble in polar solvents butt 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 is shared equally. However this isn't true when a covalent bond is formed between two different atoms.

The more electronic atom attract bonding electrons towards its self thus creating electric dipoles with in 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, Hl and HCl.

However carbon tetra chloride and carbondioxide molecules are non pollar because their bonds are symmetrically arranged which gives the molecules a dipole moment of covalent compounds which are polar have physical properties different from what is expected from true covalent compounds eg some of the conduct electricity.

(b) EFFECT OF POLARIZATION OF IONIC BONDS

When a cation approaches an ion during an ionic bond formation it tends to desist the electron cloud of anion towards itself. The electron then tend to be more 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 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 increase from lithium chloride (LiCl) to potassium chloride (KCl) in the order

LiCl <NaCl < KCl

Why?

Explanation

Ionic radii of the cations increases in the order $Li^+ <Na^+<K^+$. 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

LiCl <NaCl < 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 change. 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 Alumium chloride is much lower than that of calcium chloride.

    (b) Melting point of Aluminium chloride is lesser than of Aluminium oxide

Solution

    a. $AlCl_3$ a high ionic change and hence increase in change density this leads to a high polarizing power this leads to an increase in covalency character hence a low melting point.

    b. The chloride ion has a bigger ionic radius than the oxide ion and therefore the chloride ion is easily plolarised 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 increase but ionic radius reduces therefore polarizing power increases a cross the period and also electro negativity ie charge density = $\frac{change\ increase}{radius}$.

Consequently an increase in polarizing power across the period is off set by a decrease in polarizing power down the group hence diagonal elements have similar polarizing power and electro negativity.

Similarity in polarizing power and electronegatively bring about similarity in chemical properties.

Consider part of the periodic table below.

I   II   III   IV

Li Be B C

Na Mg Al Si
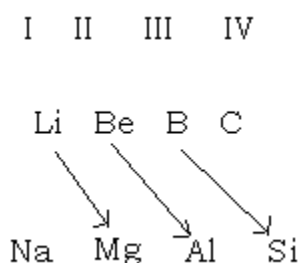
From Lithium to berrylium polarizing power increases while from beryllium to magnesium polarizing power reduces.

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 Boran and Silcom 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 nitrogren.
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 Lithiusm 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) Berylium and Aluminium
(b) Boron and silicon

Solution

Berylium 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 an hydrous $(BeCl_2)_x$ and $(AlCl_3)_x$ which readily dissolve in organic solvents they are readily hydrolyzed by water, with the evolution of hydrogen chloride.

Beryllium cabide, Be_2C, aluminium carbide Al_4Cl_3 give methane on treatment with water, unlike the ionic carbides of the group.

2 metals, they are therefore refered to as methides.

Similar complexes of beryllium and aluminium have similar stabilities eg BeF_4^{3-} and AlF_6^{3-}. The shape is 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 toms provides a pair of electrons being shared. The donor atom must have atleast one ion pair of electrons ie a pair of electrons not being used for bonding.

The acceptor atom must have atleast a vacant obital.

Examples

Ammonia

$NH_3 + H^+ \longrightarrow NH_4^+$

$$\left[\begin{array}{c} H \\ | \\ H - N - H \\ | \\ H \end{array} \right]^+$$

$H_2C(l) + H^+(aq) \longrightarrow H_3O^+(aq)$
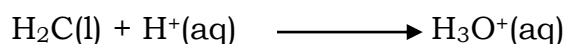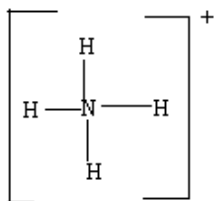
Adaptive bond is represented by an arrow pointing from the donor atom

$$\left[\begin{array}{c} H \\ | \\ H - N - H \\ | \\ H \end{array} \right]^+$$

Or

$$\left[\begin{array}{c} H \\ | \\ N \\ \diagup \diagdown \\ H \quad H \end{array} \right]^+$$

$$H_3N: + BCl_3 \longrightarrow$$

$$\begin{array}{ccc} & H & Cl \\ & | & | \\ H\!\!-\!\!\!\!&N\!\!-\!\!\!\!-\!\!Br\!\!-\!\!\!\!&Cl \\ & | & | \\ & H & Cl \end{array}$$

Boron
[trichloride]
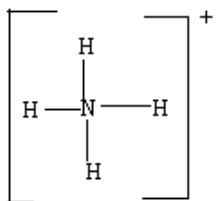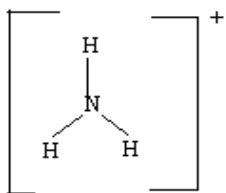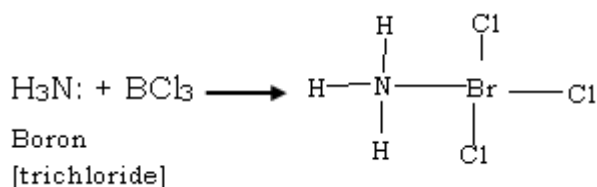
METALIC BOND

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 obitals overlap forming molecular obitals.

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 – poor 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 electrongly 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, HN_3 and H_2O.

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

Water

carboxylic acids
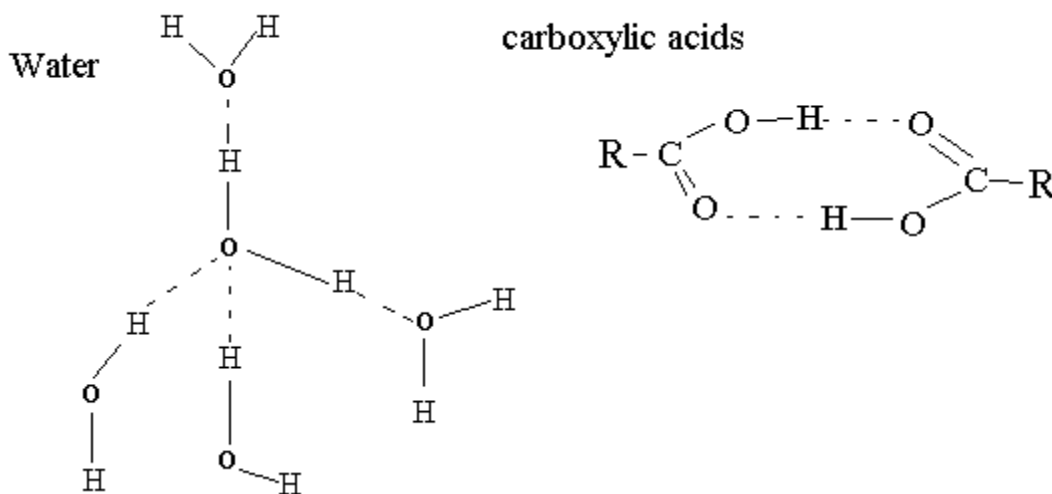
Effects of hydrogen bonding on physical properties of some compounds.

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
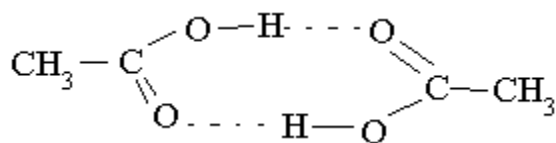
Question

Explain the following observations

Boiling points of hydrides of groups (vii) increase in the order HCl < HBr < HE< 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 HCl < HBr < 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 tetrhedrally bonded to four hydrogen atoms through covalent bonding and hydrogen bonding. This gives ice an extremely open tetrahedral structure thus a law density.

When ice melts the water molecules are kin 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 was 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 boi, points than other hydrodes of group orvi and vii respectively.

f. 2-hydroxyl benzoic acid has a lower boinding point than for hydroxyl benzoic acid.

Similarly 2 nitro phenol has a lower boiling pont than 4-nitroppenol.

Questions

Define the term hydrogen bond?

Giving the term hydrogen bond?

Giving 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

➢ Electro valent (ionic) bonding

➢ Coordinate bonding

➢ Vander waals bonding

➢ Hydrogen bonding

Structures

❖ Structure of simple molecular Cpds

❖ Structure of oxo anions

❖ Structures of ionic Cpds

❖ Structure of macro molecular covalent Cpds

❖ 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, Neom, Argon, Krypton, Xenon.

The atoms combine in two types of bonding ionic bonding of 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 must shorts 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 fores of attraction which constitute ionic bond and the energy required to break the, ionic bonds, is called lattic energy and its magnitude depends on two factors ie ionic radius and ionic charge. If ions of opposite charge have small ionic radii they approach each other strongly ie electrostatic force of attraction between the ions in high and this leads to high lattic energy.

If the ions of opposite charge have high charge density eg X^{5+} & Y^{2-} or X^{3+} & Y^{3-} they approach each 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 into ways.

Lattice energy it is the enthalapy 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 ethalapy 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

$$Na \longrightarrow \overset{x\ x}{\underset{x\ x}{Cl}}{}^{x}_{x} \longrightarrow Na^{+} - Cl^{-}$$

$$Al \xrightarrow{\hspace{2cm}} \begin{array}{c} {}^{x}_{x}\overset{x\ x}{\underset{x\ x}{Cl}}{}^{x}_{x} \\[4pt] {}^{x}_{x}\overset{x\ x}{\underset{x\ x}{Cl}}{}^{x}_{x} \\[4pt] {}^{x}_{x}\overset{x\ x}{\underset{x\ x}{Cl}}{}^{x}_{x} \end{array} \longrightarrow Al^{3+}.3Cl$$

$$Mg \xrightarrow{\hspace{2cm}} \overset{xx}{\underset{xx}{O}}{}_{xx} \longrightarrow Mg^{2+}.O^{2-}$$
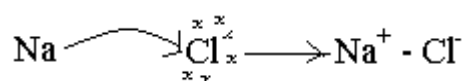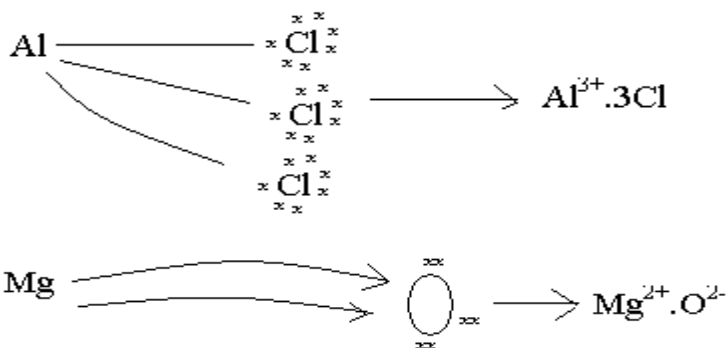
Properties of ionic C'pds

- ❖ They are crystalline solids at room temperature
- ❖ They conduct electricity either in molten state or in agaseous state.
- ❖ They are soluble in polar solvent such as water but insoluble in organic solvents such as benzene, ethanol, carbondisuphate
- ❖ 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 Lithuim chloride and Aluminium Chloride poses 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.

- ❖ Ethalapy of solution
- ❖ Enthalapy of lattice
- ❖ Enthalaphy of hydrogen

$$XY(g) + aq \xrightarrow{\underline{DH\ solutions}} X^{n+} + Y^{n-}(aq)$$

D lattice

D hydration

$X^{n+}(g) + Y^{n}(g) + aq$
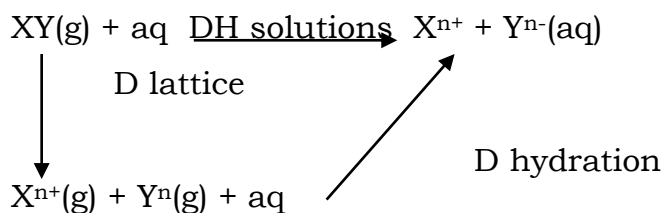
Covalent bonding

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

$$\overset{x\ x}{\underset{x\ v}{Cl}}\overset{x}{\underset{x}{:}}\ \overset{x\ x}{\underset{x\ v}{Cl}}\overset{x}{\underset{x}{:}} \longrightarrow Cl-Cl$$

Carbondioxide

$$\overset{x}{\underset{x\ x}{O}}\overset{xx}{}C\overset{xx}{\underset{xx}{}}\overset{..}{\underset{..}{O}} \rightarrow O=C=O$$

Ammonia gas

$$\underset{\overset{x}{H}}{N}\overset{xH}{\underset{H}{:}} \longrightarrow H-\underset{\overset{|}{H}}{N}-H$$
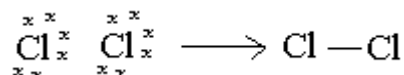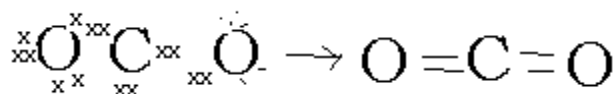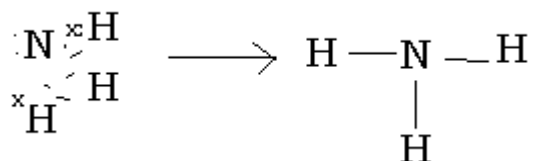
Sulphur dioxide gas

$$\overset{x}{\underset{x}{O}}S = O \rightarrow O = S = O$$

Nitrogen gas N_2

$$\overset{x}{N}:N\overset{x}{\underset{x}{:}}\longrightarrow N\equiv N$$
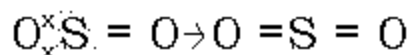
Sulphur trioxide gas
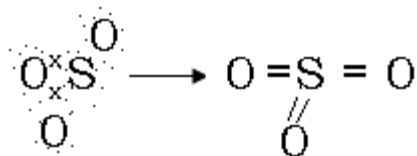
Methane gas
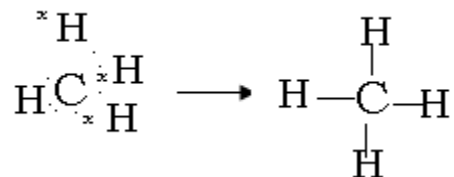
Water
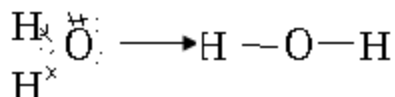
Properties of covalent C'pds

Covalent cpds are mainly gases and volatile liquids with low melting points and boiling points except silcon (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, Cl_2, NH_3, SO_2, CO_2.

Equations

$HCl(g) + H_2O(l) \longrightarrow H_3O(aq) + Cl^-$

$CO_2(g) + H_2O(g) \qquad H_2CO_3 \qquad H^+(aq) + HCO_3^-(aq)$

$NH_3(g) + H_2O(l) \qquad NH^+(aq) + OH^-(aq)$

$Cl_2(g) + H_2O(l) \quad HCl(aq) + HOCl(aq) \quad 2H^+(aq) + OCl^-(aq) + Cl^-(aq)$

$SO_2(g) + H_2O(l) \quad H_2SO_3(aq) \quad H^+(aq) + HSO_3^-(aq)$

$SO_3(g) + H_2O(l) \quad H_2SO_4(aq) \quad H^+(aq) + SO_4^{2-}(aq)$
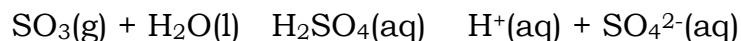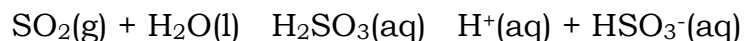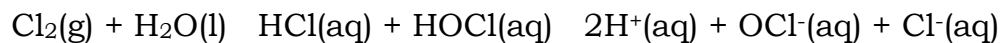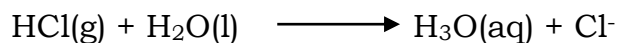
Most of the covalent Cpds consist of descrete molecules

Most covalent C'pds are insoluble in water but soluble in organic solvents eg CCl is insoluble in water but very soluble in ether.

Coordinate bonding

Accoordinate bond is a type of covalent bond in which the shared pair of electrons is provided by only one of the bonded atoms. One atoms in the donor and the other is the acceptor.

Acoordinate bond is some times called adative bond. Once adative bond is hormed if has the same x-tics as a covalent bond.

Acoordinate bond is differentiated from a normal covalent bond share electrons are coming from and where they are going.

For the atom to act as a doner, it must have atleast one pair of unsaturated electron (alone pair of electrons)

The acceptor atom should lack a pair of electrons C'pds or ions which exhibit coordinate bonding are as follows.

(a) Ammonium ion

$$NH_3 + H^+(g) \longrightarrow \left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array} \right]^+$$
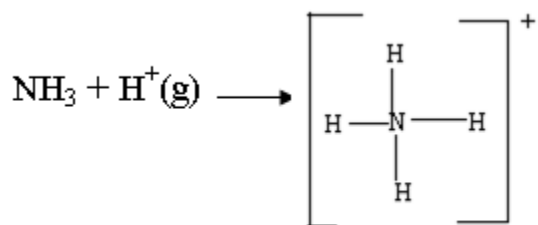
(b) Ammonium boron chloride $H_3N.BCl_3$

$$H_3N + BCl_3 \longrightarrow H_3N \longrightarrow BCl_3(s)$$

(c) Hydrozonium ion (H_2O^+)

$$H_2O(l) + H^+(aq) \longrightarrow \left[\begin{array}{c} H-O-H \\ | \\ H \end{array} \right]^+$$
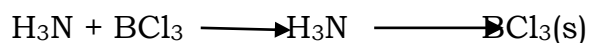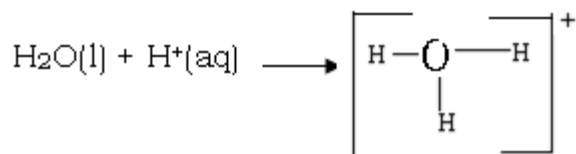
(d) Tetra amine copper (ii) ion $[Cu(NH_3)_4]^{2+}$

$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow \begin{array}{c} NH \\ \downarrow \\ H_3N \rightarrow C \leftarrow NH_3 \\ \uparrow \\ NH_3 \end{array}$$
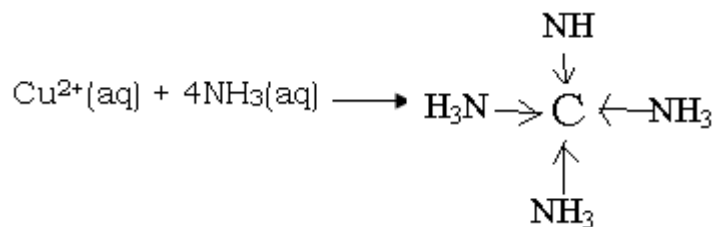
(e) Aluminium chloride in the vapour phase has a formular Al_2Cl_6 which is a dimer of $AlCl_3$ through coordinate bonds.
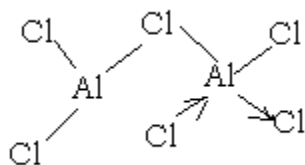
Iron (iii) chloride in vapour phase a formular $FeCl_6$ which is dimer of $FeCl_3$ through coordinate bonding.
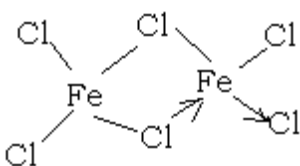
Beryllium chloride in the vapour phase has a formular Be_2Cl_4 which in a dim of $BeCl_2$ through coordinate bonding.
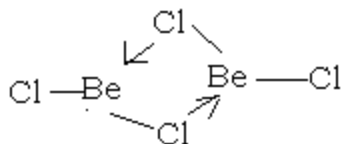
Ammonium aluminium fluorid ($NH_3.AlF_3$)
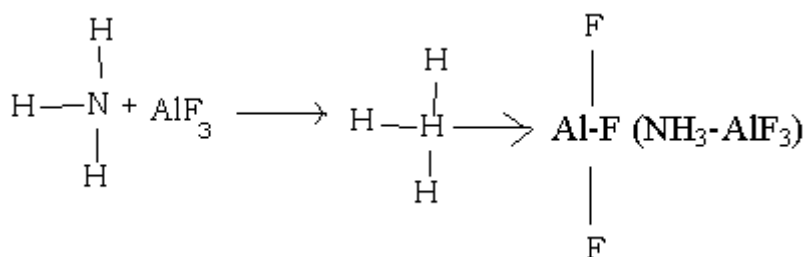
Nitrogen Chloride (NO_2)
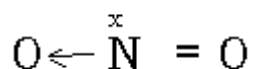
Shapes of simple covalent molecules and ions

The shapes of simple covalent molecules or ions are predicted by a theory called valence shell electron pair repulsion theory which was advanced by sidy wick and powell (VSEPR theory).

The theory is based on the following principles

The arrangement of the electron pairs around the central atom is 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 which the electron pairs around the central atom are distributed so as to minimize the repulsion an d hence to minimize the energy of the molecule or ion.

Any ion 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: alone 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 $\equiv$Y) double bond (X =Y) > single bond (X-Y)

c. The repulsion decreases with the decrease in the electro negativity 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 interms of SPDF notation

ii. Determine the number of electrons in the outer most quantum shell

iii. Determine the number of bond pairs and ion pairs of electrons in the central atom

iv. Write the formula of the C'pd in the form AX_mEn where

A-Central atom

X- Ligands (surrounding atoms)

M – number of ligands

E- Ion pair of electrons

n - Number of ion pairs of electrons

The molecule or ion can adopt any of the follow shapes / structures

Linear structure X-A-X AX_2Eo

Triagonal planor (triangular) structure

X AX_2Eo

A

X   X

T – shaped structure

AX_3E_2

X

A—X   or   X—— A —X

X

X

Sea saw (AX_4E_1)

A

X

X   X   X

Pyramidal (AX_3E_1)

A

X—   —X

X
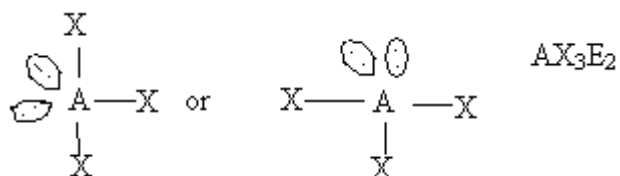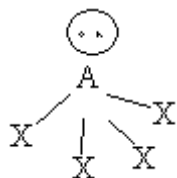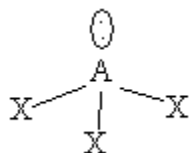
Tetra hedral (AX_3E_1)

X

A

X—   —X

X
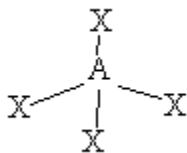
V- Shaped structure AX_2E_2 or AX_2E_1
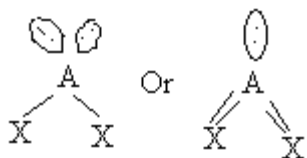
Trigonal bipyramidal (AX_5E_0)
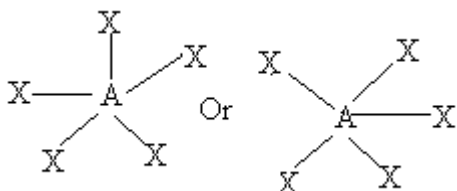
Note

1. 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

2. When a central atom has no line pair of electrons then the molecule can adopt any of the structures.
    ❖ Linear
    ❖ Trigonal planor
    ❖ Tetra hedral
    ❖ Tragonal bipynamidal

3. 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

4. An oxo anion (XO_m^{n-}) 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

CO_3^{2-} $\Longleftrightarrow$ Trigonal planon

SO_4^{2-} $\Longleftrightarrow$ Tetra hedral structure

PO_4^{3-} Tetra hedral structure

ClO_4^{-} Tetra hedral structure

SO_3^{2-} Pyramidal structure

Linear structure

BeCl$_2$ Cl-Be-Cl

CO$_2$ O = C= O

CO   C = O
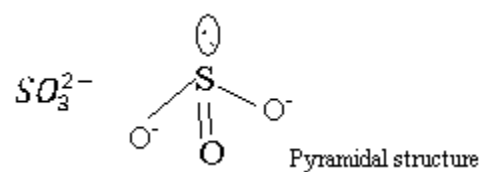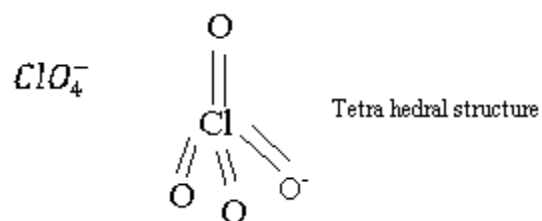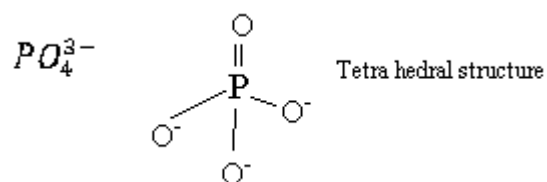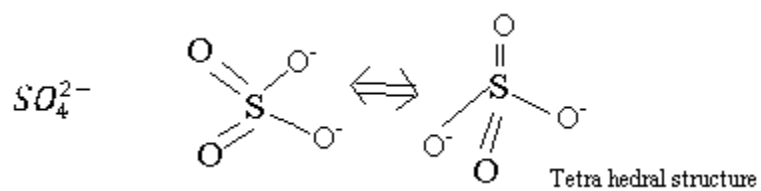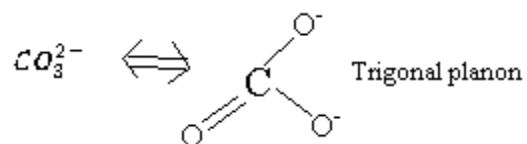
Trigonal planor structure AX_3E_0

BCl_3

SO_3

CO_3^{2-}

NO_3^{2-}
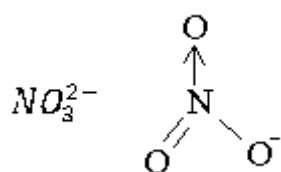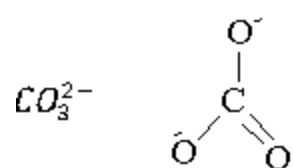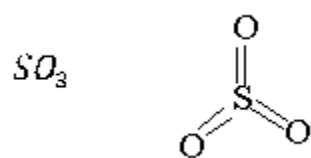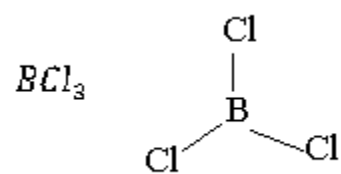
Pyramidal structure (AX₃E₁)
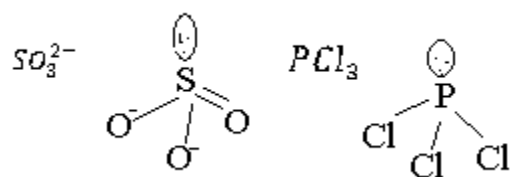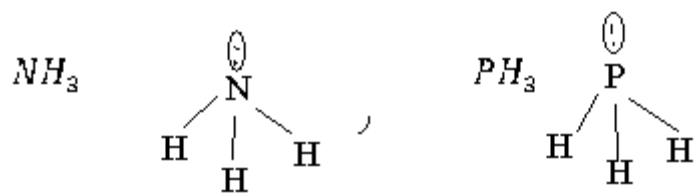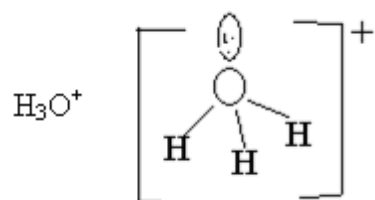
NH_3

PH_3

SO_3^{2-}

PCl_3

H_3O^+

Tetrahedral structure (AX_4E_0)
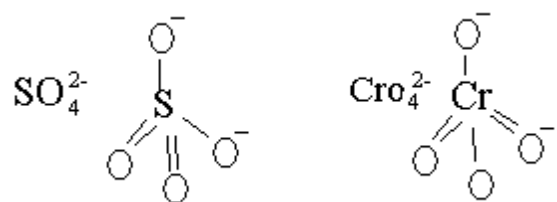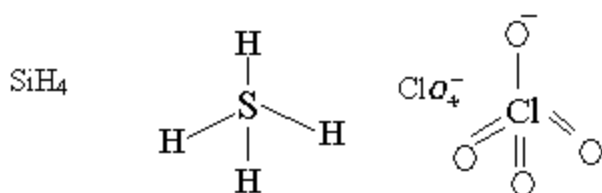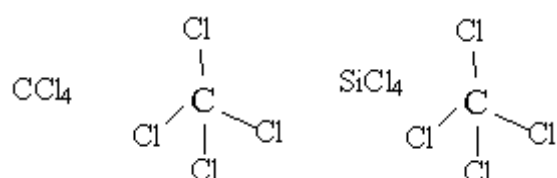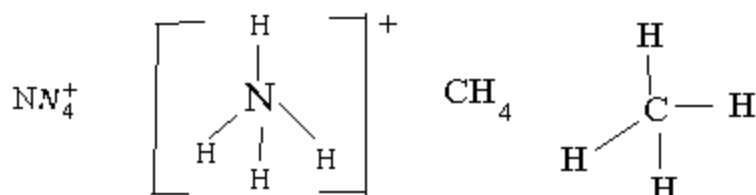
NN_4^+

CH_4

CCl_4

$SiCl_4$

SiH_4

ClO_4^-

SO_4^{2-}

CrO_4^{2-}

V- Shaped structure

H_2O

SO_2

NH_2

$[\quad N \quad H \quad H \quad H \quad]^{+}$

Trigonal bipyramidal (AX$_5$E$_0$)

PCl_5

Cl — P — Cl (with Cl, Cl, Cl)

PBr_5 Br — P — Br (with Br, Br, Br)

T- Shaped structure (AX$_3$E$_2$)

X — A — X
|
X

Eg CCF$_3$

F — Cl — F
|
F

ICl$_3$

Cl — I — Cl
|
Cl
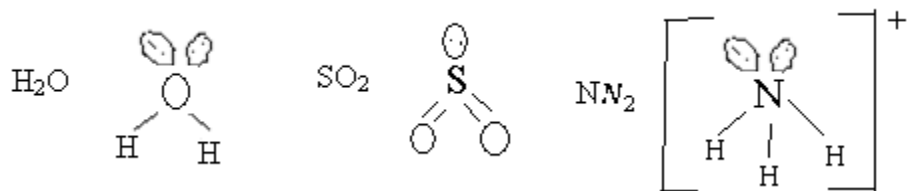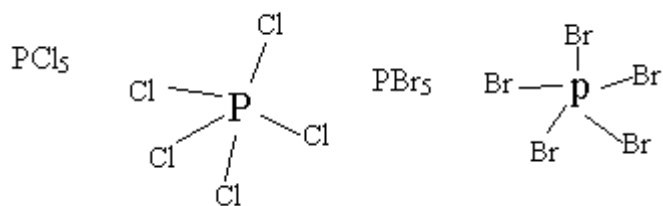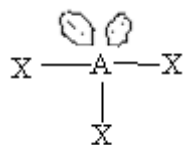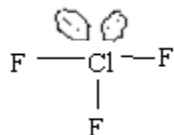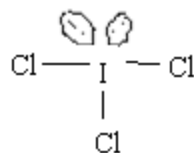
See-saw AX$_4$E$_1$

Eg SF₄, Sulphur tetra fluolide
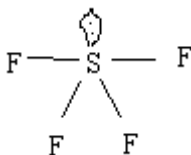
Effect of electro negativity of the central atom on the bond angle

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
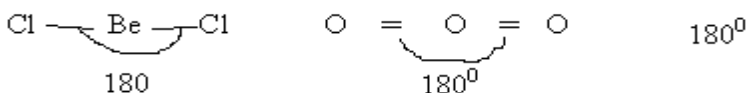
Trigonal planor structures have a bond angle of 120^0
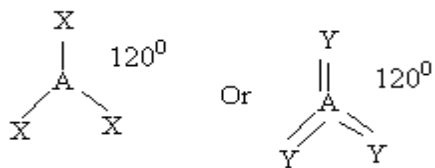
Eg
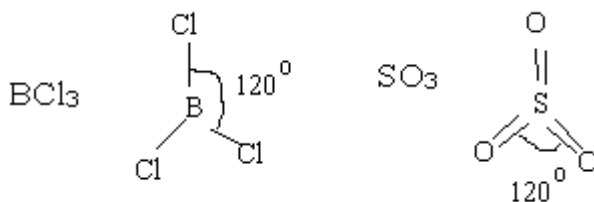
Tetrahedral structures are expected to have a bond angle of 90^0C but some time it is either less or greater then 90^0 due to the differences in the electro negativity of the central atom and the ligands eg
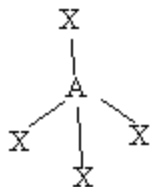
When the electro negativity of the central atom is high then there is a strong attraction of the bonding electrons towards itself and this results into a high concentration of bonding electrons around the central atom and this increases the repulsion between the bonding electron pairs and thus the bond 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 atleast along pair of electrons on the central atom.

Considering the hydrides of group V and group VI

Group V: NH_3, PH_3, AgH_3 (pyramidal)

Group VI: H_2O, H_2S, SbH_2 (V –shaped structure)
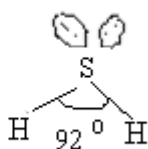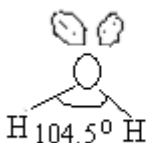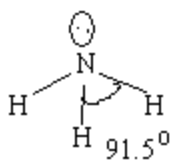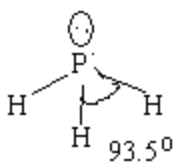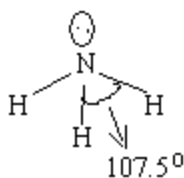
The hydrides of gpV adopt a pyramidal structure because the central atom has a lone pair of electrons but the bond angle decreases from the hydride of nitrogen to the hydride of Ascenic. This is because the electronegativity of nitrogen is higher than that of phosphorous which in turn is higher than that of a senic.

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 explation applies to the hydrides of group VI elements.

Metallic bonding

A metallic bond is a strong attraction between the metal ion and the allocalised electrons

In a melai structure positive ions of the metal are packed in a regular array with in a sea of electrons liberated from the metal atoms.
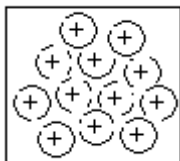
The more the no. of valecy electrons of the metal, the stronger the metallic bond.

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 shaltering.

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 ground 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, bromide is a volatile liquid while iodine is a volatile solid which sublimes on warming.

The vander waals forces because 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 formular mass eg methane, ethane, propane and butane are gases at room temp, although their boiling points are different. Fro 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 un branched 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.
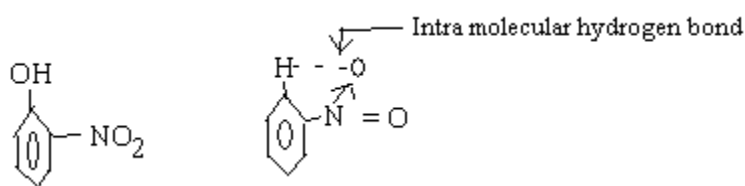
4- nitro phenol exhibits enter molecular hydrogen bonds
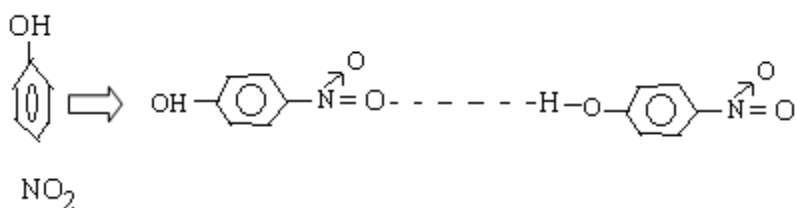
Intermolecular hydrogen bonding is stronger than intra molecular hydrogen bonding because there are many molecules involved in the hydrogen bond formation while intra molecular hydrogen bonding there is only one molecule.

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 100^0C but hydrogen sulphide its boiling point is -60^0C.

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.
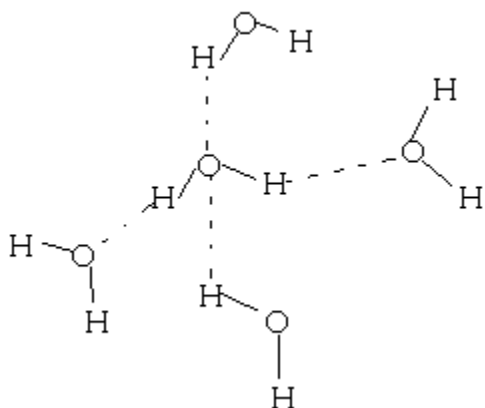
Similarly the boiling point of hydrogen fluoride is 20^0C while that of hydrogen chloride is -80^0C. this is because fluorine is more electronegative than chlorine and therefore hydrogen fluoride molecules associate through strong hydrogen bonds which require a lot of energy to break while hydrogen chloride 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 -35^0C and -86^0C 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 Hydrodrides 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 O^{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(^{0}C)	-161	-112	-95	-52	-35	-56	-20	-86
Period No.	2	3	4	5	2	4	5	3

	Gp VI					GpVII		
Hydride	H$_2$O	H$_2$S	H$_2$	HiTc	Hp	HCl	HBr	HT
Bpt(^{0}C)	100	-60	40	-5	20	-80	-60	-35
Period No.	2	3	4	5	2	3	4	5

Question

a. On the same axes, plot graphs of boiling points of the hydrides of gp IV, gpV, gp IV and gp VII against period number.

b. Explain the shape of the graph.

THERMOCHEMISTRY
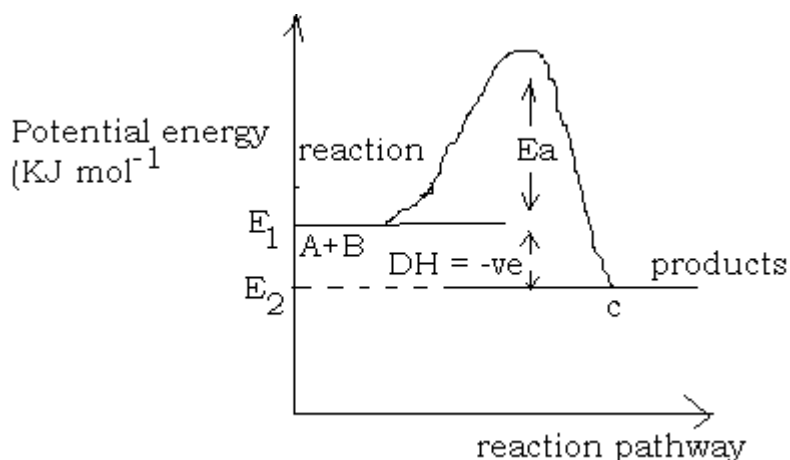
For endothermic reactions, since the products are at a higher energy are at a higher energy content than the reactants, the products are energetically unstable compared to the reactants from which they are made.

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.

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $\Delta H = 286KJmol^{-1}$
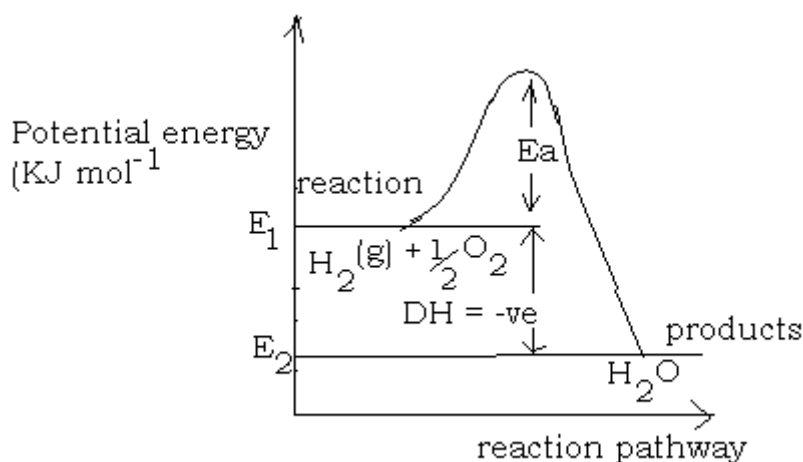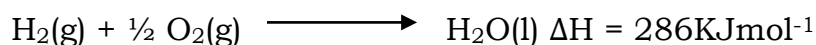
Since water is formed exothermically it is more stable relative to its elements.

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 over come by increasing temperature which activates many molecules that can over come 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.

$H_2(g) + ½ O_2(g) \longrightarrow H_2O(l) \Delta H = -286KJmol^{-1}$

$H_2(g) + ½ O_2(g) \longrightarrow H_2O(l) \Delta H = -245.4Kmol^{-1}$

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.

$H_2O(l) \longrightarrow H_2O(g) \Delta H = +40.6KJMol^{-1}$
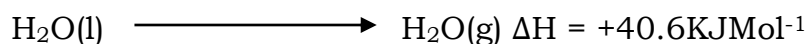
Similarly in the reactions

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) \Delta H = -57.3 KJmol^{-1}$

$NaOH(aq) + HCl(q) \longrightarrow NaCl(aq) + H_2O(l) \Delta H = -130 KJmol^{-1}$
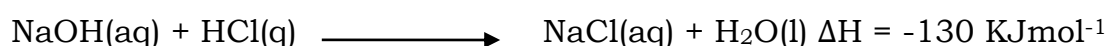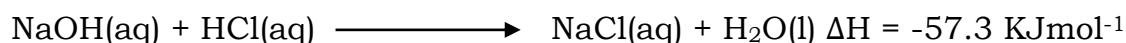
More heat is given out when hydrogen chloride gas is used instead of hydrochloric acid. The difference is because hydrogen chloride gas dissolves in water to form acqueous hydrochloric acid with evolution of heat.

$HCl(g) \longrightarrow HCl(aq) \Delta H= -72.7KJMol^{-1}$
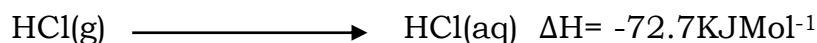
2. Concentration of the participating species. If the reacting species are in acqueous solution, their concentration should be 1 molar (1M)

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 satisified, then the symbol ΔH bears superscript and a sub script and is written.

Note: if conditions 1-3 are satisfied, then the symbol ΔH bears a superscript and a subscript and is written.

$\Delta H^{\theta}_{-298K}$

Or simply

ΔH^{θ}. This means that the energy charge a companying such a reaction is under standard conditions ie standard physical states, concentration of 1. If solutions are involved, pressure of 1 atm and temperature of 298K.

Other factors affecting enthalpy changes a company of a reaction include.

1. Allotropic modifications

An enthalpy change is involved in conversion of one allotrope into another such that the patroallotrope used affects the value of the anthalpy accompanying reaction.

Consider the formation of sulphure dioxide.

S(s) + O₂(g) ⟶ SO₂(g) ΔH^{θ} = KJmol⁻¹
(Rhombic)

S(s) + O₂(g) ⟶ SO₂(g) ΔH^{θ} = KJmol⁻¹
(monoclinic)
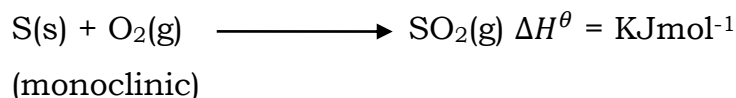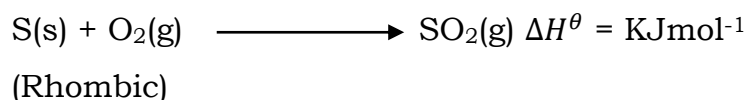
More heat is absorbed when rhombic sulphur is used than monoclinic sulphur showing that the transformation of monoclinic to rhombic is endothermic.

ᵛS(s) ⟶ ᵛS(s) ΔH^{θ}= +0.3KJmol⁻¹
(monoclinic)   (Rhombic)
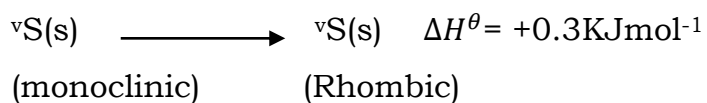
Similarly less energy is absorbed when monoclinic sulphur is used to form sulphur dioxide showing that a conversion of Rhombic to monoclinic sulphur is exothermic.

S(s) ⟶ S(s) ΔH^{θ}= +0.3KJmol⁻¹
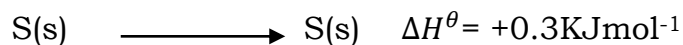
An increase in the amount of reacting substances increases the heat evolved or absorbed during the courses of a reaction.

Types of entmlpies/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

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ ΔH^{θ} = -
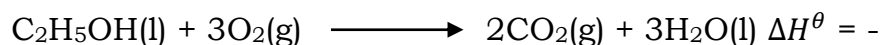
For all combustion reactions the enthalpy of reaction is negative since heat is given out when a sample is bus in excess oxygen.

Experimental determination of enthalpy of combustion of a liquid fuel eg Ethanol.
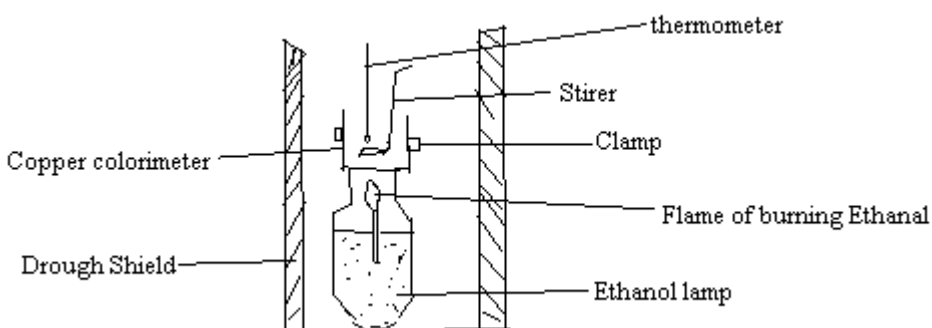
A known volume of water is put in a copper calorimeter fitted with a thermometer and s stirrer.

The calorimeter is damped and put in a shield which minimizes heat losses to the sorroundings.

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 ethand burnt is used to raise the temperature of water which stired 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 $\theta_1 {}^0C$

Final temperature of water be $\theta_2 {}^0C$

Initial weight of lamp be W_1g

Final weight of lamp be W_2g

Weight of ethanol burnt = (W_1-W_2)g

Volume of water used = Vcm^3

Water   g/cc

Heat given out in burning (W_1-W_2)g of ethanol = Heat gained by water.

$= M_wC_w\theta$

M_v = density x Vol

$= $ (Density x Vol) x $C_w(\theta_2-\theta_1)$J

Heat given out in burning 1g of ethanol $= \dfrac{PV.C_W(\theta_2-\theta_1)}{(W_1-W_2)}$J

$C_2H_5OH = (12x2) + (1x6) + (16)$

$= 4.6$g

Heat given out in burning $= [\dfrac{PV.C_W(\theta_2-\theta_1)x\ 46}{(W_1-W_2)}]$ J

46g of ethanol

$$= \frac{PV.C_W(\theta_2 - \theta_1)x\ 46}{(W_1 - W_2)x\ 1000}$$

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^{0}C

O_2 temperature of H_2O = 33.0^{0}C

Density of H_2O = 1g/cc

Vol of H_2O used = 100cm^3

SHC of H_2O = 4.27 mol^{-1}K^{-1}

Solution

Mass of ethanol burnt = 24.63 – 24.4

= 0.23g

Temperature rise = 33-18

= 15^{0}C

Molar mass of C_2H_5OH = (12x2) + 1x6) + (16 x)

= 46g

Heat given out in burning = heat gained by water 0.23g of ethanol

= mass of x SHC of x temp

Water H_2O rise

(100x1) x 4.2 x 15

6300J

Heat given out in burning = $[\frac{6300}{0.23}]$ J

1g of ethanol

Heat given out in burning = $[\frac{6300}{0.23}$ x 46]J

46g of ethanol

= 1.26 x 10^6 $Jmol^{-1}$

$\frac{1.26 \ x \ 10^6}{1000}$ $KJmol^{-1}$

= 1.26 x 10^3 $KJmol^{-1}$

= 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
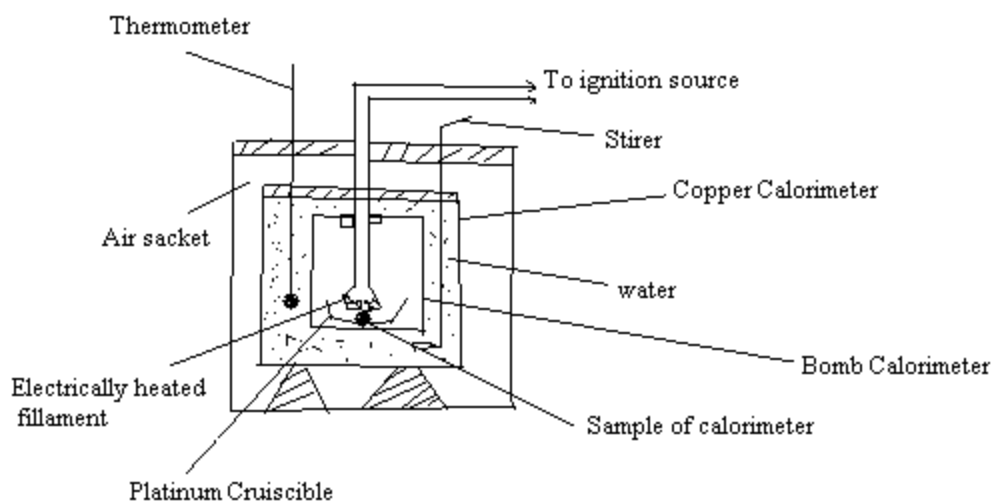
A known mass of the sample whose heat of combustion is under investigation is put on the plantinum cruiscible in a tomb calorimeter.

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 ingited 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
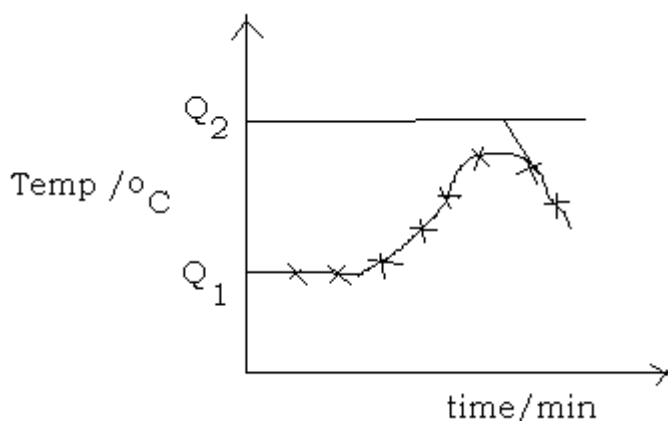
The final maximum temperature is obtained by extroparatic.

Treatment of results

Let volume of water b Vcm^2

Density of water be ρ g/cc

Specific heat capacity of water be C Jg^{-1}K^{-1}

Initial temperature of water be θ_1 ^{0}C

Final temperature of water be θ_2 ^{0}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 x temperature water capacity of water change.

Vρ.C $(\theta_2 - \theta_1)$J

Heat given out in burning /g of sample

$$\frac{V\rho C\,(\theta_2 - \theta_1)}{a}$$

Heat given out in burning 1 mole of sample –mr

$$\frac{V\rho C\,(\theta_2-\theta_1)xMr}{a}\ \text{Jmol}^{-1}$$

$$\frac{V\rho C\,(\theta_2-\theta_1)}{a\ x\ 1000}\ \text{x Mr}\ \ \text{KJ mol}^{-1}$$

Therefore heat of combustion of the sample

$$\frac{V\rho C\,(\theta_2-\theta_1)Mr}{a\ x\ 1000}\ \text{KJ Mol}^{-1}$$

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 25^0C and 1 atmosphere pressure.

Consider the following neutralization reactions

$H_3PO_4(aq) + 3NaOH(aq) \longrightarrow Na_3PO_4(aq) + 3H_2O(l)$

$3H^+(aq) + 3\bar{O}H(aq) \longrightarrow 3H_2O(l)$

$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$
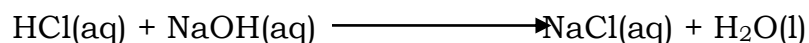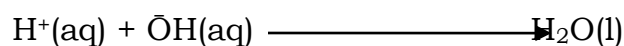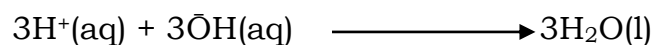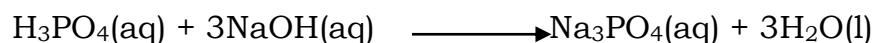
The above neutralization reactions show that in neutralization of a strong acid by strong base, the same ionic equation can be used to represent the reaction and if the acid and base in question are of concentration 1 mole dm^{-3} the same amount of heat is evolved and is approximately 57.3KJmol^{-1}

Ie

$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$ $\Delta H\theta$neut = -57.3KJmol^{-1}
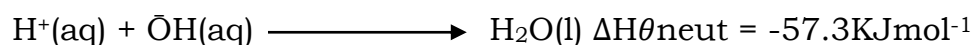
This is only true for strong acid strong base neutralizations but if the acid is weak the heat evolved is less eg the neutralization ethanoic acid by sodium hydroxide.

$CH_3OOH(aq) + NaOH(aq) \longrightarrow CH_3O\bar{O}Na(aq) + H_2O(l)$ $\Delta H\theta neut = -57.3 KJmol^{-1}$

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.

$CH_3OOH(aq)$ $CH_3CO\bar{O}(aq) + H^+$

$CH_3CO\bar{O}Na \longrightarrow CH_3CO\bar{O}(aq) + Na^+(aq)$
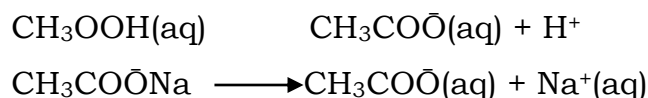
Ethanoate ions from the salt suppress the ionization hydrogen ions (H^+) in solution. Since a neutralization reaction occurs between hydrogen ions and hydroxyl ions, this reduces the heat evolved.

Experimental determination of heat of neutralization of 1M HCl(aq) by 1M NaOH(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.
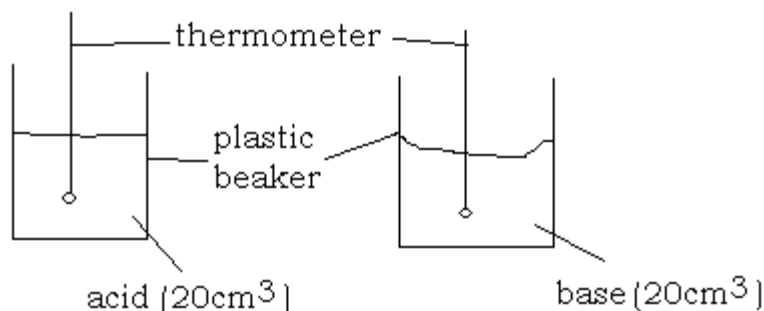
The temperature of the two solution are noted at 1 minute interval for about 5min.

The solutions are mixed together and stired 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
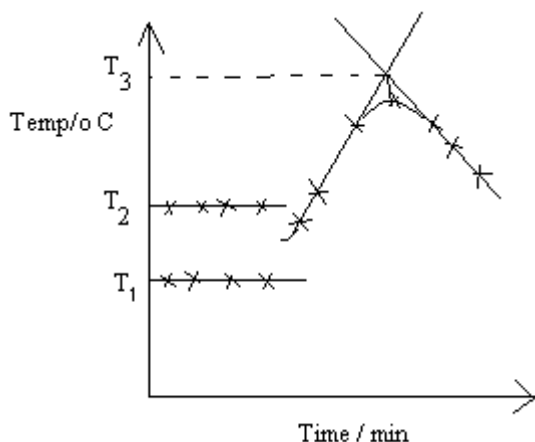
The final maximum temperature is obtained by extraporation of the curves

Treatment of results

Volume of acid and base be $V cm^3$ each

Total vol of solution $(V_1 + V_2)$

Initial temperature of base T_2 ^0C

Initial temperature of acid T_1 ^0C

Initial average temperature $= (\frac{T_1+T_2}{2})^0C$

Final temperature of solution $= T_3$ ^0C

Change in temperature $T_3 - (\frac{T_1+T_2}{2})^0C$

Density of the salt solution ρ g/cc

S.H.C of solution $= C$ $Jg\text{-}K^{-1}$

Conc of a cid and base $= 1$ $moldm^{-3}$ each

$\rho (V_1 + V_2)C (T_3 - (\frac{T_1+T_2}{2})]$ J

From the reaction

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$
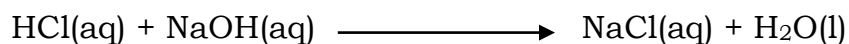
Moles of NaOH used to neutralize the acid

$= (\frac{1.0}{1000}$ x V)

From the equation 1 mole of NaOH reacts with 1 mole of acid forming 1 mole of H_2O.

Moles of water formed $= (\frac{1.0}{1000}$ x V)

Heat evolved in neutralizing the acid by the base to form

$\rho (V_1 + V_2)C [T_3 - (\frac{T_1+T_2}{2})]$ J $(\frac{1.0\,V}{1000})$ moles of water

Heat evolved in neutralizing the acid by the base to form 1 mole of water

$$\frac{\rho (V_1 + V_2)C [T_3 - (\frac{T_1+T_2}{2})] \quad J}{\frac{1.0V}{1000}}$$

$$\frac{\rho (V_1 + V_2)C [T_3 - (\frac{T_1+T_2}{2})] \quad K.Jmol^{-1}}{1.0V}$$

Qn. Find the heat neutralization of reaction (HCl + NaOH) from the following experimental data

Vol of 2M HCl = 20cm^3

Vol of 2M NaOH = 35cm^3

Initial temperature eg NaOH = 15.5^{0}C

Initial temp of HCl = 15.0^{0}C

Final temperature of the mixture = 28.3^{0}C

SHC of water = 42Jg^{-1}K^{-1}

Density of water = 1g/cc

Solution

Total vol of solution = (20 + 35) = 55cm^3

Average initial temperature = $(\frac{15+15.8}{2})$ = 15.4^{0}C

Change in temperature = 28.5 – 15.4

= 12.9^{0}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 = $\frac{2}{1000}$ x 20

= 0.04

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$
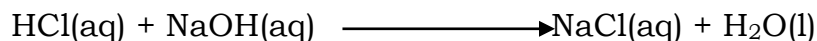
1 mole of HCl neutralizes 1 mole of NaOH forming 1 mole of water.

0.04 moles of water are formed with evolution of 2979.9J of heat

1 mole of water is formed by evolution of

$= \dfrac{2979.9}{0.04}$

$= 74497.5$ Jmol^{-1}

Heat of neutralization = - 74.4975 Kjmol^{-1}

Qn. 25cm^3 of 2M sodium hydroxide at a temperature of 13.4^{0}C were mixed with 50cm^3 of 2M sulphurioc acid at a temperature of 12.9^{0}C. if the maximum temperature of the solution was 15.2^{0}C. Calculate the heat of neutralization of sodium hydroxide by H_2SO_4 (SHC of soln = 4.2 Jg^{-1}K^{-1}, ρ = lg/cc)

Solution

Total volume of solution

= 25 + 50

= 75cm^3

Average initial temperature = $\dfrac{13.4+12.9}{2}$

= 13.15^{0}C

Change in temperature

= 15.2 – 13.15

= 2.05^{0}C

Heat given out in neutralizing of NaOH by H_2SO_4 = Heat gained by salt solution

= mass X SHC X Temperature

  Of soln of soln   rise

= (75x1) x 4.2 x 2.05

= 645.75J

$2NaOH(aq)\ H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$
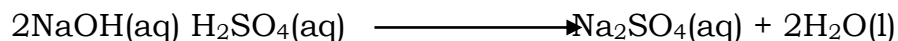
Moles of NaOH used = $(\dfrac{2\ x\ 25}{1000})$ = 0.05moles

Moles of H_2SO_4 reacted = $(\dfrac{2\ x\ 25}{1000})$ x ½

= 0.025 moles

1 mole of H_2SO_4 reacts with 2 moles of NaOH forming 2 moles of H_2O

Moles of water formed

= 0.025 x 2

= 0.05 moles

0.05 moles of water are formed with evolution of 645.75J of heat

1 mole of water is produced with evolution of ($\frac{645.75}{0.05}$ x 1) Jmol^{-1} = 12915 Jmol^{-1}

$= \frac{645.75}{5\ x\ 10^{-2}x\ 10\ x\ 10^{+3}}$

$= \frac{645.75}{5\ x10}$

12.915KJmol^{-1}

Heat of neutralization

= -12.915 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.

$H_2(g) + O_2(g) \longrightarrow H_2O_2(l)$ ΔH_f^0 = -242 Kj mol^{-1}
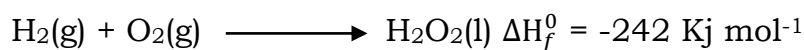
Hydrogen perioxide is expected to be very stable but it readily decomposes each in absence of a catalyst. This shows that hydrogen perioxide is stable relative to its elements but unstable relative to water and oxygen to which it readily decomposes.

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

$$Sn(s) + 2H_2(g) \longrightarrow SnH_4(l) \quad \Delta H_f^0 = +162.8 \text{ KJ mol}^{-1}$$

$$Cl_2(g) + O_2(g) \longrightarrow Cl_2O_7(l) \quad \Delta H_f^0 = +175.75 \text{ KJ mol}^{-1}$$
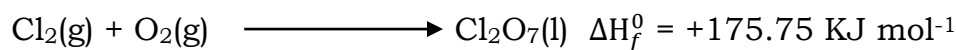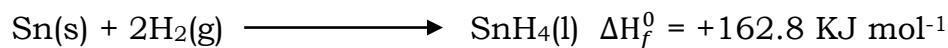
All those compounds that are formed exothermically are very stable eg

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s) \quad \Delta H_f^0 = -1675 \text{ KJ mol}^{-1}$$

$$Na(s) + \frac{1}{2} Cl_2(g) \longrightarrow NaCl(s) \quad \Delta H_f^0 = -411 \text{ KJ mol}^{-1}$$
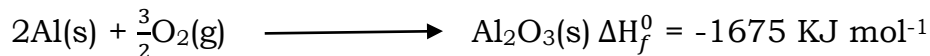
Stability can also be measured by using the entropy of the reaction.

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

$DS = \frac{q}{T}$ 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 ΔH and the difference G_1-G_2 is DG. The difference between DH and DG is called the entropy TDS.

Ie DH – DG = TDS

Or DG = DH-TDS

The reaction is possible if DG is negative at OK the entropy is O 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, $Na_2S_2O_3$ and $NaNO_3$ have positive enthalpies of solution would expect to be insoluble if enthalpy of solution would depend on DH alone but also depends on the entropy.

Measurements of standard heats of formation

The standard enthalpies of formation of many oxides such as carbondioxide, 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 respect 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 carbondioxide 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 he summation.

It states in transforming reactants into products the total heat change is the same regardless of the taken provided the initial and final states are the eg in transforming A and B it can be done at once or it can in stages.
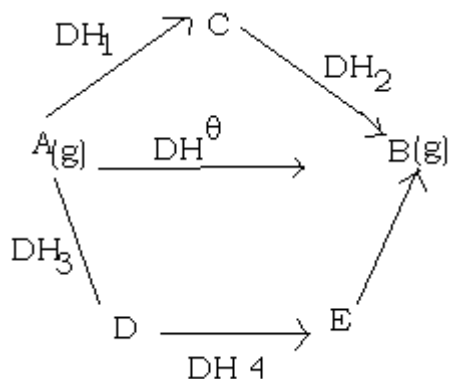
By Hess's law

$DH^\theta = DH_1 + DH_2$

OR

$DH^\theta = DH_3 + DH_4 + DH_5$

Example's using Hess's law

1. Consider the formation of gaseous water

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$ $DH^\theta = ?$

The value above can be obtained from

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$ $DH^\theta = -286KJmol^{-1}$

$H_2O(g) \longrightarrow H_2O(l)$ $DH^\theta = -44$ KJ mol^{-1}

Solution

By Hess's law

$H_2(g) + \frac{1}{2} O_2(g)$ $DH^\theta = -286$ $H_2O(g)$

DH_2

$H_2O(g)$ $DH_3 = -44$
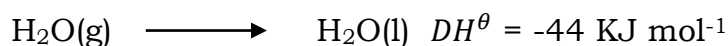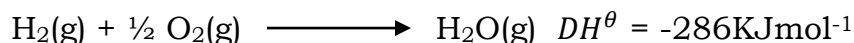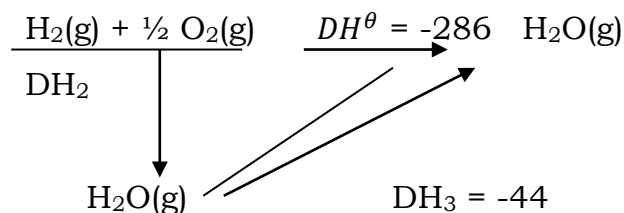
By Hess's law

$DH_1 = DH_2 + DH_3$

$-286 = DH_2 + -44$

$DH_2 = -242$ 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 that water

Energy level diagram
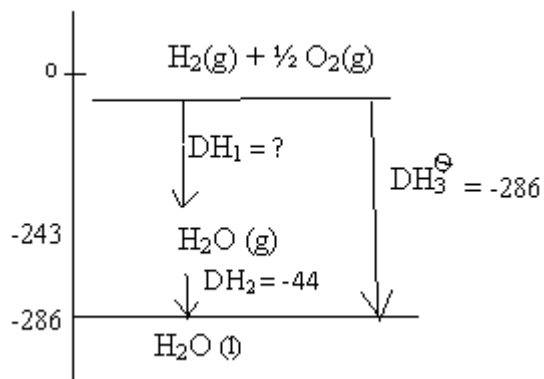
By Hess's law

$DH_1 = DH_2 + DH_3^\theta$

$DH_1 = -286 - {}^-44$

-242 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}
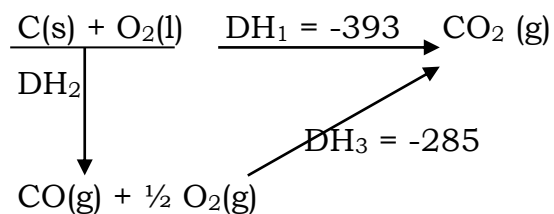
$DH_1^\theta = DH_2 + DH_3$

$DH_2 = DH_1^\theta - DH_3$

= -393 + 285

= -108 KJmol^{-1}
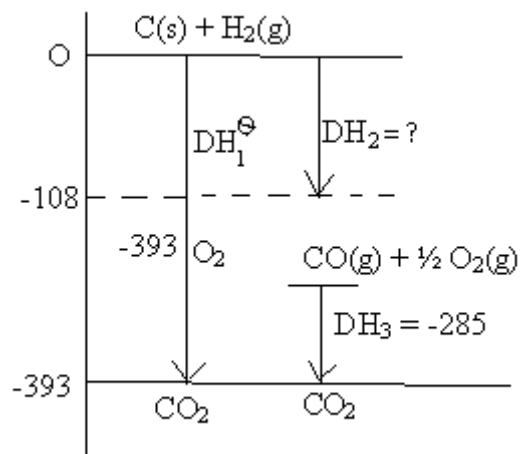
Qn: Find standard enthalpy of formation of ethyne given the standard enthalpies of combustion in KJmol^{-1}

$C_2H_2(g)$ = -1300

C(i) = -394

$H_2(g)$ = -286
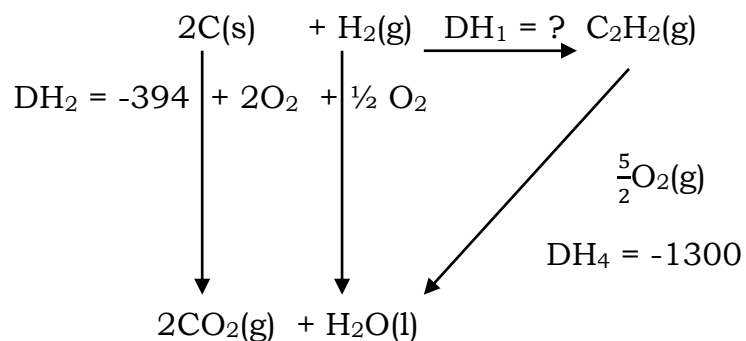
By Hess's law

DH_1^0 = DH_2 + DH_3 − DH_4

(-394) + (-286) − (1300)

KJ mol$^-$

Graph

DH_3 = DH_1 + DH_2

DH_1 = DH_3 − DH_2

DH_1 = (2 x -394) + -286) - $^-$1300

= 226 KJ mol-1

Alternatively

$C_2H_2(aq) + \frac{5}{2}O_2(q) \longrightarrow 2CO_2(g) + H_2O(l)$
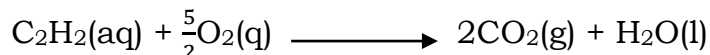
-1300 + 0   =   (2 x -394) + (-286)

DH_f^θ of C_2H_2 = (heat content of reactants) – (heat content of product)

(-1300) – (-1074)

= -226KJmol-1

Alternatively writing equations and manipulating them

$C_2H_2(aq) + \frac{5}{2}O_2(q) \longrightarrow 2CO_2(g) + H_2O(l)$ DH_c^θ = -1300KJ mol-

$H_2(g) + ½ O_2(g) \longrightarrow H_2O(l)$ DH_c^θ = -286KJ mol-
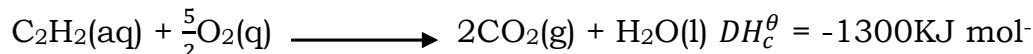
Required equation is

$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$ DH_f^θ = ?
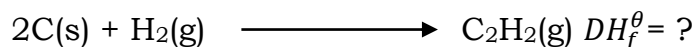
Multiplying (iii) x 2, then reverse eqn (i) and sum up all the eqns.

$2C(s) + H_2(g) \longrightarrow H_2C_2$ DH^θ = +226KJmol-1
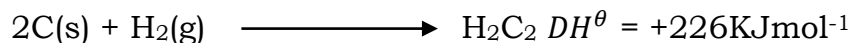
Example

Calculate the enthalpy of formation of ethene given that is combustion is -891 KJ mol-1 and those in carbon and hydrogen are – 286 KJmol-1

DH_f^θ = (-393 + (-286 x 2) + 891

= -74KJ mol-1

Method 2

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ DH_f^θ = -891

$C(s) + O_2(g) \longrightarrow CO_2(g)$ DH_c^θ = -393

$H_2(g) + ½ O(g) \longrightarrow H_2O(l)$ DH_c^θ = -286

Required eqn

$C_2(g) + 2H_2(g) \longrightarrow CH_4(g) DH(g)$ DH_f^θ =?
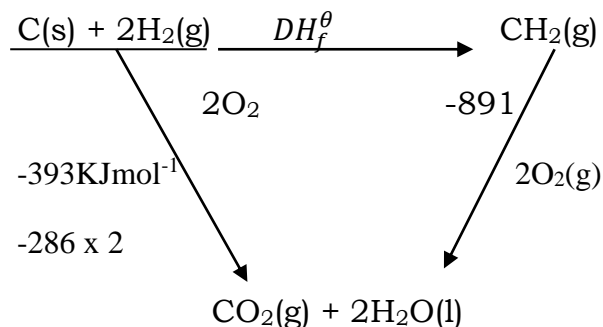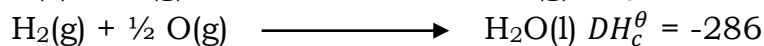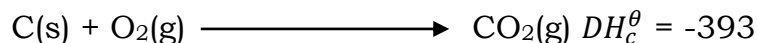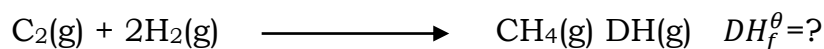
Multiplying (eqn) (iii) by 2 and reverse eqn (i) then sum up all equations.

Or

C(s) + 2H$_2$(g) $\longrightarrow$ CH$_4$(g)

(-393) + (-286 x 2)   -891 + x
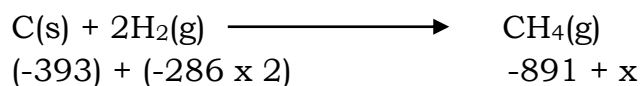
Introduce an unknown on the side where we want to get the energy term.

X = 891 + (-393) + (-286 x 2)

X = -74KJmol^{-1}

Example 4

Given the ethalpies of combustion of carbon graphite and carbon monoxide as -393.5 and -283 KJmol^{-1} respectively. Calculate the enthalpy of formation of carbonmonoxide.

C(s) + ½ O$_2$(g) $\underline{\quad DH_f^\theta =?\quad}$ CO(g)

½ O$_2$ ½ O$_2$

-393.5

CO$_2$(g)

DH_f^θ = -393.5 + 283

= -110.5KJmol^{-1}

Or

C(s) + O$_2$(g)   CO$_2$(g) DH_c^0 = -393.5

CO(g) + ½ O$_2$(g)   CO$_2$(g) DH_c^0 = -286
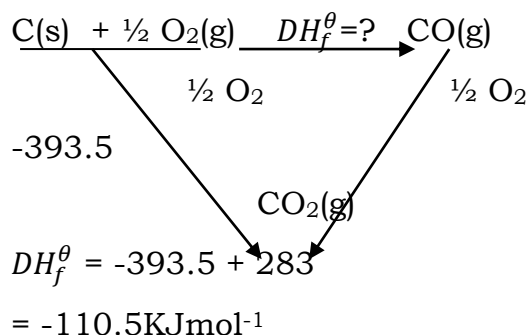
Reversing eqn (ii) and suming up both eqns

+286 + -393-5

= -110.5KJmol^{-1}

Or

C(s) + ½ O$_2$(g) $\longrightarrow$ CO$_2$(g)

-393.5 + O   -283 + x
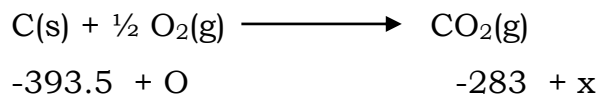
X – 283 = -393.5

X = -393.5 + 283

X = -110.5KJmol^{-1}

Question

The heat changes for some reactions are given below all in KJmol^{-1}

$H_2(g) + S(s) + 2O_2(g) \longrightarrow H_2SO_4(l)$ DH^θ = 8148

$H_2SO_4(s) \longrightarrow H_2SO_4(aq)$ DH^θ = -911.4

$ZnSO_4(s) \longrightarrow ZnSO_4(aq)$ DH^θ = -81.9

$Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$ DH^θ = -153.1
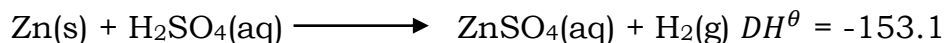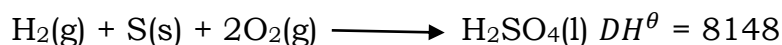
Calculate the heat of formation of hydrous zinc sulphate

$Zn + S(s) + 2O_2(g) \longrightarrow ZnSO_4(s)$
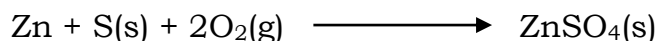
Reversing equation (ii) and suming up all the equations

-814.8 + -911.4 + 81.9 + -153.1

= -1797.4 KJ mol^{-1}

Given the data below, calculate the enthalpy of formation of Rabidium sulphate (Rb_2SO_4)

$H^+(aq) + \bar{O}H(aq) \longrightarrow H_2O(l)$ DH^θ = -57.3KJ mol^{-1}

$RbOH(s) \longrightarrow Rb^+(aq) + \bar{O}H(aq)$ DH^θ = -62.8KJ mol^{-1}

$Rb_2SO_4(s) \longrightarrow 2Rb^{2+}(aq) + SO_4^{2-}(aq)$ DH^θ = +929.3KJ mol^{-1}

$Rb(s) + \frac{1}{2} O_2(g) + \frac{1}{2} H_2(g) \longrightarrow 2RbOH$ DH^θ = -44

$H_2(g) + S(s) + \frac{1}{2} O_2(g) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$ DH^θ = -907.5

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ DH^θ = -286

Solution

$2Rb(s) + S(s) + 2O_2(g) \longrightarrow Rb_2SO_4(s)$
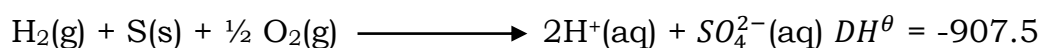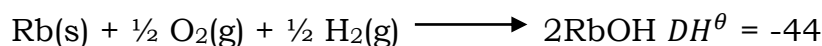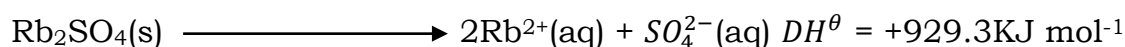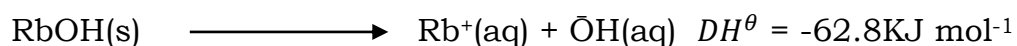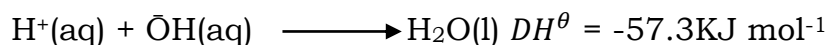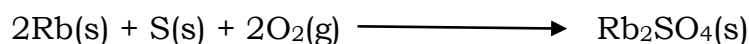
Multiplying eqn (iii) (vi) by 2 then reverse (viii) and (vi) gives

(-57.382) + (-62.8 x 2) + -929.3 + (414 x 2) + -907.5 + (285 x 2)

= -2335KJmol^{-1}

Calculate the enthalpy change for the reaction

$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$
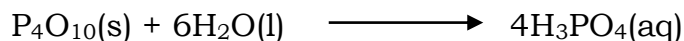
Given that the DH$_f$ of H$_3$PO$_4$, P$_4$O$_{10}$, H$_2$O are -1279 KJ mol^{-1}, -2984, -286 respectively

Solution

$4O(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$ DH_f^0 = -2984

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ DH_f^0 = -286

$\frac{3}{2}H_2(g) + P(s) + 2O_2(g) \longrightarrow H_3PO_4(aq)$ DH_f^0 = -1279
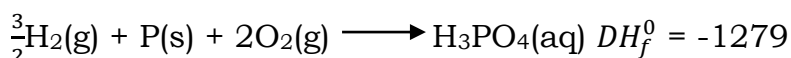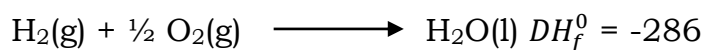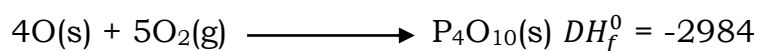
Multiply equation 11 by 6 eqn (iii) by 4 then reverse equation (i) and (ii) and sum up all equations.

+2984 + 286 x 6 – 1279 x 4

= -416 KJ mol^{-1}

$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$
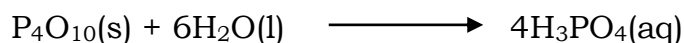
4x-12798*x

BOND ENTHALPIES

This is defined as the energy change that occurs in forming abond 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 acovalent bond and is from free gaseaous atoms.

Bond enthalpy (energy) is the energy required to break 1 mole of a covalent bond forming free gaseous atoms eg

$Cl\text{-}Cl(g) \longrightarrow Cl(g) + Cl(g)$ $DH^{\theta} = BE = +ve$
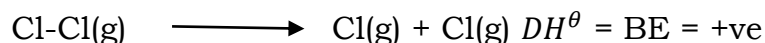
Or

It is the energy given out by free gasous atoms when they combine to form 1 mole of a covalent bond.

The free gaseous atoms posses potential energy of a tomisation 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.

$Cl(s) + Cl(g) \longrightarrow Cl(g) - Cl(g)$ $DH^{\theta} = BE = -ve$
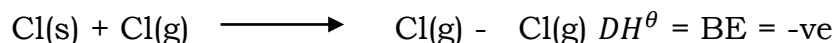
Calculating bond energies

Consider formation of methane

$C(s) + 2H_2(g) \xrightarrow{\quad DH_f^0 \quad} CH_4(g)$ --------(i)
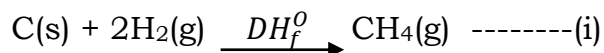
Alternatively

It can be formed from its gaseous atoms

$C(g) + 4H(g)$ DH_{BE} $CH_4(g)$ ………….(ii)

Combining eqn (i) and (ii)

$$C(g) \quad + \quad 4H(g) \xrightarrow{\quad DH_{BE} \quad} CH_4(g)$$

DH^{θ}_{atmis} BDE/

DH^{θ}_{atmis}

B.E

$$C(g) \quad + \quad 4H(g)$$
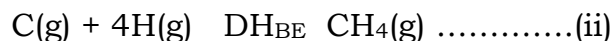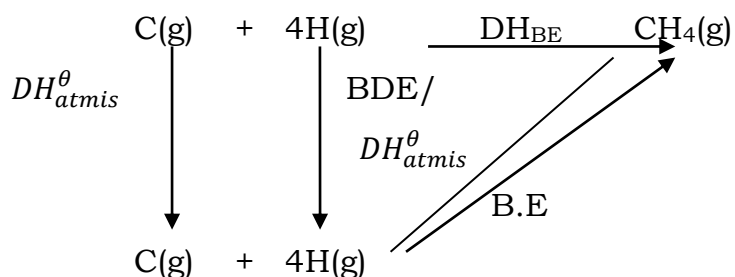
The BE is given out in forming 4 (C-H) bonds

For every C-H bond, the energy given out is $\frac{BE}{4}$

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 CH$_4$ = -74

$$C(g) + 4H(g) \xrightarrow{\quad DH^o_f = -74 \quad} CH_4(g)$$

+720   +431

BE

$$C(g) + 4H(g)$$
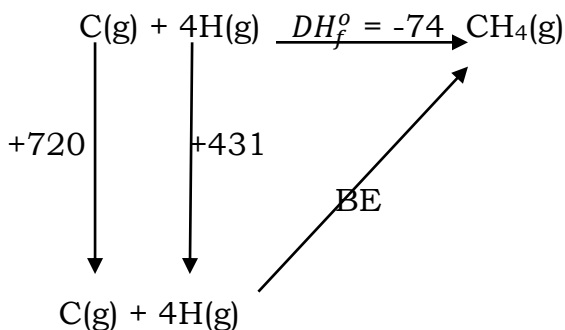
By Hess's law

-74 = +720 + (431 x 2) + BE

BE = -1656KJmol^{-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 KJmol^{-1}.

$$2C(s) \quad + \quad 3H_2(g) \xrightarrow{\quad DH^o_f = -818 \quad} C_2H_6(g)$$

(2 x 720)   (3 x 431)

BE

$$2C(g) \quad + \quad 6H(g)$$
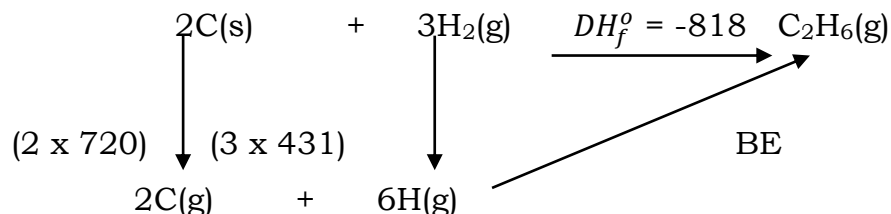
-818 = (2 x 720) + (3 x 431)+ BE

BE = -2821KJmol^{-1}

-2821 = 6(C-H) + 1(C-C)

-2821 = (6x -414) + (C-C)

(C-C) = -337KJ mol^{-1}

Similar calculation can be used to determine the bond enthalpy of carbon to carbon double bond and C=C eg in ethene given the enthalpy of formation of ethene as -92KJmol^{-1}

$$2C(s) \quad + \quad 2H_2(g) \quad DH^o_f = 92 \quad C_2H_4 (g)$$

+120 x 2   +431 x 2   BE

2C(g)   +   4H(g)

By Hess's law

-92 = (720 x 2) + (431 x 2) + BE

BE = -2394KJ mol^{-1}

$$C_2H_4 \quad = \quad \overset{H}{\underset{H}{>}} C = C \overset{H}{\underset{H}{<}}$$
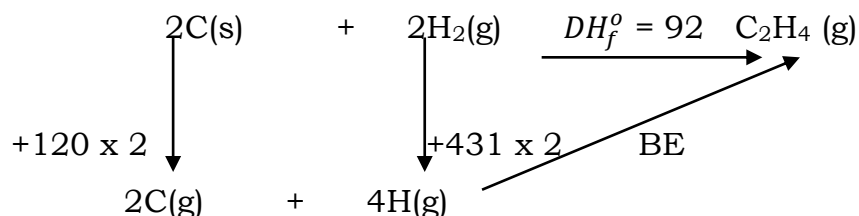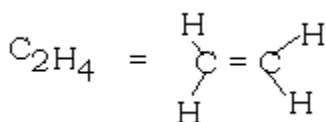
4(5-H) + (C=C) = -2394

4x – 44 + C = C = -2394

(C = C) = -738KJmol^{-1}

For C ≡C as in ethyne given the enthalpy of formation of ethyne of formation of ethyne as -96KJ mol^{-1}

$$2C(s) \quad + \quad H_2(g) \quad DH^o_f = -96 \quad C_2H_4 (g)$$

+120 x 2   +431 x 2   BE

2C(g)   +   2H(g)

By Hess's law

-96 = (720 x 2) + (431 x1) + BE

BE = -1967 KJ mol^{-1}

$C_2H_2 = H – C \equiv C – H$
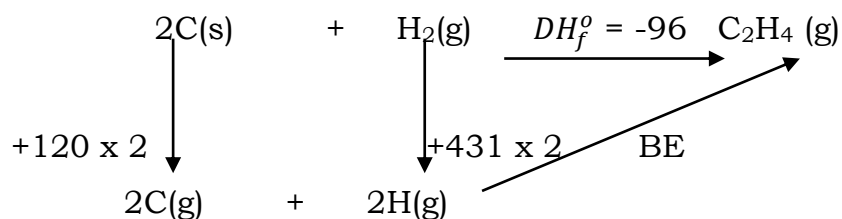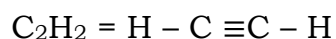
-1967 = 2(C-H) + 1(C≡C)

-1967 = 2(-414) + (C≡C)

$(C \equiv C)$ = -1139 KJmol^{-1}

(a) What is meant by the term bond energy.

(b) The figure 1 nbelow represents energy diagram for the formation of methane.

C(s) + 2H(g) $\xrightarrow{\quad DH_1 \quad}$ CH$_4$ (g)

DH$_3$ DH$_2$ DH$_4$

C(g)   4H(g)
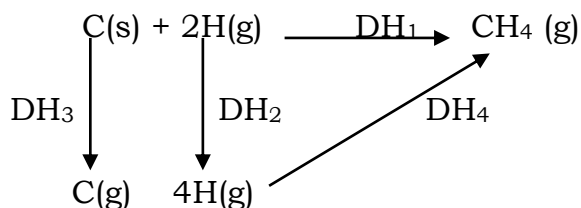
Identify the following energy changes   DH$_3$ DH$_2$ DH$_4$

Given that DH$_1$ = -75 KJmol^{-1} DH$_2$ = +218KJ mol^{-1} of hydrogen atom, DH$_3$ = +715KJ mol^{-1}. Calculate the

    (i)   Value of DH$_4$

    (ii)   Bond energy for carbon hydrogen bond

Solution

(b) DH$_1$ enthalpy of formation of 1 mole of methane

DH$_2$ Atomisation energy of hydrogen atoms (bond desociation energy of hydrogen molecule)

DH$_3$ Atomisation energy of carbon atoms

By Hess's law

DH$_1$ = DH$_2$ + DH$_3$ + DH$_4$

DH$_4$ = DH$_1$ – DH$_2$ – DH$_3$

= -75 – (218 x 4) – 715

DH$_4$ = -1662 KJ mol^{-1}

H–C–H (with H above and H below the central C)
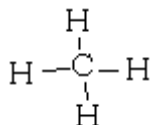
4(C-H) = -166.2

C-H = $\frac{-1662}{4}$

= -415.5 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=0	605

Calculate the enthalpy change for the following reactions

H_2(g) + Cl_2(g) $\longrightarrow$ 2HCl (g)

Bonds broken

(H-H) + (Cl – Cl)
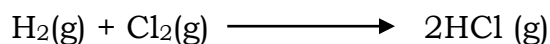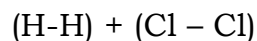
436 + 242   = +678 KJmol^{-1} (Bond broken +) (form bond -1)

Bonds formed

2(H-Cl) = 2 x 431
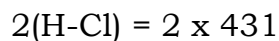
= -862 KJmol^{-1}

Heat of reaction = +678 – 862

= -184 KJmol^{-1}

CH_3CH_3(g) + Cl_2(g) $\longrightarrow$ CH_3CH_2Cl (l) + HCl(s)

Bond broken

= 1(C-H) + (Cl – Cl)
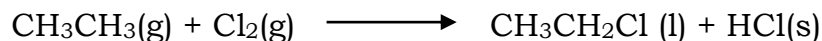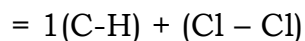
= (414 x 1) + (242 x 1)

= +656 KJmol^{-1} (breaking bond$^+$)

Bonds formed

1(C-Cl) + (H-Cl)
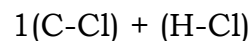
= 315 x1) + (431 x 1)

= -746 KJmol^{-1}

Heat of reaction = -746 + 656

= -90 KJmol^{-1}

$CH_2 = CH_2 + Cl_2$ CCl_4 $CH_2 - CH_2$
                                           | |
                                          Cl   Cl
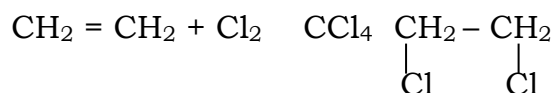
Bonds broken

1(C-C) + 1(Cl – Cl)

(348 x 1) + (242 x 1)

= +590KJ mol^{-1}

Bonds formed

2(C-Cl)

= 2 x 315

= -630 KJmol^{-1}

Heat of reaction = -630 + 590

= -40KJmol^{-1}

Question

Calculate the heat of combustion of cyclohexane using the above bond energies.

Soln

C_6H_{12} (l) + $9O_2$(g) $\longrightarrow$ $6CO_2$(g) + $6H_2O$(l)
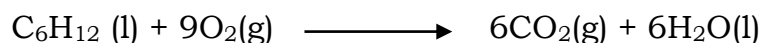
Bonds broken
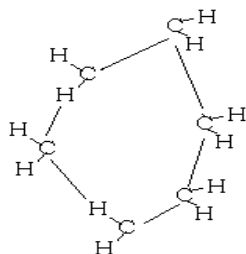
6(C-C) + 12(C-H) + 9(O=O)

(348 x 6) + 414 x 12) + (496 x 9)

= +11520 KJmol^{-1}

Bonds formed

O = C = O   H – O - H

2 x 6 (C =O)   2 x 6 (O-H)

12 (C=O) + 12(H-O)

= (12 x 605) + (12 x 463)

= -12816 KJ mol^{-1}

Heat of reaction = +11520 + -12816

= 1296 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

$6C (s) + 3H_2(g) \longrightarrow C_6H_6(l)$
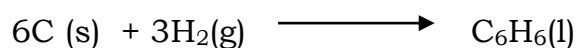
Bonds broken

Atomisation energy

= 3(H-H) + 6C(g)

(3 x 436) + (6x720)

= +5628 KJmol^{-1}

Bonds formed

6(C-H) + 3(C-C) + 3(C≡C)

(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

$HC ≡CH (g) + 2H_2(g) \longrightarrow H_3C – CH_3$
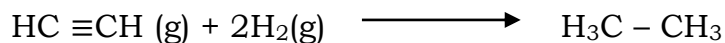
Bonds broken

(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

Enery cycle
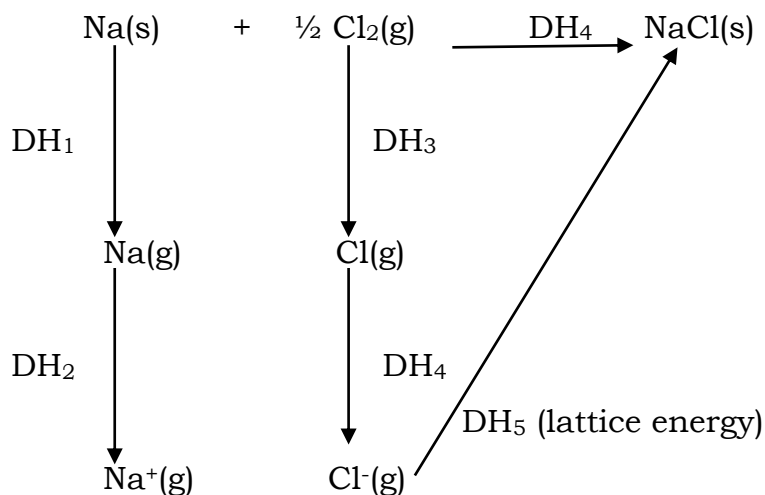
Born harber cycle is a complete energy cycle linking many enery terms and can be used to determine the latice energyof an ionic crystal which can not be determined experimentally it can be represented as either anenergy cycle or an energy level diagram.

Energy level diagram
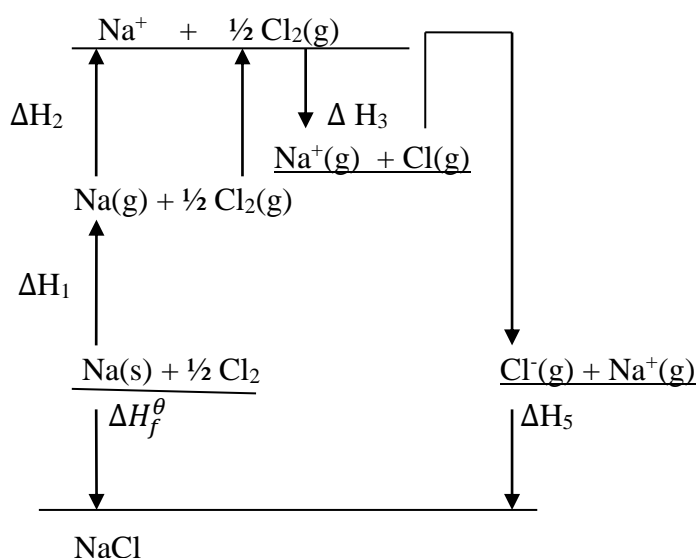
To construct the energy level diagram, enthalpy changes that are negative are identicated by an arrow pointint downwards while those that are positive are idicated by an arrow pointing upwards

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.

DH_2 is called ionisation energy and is defined as the energy required to remove 1 mole of an electric from gaseous atoms forming 1 mole of unpositively charge cations.

DH_3 is bond dessociation energy for chlorine moles 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 gasous molecules.

DH_4 kis 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.

DH_5 is called lattice energy defined as the potential energy possed by free gasous ions which is given out when they combine to form 1 mole of an ionic crystal in the solid state.

$[Cl(g) + e \longrightarrow Cl^-(g)]$
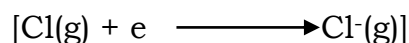
Or

It is the energy required to split 1 mole of an ionic crystal in the solid state into free gaseous ion.

By Hess's law, lattice energy can be obtained

DH_f^θ = DH_1 + DH_2 + DH_3 + DH_4 + DH_5

DH_5 = DH_f^θ - (DH_1 + DH_4 + DH_3 + DH_2)

Qn: Using the following information to work out the lattice energy of sodium chloride.

$Na(s)$ + ½ $Cl_2(g) \longrightarrow NaCl$ DH_c^0 = -410.9KJmol^{-1}

$Na(s) \longrightarrow Na(g) \longrightarrow 107.5$ KJ Mol

$Na(s) \longrightarrow Na^+(g) \longrightarrow 493$ KJ Mol-

$Cl(g) \longrightarrow Cl^-(g) = DH^\theta = -365$KJmol^{-1}
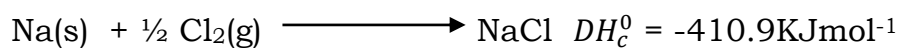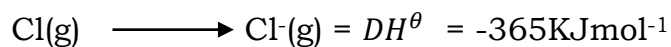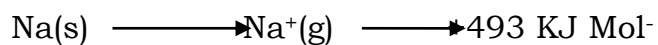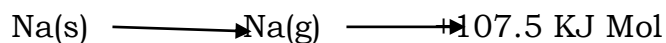
Solution

Using an energy cycle

$$Na(s) \quad + \quad \tfrac{1}{2} Cl_2 (g) \xrightarrow{\;\Delta H_1^\theta = 10.9\;} NaCl(s)$$

ΔH_2^θ $^+107.5$ ΔH_4^θ $+\dfrac{+242}{2}$

Na(g)   Cl(g) ΔH^θ

Lattice energy

ΔH_3^θ $^+493$ $\Delta H_5^\theta = -365$

$Na^+(g) \quad + \quad Cl^-(g)$
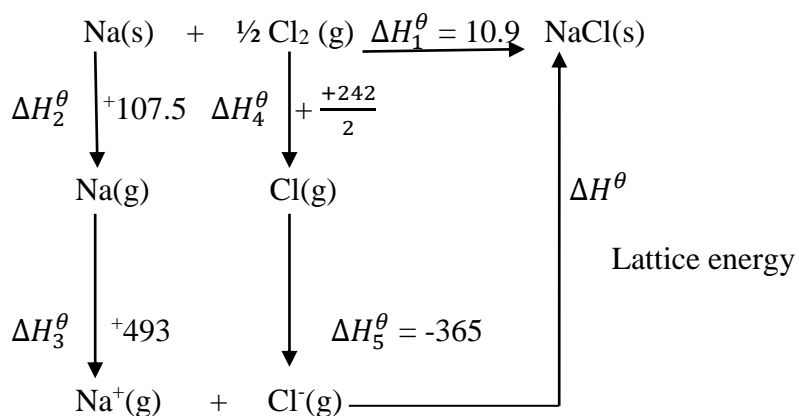
By Hess's law

$DH_1^\theta = DH_2^\theta + DH_3^\theta + DH_4^\theta + DH_5^\theta + DH^\theta$lattice

$DH_{lattice}^\theta = 40.9 - (102.5 + 493 + \dfrac{242}{2} + -365)$

$DH_{lattice}^\theta = 775.9 - 716.5$

$= +59.4$ KJ mol

Using an energy level diagram

$Na^+(g) \quad + \quad Cl^-(g)$

$\Delta H_4^\theta = \dfrac{+242}{2}$ $\Delta H_5^\theta = -365$

$Na^+(g) \quad + \tfrac{1}{2} Cl_2 (g)$

$\Delta H_3^\theta = +493$

$Na(g) + \tfrac{1}{2} Cl_2(g)$

$Cl^-(g) + Na^+(g)$

$\Delta H_2^\theta = +107.5$

$Na(s) + \tfrac{1}{2}Cl(g)$

$\Delta H_1^\theta = -410$ $\Delta H_{Lattice}^\theta$

NaCl(s)
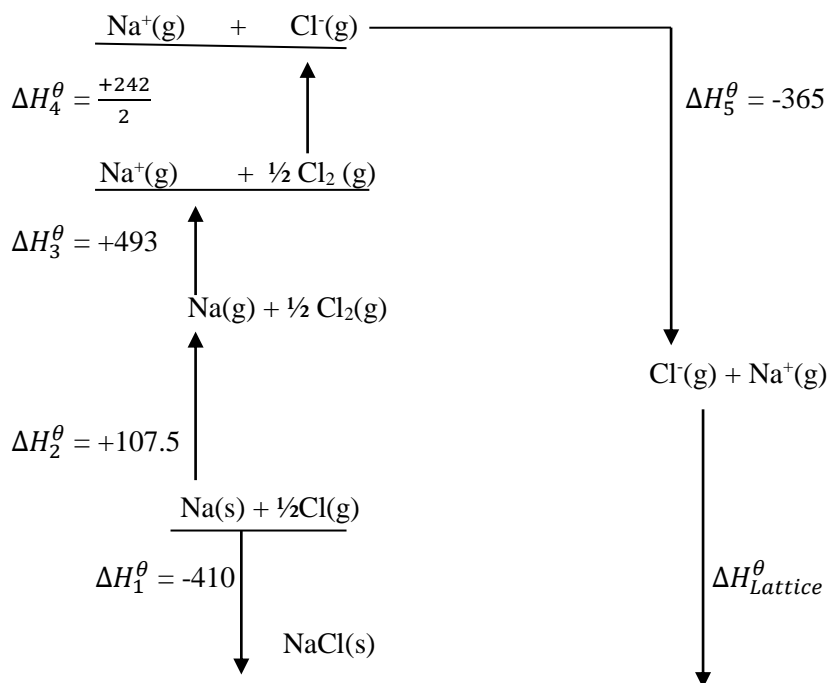
By Hess's law

$DH^\theta_{lattice} = DH^\theta_1 - (DH^\theta_2 + DH^\theta_3 + DH^\theta_4)$

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 ioniasation energy of copper = +716

Atomisation energy of oxygen molecule = +245

2nd electron affirnity of oxygen = +791

Enthalapy of formation y = -115

Copper (ii) oxide

3rd electron affinity of oxygen = -141
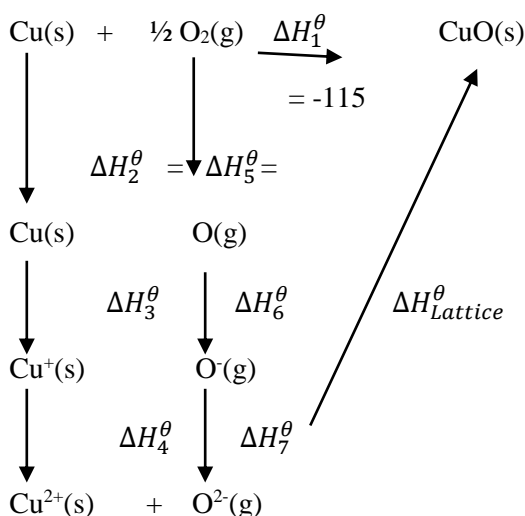
By Hess's law

$DH^\theta_{lattice} = DH^\theta_1 - (DH^\theta_2 + DH^\theta_3 + DH^\theta_4 + DH^\theta_5 + DH^\theta_6)$

(339 + 716 + 791 + 1225 – 141)

= -1942.5 1 mole

$$O^{2-}(g) + Cu^{2+}(g)$$

$$Cu^{2+}(g) \quad + \quad O(g)$$

$$\Delta H_5^\theta \qquad\qquad\qquad\qquad \Delta H_6^\theta$$

$$\underline{Cu^{2+}(g) + \tfrac{1}{2}\,O_2(g)} \qquad\qquad \Delta H_7^\theta$$

$$\Delta H_4^\theta$$

$$\underline{Cu^+(g) + \tfrac{1}{2}\,O_2(g)} \qquad \underline{Cu^{2+} + O^-(g)}$$

$$\Delta H_3^\theta$$

$$\underline{Cu(g) + \tfrac{1}{2}\,O_2(g)} \qquad\qquad \Delta H_{Lattice}^\theta$$
$$\Delta H_2^\theta$$

$$\underline{Cu(g) + \tfrac{1}{2}\,O_2(g)}$$

$$\Delta H_1^\theta = 115$$

$$\underline{CuO(s)}$$
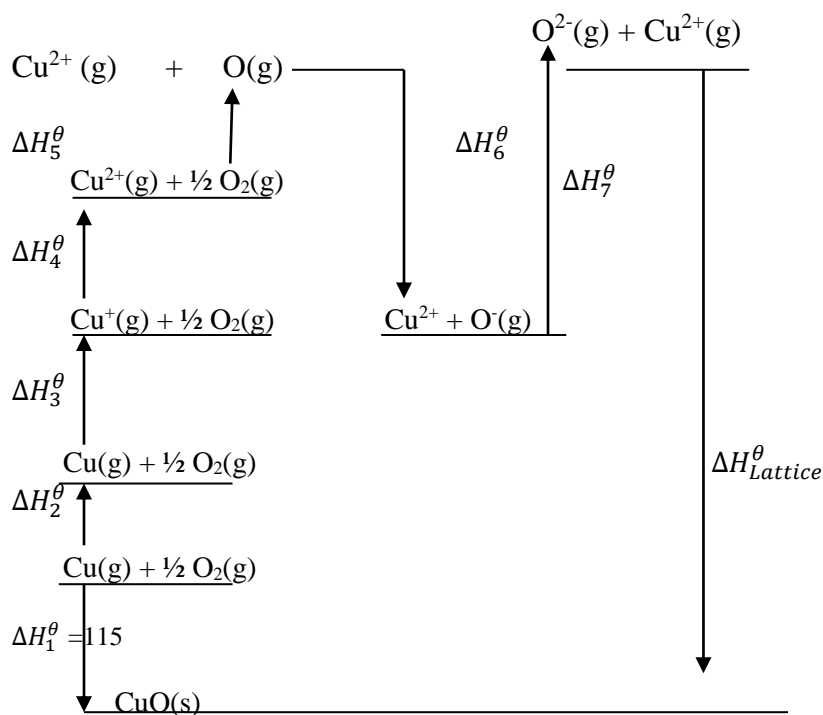
$DH_{lattice}^\theta = DH_1^\theta - (DH_2^\theta + DH_3^\theta + DH_4^\theta + DH_5^\theta + DH_6^\theta + DH_7^\theta)$

-115-[339+746+1960+$\frac{248}{2}$+791 + -141

Use the thermochemical data below to determine the lattice energy of copper (ii) chloride)

DH_f^θ CuCl$_2$ = -220 KJmol^{-1}

$DH_{sublimation}^\theta$ Cu = +338.3 KJmol^{-1}

1st IECu = $^+$475 KJmol^{-1}

2nd F.E Cu = $^+$1958 KJmol^{-1}

1st EA of Cl = -346 KJmol^{-1}

Bond dissociation energy of chlorine molecule = 121.1 KJmol

$$\underline{2Cl^-(g)\ +Cu^{2+}}$$

$\Delta H_6^\theta =$ -396 x 2

$$\underline{Cu^{2+} + 2Cl(g)}$$

ΔH_5^θ 121.1   3

$$\underline{Cu^{2+}(g) + Cl_2(g)}$$

ΔH_4^θ 1950

$$\underline{Cu^+(g) + Cl_2(g)}$$ lattice energy

ΔH_3^θ 475

$$\underline{Cu(s) + Cl_2(g)}$$

ΔH_2^θ 338.3

$$\underline{Cu(s) + Cl_2(g)}$$

$\Delta H_1^\theta =$ -220

$$\underline{CuCl_2(s)}$$
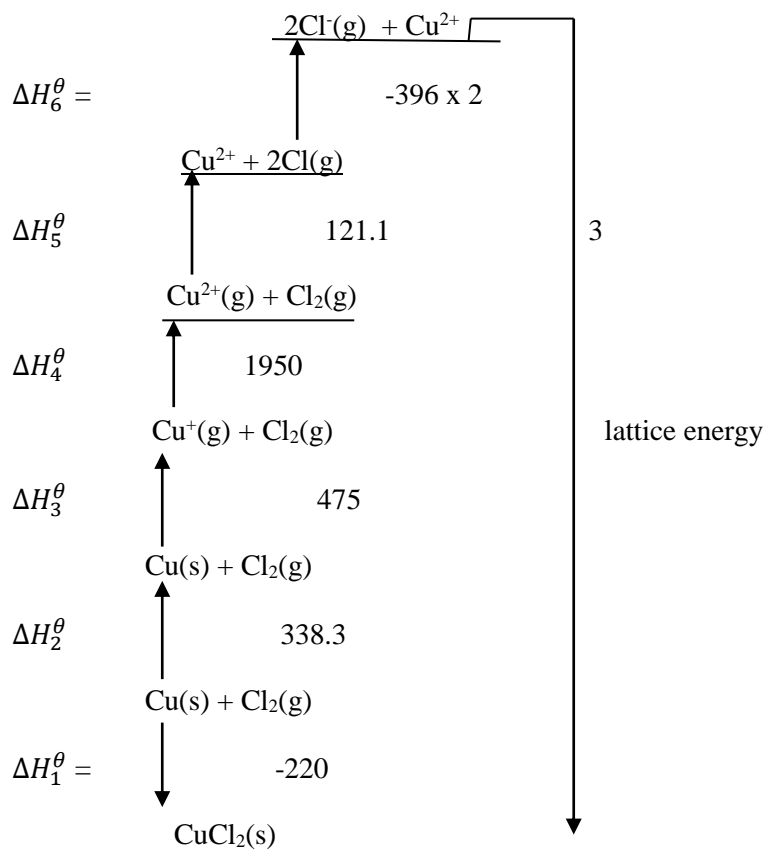
$DH_{lattice}^\theta = DH_1^\theta - (DH_2^\theta + DH_3^\theta + DH_4^\theta + DH_5^\theta + DH_6^\theta)D$

$= -220 = (338.3 + 475 + \dfrac{195\ x\ 2}{2} + -346 + 121.1)$

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

$F = Q^+Q^-$

$F = 1$

$r_1^+ + r_2^-$

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

$$F = \frac{1}{(r^+ + r^-)^2}$$

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 floride has a higher lattice energy than Barrum Chloride ($Ba^{2+}Cl^-$).

Lattice energy decreases in magnitude from lithium Fluoride (L_1F) 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 cowleny is higher in Aluminium Chloride.

Applying lattice energy

1. Determining the stectrometry of salts

Eg Magnesium Chloride is $MgCl_2$ and not $MgC6$

2. Solubility of ionic compounds

3. Thermo decomposition of salts

Stochiometry of salts

Stoichiometry refers to the cation in which atoms react. Consider the born habers cycles $Mg^{2+}Cl^-$

$Mg\ (s) + \frac{1}{2}\ Cl_2(g)\quad Mg^{2+}\ (Cl_2^-)_2$
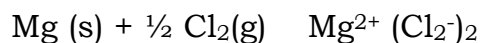
Sublimation energy of magnesium = 150 KJ/mol

1st I.E of magnesium = +736

2nd IE of magnesium = +1450 KJmol^{-1}

Bond dissociation energy per = +242

Moles of chlaire

EA of chlorine = -364

Lattice energy of $MgCl_2$ = -770 KJ/Mol

Lattice energy of $Mg^{2+}Cl^-)_2$ = -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
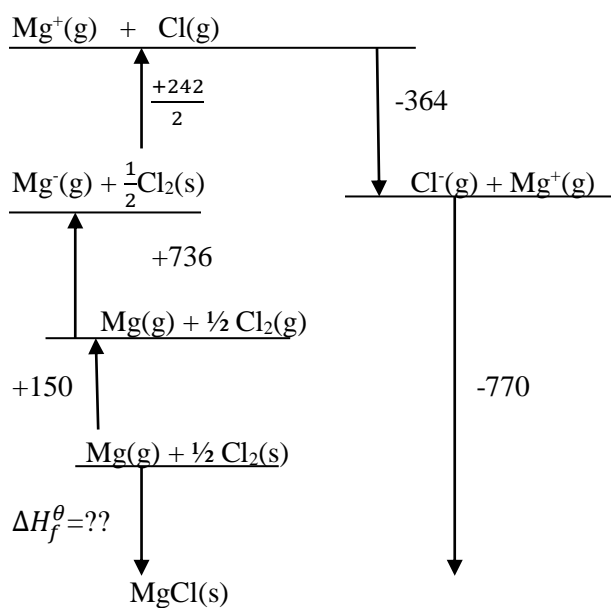
$\Delta H_f^{\theta} = 150 + \frac{242}{2} + $ -364 − 770 + 736

= 127 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

   a) Lattice energy of the solid
   b) Hydration enthalpy of the ions

Hydration energy is defined as the heat charge 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 spearing soluble on insoluble salt lattice enthalpy is higher than hydration energy.

For an ionic solute MX_2 its solubility is shown by the energy cycle below.

$Mx(s) + aq \longrightarrow M^+(q) + X(aq)$

Lattice energy

$M^+_Q + x^-(g) + aq \qquad\qquad DH^\theta$ Hydration
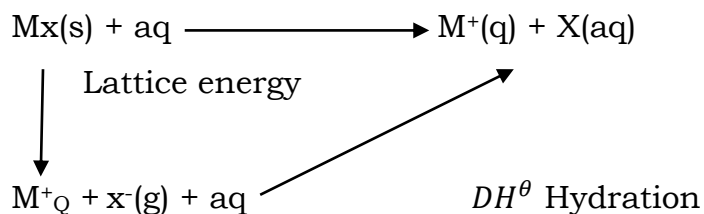
By Hess's law

DH^θ 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 ie its charge and the smaller are less the more isotherme the hydration enthalpy.

Solubility trends for group II sulphases and hydroxides

   (a) Sulphates

The solubility of sulpate depends on charge on the cotton 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 catio has the most important effect since the anion is large and does not change, therefore lattice enthalpy doesnot change significantly as the cation radius increases. However the hydration energy of the cation fall, 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

$MX_{(s)} + (aq)$

Experimental determination of Enthalpy of solution

A known volume of water say Vcm^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 Vcm^3

Mass of solution be a g

Initial temperature of water be T_1 ^0C

Final temperature of solution be T_2 ^0C

Assuming heat capacity of the solution to be $4.2\ Jg^{-1}K^{-1}$

Density of solution is lg/cm^3

Neglecting the heat capacity of the beaker and the thermometer.

Then volume of solution = $(V + a)cm^3$

Mass of the solution = $(V + a)$ x $1 = (V + a)g$

Heat change for the solubility of a g

= mass of solution X SHC X Temperature

= $(V + a)$ x 4.2 x $(T_2 - T_1)$

Heat change for Mrg of solute = $\frac{(V+a)x\ 4.2\ x\ (T_2-T_1)}{a}$ x Mr $Jmol^{-1}$

= $\frac{(V+a)x\ 4.2\ x\ (T_2-T_1)x\ Mr}{1000a}$ $KJ\ mol^{-1}$

Example

15.95g of an hydrous copper sulphate were dissolved in 1 litre of water. The temperature of water was 17^0C and that of solution 18.5^0C. What is the heat of solution of anhydrous copper sulphate (density of solution 1g/cc and specific heat capacity of solution is $9.2\ Jg^{-1}K^{-1}$)

Total volume of solution = Volume of water + Mass of solute

= $(1000 + 15.95)\ cm^3$

$1015.95cm^3$

Mass of solution 1015.95 x 1 (volume x density

= 1015.95g

Enthalpy of solution of

15.95g of solute   = Mass of X SCH of X Temperature

(anhydrous copper (ii) sulphate)   solution   solution   change

= 1015.95 x 4.2 x (18.5 – 17)

= 1015.95 x 4.2 x 1.5

= 6400.85

$CuSO_4$ = (64 x 1) + (32 x 1) + (16 x 4)

= 160g

Enthalpy of solution for 1 mole of anhydrous $CuSO_4$

= $\frac{6400.55}{15.95}$ x 160

= 64205.49 Jmol^{-1}

= 64.2055 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 palarises 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. $(CH_3CH_2CH_2CH_3)$ and methyl propane CH_3CHCH_3 are
$$CH_3$$

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
$CH_3CH_2CH_3$	-7220	-660
$CH_3CH_2CH_2CH_3$	-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.

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

$$CH_3(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$$CH_3CH_2CH_3(g) + \frac{10}{2}O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$
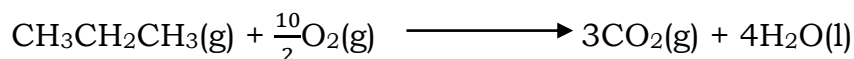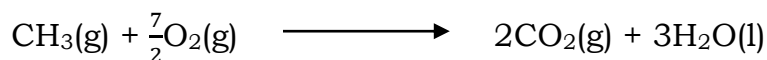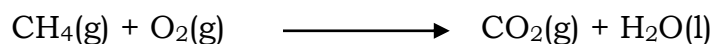
The heat of combustion gets larger by constant amount as you progress along homologous series not only for alkanes but other organic compounds.

The idea is confirmed by plotting heats of combustion against number of carbon atoms for alkanes and alcohols.
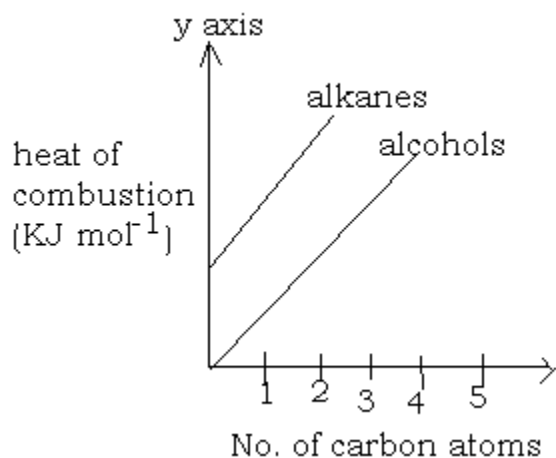
The graph for alcohols passes through the origin while that of alkanes has the intercept along the y-axis for alcohol, using the general formular.

$C_nH_{2n+1}OH$ 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_{n2+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.

DH_C^0 of ethene = -1393 KJ mol^{-1}

DH_C^0 of ethyne = -1310 KJ mol^{-1}

DH_C^0 of $H_2O(l)$ = -286 KJ mol^{-1}

$HC \equiv CH(g) + H_2(g) \longrightarrow H_2C = CH_2(g)$

$H_2C = CH_2 + 3O_2(g) \longrightarrow 2CO_2(q) + 2H_2O(l)$ -1393-----(i)

$HC = CH + \frac{3}{2}O_2(g) \longrightarrow H_2O(l)$ -1310------(ii)

$H_2(g) + ½ O_2(g) \longrightarrow H_2O(l)$ -286------(iii)
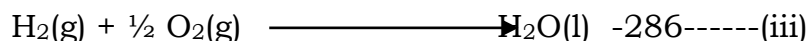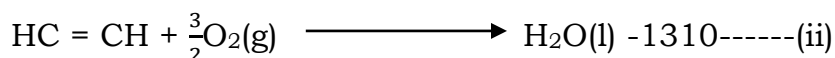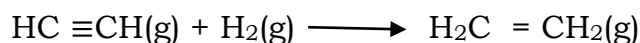
ELECTRO – CHEMISTRY

Electro chemical cells

An electrochemical cell is advice which allows xxxxx action is proceed in such a way that the flow of electrons is produced. An electro chemical cell has two half cells with one involving oxidation reaction and another involving reaction.

xxxxreaction involves simultaneous loss and gain as electrons. A reducing agent losses electrons. A reducing agent loses electrons while an oxidizing agent gains electrons.

Consider the zinc and copper half cell reactions, zinc involves electrons while copper gains electrons. The flow is electrons from the zinc half cell to the copper half cell cases a current to flow in the opposite direction.

The half cell reaction

$Zn(s) \longrightarrow Zn^{2+} + 2e^-$ (oxidation)

Copper half cell reaction
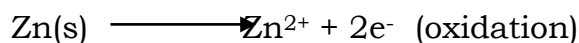
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$ (reduction)

A cell diagram can be used to represent the above

Zn(s) + Cu^{2+} $\longrightarrow$ Zn^{2+} + 2e$^-$

Write the equation for the reaction

Zn(s) + Cu^{2+} $\longrightarrow$ Zn^{2+} + Cu$^-$(s)
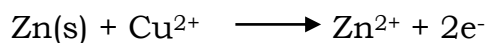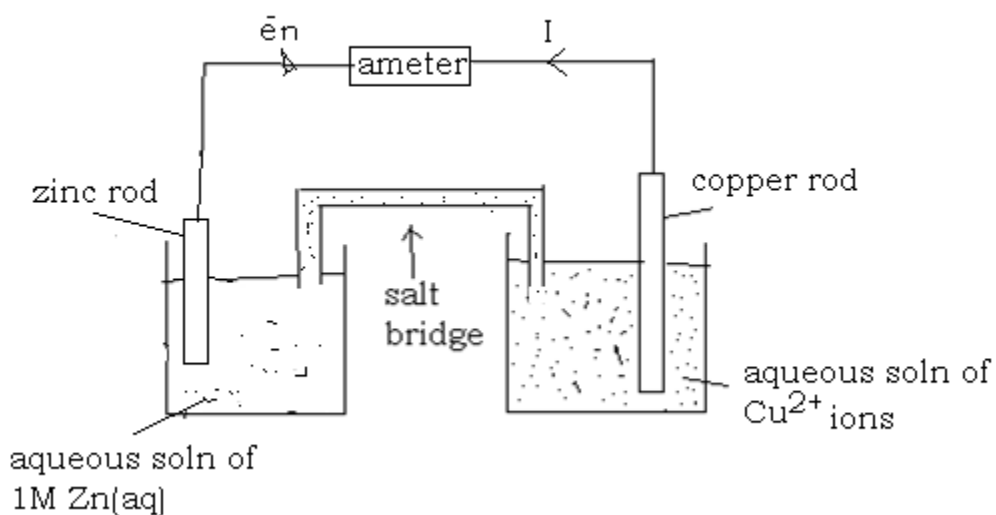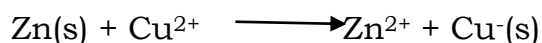
Electrons flow the zinc cell to the copper half cell through the wire the extanal circuit this creates a current in the wire which shows in the opposite direction and measured using an Amnster. This current can be used to do some work like lighting balls.

The redox reaction can be proceed.............are in isolation so the salt brighe comptetes 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 ship of a filter paper sooked in other an acqueous solution of potassium nitrate in KCl

Alternatively a porous partion can be used to separate the two solutions instead of the salt bridge.

a porous partition

zinc rod

copper rod

1M Zn^{2+}(aq) ions

1M Cu^{2+}(aq)

porous
partition
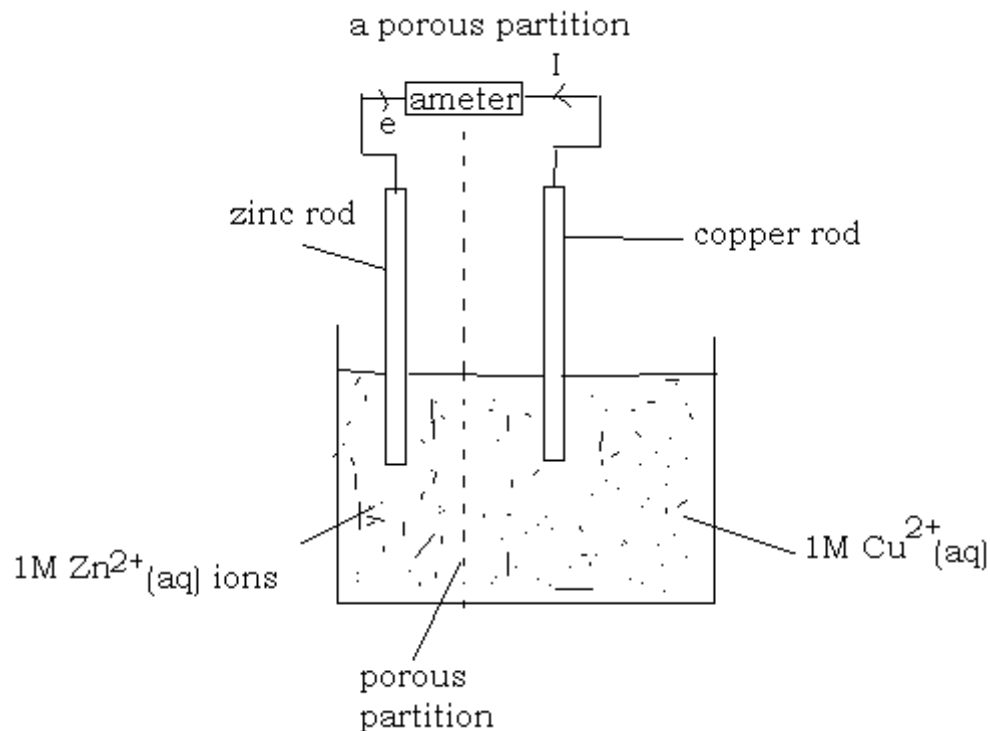
Electrode potential

When a metal rid is dipped into a solution of its ions thing may happen

The metal and may use electrons to form ion which point.

Solution

$$M(s) \longrightarrow M^{n+}(aq) + ne^-$$
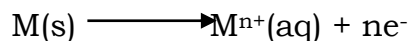
The ions in solution may gain electrons and are deposited as metal on the rod.

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

Whether the metal loss electrons to go into solution ....gaining electrons to deposit as metal depends on the ele...........

Consider the zinc and copper electrodes diping in their acqueous solutions of concentration 1 molar. Sinc being electropositive gas 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 change relative to the outside.

Zinc rod

Zn²⁺

Zn(s)   Zn²⁺(aq) +2e⁻
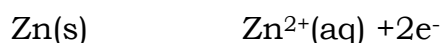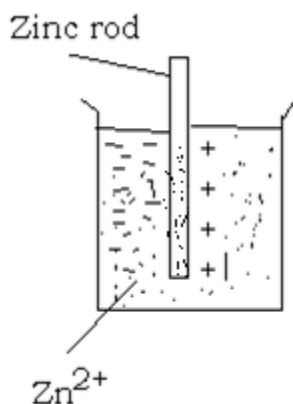
An electric double layer is created called electric pressure difference between the inside of the electrode and the solution. This is called the electrode potential.

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 posit change relative to the solution.

copper rod

Cu²⁺

Cu^{2+} (aq) + 2e   Cu(s)
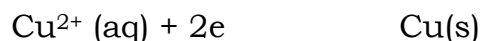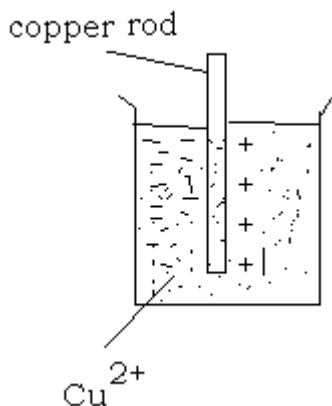
Similarly an electric double layer is created between the electrode and the solution giving the electric pressure difference called an electrode potential.

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 ammeter dipped in a solution of its ions, the standard hydrogen bond is used 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.

hydrogen gas at latm & 298k →

1 m solution of HCl

platinum electrode
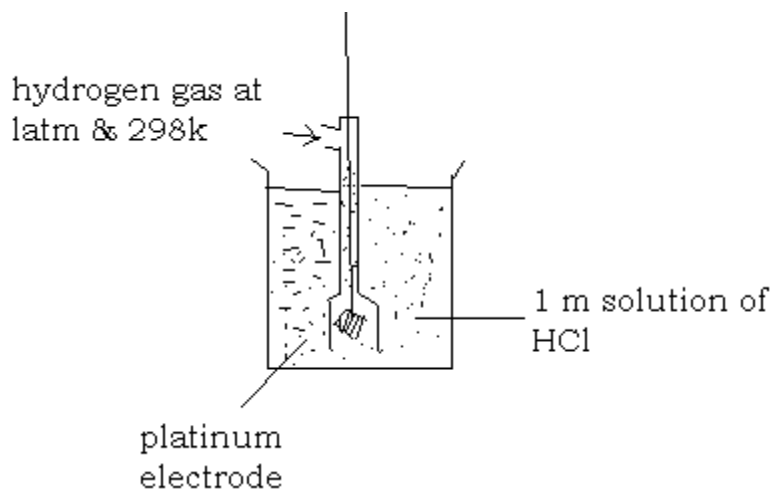
On the platinum electrode

$H^+ + e^-$ $\frac{1}{2} H_2$

$\frac{1}{2} H_2$ $H^+ + e^-$
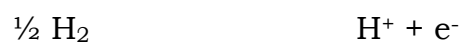
This gives the standard hydrogen electrode (SHE) half cell reaction.

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.

potential meter

hydrogen gas at 25°C and 1 atm

zinc rod

1 M hydrochloric acid

salt bridge

1 M Zinc II irons

platinum electrode
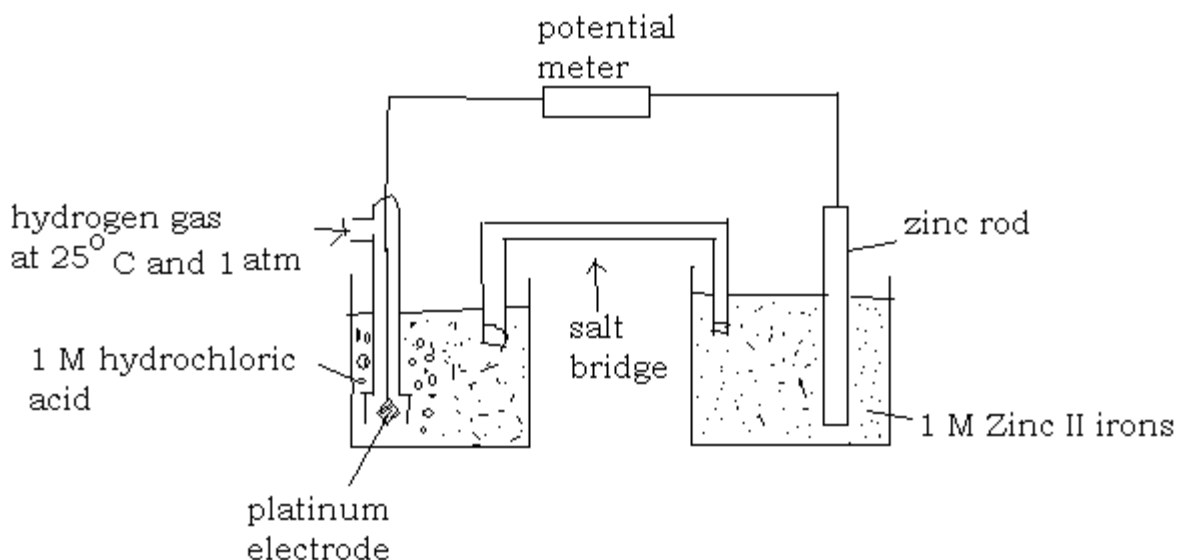
The zinc half cell is constructed from a zinc rod dipped into a solution of zinc II ions of concentration 1M as shown above. The standard hydrogen electrode is constructed by bubbling pure hydrogen gas at a temperature of 298K and a pressure of 1 atm over a plantinum electrode dipping in a solution of HCl bridge. The potential difference between the two half bride, 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 satisified the of a standard electrode potential of a metal is given a symbol E^θ. The superscript θ 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)

Match 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 detouch 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.

Hydrogen energy of the metal ion

$Z^{2+}(s)$ + aq $Zn^{2+}(aq)$

This is the energy given out when a gaseous ion is surrounded of a sphere of an infinite number of water molecules. The higher the hydrogen 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 cases 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.

Temperating

For standard electrode potential temperature should be 298K.

Pressure

The pressure should be / atmosphere under standard conditions.

The convention used are those reummeded by the IUPAC

A cell made up of two half cells

The emf of the cell is given by

E^θ cell = E^θRHS - E^θLHS

The standard hydrogen electrode (SGE) 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 is both are negative the more negative is the left.

Question

Given the following half cell reactions

Cu^{2+}(aq) + 2e⁻   Cu(s) E^θ = +2.34

Ag^{2+} + e⁻   Ag(s) E^θ = +0.80v
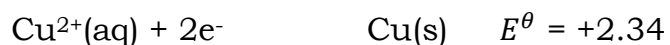
Calculate the emf of the cell

E^θcell = $E^\theta 2HS - E^\theta$ LHS

= 080 – 0.34

= +0.46v

Given the following reaction potentials, calculate the E^θ cell

$Al^{3+}(aq) + 3e^-$ Al (s) E^θ = -1.66v

$Mg^{2+} + 2e^-$ $Mg(s)$ E^θ = -2.39v

$E^\theta cell = E^\theta RHS - E^\theta$ LHS

= -1.66 - -2.37

= +0.718

Using the Daniel half cell reactions

$Zn^{2+}(aq) + 2e^-$ $Zn(s)$ E^θ = -0.76v

$Cu^{2+} + 2e^-$ $Cu(s)$ E^θ = +0.31v

Calculate the E^θ cell

$E^\theta cell = E^\theta RHS - E^\theta$ LHS

= 0.34 - -0.76

= +1.10V

Combining half cells

Consider the Daniel cell made up of copper and zinc half cells

$Zn^{2+} + 2e^-$ $\rightarrow$ $Zn(s)$ E^θ = -0.76v

$Cu^{2+} + 2e^-$ $\rightarrow$ $Cu(s)$ E^θ = -0.34v

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.

$Zn^{2+} + 2e^-$ $\rightarrow$ $Zn(s)$ E^θ = -0.76v

$Cu^{2+} + 2e^-$ $\rightarrow$ $Cu(s)$ E^θ = -0.34v

$Zn(s)$ + Cu^{2+} $\rightarrow$ $Zn^{2+} + Cu(s)$ E^θ = -0.76v
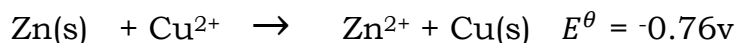
If both have cell reactions are having negative potentials. The more one with a more negative potential is reversed eg the galvanic cell based on the half reactions.

$Al^{3+}(aq) + 3e^-$ $\longrightarrow$ $Al(s)$ E^θ = -1.66v.............(1)

$Mg^{2+}(aq) + 2e^-$ $\longrightarrow$ $Mg(s)$ E^θ = -2.57v.......(2)
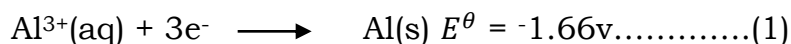
Reversing eqn (3) and multiplying eqn (1) by 2 and eqn (2) by 3

$2 \times Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$ E^θ = +1.66v

$3 \times Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$ E^θ = $^+$2.57v

$2Al^{3+}(s) + 3Mg(s) \longrightarrow 2Al(s) + 3Mg^{2+}$ $E^\theta cell$ = $^+$0.91v
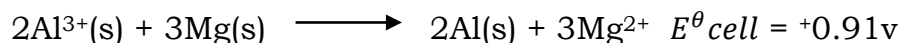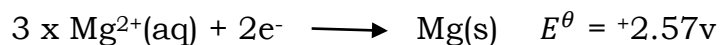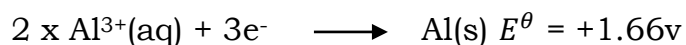
If both half cell reactions have positive electrode potentials, the half cell reaction with less positive electrode potential is reversed eg for the half cell reactions.

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mg^{2+}(aq) + 4H_2O(l)$ E^θ = +1.5v

$ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_4^-(aq) + H_2O(l)$ - E^θ = +1.19v
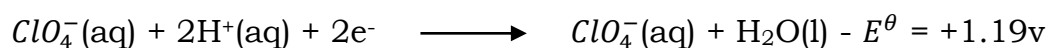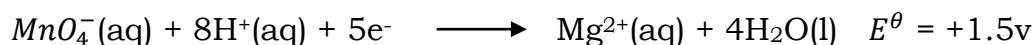
Reversing eqn (s) + multiplying eqn (1) by 2

$2 \times MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mg^{2+}(aq) + 4H_2O(l)$ E^θ = +1.5v

$5 \times ClO_4^-(aq) + 2H^+(aq) + 2e^- \longrightarrow ClO_3^-(aq) + H_2O(l)$ - E^θ = +1.19v

$2MnO_4^-(aq) + 5ClO_3^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5ClO_4^-(aq) + 3H_2O(l)$ $E^\theta cell$ = +0.32v
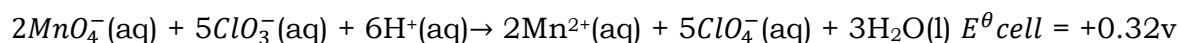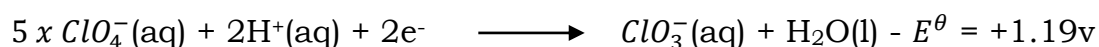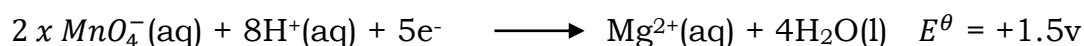
Note

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

$Li^+(aq) + e^- \rightarrow Li(s)$	-303	
$K^+(aq) + e^- \rightarrow K(s)$	-2.92	Strongest reducing agent
$Ca^{2+}(aq) +2e^- \rightarrow Ca(s)$	-2.87	(electropositive)
$Na^+(g) + e^- \rightarrow Na(s)$	-2.71	
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37	
$Al^{3+}(aq) + 2e^- \rightarrow Al(s)$	-1.66	
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(l)$	-0.76	
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(l)$	-0.13	
$H^+(aq) + e^- \rightarrow ½ H_2(g)$	-0.00	
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34	Weakest reducing agent
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80	

The more negative the potential the easier is for oxidation to take place ie

$M(s) \longrightarrow M^{n+}(aq) + ne^-$
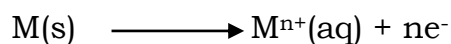
This is true for highly electropositive metals with loosely attached electrons. These are mainly group I elements which are electron donors, making them strong reducing gents.

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.

$Zn^{2+} + 2e^- \longrightarrow Zn(s) = 0.76v$

$Cu^{2+}(aq) + 2e^- \longrightarrow E^\theta = +0.34v$
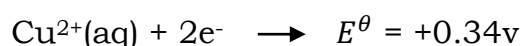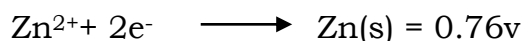
The zinc electrode is the negative electrode therefore it is the anode and oxidation takes place at this electrode according to the equation.

$Zn^{2+} \longrightarrow Zn^{2+} + 2e^- \qquad E^\theta = +0.76v$
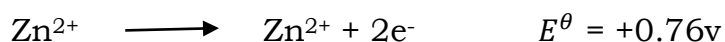
In the process electrons are given a way to the electrode which acquires a negative change relative to the solution.

The copper electrode is the positive electrode and is the cathode on the electrode giving it a positive change relative to the solution. The cathode reaction is therefore;

$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \; E^\theta = +0.34V$
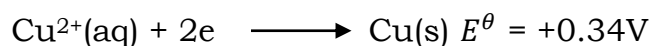
THE PLANTINUM ELECTRODE (PE)

Consider half cell reactions below involving ion –ion type without a metal

$Fe^{2+} + e^- \longrightarrow Fe^{2+}(aq)$

$Sn^{4+} + 2e \longrightarrow Sn^{2+}(aq)$

$Cu(s) / Cu^{2+}(aq) (1M) // Fe^{3+}(aq) (1M) – Fe^{2+}(1M) / Pt(s)$

Again for the reaction

$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

$Pt(s)/Fe^{2+}(aq) (1M), Fe^{3+}(aq) (1M) // MnO_4^-(aq) (1M), H^+(aq) + Mn^{2+}(aq)(1M)/ Pt(s)$
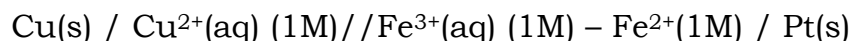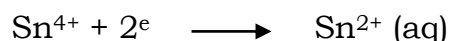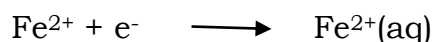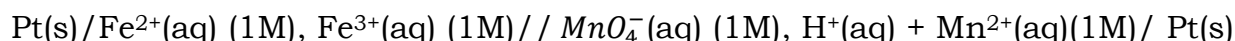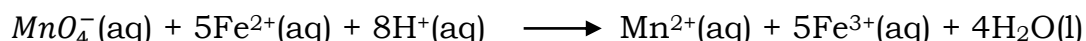
(oxidation)   (Reduction)

If one of the electrodes is the SHE then it is used as the left hand side electrode.

$\frac{1}{2}H_2(g) \longrightarrow H^+ + e$

$Pt(s) / \frac{1}{2}H_2(s), H^+(g)$

Or $Pt(g)$ ½ $H_2(g)/H^+(aq)$
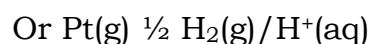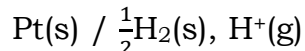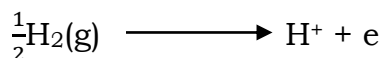
Emf of cell / $E^\theta cell$

This is defined as the potential difference between two half cells each with its electrode dipping in its acqueous 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 the left to the right and the current to flow kin the opposite direction.

Consider the Daniel cell of made up of the 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 electrodes in the rod giving it a negative potential.

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
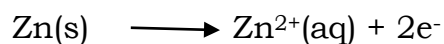
These electrons flow in the external circuit connected to the copper electrode. The copper ions gain electrons to deposit as copper metal. As more copper ions deposit on the electrode, the electrode acquires a positive charge relative to the solution giving it a positive potential.

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
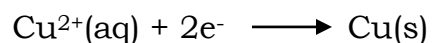
The flow of electrons from the zinc half cell to the supper half cell causes a current to flow in the opposite direction generating and emf which can be measured using a potentiometer.

Measuring e.m.f ($E^\theta cell$)

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.
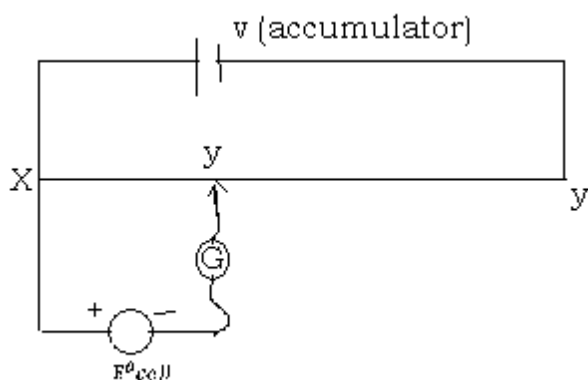
A jockey J is moved on a uniform wire xy(100cm) until when a condition of a current flow in the galvanometer is achieved (null point) or balance point. At balance point the ratio of the length xy/xy = to the ratio of emf of the standard cell y to the emf of the cell under investigationE^θ.

$$\frac{xy}{xy} = \frac{V}{E^\theta}$$

$$E^\theta = \frac{V\,[xJ]}{xy}$$

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

DG^θ = -nFE^θ, where

N = number of moles of electrons transferred

F = Faraday's constant

E^θ = Emf of a cell

Consider the Daniel cell

Zn(s) + Cu^{2+}(aq) $\longrightarrow$ Zn^{2+}(aq) + Cu(s) E^θ = +1.1V

$\Delta G^\theta = -Fe^\theta$
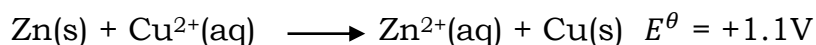
= -2 x 96500 x 1.10

= -212300J mol^{-1}

-212.3 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 E^θ cell is positive and the free

energy change DG^θ is negative.

Qn

The electrode potentials for some reactions are given below

2H$^+$(aq) + O$_2$(g) + 2e$^-$ $\longrightarrow$ H$_2$O$_2$(aq) E^θ = +0.68V

Ag$^+$(aq) + e$^-$ $\longrightarrow$ Ag(s) E^θ = +0.8V

H$_2$O$_2$(aq) + 2H$^+$(aq) + 2e$^-$ $\longrightarrow$ 2H$_2$O(l) E^θ = +1.72V
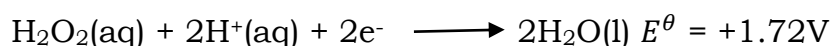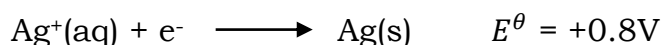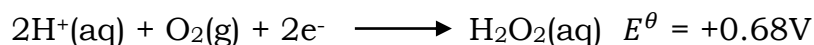
Write an equation for the reaction between silver nitrate and H$_2$O$_2$ and work
out the E^θ cell and state whether the reaction is feasible or not give a reason.

Solution

2 x Ag$^+$ + e$^-$ $\longrightarrow$ Ag$^+$ E^θ = +0.80V

H$_2$O$_2$(aq) $\longrightarrow$ 2H$^+$(aq) + O(g) + 2e$^-$ E^θ = -0.68V

2Ag$^+$(aq) + H$_2$O$_2$(aq) $\rightarrow$ 2Ag(s) + 2H$^+$(aq) + O$_2$(g) E^θcell = (0.8 + 0.65) = 0.12V
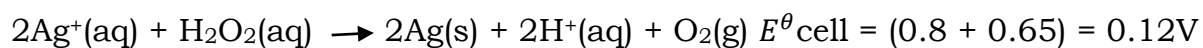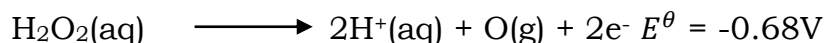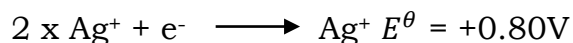
Or E^θcell = E^θ_R - E^θ_L

= (+0.80 - +0.68)

= +0.12V

The reaction is feasible because of the cell is positive

Question

Below are half cell reactions

MnO_4^-(aq) + 8H$^+$(aq) + 5e$^-$ $\longrightarrow$ Mn^{2+} (aq) + 4H$_2$O(l) E^θ = +1.51V

Cl$_2$(aq) + 2e$^-$ $\longrightarrow$ 2Cl$^-$(aq) E^θ = +0.75V
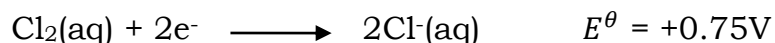
    a) Write the equation for the spontaneous cell reaction

    b) Calculate the emf of the cell made by combining the two half cell reactions

    c) Using four result in (b) explain why HCl is not used to acidify potassium permanganate titration

Solution

For a feasible reaction, E^θcell should be positive so reversing equation 2.

$2x\ MnO_4^-$(aq) + 8H$^+$(aq) + 5e$^-$ $\longrightarrow$ Mn^{2+} (aq) + 4H$_2$O(l) E^θ = +1.51V

5x Cl$_2$(aq) + 2e$^-$ $\longrightarrow$ 2Cl$^-$(aq) E^θ = +0.75V

2 MnO_4^-(aq) + 10Cl$^-$(aq) + 16H$^+$(aq) $\rightarrow$ 2Mn^{2+}(aq) + 8H$_2$(l) + 5Cl$_2$ E^θ = +0.76V
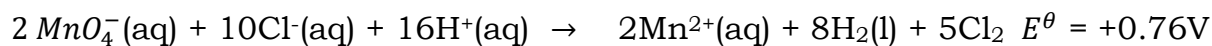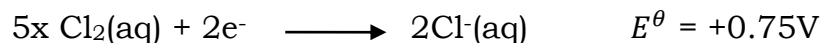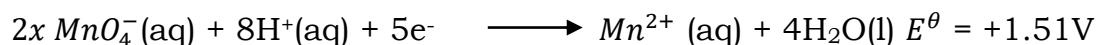
E^θcell = $E^\theta R$ $E^\theta L$

+1.51 - +0.75

= +0.76V

Since the oxidation of chloride ions to chlorine by the permanganent ions gives a positive E^θcell 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

Cu$^+$/Cu = +0.52V

Cu^{2+}/Cu$^+$ = +0.15V

Cu + Cu^{2+} $\longrightarrow$ 2Cu$^+$
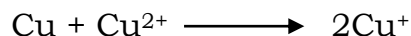
Calculate the cell voltage of the reaction and state whether the reaction is feasible or not.

Cu + Cu^{2+} $\longrightarrow$ 2Cu$^+$

Cu(s) $\longrightarrow$ Cu$^+$ + e$^-$ E^θ = -0.52V

Cu^{2+} + e$^-$ $\longrightarrow$ Cu$^+$(aq) E^θ = -0.15V

Cu + Cu^{2+} $\longrightarrow$ 2Cu$^+$(aq) E^θcell = -0.37V

317
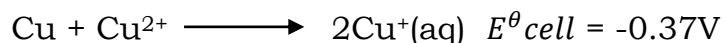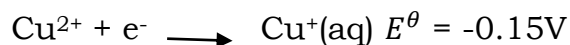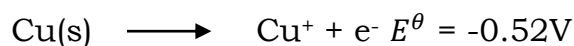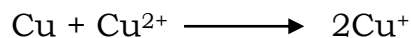
The reaction is not feasible because the emf of the cell is negative.

Which ion is more stable in the acqueous solution and why.

Copper (ii) is more stable in the acqueous 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

$2Cu^+ \longrightarrow Cu(s) + Cu^{2+}(aq)$ $E^\theta cell$ = +0.37V
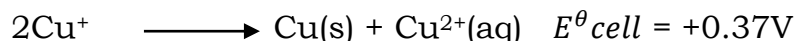
Therefore Cu^{2+} readily despoortianates into element copper (ii)

A disproportionation reaction is one involving self oxidation and reduction of a chemical species.

Question

Given

MnO_4^-(aq) + 4H$^+$(aq) + 2e$^-$ $\longrightarrow$ MnO$_2$(s) + 2H$_2$O(l) E^θ = +2.26V

$2MnO_4^-$ + 2e$^-$ $\longrightarrow$ $2MnO_4^{2-}$(aq) E^θ = +0.56V

Comment on the feasibility of the reaction

$3MnO_4^-$(aq) + 4H$^+$(aq) $\longrightarrow$ $2MnO_4^-$(s) + MnO$_2$ + 2H$_2$O(l) and the stability of the MnO_4^-(aq) ion. (F = 96500C)

Solution

Reverse equation (2)

MnO_4^-(aq) + 4H$^+$(aq) + 2e$^-$ $\longrightarrow$ MnO$_2$(s) + 2H$_2$O(l) E^θ = +2.26V

$2MnO_4^-$ $\longrightarrow$ $2MnO_4^{2-}$(aq) + 2e$^-$ E^θ = +0.56V

$3MnO_4^{2-}$(aq) + 4H$^+$(aq) $\longrightarrow$ $2MnO_4^-$(s) + MnO$_2$ + 2H$_2$O(l)
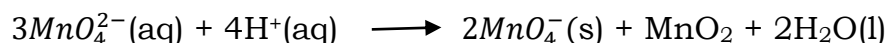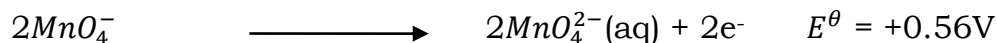
$E^\theta Cell = E^\theta R - E^\theta L$

= +2.26-0.56

=+1.70V

$E^\theta cell$ = +1.70V

$\Delta G^\theta cell = nFE^\theta$

= -2 x 96500 x 1.70

= -328.1KJMol^{-1}

The reaction is feasible because the free energy change for the cell reaction is negative.

Since the forward reaction is feasible the MnO_4^{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

Zn(s) + Cu²⁺ $\longrightarrow$ Zn²⁺(aq) + Cu(s) E^θ = +1.1V
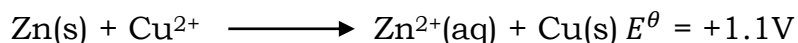
The above cell reaction generates an emf of 1.10V under standard conditions and any ions involved having a concn of 1 molar.

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
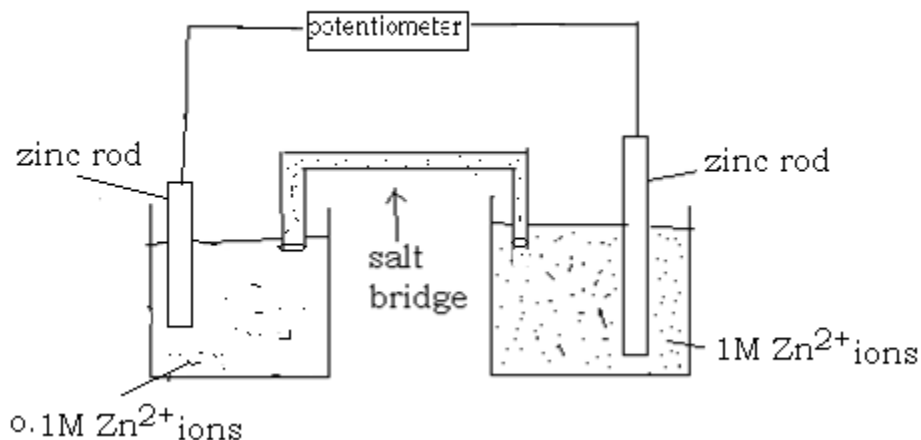
A concentration cell is one in which both compartment have the same chemical species but at different concentrations, the difference in concentration is the only factor that produces a cell voltage.

Equilibrium is achieved when the two concentrations are equal.

The higher concentration is reduced and the lower concentration is increased therefore a dilute solution under goes oxidation ie more of the zinc electrode dissolves releasing zinc ions in solution.

Zn(s) $\longrightarrow$ Zn²⁺ + 2e⁻
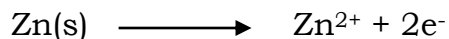
Therefore the dilute compartment forms the left half cell

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.

$$Zn^{2+} + 2e \longrightarrow Zn(s)$$
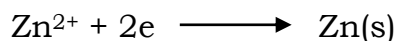
Therefore the concentrated compartment forms the right half cell. The conventon used here is electrons flow from the less concentrated to the more concentrated and the less concentrated in the negative half cell while the more concentrated is the positive half cell.

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.

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \text{ (oxidation)}$$
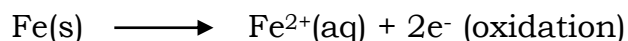
The electrons travel to the cathodic area and reduce oxygen so at the cathodic area the following reaction takes place.

$$\frac{1}{2}O_2(l) + 2e^- + H_2O(l) \longrightarrow 2\bar{O}H(aq)$$
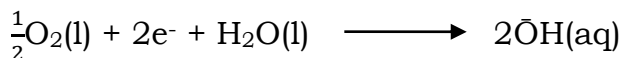
The iron (ii) ions and hydroxyl ions meet and ions (iv) hydroxide is precipitated

$$Fe^{2+}(aq) + 2\bar{O}H(aq) \longrightarrow Fe(OH)_2$$
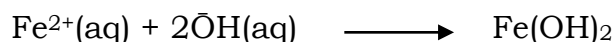
Finally oxygen oxidizes the iron (ii) hydroxide to iron (iii) oxide which is rust.

$$2Fe(OH)_2 (s)+ \frac{1}{2} O_2(l) \longrightarrow Fe_2O_3 + 2H_2O (s)$$
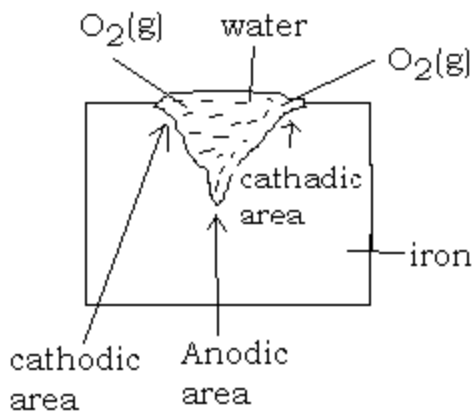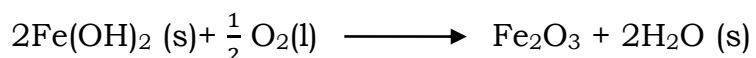
Stainless steel is iron containing a high proportion of chromium which forms a protective layer of chromium (iii) oxide over the whole surface of the metal. If the surface is scratched, a new protective layer of chromium (iii) oxide is formed and iron does not rust.

It scratched, at the anodic area chromium atoms became oxidized since chromium is more electropositive than iron.

$$Cr(s) \longrightarrow Cr^{2+} + 2e^-$$
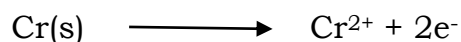
At the cathodic area water splits into $\bar{O}H$ and hydrogen ions the hydrogen ions are discharged as hydrogen gas at the cathode but the $\bar{O}H$ ions meet with the Cr^{2+} ions forming Cr^{2+} hydro chromium (ii) hydroxide.

$$Cr^{2+}(aq) + \bar{O}H(aq) \longrightarrow Cr(OH)_2(s)$$

Finally chromium (ii) hydroxide undergoes oxidation aerial oxidation to form chromium (iii) oxide.

$$2Cr(OH)_2(s) + \tfrac{1}{2} O_2 \longrightarrow Cr_2O_3(s) + 2H_2O$$

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

Zn(s) $\longrightarrow$ Zn^{2+}(aq) + 2e$^-$

Cathode reaction

2H$^+$(aq) + 2e$^-$ $\longrightarrow$ H$_2$(g)
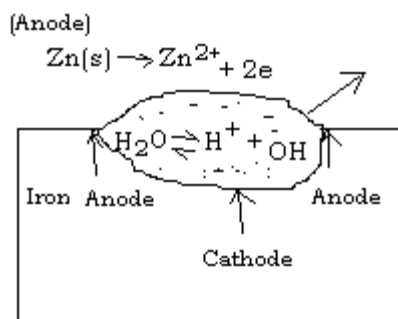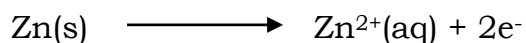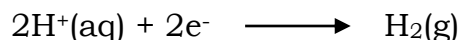
Zinc is more electropositive than iron so it goes into solution liberating zinc ions and electrons. This surface becomes the anodic area where oxidation takes place.

Iron acts as a cathode where water splits into hydrogen ions and ŌH 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.

Zn^{2+}(aq) + 2ŌH $\longrightarrow$ Zn(OH)$_2$ (s)
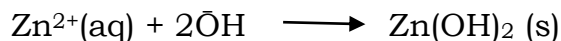
This solid forms a protective covering that prevents iron under health from rusting. During this process zinc is sacrificed hence acts as a sacrificial metal.

Suppose tin plated iron is scratched creating a depression where water fill, the following reactions takes place.
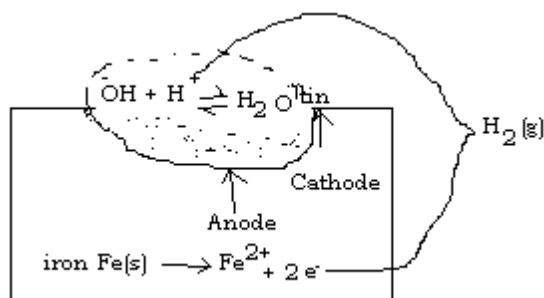
Iron is more electropositive than tin so it undergoes oxidation and forms the anodic area.

Fe(s) $\longrightarrow$ Fe^{2+}(aq) + 2e

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.

H_2O(l) $\bar{O}H$(aq) + H$^+$

2H$^+$(aq) + 2e$^-$ H$_2$(g)

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.

Fe^{2+}(aq) + 2$\bar{O}$H $\longrightarrow$ Fe(OH)$_2$ (s)
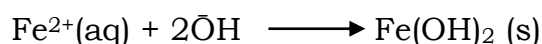
The hydrogen undergoes aerial oxidation to form hydrated iron (iii) oxide which is rust.

2Fe(OH)$_2$ (s) + $\frac{1}{2}$O$_2$(g) $\longrightarrow$ Fe$_2$O$_3$.2H$_2$O(s)
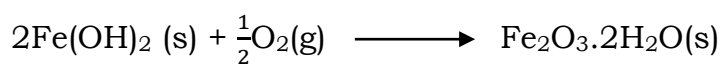
Therefore tin can not protect iron from rusting.

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 acqueous or molten state eg salts, acids, alkalis etc.

2. Non – electrolytes

Substances which do not conduct electricity in acqueous solution or molten state eg glucose, sucrose and many organic compounds.

3. Weak electrolytes

Substances which only slightly ionize in acqueous 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 acqueous solution eg salts of metals and all mineral acids

5. Covalent electrolytes

These only ionize when only in acqueous 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 acqueous 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 fussed 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. T here fore 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 ∝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 Ampire is used for 1 second

M=Z

Z is aproportionality constant called the electrochemical equivalent

It is defined as the mass of a substance liberated or deposited when a current of one ampire 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 it constant. It was given the value 96500C and is calleda 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 x 25 x 60

= 4500C

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
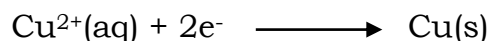
2F deposit 64g of Cu

4500C will deposit $(\frac{64}{2F} \times 4500)$

$= \frac{64}{2 \times 96500} \times 4500$

= 1.49g

Assume that during the electrolysis of $250cm^2$ 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

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
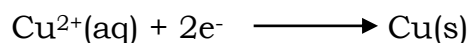
Moles of $CuSO_4$ used = $(\frac{0.1}{1000} \times 250)$

$= 2.5 \times 10^{-2}$ moles

$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$

1 mole of $CuSO_4$ gives 1 mole of $Cu^{2+}aq$

Moles of Cu^{2+}

$= (\frac{0.1 \times 250}{1000})$

= 0.025moles

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

= 4825C

= 4825

Name the gas obtained at the positive electrode and write the equation to its release.

$4\bar{O}H(aq) \longrightarrow 2H_2O(l) + O_2(g0 + 4e^-$
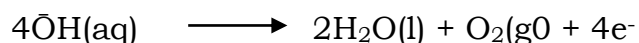
(c)calculate the volume of the gas at stp obtained at the positive electrode (I= 96500Cmol^{-1}, molar gas volume of stp = 22.4 dm³)

Solution

$4\bar{O}h(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e^-$
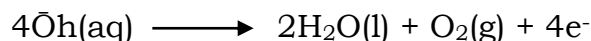
4F are required to discharge 1 mole of O_2

(4 x 96500)C are required to discharge 22.4dm³ of O_2

1C will discharge $\frac{22.4}{4\ x\ 96500}$ of oxygen

4825C will discharge $[\frac{22.4}{4\ x\ 96500}$ 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.
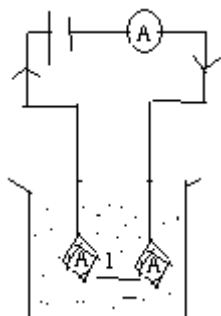
The resistance offered by a given volume of he electrolytic solution between the two electrodes to the flow of current is in line with the one offered by metallic conductors.

At constant temperature, the electrical resistance offered by the electrolyte is

    (i)   Directly proportional to the distance of separation 1 between the two electrodes.

    (ii)   Inversely proportional to the cross-sectional area of the electrodes ie

R $\propto$l ....(1)

R $\propto \frac{l}{A}$..............(2)

Combining (1) and (2)

$R \propto \dfrac{l}{A}$

Or

$R = \rho\dfrac{l}{A}$

Where ρ is proportionality constant called resistivity

Resistivity $(\rho) = R\dfrac{a}{l}$

The electrodes are of a unit cross – sectional area and the distance of separation between two electrodes is a unit length.

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.

From $R = \rho\dfrac{l}{A}$

$\dfrac{1}{R} = \dfrac{1}{\rho} \cdot \dfrac{A}{l}$

The receprical of resistance $\dfrac{1}{R}$ is the conductance electrolyte. It is given the symbol C

$C = \dfrac{1}{\rho} \cdot \dfrac{A}{l}$

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 receprical of electrolyte resistivity is called electrical conductivity $\left(\dfrac{1}{\rho}\right)$ and is given the symbol K.

From $\dfrac{1}{\rho} = \dfrac{1}{R} \cdot \dfrac{l}{A}$

$K = \dfrac{1}{R} \cdot \dfrac{l}{A}$

$K = C\cdot\dfrac{l}{A}$

If l = aunit, & A=a unit

K = C

Electrolytic conductivity K is defined as the reciprocal of resisitivy 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 $\frac{l}{A}$

If l is in metres and A is square metres

$$K = \frac{1}{ohm}.\frac{m}{m^2}$$

And if l = cm and A in cm

Then

$$K = Ohm^{-1}cm^{-1}$$

Siemen metre^{-1} (sm^{-1}) or siemen centi metre (S cm^{-1}) are also used since $\frac{1}{ohm}$ = Siemen.

(1 Scm^{-1} = 100Sm^{-1})

Measurement of conductivity of solutions
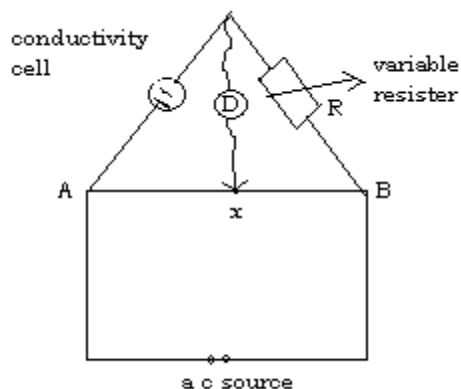
A wheatstone bridge circuit is used be.

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

$$\frac{Resistance\ offered\ by\ conductivity\ cell}{Resistance\ of\ the\ variable\ resistor} = \frac{Length\ of\ Ax}{Length\ of\ XB}$$

Resistance of the variable of the conductivity cell is obtained and the conductivity K can be determined using the expression $K = \dfrac{1}{R} \cdot \dfrac{l}{A}$

The value of the cell constant $\dfrac{l}{A}$ 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(CH₃COOH)	0.0107	0.041	0.143	0.46		1.32	1.60	1.62

This is shown graphically below
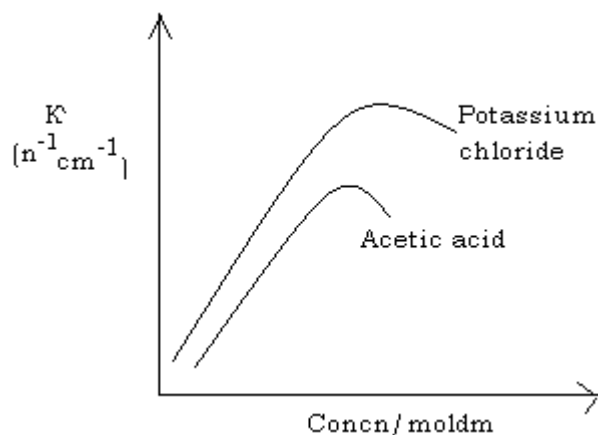
Strong electrolytes are fully dissociated in solution releasing many conducting ions per unit volume showing a higher conductivity.

Weak electrolytes are only slightly ionized releasing few conducting ions kin solution hence a lower conductivity 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
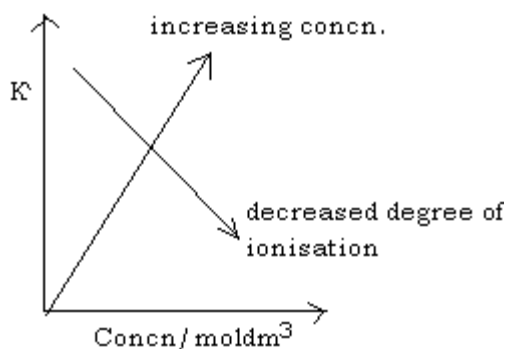
Strong electrolytes
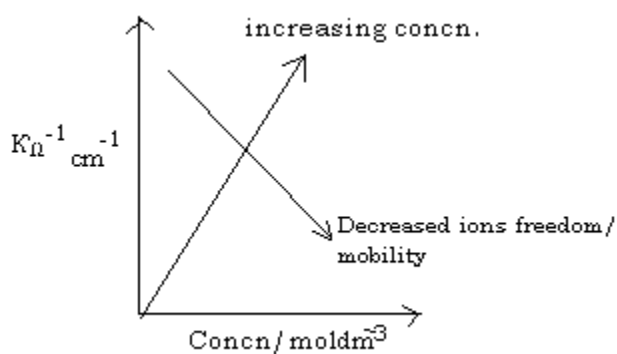
For weak electrolyte the degree of ionization is high at low concentration, so many conducting ions per unit volume. The degree of ionization decreases with increase in concentration educing the number of conducting species per unit volume. Therefore the conductivity K is lowered at high concentration. For concentration because of a lowered ionic interference or increased ionic freedom.

At high concn there is an increase in ionic interprence lowering ionic freedom reducing the conductivity.

Molar conductivity λc/λc

This is defined as the conductante of a given volume of an electrolyte containing 1 mole of a solute between two electrodes of $1cm^2$ cross-sectional area seperated by a length of 1 cm.

Molar conductivity $\lambda c = \dfrac{Electrolytic\ conductivity}{concentration}$

$$= \frac{K}{c}$$

C = mold m^{-2}

$K = \Omega^{-1}cm^{-1}$

$\Lambda_c = \dfrac{\Omega^{-1}cm^{-1}}{moldm^{-3}}$

10cm = 1dm

10^{-3}cm^{-3} = 1dm^{-3}

$= \dfrac{\Omega^{-1}cm^{-1}}{mol.10^{-3}cm^{3}}$

1000Ω^{-1}cm^{2}mol^{-1}

Units are Ω^{-1}cm^{2}mol^{-1}

$\Lambda_c = \dfrac{1000\ K}{c}$ Or molar conductivity $= \dfrac{K}{c}$

10dm = 1m

1 dm = $\left(\dfrac{1}{10}\right)$m = 10^{-1}m

$\dfrac{\Omega^{-1}cm^{-1}}{moldm^{-3}}$

1 dm^{-3} = (10^{-1})$^{-3}$m^{-3}

1 dm^{-3} = 10^{3}m^{-3}

$\Lambda_c = \dfrac{\Omega^{-1}m^{-1}}{mol.10^{3}m^{-3}}$

$= \dfrac{\Omega^{-1}m^{2}mol^{-1}}{10^{3}}$

Units are Ω^{-1}m^{2}mol^{-1} and $\boxed{\Lambda_c = \dfrac{1000\ K}{c}}$

Variation of molar conductivity with concentration

Λ_0

Λ_c

Strong electrolyte
eg KCl

weak electrolyte
eg CH_3COOH

$\sqrt{\text{concentration (moldm}^{-3})}$

Λ_0

Strong electrolyte
eg KCl

weak electrolyte
eg CH_3COOH

Λ_c

$\Omega^{-1}cm^2mol^{-1}$

$\frac{1}{C}$ (dillution)
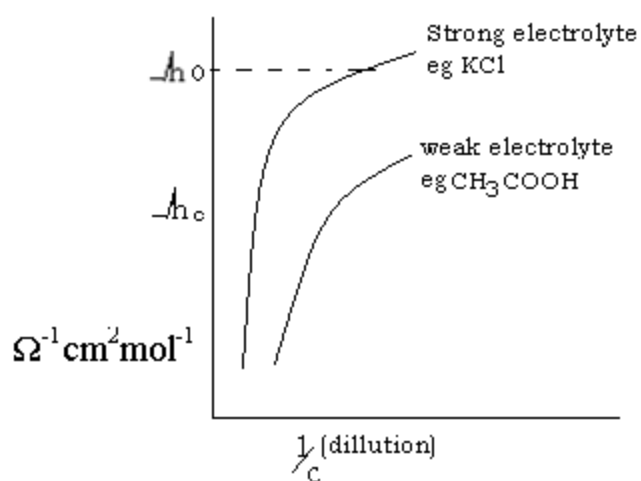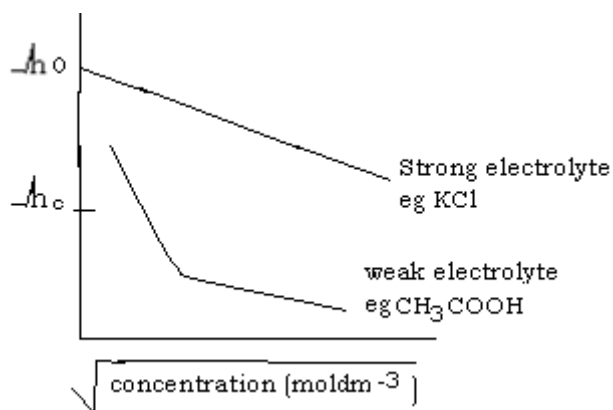
(a) Strong electrolytes

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 affects (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;

$$\Lambda_c = \Lambda_c^\circ - K\sqrt{C}$$

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
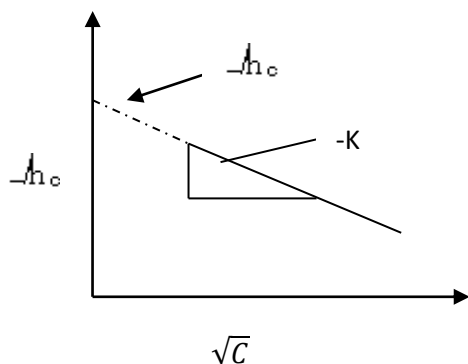
A strong electrolyte molar conductivity is highest at zero concn at infinite dilution because at this point positive and negative ions are very free from each other. The value of molar conductivity at zero (0) concn or infinite dilution is called the molar conductivity at zero concentration and is obtained by extra polation.

   (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 conducing ions in the solution.

At high concentration (low dilution), the degree of ionization is greately reduced reducing the number of conducting ions in solution and reducing the molar conductivity.

For a weak electrolyte, Armheneous found out that the degree of ionization $\propto$ is given by

$$\propto = \frac{\Lambda_c}{\Lambda_0}$$

And at zero concn (inifinte dilution) $\propto$ is proximately equal to 100% or 1 but a high concentration $\propto$ is less than 100% or 1

The value of Λ_c at a given concentration is got from conductivity measurement by using an electrolyte of a known concentration ($\Lambda_c - \frac{K}{c}$) while for Λ_c it is got indirectly by using Kohlauseh'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.

$\square$(NaCl) = $-h°$Na$^+$ + $-h°$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

$\square$(CH$_3$COOh) = $-h°$(CH$_3$CO$\bar{O}$) + $-h°$(H$^+$)

Alternatively the value of $-h°$ for ethanoic can be obtained from the molar conductivity at zero concn for selected strongy electrolytes eg NaCl, HCl and CH$_3$CO$\bar{O}$Na$^+$

i.e HCl(aq) + CH$_3$CO$\bar{O}$Na$^+$ (aq) $\longrightarrow$ NaCl(aq) + CH$_3$COOH(aq)

$\square$CH$_3$COOH = ($-h°$HCl + $-h°$CH$_2$CO$\bar{O}$Na$^+$) - $-h°$NaCl
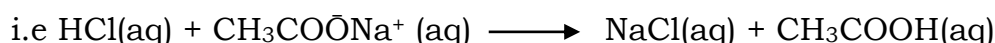
The olar conductivity of KNO$_3$. KCN and nitric acid at infinite dilute are, respectively 145, 156 and 425 Ω^{-1}cm^{2}mol^{-1}. Calculate the molar conductivity of hydrocyanic and acid at infinite dilution.

Solution

KCN (aq) + HNO$_3$(aq) $\longrightarrow$ HCN(aq) + KNO$_3$
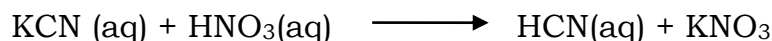
$-h°$HCN = ($-h°$KCN + $-h°$HNO$_2$) - $-h°$KNO$_3$

= (156 + 421) – 145

= 432 Ω^{-1}cm^{2}mol^{-1}

Worked example

The olar conductivities of Ammonium chloride NaOH and NaCl are respectively 141, 252, 280 Ω^{-1}cm^{2}mol^{-1}. Calculate the $-h$ of ammonium hydroxide.

NH$_4$Cl(aq) + NaOH(aq) $\longrightarrow$ NH$_4$OH(aq) + NaCl(aq)
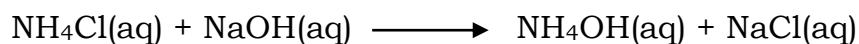
$\square$NH$_4$OH = ($-h°$NH$_4$Cl + $-h°$NaOH) - $-h°$NaCl

= (141 + 252) – 280

= 113 Ω^{-1}cm^{2}mol^{-1}

Worked examples

The resistance of a cell containing 0.1 mold m NaCl at 25^{0}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

   a) The cell constant

b) The conductivity of KNO_3

c) The molar conductivity of a 0.0116M solution of KNO_3

Solution

$$P = \rho \frac{l}{A}$$

$$\rho = R\frac{A}{l}$$

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{A}$$

$$K = \frac{1}{R} \cdot \left(\frac{l}{A}\right)$$

$$\left(\frac{l}{A}\right) = K R$$

$$= 1.3 \times 10^{-2} \times 50.62$$

$$= 0.65806 cm^{-1}$$

$$K\, KNO_3 = \frac{1}{R}\left(\frac{l}{A}\right)$$

$$= \frac{1}{185} \times 0.65806$$

$$= 3.55708 \times 10^{-3} \Omega^{-1}cm^{-1}$$

$$\Lambda_m(KNO_3) = \frac{1000K}{c}$$

$$= \frac{1000 \times 355708 \times 10^{-3}}{0.116}$$

$$= 306.645 \ \Omega^{-1}cm^2mol^{-1}$$

The electrolytic conductivity of a solution of 0.1m of acqueous amino ethane is

$1.5 \times 10^{-1}\Omega^{-1}m^{-1}$. If the molar conductivity of solution of infinity is $\Lambda_m^0 = 2.04 \times 10^{-2} \ \Omega^{-1}m^{-2}mol^{-1}$.

Calculate

The percentage dissociation of amino ethane

The basic dissociation constent of amino ethane

Solution

$$\propto = \frac{\Lambda_m^c}{\Lambda_m^\circ} \times 100$$

$$\Lambda_m CH_3CH_2NH_2 = \frac{K}{1000C} = \frac{1.5 \times 10^{-1}}{1000 \times 0.1}$$

$$= 1.5 \times 10^{-3} \ \Omega^{-3}m^2mol^{-1}$$

$$\propto = \frac{1.5 \; x \; 10^{-3}}{2.04 \; x \; 10^{-2}} \; x \; 100$$

= 7.35%

| $CH_3CH_2NH_2(aq) + H_2O \; (l)$ | | $CH_3CH_2NH_3(aq) + \bar{O}H(aq)$ | |
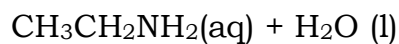
Initially   1   0   0

If $\propto$ in degree C $(1-\propto)$ $C\propto$ $C \propto$

$$Kb = \frac{[CH_3CH_2NH_3][\bar{O}H]}{[CH_3CH_2NH_2]}$$

$$= \frac{C\propto.C\propto}{C(1-\propto)}$$

$$Kb = \frac{C\propto^2}{1-\propto}$$

$$= \frac{0.1 \; x \; (0.0735)^2}{(1-0.0735)}$$

583 x 10^{-4} mold m^{-3}

583 x 10^{-4} mold m^{-3}

$$Kb = \frac{[CH_3CH_2NH_3][\bar{O}H]}{[CH_3CH_2NH_2]}$$

At equilibrium $[CH_3CH_2NH_3] = [\bar{O}H]$

$$Kb = \frac{[OH^2]}{[CH_3CH_2NH_2]}$$

$$[\bar{O}H] = \sqrt{kb \; [CH_3CH_2NH_2]}$$

$$= \sqrt{(5.83 \; X \; 10^{-4}) X \; 0.1}$$

= 7.63 X 10^{-3} Mold m^{-1}

$$[H^+] = \frac{kw}{[\bar{O}H]}$$

$$= \frac{1.0 \; x \; 10^{-14}}{7.631 \; x \; 10^{-3}}$$

= 1.3097 x 10^{-11} mold m^{-3}

PH = -log(H$^+$] = -log(1.3097 x 10^{-11})

= 10.88

pH = 10.88

FACTORS AFFECTING CONDUCTIVITY OF AN ION

Size of the ion
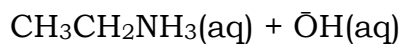
The smaller the size of the ion the higher the conductivity. This is because smaller ions are highly mobile and therefore highly conducting. This explains why the most highly conducting ions is the hydrogen ions because it is the smallest ion.

Charge on the ion

The greater the charge on the ion the higher is its conductivity because a highly charges ion is more readily attracted to the electrodes than a less charged ion. This explains why the conductivity of magnesium ion (K= 106$\Omega^{-1}cm^{-1}$) is higher than that eg sodium.

Similarly the surrounding of a sulphate ion SO_4^{2-} is higher than that of a chloride ion (Cl-).

Charge density

The higher the charge density the lower is the a conductivity ions with a higher charge density attract their mobility hence 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.
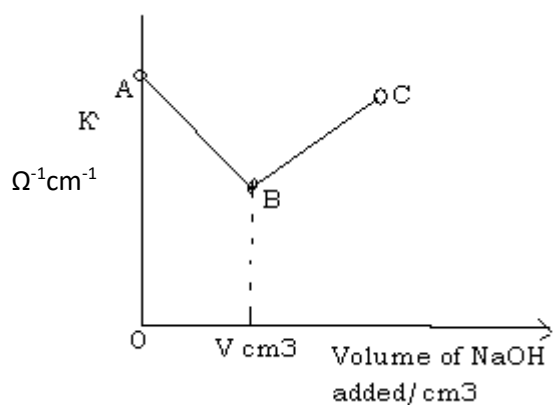
The conductivity decreases rapidly along AB and increases gradually along BC. Initially the conductivity is high because HCl is a strong acid and completely dissociates into many and by highly conducting hydrogen ions.

$$HCl (aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

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

$$H^+(aq) + \bar{O}H \longrightarrow H_2O(l)$$
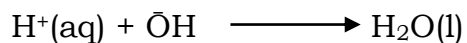
The fast moving and highly conducting H^+ ions are being replaced by the slow melting and less conducting Na^+ ions.

Point B gives the conductivity of the solution at end point and the volume of the base required is Vcm^3. At the end point is the minimum conductivity due to conductivity or 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 wrong base eg ethanoic acid, sodium hydroxide pair.
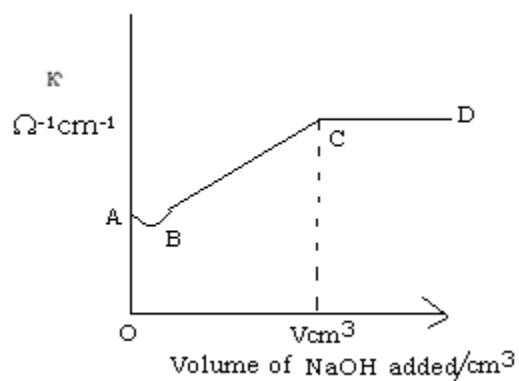
Initially the conductivity low because ethanoic acid is a weak acid which enter slightly ionizes releasing few highly conductivity and fast moving hydrogen ions.

$$CH_3COOH \qquad CH_3CO\bar{O} + H^+$$
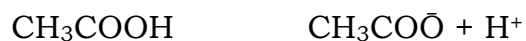
Conductivity decreases along AB due to

(i)   Removal of the few hydrogen ions in the neutralization reaction by the hydroxide ions in the solution.

$$H^+ + \bar{O}H \longrightarrow H_2O(l)$$
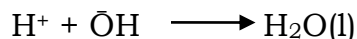
(ii)   Suppression of ionization of ethanoic acid by the strong salt formed due t o common ion effect, addition of a small amount of sodium hydroxide to ethanoic acid forms sodium ethanoate that suppresses the ionization of ethanoic acid.

$$CH_3COOH(aq) \qquad CH_3CO\bar{O}(aq) + H^+(aq)$$

$$CH_3CO\bar{O}Na^+(aq) \qquad CH_3CO\bar{O}(aq) + Na^+(aq)$$

There is a sharp increase in conductivity in the region BC due to the salt formed which fully ionizes releasing many sodium ios in solution.

$$CH_3CO\bar{O}Na^+ \longrightarrow CH_3CO\bar{O}(aq) + Na^+(aq)$$
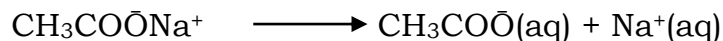
Point C is the end point of the titration and the volume requires to reach end point is V cm³. The conductivity at the end point is higher than the initial conductivity because the solution at the end point has conductivity ions than the initial solution.

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**
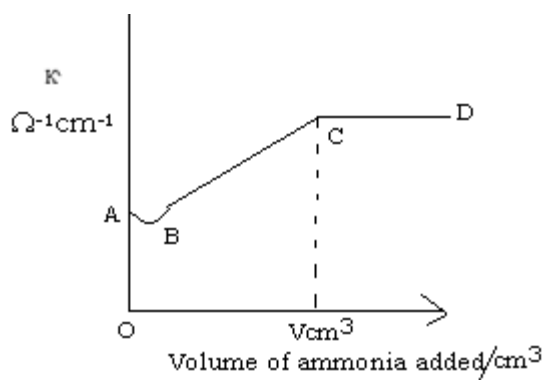
At point A conductivity is low because ethanoic acid is weak and only slightly ionizes in solution releasing few hydrogen ions in solution.

Neutralization of the hydrogen ions by ammonia (ŌH from NH₄OH). The fast moving hydrogen ions are being replaced by the less moving ammonia ions with formation of neutral water molecules.

$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

$NH_4OH + H^+(aq) \longrightarrow NH_4^+ + H_2O$
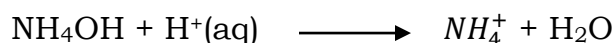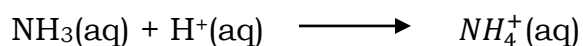
Suppression of the ionization of ethanoic acid due to common ion effect

$CH_3COOH(aq) \qquad\qquad CH_3CO\bar{O}(aq) + H^+(aq)$

$CH_3CO\bar{O}NH_4^+(aq) \longrightarrow CH_3CO\bar{O}(aq) + NH_4^+$
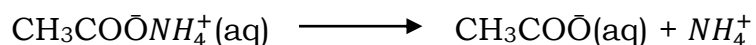
Atom BC conductivity increases due to formation of a strong electrolyte ethanoate which fully desociates releasing many conducting ions. The end point is at point C and the volume of ammonia needed to reach end point is Vcm³. The conductivity at all the end point is high due to strong electrolyte formed 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

Volume of ammonia added
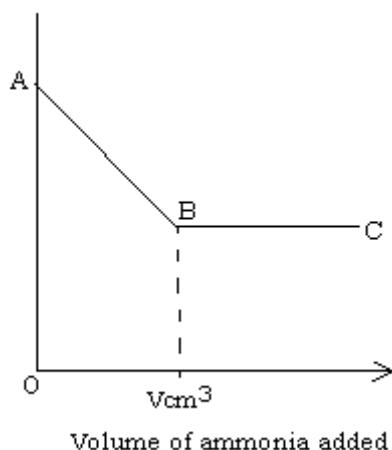
The initial conductivity is high because the acid is a strong electrolyte and fully dissociated releasing many and highly conducting hydrogen ions. Conductivity decreases a long AB because of the removal of the hydrogen ions due to their neutralization by ammonia. The hydrogen ions are being replaced by the ammonia ions which are less conducting.

NH_3 + H$^+$(aq) $\longrightarrow$ NH_4^+(aq)
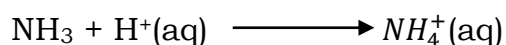
Point B is the end point of the titration end the volume of ammonia required to reach end point is Vcm^3. Any increase in conducting after the end point would be due to axcess ammonium hydroxide added but its ionization is suppressed by the ammonium ions from the strong ion effect to conducting remains constant along BC.

NH_4OH(aq) $\qquad$ NH_4^+(aq) + $\bar{O}H$(aq)

NH_4Cl(aq) $\longrightarrow$ NH_4^+ + Cl(aq)
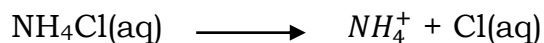
Changes in conductivity when a mixture of a strong acid and a weak acid is titrated with a weak base eg a mixture by HCl and CH$_3$COOH with Ammonia.

Volume of ammonia added
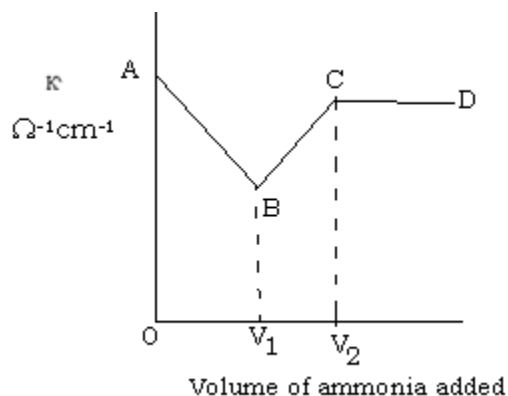
It is the strong acid that titrates fast. The initial conductivity is high because HCl is a strong electrolyte and releases many hydrogen ions in solution. The fall in conductivity along AB is due to neutralization of the H^+ ions from strong acid.

At point B all strong acid has been neutralized and volume required is V_1 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 cm^3 and the volume required for only ethanoic acid is (V_2-V_1)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.

volume of silver
nitrate added / cm3
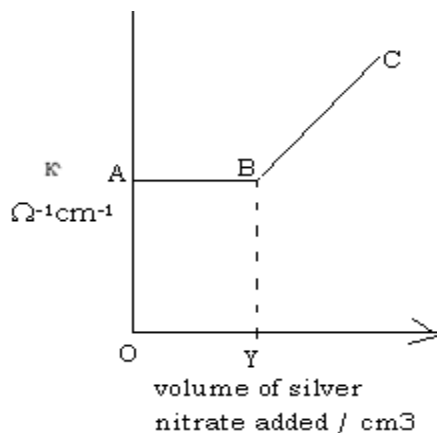
The initial conductivity is high because sodium chloride is a strong electrolyte and fully dissociated releasing many conductivity ions in solution.

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 cm³.

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

K Solution = K solution - K solvent.

Then molar conductivity of the solute is $\dfrac{1000\,K}{C}$ and for saturated solutions the concentration of the solute is equal to its solubility in mol per litre.

$$\square\text{solute} = \dfrac{1000\,K\,(solute)}{solubilities}$$

Solubility $= \dfrac{1000\,K\,(solute)}{\lambda_{\text{solute}}}$

Example

Calculate solubility of a saturated solution of AgCl at 25⁰C whose electrolyte conductivity is 4.36 x $10^{-6}\,\Omega^{-1}cm^{-1}$ and that of water is 2.50 x $10^{-6}\,\Omega^{-1}cm^{-1}$ given that the molar conductivity of silver chloride at the same temperature is 1.46 x $10^{-2}\,\Omega^{-1}cm^{-2}\,mol^{-1}$.

Solution

K Solution = K solution - K solvent.

= (4.36 x 10^{-6} – 2.50 x 10^{-6})

= $1.86 \times 10^{-6} \Omega^{-1} cm^{-1}$

$$\text{Solubility} = \frac{1000 \, \kappa_{(solute)}}{\Lambda_{solute}}$$

$$= \frac{1000 \times 1.8 \times 10^{-6}}{1.46 \times 10^{-2}}$$

= 0.1274 moldm^{-3}

Molar mass of AgCl = 108 + 35.5

= 143.5

Solubility in g/l

= 143.5 x 0.1274

= 18.2819 gl^{-1}

Question

At 25^{0}C the molar conductivity of silver nitrate, potassium nitrate and potassium chloride are 133.4, 145.0 and 149.9 Ω^{-1}ohms respectively. At the same temperature the conductivity of a saturated solution of silver chloride is $3.1 \times 10^{-6}\Omega^{-1}cm^{-1}$ while that of pure H_2O is $1.6 \times 10^{-5} \Omega^{-1}cm^{-1}$.

(i)   Calculate the solubility of silver chloride in mols l^{-1} at this temperature.

(ii)   Determine the solubility product of solver chloride at this temperature.

$$\Lambda (AgCl) = \frac{1000 \, \kappa_{(AgCl)}}{S}$$

AgNO$_3$(aq) + KCl(aq)   AgCl(aq) + KNO$_3$(aq)
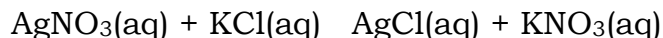
$\Lambda(AgCl) = \Lambda(AgNO_3) + \Lambda(KCl) - \Lambda(KNO_3)$

=(133.4 + 149.9)-145.0

= 138.3 $\Omega^{-1}cm^{-2}mol^{-1}$

$\kappa(AgCl) = \kappa$solution- κsolvent

= 3.14 x 10⁻⁶ – 1.6 x 10⁻⁶

$= 3.14 \times 10^{-6} - 1.6 \times 10^{-6}$

$= 1.54 \times 10^{-6} \, \Omega^{-1}cm^{-1}$

Solubility of AgCl

$$= \frac{1000 \, \kappa_{(solute)}}{\lambda_{AgCl}}$$

$$\frac{1000 \times 1.54 \times 10^{-6}}{138.5}$$

$1.11 \times 10^{-5} \, moldm^{-3}$

$AgCl(aq) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
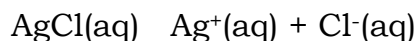
$Ksp(AgCl) = (Ag^+).(Cl^-)$

1 mole of AgCl gives 1 mole of Ag^+ ions and 1 mole of Cu^+ ions.

$[Ag^+] = 1.11 \times 10^{-5} \, moldm^{-2}$

$[Cl^-] = 1.11 \times 10^{-5} moldm^{-3}$

$Ksp(AgCl) = (Ag^+).(Cl^-)$

$=(1.11 \times 10^{-5}) \times (1.115 \times 10^{-5})$

$= 1.2321 \times 10^{-10} \, mol^2 \, dm^{-6}$

Question

Given that the mole conductivity at infinite dilution of 5cm ionic species below

Ion	$\lambda \, \Omega^{-1}cm^2mol^{-1}$
Na⁺	00.1
ŌH	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

$\lambda^0 HCl = \frac{1000\ K}{C}$

$\lambda^0 HCl = \lambda^0 H^+ + \lambda^0 Cl^-$

$=(349.8 + 76.4)$

$= 426.2 \Omega^{-1} cm^2 mol^{-1}$

$K\ HCl = \frac{C\lambda^0 HCl}{1000}$

$\frac{0.1\ x\ 426.2}{1000}$

$= 4.262\ x\ 10^{-2} \Omega^{-1} cm^{-1}$

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

At the end point the conductivity solution in salt solution of NaCl

Since 1 mole of HCl gives 1 mole of NaCl the [NaCl] = 0.1M

$\lambda^0 NaCl = \lambda^0 Na^+ + \lambda^0 Cl^-$

$50.1 + 74.6$

$= 124.7 \Omega^{-1} cm^2 mol^{-1}$

$K\ NaCl = \frac{C\lambda^0 NaCl}{1000}$

$= 1.247\ x\ 10^{-2} \Omega^{-1} cm^{-1}$

When twice as much NaOH been added conductivity is due to the salt formed and the excess NaOH

But from

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2o(l)$
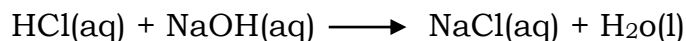
1 mole of HCl reacts with 1 mole of NaOh at the end point.

[Hcl] reacted at end point = 0.1M

[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

$\lambda^0 NaOH = \lambda^0 Na^+ + \lambda^0 OH$

=50.7 + 198.6

= 245.7 $\Omega^{-1}cm^2mol^{-1}$

$$K^\circ \ NaOH = \frac{C\lambda^0 NaOH}{1000}$$

$$= \frac{0.1 \ x \ 248.7}{1000}$$

= 2.487 x $10^{-2}\Omega^{-1}cm^{-1}$

Total $K^\circ = K^\circ_{NaCl} + K^\circ_{NaOH}$

= 3.752 x $10^{-2}\Omega^{-1}cm^{-1}$
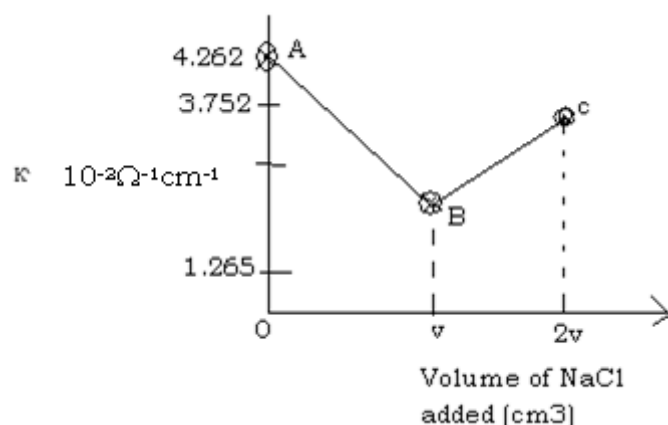
Initially the conductivity is very high because hydrochloric acid is a strong electrolyte and fully dissociated in solution releasing many fast moving and highly conducting hydrogen ions. The conductivity decreases a long AB because of the removal of hydrogen ions by the hydroxide ions forming molecules 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 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
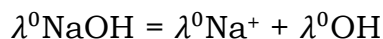
$\lambda^0 NaOH = \lambda^0 Na^+ + \lambda^0 OH$

= (50.1 + 198.6)

$248.7\Omega^{-1}cm^{-1}mol^{-1}$

$NaOH = \dfrac{\lambda^0 NaOH \; x \; C}{1000}$

$= \dfrac{248.7 \; x \; 0.01}{1000}$

= 2.487 x $10^{-2}\Omega^{-1}cm^{-1}$

NaCH(aq) + HCl(aq) NaCl(aq) $\longrightarrow$ NaCl(aq) + H_2O(l)
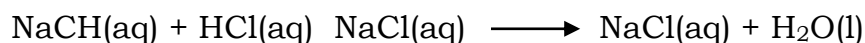
Conductivity is due salt formed and excess HCl

Moles of NaOH used = ($\dfrac{0.01}{1000}$ x 50) moles

Moles of HCl used = ($\dfrac{0.02}{1000}$ x 50) moles

Moles of excess HCl acid ($\dfrac{0.02 \; x \; 50}{1000}$) $-$ ($\dfrac{0.01 \; x \; 50}{1000}$)

$= \dfrac{0.01 \; x \; 50}{1000}$

= 5.0 x 10^{-4} moles

100cm³ of solution contains 5.0 x 10^{-4} of excess HCl

1000cm³ of solution will contain $\dfrac{5.0 \; x \; 10^{-4}}{100}$ x 1000

= 5.0 x 10^{-3}M

$\lambda^0 HCl = \lambda^0 H^+ + \lambda^0 Cl$
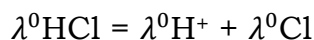
349.8 + 76.4

= $426.2\Omega^{-1}cm^{-1}mol^{-1}$

$= \dfrac{\lambda^0 HCl \; x \; C}{1000}$

$\dfrac{426.2 \; x \; 5 \; x \; 10^{-3}}{1000}$

= 2.13 x 10^{-3} $\Omega^{-1}cm^{-1}$

Since 1 mole of NaOH completely reacts with the acid to form 1 mole of NaCl then moles of NaCl formed.

$=(\frac{0.01}{1000}$x50) moles of NaCl

100cm^3 of solution will contain $\frac{0.01}{1000}$x50 moles of NaCl

1000cm^3 of solution will contain $\frac{0.01\ x\ 50}{1000}$ x $\frac{1000}{100}$

= 5.0 x 10^{-3}M

λ^0NaCl = λ^0Na$^+$ + λ^0Cl

= 50.1 + 16.4

= 126.5 Ω^{-1}cm^{-1}mol^{-1}

$K_{NaCl}=\frac{\lambda^0 NaCl\ x\ C}{1000}$

$=\frac{126.5\ x\ 5\ x\ 10^{-3}}{1000}$

= 6.325 x 10^{-4} Ω^{-1}cm^{-1}

Total conductivity

K_{NaCl}+ K_{HCl}

6.325 x 10^{-4} + 2.131 x 10^3

= 2.7635 x 10^{-3} Ω^{-1}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 form t he system and the system may lose heat to the surrounding or may gain heat from the surrounding.

A system that losses 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

Energy

Reactants

H_1

$DH = H_2 - H_1$ Since H, $>H_2$

$DH = $ -ve

products

H_2

Reaction path

Endothermic reaction

Energy

H_2 products

$DH = H_2 - H_1$ Since H, $>H_2$

$DH = $ +ve

H_1 Reactants

Reaction path
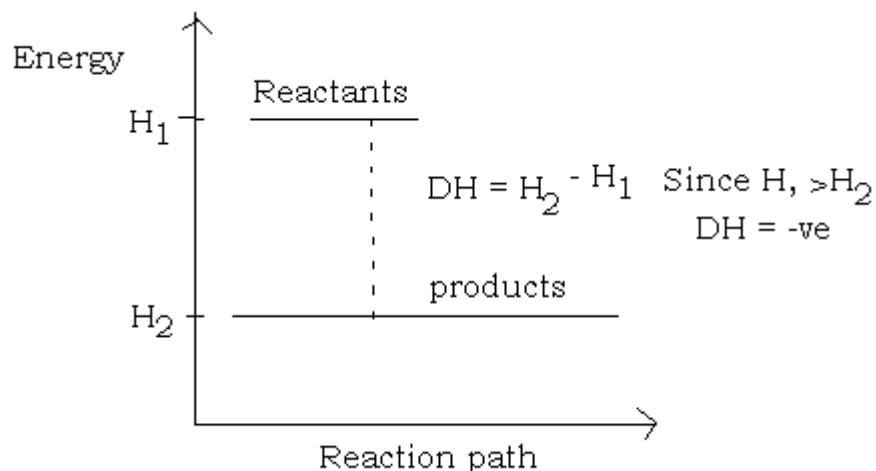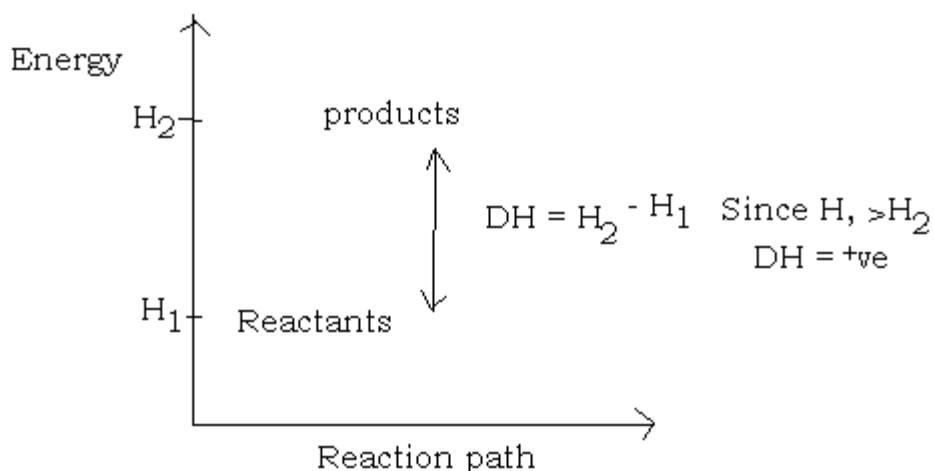
Note

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 enthalapy changes are measured at standard conditions ie temps of 25^0C or 298K. pressure of 1 atmosphere or 760mmHg or 101325 pa or $101325NM^{-2}$.

Therefore standard enthalapy of reaction is denoted by DH_r^θ

Standard enthalpy of formation is denoted by DH_f^θ

Standard enthalpy of combustion is denoted by DH_0^θ

Standard enthalpy of neutralization is denoted by DH_n^θ

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.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \quad DH_r^\theta = -575KJ$$
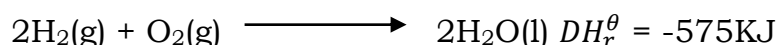
Standard enthalpy of formation standard enthalpy of combustion.

Standard enthalpy of formation (DH_r^θ) 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, $N_2(g)$ $O_2(g)$ 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 $O_2(g)$ under standard conditions

$Mg(s) + \frac{1}{2} O_2(g) \rightarrow MgO(s)$ ΔH_f^θ = -602 KJ mol^{-1}

$C_2H_5OH(l) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ ΔH_c^θ = --1368KJ mol^{-1}

$C(s) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ ΔH_f^θ = -285KJ mol^{-1}

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ ΔH_f^θ = -110 KJ mol^{-1}

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl \rightarrow HCl(g)$ ΔH_f^θ = -92 KJ mol^{-1}

$C(s) + O_2(g) \rightarrow NaCl(s)$ ΔH_c^θ = -393 KJ mol^{-1}

$Na(s) + \frac{1}{2} Cl_{(s)}$ ΔH_f^θ = -418 KJ mol^{-1}

$C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH_c^θ = -395 KJ mol^{-1}
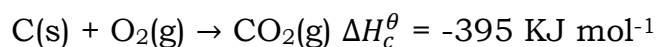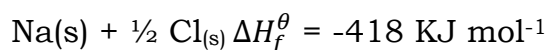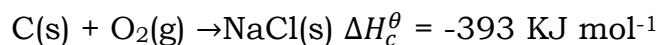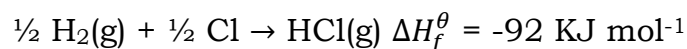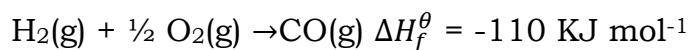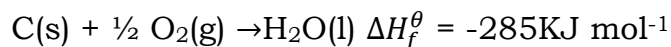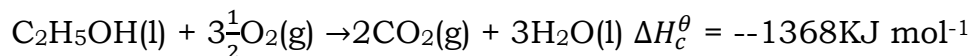
Experiment: Determination of heat enthalpy of combustion

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 planted 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 each a pressure of 20-25 atmospheres.

The bomb calorimeter is then closed by screw value 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.
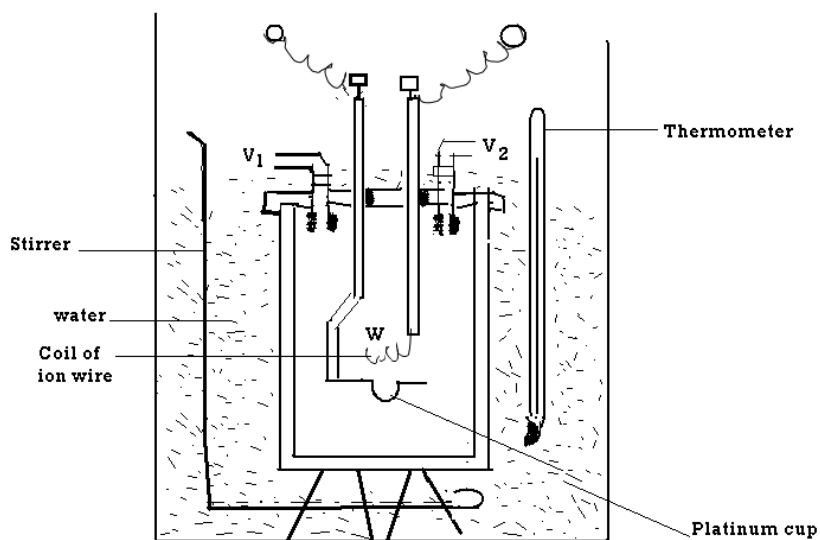
A graph of temp against time is plotted and the graph can be used to determine the max temperature as follows.
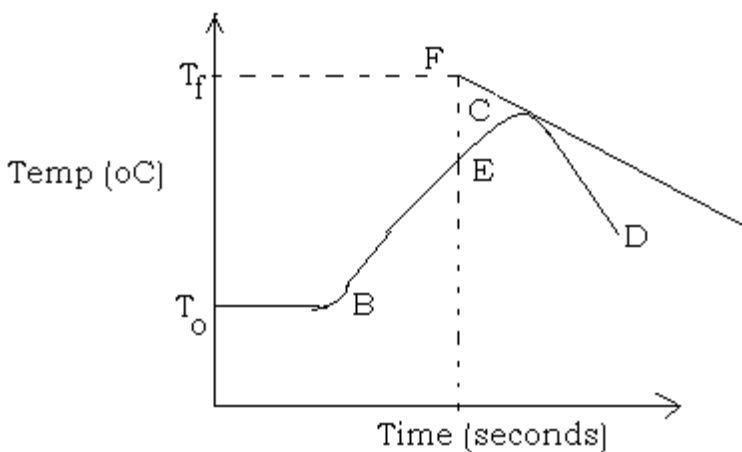
A targent is drawn on the cooling curve, if E is the mid point of BC and EF is parallel the temp axis the highest temp reached can be taken as for T_f.

Treatment of results

Let a g be the mass of the substance under investigation.

bg be the mass of water

T_o – initial temp of the water

T_f – final temp of the water

Let the S.H.C of water be 4.2Jg^{-1}K^{-1}

Let the heat capcity of bomb calorimeter be CJK^{-1}

DT absorbed by the water = $M_wC_wDT_4CD_T$

= (b x 4.2) (T_f – T_0) + C(T_f – T_0)

ag of the substance produce (b x 4.2) (T_f – T_0) + (C T_f – T_0)^J

about Mr of the substance

Mr of the substance will produce $\frac{(b\ x\ 4.2)(T_f-T_o)+\ C(T_f-T_o)x\ Mr}{a}$

Enthalpy of combustion of the substance

- $[\frac{(b\ x\ 4.2)(T_f-T_o)+\ C(T_f-T_o)x\ Mr}{1000a}]$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 and a thermometer.
- The set up of the apparatus is shown below.

Shield reduced heat loss to surrounding

Thermometer

Metal colorimeter tains a knwon mass of water

Spirit burner containes fuel
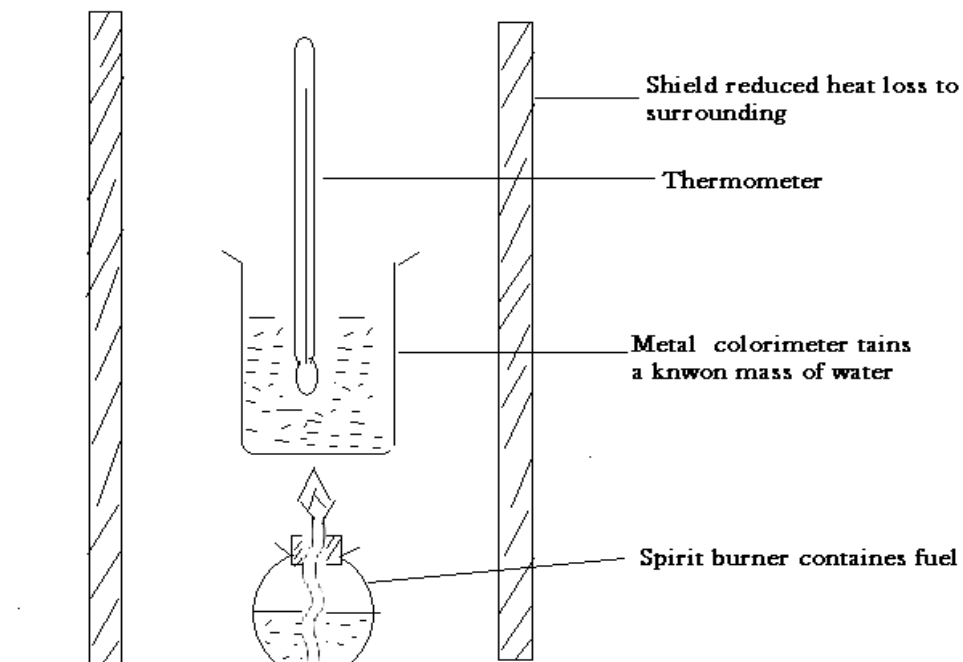
- The initial temperature of water is read and recorded as T_0 °C.
- The spirit lamp is lit and the flame is placed in position so that it just touches the bottom of the metal can and is allowed to heat up the water.
- A stired is arranged to allow the flame to remain steady
- When the temperature of 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°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 Jg⁻¹K⁻¹.

Let the mass of the water be a g

$DT = (T_1 - T_0)$ °C

Mass of ethanol that burnt = $M_1 - M_2$

Heat absorbed by the water = mass of water x ShCw x DT

$= a \times 4.2 \times (T_1 - T_0)$

RFM of ethanol = 46

(M_1-M_2)g of ethanol produce $a \times 4.2 \times (T_1 - T_0)$J of heat

46g of ethanol will produce $\frac{a\ 4.2\ (T_1-T_0)}{M_1-M_2}$ X 46

DH_C^θ of Ethanol $= -[\frac{4.2a\ (T_1-T_0)}{100(M_1-M_2)} \times 46]$KJ mol⁻¹

NOTE

i. The ΔH_c^θ of any substance is negative (ie it is an exothermic reaction

ii. The Δ_c^θ 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

1. When 1.5g of ethanol was burnt, the heat produced raised the temperature of 500g of water from $25°c$ to $44.5°c$

   Calculate the Δ_c^θ of ethanol (Shc of water = $4.2\ Jg^{-1}k^{-1}$

   ΔT = 44.5 − 25

2. What mas of methane (natural gas) must be burnt to raise the temperature of 2kg of water from $20°c$ to $100°c$

   Assume no heat is lost (Shc of water = $42Jg^{-1}k^{-1}$

   ΔH_c^θ of methane = -890 $Jmol^{-1}$

   No. 1 $\Delta T = 44.5 − 25$

$$= 19.5°c$$

Heat absorbed by water = 500 x 42 x 19.5 = 40950.J

1.5g of ethanol produce 40950J

46g of ethanol produce $\frac{40950}{1.5}$ x 46 x $\frac{1}{1000}$

= ⁻6255.8 kJmol⁻¹

1. RFM CH_4 = 12 + 4 = 16

$$\Delta T: 100 − 20 = 80°c$$

Heat absorbed by water = 2000 x 4 .2 x 80

   = 672000.5

ΔH_c^θ of CH_c = - 890 kJmol⁻

890 *kj are produced by* 16

612kJ are produced by $\frac{16}{890}$ x 672

$$= 12.1g$$

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 theme dynamic data

$C_{(g)} + O_{2(g)} CO_{2\,(g)}$ 393 kJmol^{-1} --- 2

CH4(g) + 2O$_2$(g) CO$_2$(g) + 2H$_2$)(g) OHc = -890 kJmol-1

C(g) 2H2(g) --Cha(g) ....
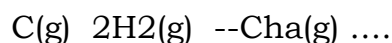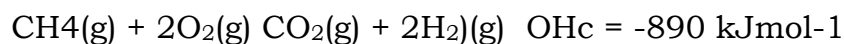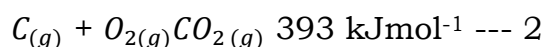
  iii. When the equations are added or subtracted

  iv. The enthalpies are also added or subtracted

Eqn 4 = (1) + x (ii) + - (iii)

C$_{(2)}$ + O$_2$(g)   →   CO$_2$(g)   →   - 393kJmol^{-1}

2H$_2$(g) + O$_2$(g)   →2H$_2$O(g) →-572kJ

C(g) + 2H$_2$(g) +2 $\cancel{O_2}$(g) → $\cancel{CO_2}$+ 2$\cancel{H_2O}$ (1) ΔH = −965kJ

$\cancel{CO_2}$(g) + 2$\cancel{H_2O}$(1) → CH$_2$(g) + 2θ$_2$(g) ΔH 890 kJmo^{-1}

C(g) + 2H2(g) → CH4(g) ΔH_F^θ -75kJmo^{-1}
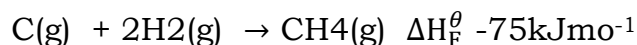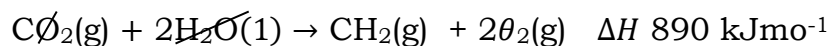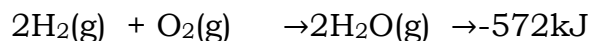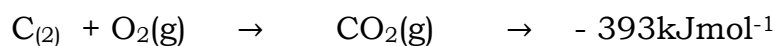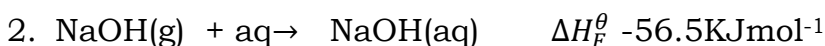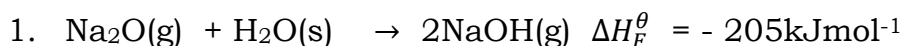
2. Find the standard enthaling of formation of carbon monoxide. If the standard enthalpies of combustion of carbon and carbon monoxide are - 393kJmol-1 and – 285kJmo-1 respectively.

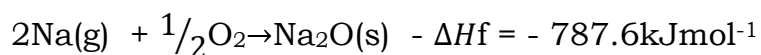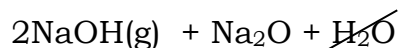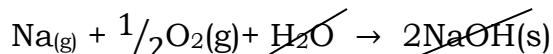C(g) + O$_2$(g) → CO2(g) ΔH_c° = -393kJmol^{-1}

2CO2(g) + O2(g) → 7CO(g) ΔH_c° = - 285kJmol^{-1}

C(2) + $\frac{1}{2}$ O$_2$(g) CO(g) → 3

C (g) + O$_2$(g) $\cancel{CO_2}$(g)   - 393

$C\theta 2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)\ \frac{1}{2}(285)$

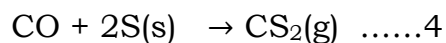$C(g)\frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}\ \Delta H_s^{\epsilon} = -250.5\ kJmol^{-1}$
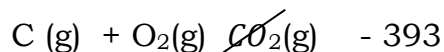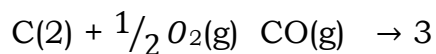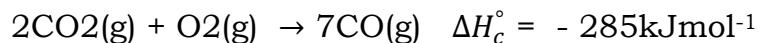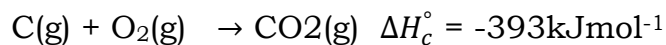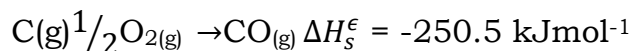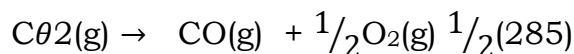
Calculate the standard enthalpy of formation of sodium oxide from the following date

1. $Na_2O(g) + H_2O(s) \rightarrow 2NaOH(g)\ \Delta H_F^{\theta} = -205kJmol^{-1}$
2. $NaOH(g) + aq \rightarrow NaOH(aq)\ \ \ \Delta H_F^{\theta}\ -56.5KJmol^{-1}$
3. $Na(g) + H_2O(1) + aq \rightarrow NaOH(aq)\ \ \Delta H_2^{\theta}(G) - \Delta H_6^{\theta} = -410Jmol^{-1}$
4. $H2(g) + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}\ - \Delta H_J = -285.6\ Kmol^{-1}$
5. $2Na(g) + \frac{1}{2}O_2(g) \rightarrow 2Na_2O_{(g)}$

$2Na\cancel{OH}_2 \rightarrow Na_2O(2) + H_2O$

$2Na\theta Hs + aq \rightarrow 2Na\cancel{OH}(aq)$

$-2\cancel{Na}OH_{(aq)} \rightarrow Na(g) + 2H2O_{(1)}$

$Aq \rightarrow Na_2O(g) + 2Na(g) + H_2O_{(1)}$

$Na + H_2O_{(g)} \rightarrow NaOH$

$5 = 2-(2) + 2(s) + 4 - (1)$

$2NaOH(aq) + aq \rightarrow 2NaOH(g)\ \ -113kJ$

$2Na(s)\ 2H_2O +aq \rightarrow 2MaOH(aq) + \frac{1}{2}\ -825kJ$

$Na_{(g)} + \frac{1}{2}O_2(g) + \cancel{H_2O} \rightarrow 2Na\cancel{OH}(s)$

$2NaOH(g) + Na_2O + \cancel{H_2O}$
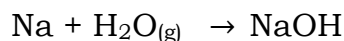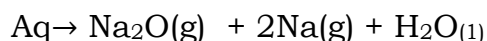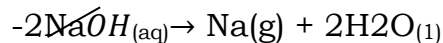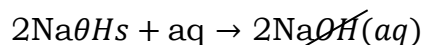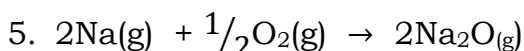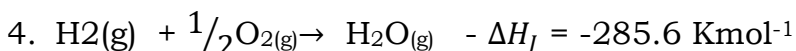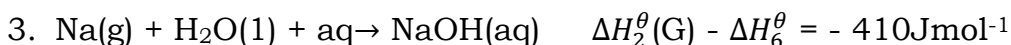
$2Na(g) + \frac{1}{2}O_2 \rightarrow Na_2O(s)\ - \Delta Hf = -787.6kJmol^{-1}$
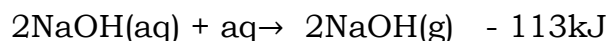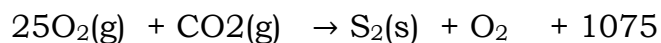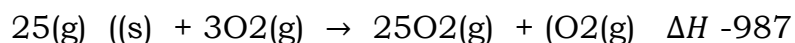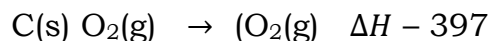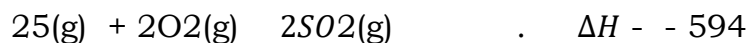
Find the standard enthalpy of formation of carbondisulphide[$CS(g)$] carnon disulphide burns in air to form carbondioxide and sulphur dioxide. The ΔH_c^{θ} of carbondisulphide, sulphur and carbon are -1075 – 297 & -393 kJmol-1 respectively
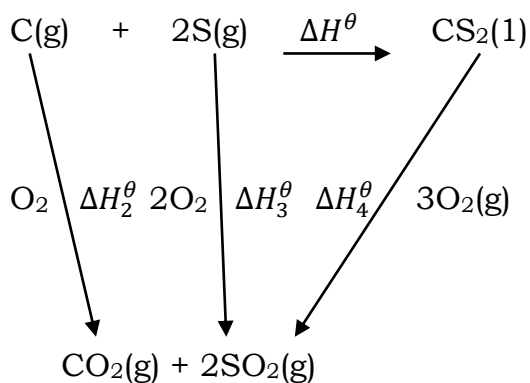
$CS(1) - 3O_2(g) \rightarrow CO2(g) + 250_2(g)\ \Delta H_c^{\theta} - -1075$

$C(s) + O_2(g) \rightarrow CO2(s)\ ..... \Delta H = -393$

$S(s) + O_2(g) \rightarrow SO2(g)\ ....3\ \Delta H_c^{\theta} = 397$

$CO + 2S(s) \rightarrow CS_2(g)\ ......4$

4 = 2(3) + (2) - (1)

$25(g) + 2O2(g)$ $2SO2(g)$. ΔH - - 594

$C(s)\ O_2(g)\ \rightarrow\ (O_2(g)$ $\Delta H - 397$

$25(g)\ ((s) + 3O2(g)\ \rightarrow\ 25O2(g) + (O2(g)$ ΔH -987

$25O_2(g) + CO2(g)\ \rightarrow\ S_2(s) + O_2$ + 1075

$C(s) + 2S(2)\ \rightarrow\ CS2(1)$. ΔH_f^θ = + 88 kmol^{-1}

Born Haber cycle

$C(g)$ + $2S(g)$ $\xrightarrow{\Delta H^\theta}$ $CS_2(1)$

O_2 ΔH_2^θ $2O_2$ | ΔH_3^θ ΔH_4^θ $3O_2(g)$

$CO_2(g) + 2SO_2(g)$
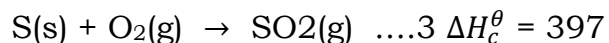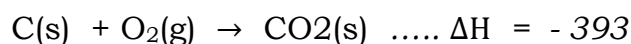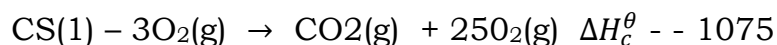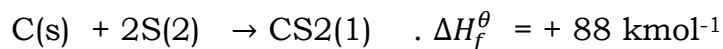
$\Delta H_1^\theta \Delta H_2^\theta$ + $2\Delta H_3^\theta$

ΔH_2^θ = 85kJmol^{-1}

Calculating enthalpies of reactions from standard enthalpies of formation

ΔH^θreaction = $\sum \Delta H_R^\theta$ (reactants)

1. Given the standard enthalpies of formation of some prds

ΔH_6^θ (NH$_3$) = - 46kJml^{-1}

ΔH_f^θ (HCl) = - 92.3 kJmol^{-1}

ΔH_F^θ (NH$_2$(1)   = - 315kJmol^{-1}Calculate the standard enthalpy of the following reaction

HCl(g) + NH^3 (g)   NH4Cl(s)
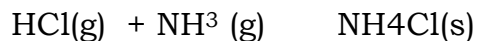
$\Delta H_{reaction}^\theta$ = - 315 – (-46 + - 42.3)

= 196.7 kJmol^{-1}

2. Given the standard enthalpies of formation of some prods

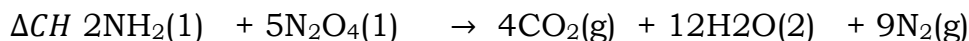ΔH_8^θ (H2O2..) = - 20kJmol^{-1}

$H\theta_F^\theta$ ($CO_2(g)$ = - 393kJmol

ΔH_F^θ ($CH3\ NHNH_2(1)$ = - 53kJmol-1

ΔH_f^θ (2C..) = - 286 kJmol^{-1}

Calculate the standard enthalpy of the following reaction

$\Delta CH\ 2NH_2(1)\ +\ 5N_2O_4(1)\ \rightarrow\ 4CO_2(g)\ +\ 12H2O(2)\ +\ 9N_2(g)$

$\Delta H_{Reaction}^\theta\ =\ \Sigma \Delta H_6^\theta$ (products - $\Sigma \Delta H_R^\theta$ (reactant)

$= 4(-393) + 12\ x - 196)\ [4 \times 53 + 5 \times\ -20]$

$= -5116\ kJmol$-1

HESS'S Law

Hess's law states that if a reaction can have place by more than one root, the overall change in enthalpy is the same which ever route is followed
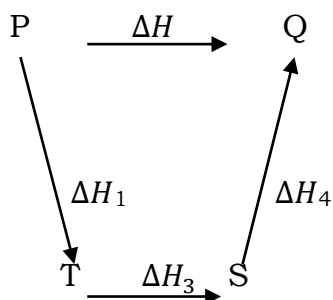
By Hess's law

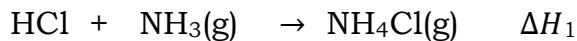$\Delta H_1 = \Delta H_2\ \Delta H_3\ _+\Delta H_4$

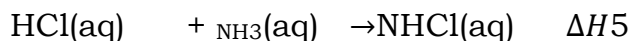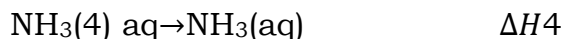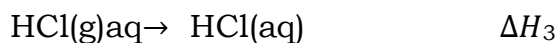**The closed energy cycle is what we call a born – haber cycle**

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 NHaCl(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$_2$Cl

$HCl\ +\ NH_3(g)\ \rightarrow\ NH_4Cl(g)\ \ \ \ \Delta H_1$

$_{NH4Cl})g)\ \ \ aq\rightarrow\ NH_4Cl(aq)\ \ \ \ \ \ \Delta H_2$

Total enthalpy $= \Delta H1 + \Delta H_2$

HCl(g)aq→ HCl(aq) $\Delta H3$

NH₃(4) aq→NH₃(aq) $\Delta H4$

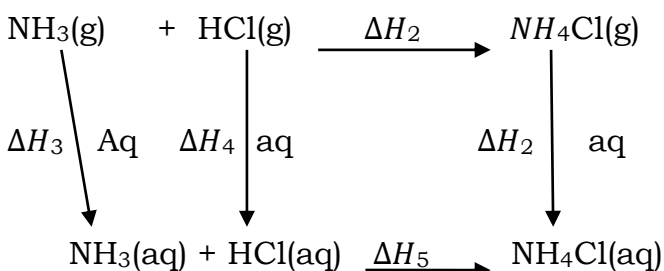HCl(aq) + $_{NH3}$(aq) →NHCl(aq) $\Delta H5$

Total enthalpy change

$\Delta H_3 \Delta H_3$

By Hess's law

ΔH_1 + ΔH_2 = ΔH_3 + ΔH_4 + Δ_5

Born - haber cycle

NH₃(g) + HCl(g) $\xrightarrow{\Delta H_2}$ $NH_4Cl(g)$

ΔH_3 Aq ΔH_4 aq ΔH_2 aq

NH₃(aq) + HCl(aq) $\xrightarrow{\Delta H_5}$ NH₄Cl(aq)

By Hess's law

ΔH_1 + ΔH_2 = ΔH_3 + ΔH_4 + ΔH_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 CH2 , C Hydrogen and these results can be used to calculate the standard enthalpy of formation of methane which can not be determined directly.
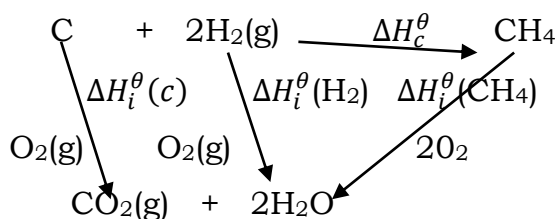
e.g

ΔH_c^θ (CH4) - 890JHnak⁻¹

ΔH_c^θ (H₂) = 286kJmal

ΔH_c^θ (CO₃) = - 393 kJmol⁻¹

Calculate the standard enthalpy of formation of methane

By Hesse's law

ΔH_f^{θ} (CH4) $+ \Delta H_c^{\theta}$ (CH4) $= \Delta H_c^{\theta}$ (c) $+ \Delta H_c^{\theta}$(H$_2$)

$\Delta H_c^{\theta} = \Delta H_c^{\theta}$ (C) $+ \Delta H_c^{\theta}$ (H$_2$) $- \Delta H_c^{\theta}$(CH$_2$)

$\qquad\qquad$ = $^-$393 $+2(-286)$ $-$ (-890)

$\qquad\qquad\quad$ = $^-$75kJmol^{-1}

Calculate the standard enthalpy of formation of ethanol given that the
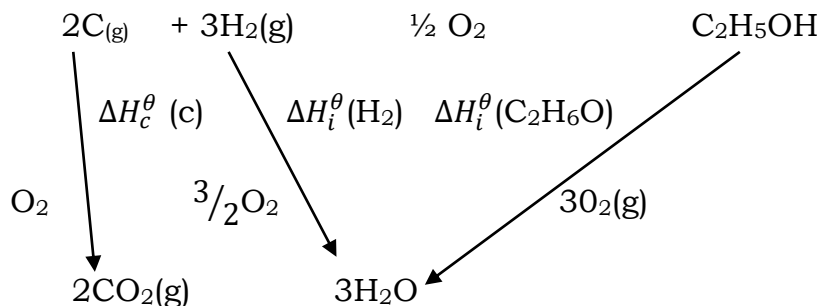
ΔH_c^{θ}(C$_2$H$_2$O) = $^-$393 Jkmol^{-1}

ΔH_c^{θ} = - 286 kJmol^{-1}

ΔH_c^{θ} $+ \Delta H_c^{\theta}$ (C$_2$H$_6$O) $= \Delta H_c^{\theta}$ (H$_2$) $+ \Delta H_c^{\theta}$ (C$_2$)

ΔH_f^{θ} = $2\Delta H_c^{\theta}$(H$_2$) $+ 3\Delta H_c^{\theta}$ (H$_1$) $- \Delta H_c^{\theta}$ (C2H$_6$O)

= 2(-393 + 3(-286) - (-136....)

= -276kJmol^{-1}

Standard enthalpy of automation 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

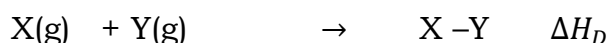e.g $Na(g) \rightarrow Na(a)$ $\Delta H_{atom} = -108kJmol^{-1}$

$\frac{1}{2}H_2 \rightarrow H(g)$ $\Delta H_{tom} = +218kJmol^{-1}$

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \rightarrow \Delta H_{atom} = 121kJmol^{-1}$

$C(g) \rightarrow C(g) - \Delta H_{atom} = 121 kJmol^{-1}$
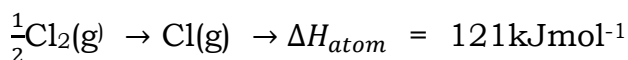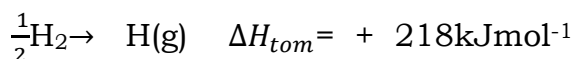
Bond energy

This is the heat required to break one mole of a continent and between two atoms in gaseous state

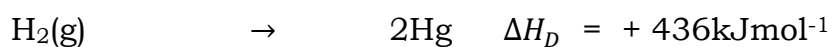$X - Y_{(g)} \longrightarrow X(g) + Y_{(g)}$
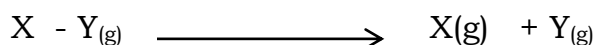
This bond energy is some times called, bond dissociation energy which is an endothermic process.

Bond energy is the heat required when one mole of a revalent bond is formed from two atoms in gaseous state
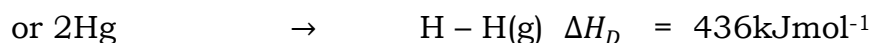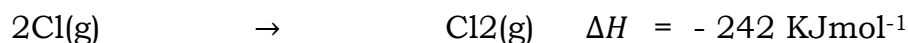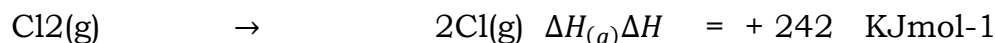
This is an exothermic process

$X(g) + Y(g) \rightarrow X-Y$ ΔH_D

e.g

   $H_2(g) \rightarrow 2Hg$ $\Delta H_D = +436kJmol^{-1}$

   H-H

or $2Hg \rightarrow H-H(g)$ $\Delta H_D = 436kJmol^{-1}$

                    $H_2(g)$

$Cl_2(g) \rightarrow 2Cl(g)$ $\Delta H_{(g)}\Delta H = +242$ KJmol-1
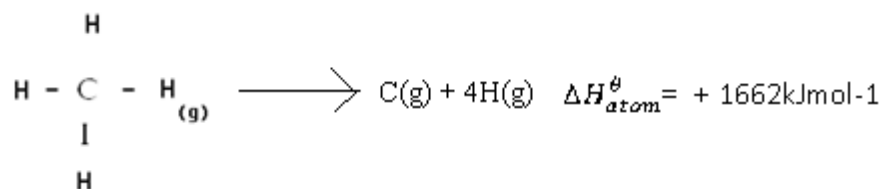
$2Cl(g) \rightarrow Cl_2(g)$ $\Delta H = -242$ KJmol^{-1}

Enthalpy of atomization and bond energy are related by the fact that bond energy is hence enthalpy of atomization.
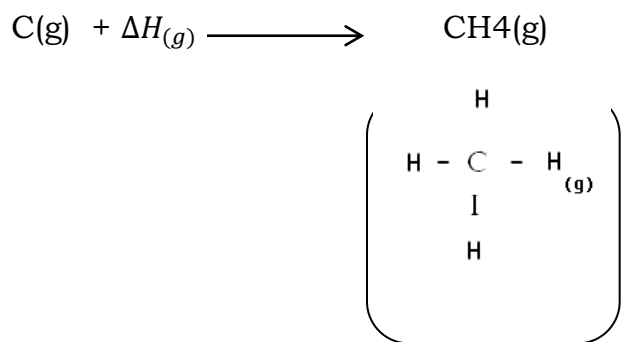
AVERAGE BOND ENERGY

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

$$\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}_{(g)} \longrightarrow C(g) + 4H(g) \quad \Delta H^{\theta}_{atom} = + 1662 kJmol\text{-}1$$

4 x E(C-H) = 1662

$\quad$ E(C-H $= \frac{1662}{4}$ = 415.2 kJmol^{-1}

ΔH^{θ}_E - 1662kJmol^{-1}

$C(g) + \Delta H_{(g)} \longrightarrow \quad CH4(g)$

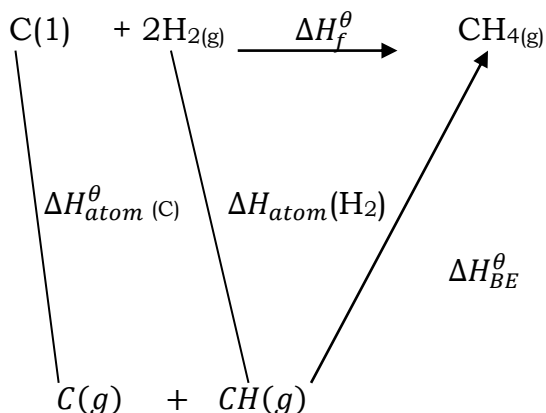$$\left(\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}_{(g)} \right)$$

Calculating bond energies form standard enthalpies of atomization and formation

1. The standard enthalpy of formation of machine is -74.8 kJmol^{-1}
    And the standard enthalpy of atomization of graphite and hydrogen are + 715kJmol^{-1} and + 218 kJmol^{-1} respectively .

Constant a born – haber cycle for the standard enthalpy of formation of methane .

Determine the average bond energy of C-H bond in methane.

$$C(1) \quad + 2H_{2(g)} \xrightarrow{\Delta H^{\theta}_f} \quad CH_{4(g)}$$

$\Delta H^{\theta}_{atom\ (C)} \quad \Delta H_{atom}(H_2)$

ΔH^{θ}_{BE}

$C(g) \quad + \quad CH(g)$

By Hess's law

$$\Delta H^\theta_{atom}(c) + \Delta H_{atom}(H_2) + \Delta H^\theta_{BE}$$

$$-14.8 = +715 + 421g + gE$$

$$\Delta E^\theta_{BE} - -1661.5 kJmol^{-1}$$

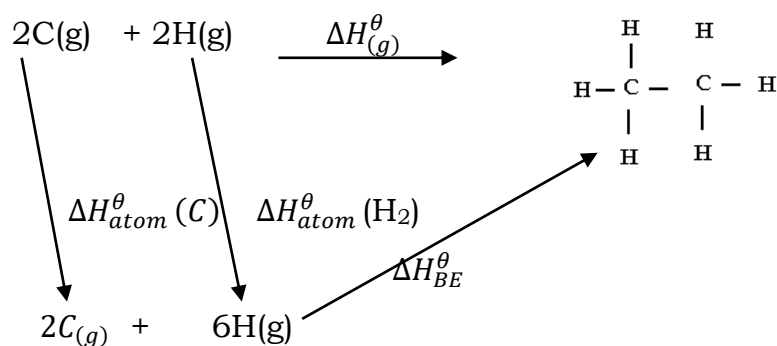(b) Average bond energy $= \dfrac{-1661.5}{4}$

$$= -415.45 kJmol^{-1}$$

2. Calculate the average C –C bond energy in ethane from the following thermo dynamic data

$$\Delta H^\theta_{atom}(c) = +715\ kJmol^{-1}$$

$$\Delta H^\theta_{atom}(H_2) = -218 kJmol^{-1}$$

$$\Delta H^\theta_{atom}(H_2) = 84.6\ kJmol^{-1}$$

$$E(C-H) = 415.45\ kJmol^{-1}$$

$$\Delta H^\theta_f\ (C_2H_2) = \Delta H^\theta_{BE} + \Delta H^\theta_{atom}(H_2) + \Delta H^\theta_{atom}(C)$$

$$84.C = \Delta H^\theta_{BE} + 6 \times 218 + 2 \times 715$$

$$\Delta E_{BE} = 6(218) + 2(715) + 84.6$$

$$\Delta E_{BE} - 2822.6\ kJmol^{-1}$$

$$\dfrac{E(C-H)}{C} = -415.45\ k\ Jmol^{-1}$$

$$E(C-H) = -2492.7 kJmol^{-1}$$

$$2\ E(C-C) = -2822.6 - -2492.7\theta$$

$$2[E(C-C)] = -329.kJmol^{-1}$$

Determination of enthalpy of reaction form the bond energies

$$\Delta H^{\theta}_{Reaction} = \Sigma \Delta H^{\theta}_{BD} \text{ Bond broken in reactants} \quad - \Sigma \Delta E^{\theta}_{BD} \text{ for bonds formed in products}$$

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	0 - 0
C = C	610	463	0 -H
C - H	415	562	F - H
C - U	360	890	C ≡ N
C = O	740	276	C - Br
C ≡ C	835	484	C - F
N ≡ 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 form the table, calculate the enthalpies of the following reactions.

(a) CH$_4$(g) + Cl2 (g) $\longrightarrow$ CH$_3$Cl(g) + HCl(g)
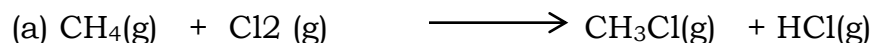
$$\Delta Hr^{\theta}_{reaction} = \Sigma \Delta H_{BD} \text{ for Bonds broken in reactants} \quad - \Sigma \forall \Delta E^{\theta}_{BD} \text{ for bonds formed in product}$$

= (415 + 242) - 431 + 339)

= -167kJmol^{-1}

(b) Cl$_2$(g) + H$_2$(g) = 2HCl
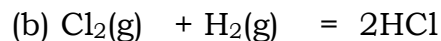
$\Delta H_{reaction}$ = (242 + 435) - 2(431)

= - 185kJmol^{-1}

(c) N$_2$(g) + 3H$_2$(g) $\rightarrow$ 2NH$_{3(g)}$

$\Delta H_{reaction}$ = 945 + 3(435) - 2(390)

= 1479KJmol

(d) N_2H_4(g) + F_2(g)   → N_2(g)   + 4H – F

$\Delta E_{reaction}$ =   2(163) + 4(380) – 4(562)

= −362 kJmol-1

```
H      H
|      |
C   =  C
|      |
H      H
```

(e) C_2H_4 (g) - H_2(g)   →   C2H6(g)
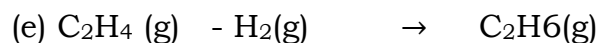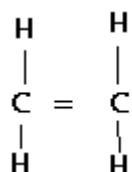
$\Delta H_{reaction}$= (435 + 610) – (345 + 2(415)
= −130 kJmol

$$CH_3 - \overset{\overset{O}{||}}{C} - CH_3 + H_2(g) \longrightarrow CH_3 - \underset{\underset{OH}{|}}{C}HCH_3$$
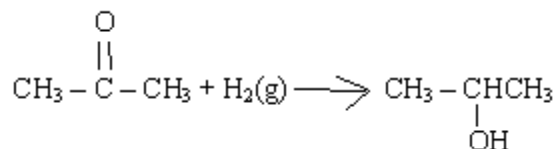
= 740 + 435 - 463
$\Delta H_{reaction}$ = 712 kJmol-1

=   712 kJmol=1

```
H  H       H-O-H
|  |
O  O
```

(g) 2H2O2(g)   ⟶   2H2O(4)   + O2(g)
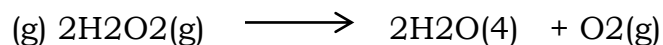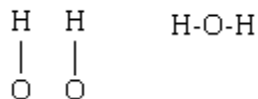
$\Delta H_{reaction}$ = 2(463) + 435 – (2(463) + 146 = 289kJmol-1
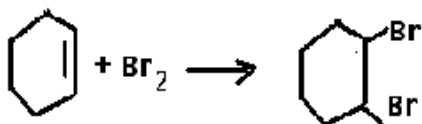
$\Delta H_{reaction}$ = 610 + 193 - [(276) x . 345]

= -94kJmol-1

Delocalization energy in Benzene

If the structure of benzene is assumed to consist of alternate double and single bonds, then, the enthalpy or hydrogenation of benzene can be calculated as follows;

Cyclehexa - 1,35 - triene
(Benzene)

Cyclohexane
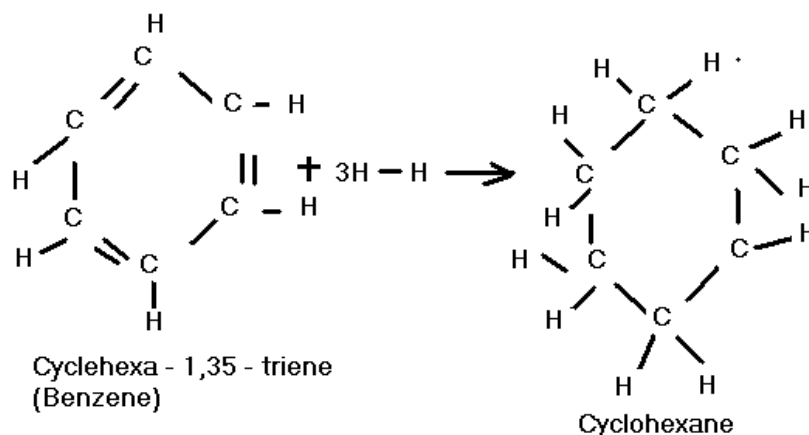
$\Delta H_{Reaction}$ = $\sum \Delta H_{For\ bond\ broken}$ - $\sum \Delta H_{for\ bonds\ formed}$

= 3E(C+C) + 3E(H----11) - C.E(C-H) + 3E(C – C)

= 3(610 + 3(435) - 6(415) + 3(345)

= 645 kJmol^{-1}

= -3390kJmol

The experementary determed 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 eqivalent to 390 – 210

= 180 kJmol^{-1}

the extra stability of the benzene ring is attributed to the delocalisation of the bonding electrons over .. all six carbon toms.

Prediction of the feasibility of a reaction

The enthralpy change of a recation is sometime, used as a rough guide to show weather the reaction is feasible or not or the likely hard that the reaction will occur.

If ΔH° 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 postive then the reactio is not feasible and such a reaction needs extrnal energy to have place.

Therefore reactions which occur spontneously are often exothermic reactions. However, some endothermic re actions can also occur sponteneously.

This is due to increase in the entropy of the reaction.

Entropy can be defined as the degre of disorce of ea system

e.g dissolving poassium iodide in water is an endothermic proces and the reaction does not need any heating. This means that such a reaction has high entropy.
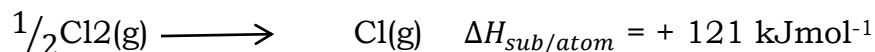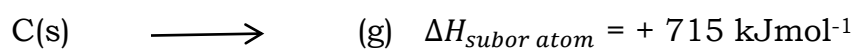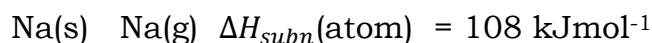
Bron-haber cycle and latice energies

The Born-Haber enegy cycle considers, the energy changes which occur during the formaton of an ionic crystal (ionic cp'd) from its elements.

We can form the ionic cp'd directly or we can use other enthalpies to reach the ionic cpd. Such enthalpies incude atomization energy ionisation energy, electron affinity and latice energy .

Atomisaiton energy

It is the enthalpy change that occurs when an element (metal) is coverted into one more of gaseous atom)

Na(s) Na(g) ΔH_{subn}(atom) = 108 kJmol^{-1}

C(s) $\longrightarrow$ (g) $\Delta H_{subor\ atom}$ = + 715 kJmol^{-1}

$\frac{1}{2}$Cl2(g) $\longrightarrow$ Cl(g) $\Delta H_{sub/atom}$ = + 121 kJmol^{-1}

Ionisation energy

It is the enthalpy change that ocurs when one mole of electrons is removed from one mole of gaseous atom to form one mole of positivelychanged gaseous ions atoms to form one mole of postivevely changed gaseous ions

Na(g) $\longrightarrow$ Na(g) + e ΔH_s = + 493 kJmol^{-1}
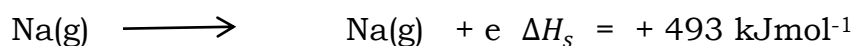
Electron affinity

This is the enthalpy change that occur when one mole or gaseous atoms of a non metal gain mole of electrons toform one mole of negatively changed gaseous ions.

Lattic energy

It is $\Delta H°$ that occurs when one mole of an ionic crystal is formed from its constantuent gaseous ions.

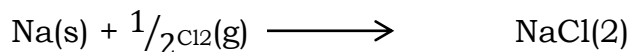Na(aq) + Cl(aq) $\longrightarrow$ NaCl(g)
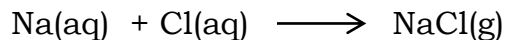
Enthalpy of solution

It is the $\Delta H°$ that formed when one mole of an ionic crystal littice is broken into its constituent gaseous ions.

ΔH

Standard enthalpy of formation is the heat reaact.. when one mole of a compound is formed from its physical state from its construent elements

Na(s) + $^1/_2$Cl2(g) $\longrightarrow$ NaCl(2)

ΔH_f^θ = 411 kJmol^{-1}

Born – Haber cycle for formation of sodium chloride
From its elements

Na(s) + $^1/_2$Cl$_2$(g) $\underrightarrow{\text{-411KJ/mol}}$ NaCl(s)

+ 108   +121

Na(g)   Cl(g)

-770

+493   -364

Na$^+$ (g) + Cl$^-$(g)
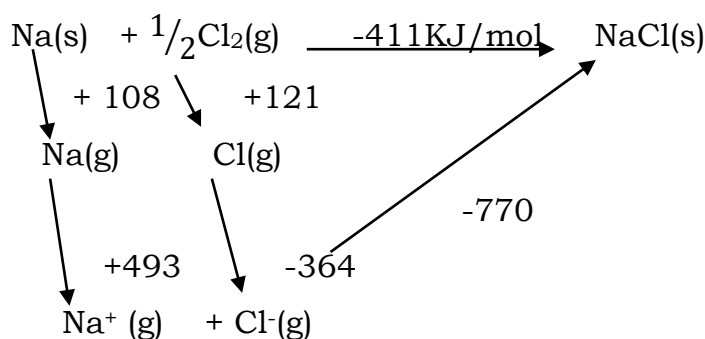
ENERGY DIAGRAM FOR FORMATION OF AN IONIC (PD) FROM IT'S ELEMENTS

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.

ΔH_f^θ(NaCl) = -411kJmol-1

ΔH_{atom}^θ(Na) = + 108kJmol^{-1}

ΔH_2(Na)   = + 493kJmol^{-1}

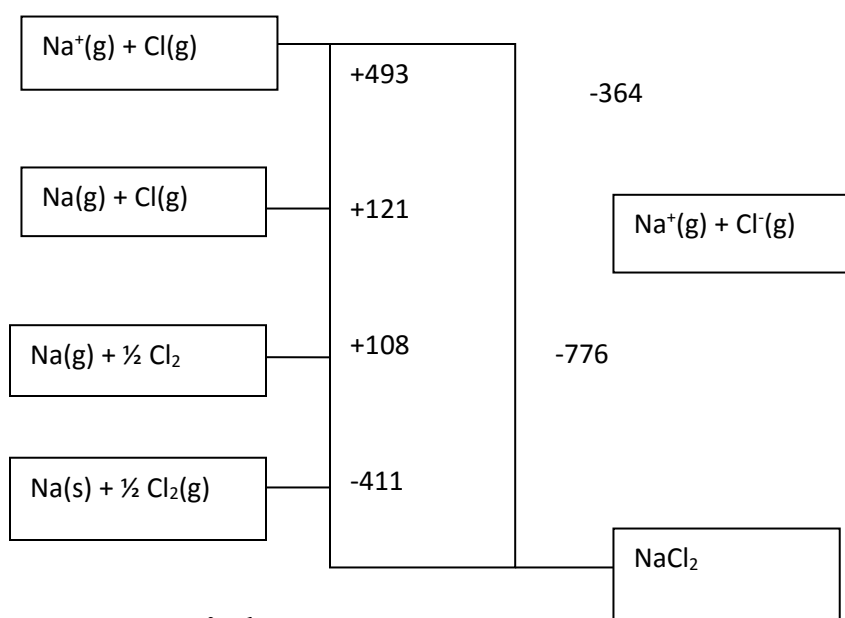ΔH_{en}^θ(Cl)   = - 364kJmol^{-1}

$\Delta H_{luttice}^\theta$ (NaCl)   = - 776kJmol^{-1}

Na$^+$(g) + Cl(g)	+493	-364
Na(g) + Cl(g)	+121	Na$^+$(g) + Cl$^-$(g)
Na(g) + ½ Cl$_2$	+108	-776
Na(s) + ½ Cl$_2$(g)	-411	NaCl$_2$

By Hess's law

$$+\Delta H_s^\theta(Na)$$

$$\Delta H_f^\theta(NaCl) = \Delta H_{atom}^\theta(Na) + \Delta H_{aq}^\theta)C) + \Delta H_{............}(Cl) + \Delta H_{(eth..}(NaCl)$$

$$= 108 + 121 + -364 - 776 +$$

$$= 108 + 121 + 493 + - 364 + 776$$

$$= - 418kJol-1$$

Construct an energy level diagram for the formation of calcium chloride from it's elements.

Calculate the latticeenergy of calcium chloride using the following thermodynamic data.

ΔH_f^θ (CaCl)   = - 795 kJmol^{-1}

ΔH^θ_{atom} (Ca+ + 177kJmol^{-1}

ΔH^θ_{atom} (Cl) = + 121 kJmol^{-1}

1st JE of Ca = 590 kJmol^{-1}

2nd JE of Ca = + 1100kJmol^{-1}

1st EA of Cl = - 364 kJmol^{-1}
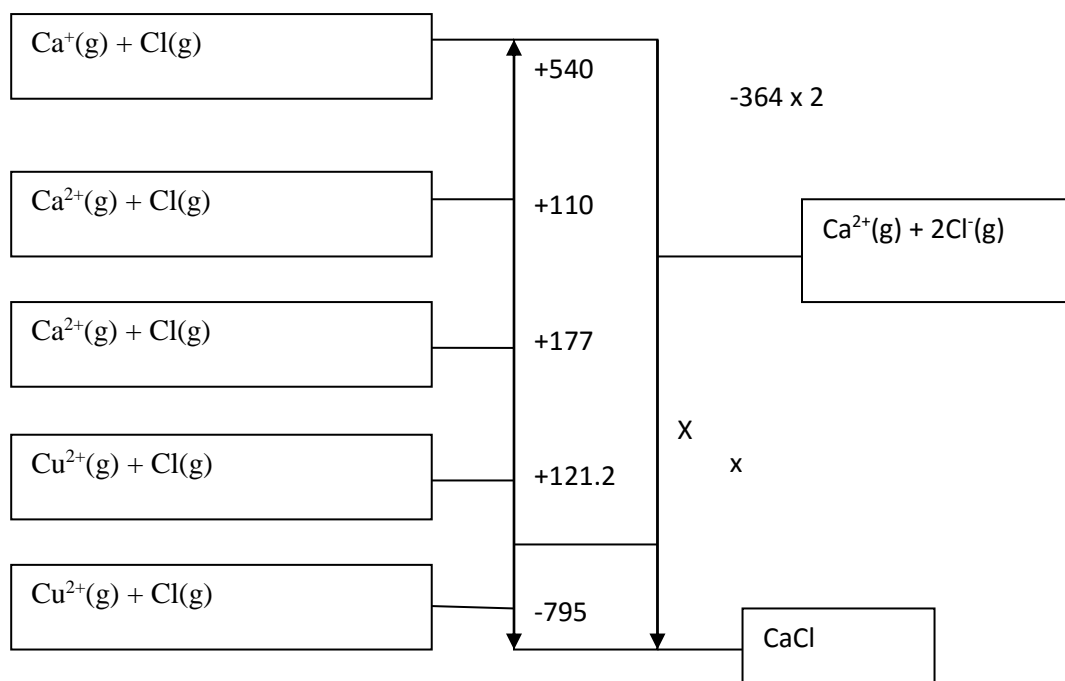
By Hess's law

ΔH^θ_f (Cash) = EACl + 1st IE (Ca + 2nd IE Ca + ΔH^θ_{atom} Ca + ΔH^θ_{atom} Ca + $\Delta H^\theta_{reaction\ Cl}$

+ $\Delta H^\theta_{lattric}$ CaCl$_2$

-795 = 364 + 590 + 1100 + 177 + 121.4 – x

x = - 2176 kJmol^{-1}

$\Delta H^\theta_{lattic(CaCl_2)}$ = 2176 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 change (change 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 attraction between the ions are very high and this results into 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 donot approach each other more closely and the electrostatic force of attraction are weak reading 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 apposite 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	ΔH lattice kJmol^{-1}	
$Na^+ - Cl^-$		
$Na . F^-$		
$Mg^{2+}. 2C^-$		
$Mg^{2+} . C^{2-}$		
$2Al^{3+} . 3C^{2-}$		
$Al^{3+} . 3Cl^-$		
$2l_1 . 0^2$		
$2k^{-1} . 0^2$		
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.

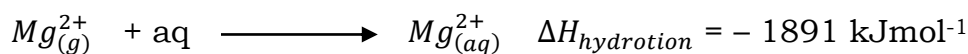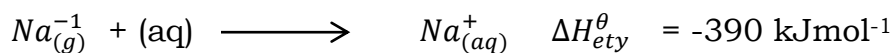Flauride ion is smaller than chloride ion and therefore CaF2 has a higher lattice energy than CaCl2

Oxygen ion is daibly charged which chloride ion is singly charged therefore CaO has a higher lattic energy than CaCl2.

Standard enthalpy of solution and standard enthalpy of hydra..

Standard enthalpy of soles is the enthalpy changes that occurs when one mole of an ionic cp'd 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

mX(2) + (aq) ΔH solution $M^+_{(aq)}$ + $X^\circ_{((aq)}$

e.gMgCl(aq) + (aq) ΔH solution $Mg^{2+}_{(aq)}$ + 2Cl⁻(aq)
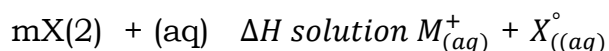
<u>standard enthalpy of hydration</u> (hydration energy is the enthalpy change that occurs when one mole of gaseous ions is completely surrounded by water molecules, such that hurther dilution causes no enthalpy change the enthalpy of hydration is always, an exothermic process because there are partial bond formed between the ions and water molecules .

$Na^{-1}_{(g)}$ + (aq) $\longrightarrow$ $Na^+_{(aq)}$ ΔH^θ_{ety} = -390 kJmol⁻¹

$Mg^{2+}_{(g)}$ + aq $\longrightarrow$ $Mg^{2+}_{(aq)}$ $\Delta H_{hydrotion}$ = – 1891 kJmol⁻¹

$Al^3_{(g)}$ + aq $\longrightarrow$ $Al^{3+}_{(aq)}$ $\Delta H_{hydrotion}$ = - 4613 k Jmol⁻¹

$Ca^{2+}_{(g)}$ + aq $\longrightarrow$ $Ca^{2+}_{(aq)}$ $\Delta H_{hydrotion}$ = - 1562kJmol⁻¹

$F^-_{(g)}$ + aq $\longrightarrow$ F(aq) $\Delta H_{hdrochation}$ = - 457 kJmol⁻¹

$Cl_{(g)}$ + aq $\longrightarrow$ $Cl^-_{(aq)}$ $\Delta H_{Hdrotion}$ =   - 381 kJmol⁻¹

$Br^-_{(g)}$aq $\longrightarrow$ $Be^-_{(aq)}$ $\Delta H_{hydrotion}$ =- 351 kJmol⁻¹
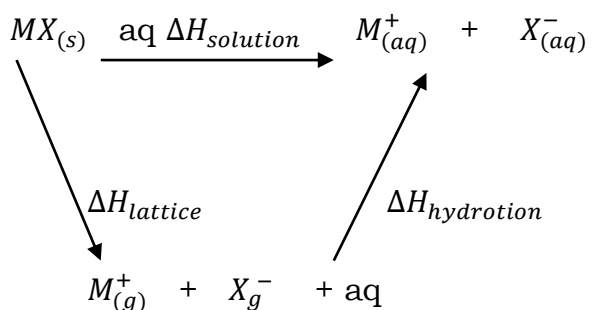
From the values above of the hydration energies, the smaller the ion the higher the hydration energy.

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 change 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 term come into pu.. ie enthalpy of solution enthalpy of lattice and enthalpy of hydration.

The three energy terms are related by the born-haber cycle below;

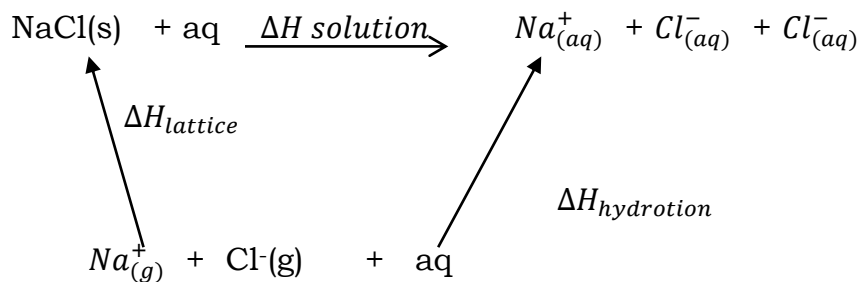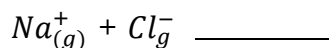$$MX_{(s)} \xrightarrow{\text{aq } \Delta H_{solution}} M^+_{(aq)} \ + \ X^-_{(aq)}$$

$\Delta H_{lattice}$ $\quad\quad$ $\Delta H_{hydrotion}$

$$M^+_{(g)} \ + \ X^-_g \ + \text{ aq}$$

By Hess's law

$$\Delta H^\theta_{solution} = \Delta H^\theta_{lattice} + \Delta H^\theta_{hydration}$$

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 energyof sodium chloride is -770 kJmol[-1] and the hydration energy of Na((g) is -766 kJmol[-1]. Calculate the enthalpy of solution of sodium chloride.

$$Na^+_{(g)} + Cl^-_g \quad \underline{\hspace{2cm}}$$

NaCl(s) + aq $\underline{\Delta H\ solution}$ → $Na^+_{(aq)}$ + $Cl^-_{(aq)}$ + $Cl^-_{(aq)}$

$\Delta H_{lattice}$ ↗
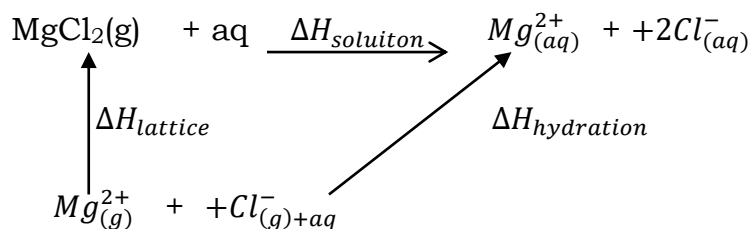
$\Delta H_{hydrotion}$

$Na^+_{(g)}$ + Cl⁻(g)   + aq

$\Delta H_{hydration}$ = $\Delta H_{lattice}$ + $\Delta H_{solution}$

-766 = -770 + $\Delta H_{soluiton}$

$\Delta H_{soluiton}$ = 4kJmol⁻¹

The lattice energy of MgCl₂ is -2484 kJmol⁻¹

The hydration energies of Mg^{2+} and Cl^- are -1891kJmol⁻¹ and -381 kJmol⁻¹ respectively. Calculate the enthalpy of solution of MgCl₂.

MgCl₂(g)   + aq $\underline{\Delta H_{soluiton}}$ → $Mg^{2+}_{(aq)}$ + +2$Cl^-_{(aq)}$

$\Delta H_{lattice}$

$\Delta H_{hydration}$

$Mg^{2+}_{(g)}$ + +$Cl^-_{(g)+aq}$

$\Delta H_{hydration}$ = $\Delta H_{lattice}$ + $\Delta H_{solution}$

-1891 + -381 x 2=   – 2484 = $\Delta h_{SOLUTION}$

-2652 + 2489   = $\Delta H_{solution}$
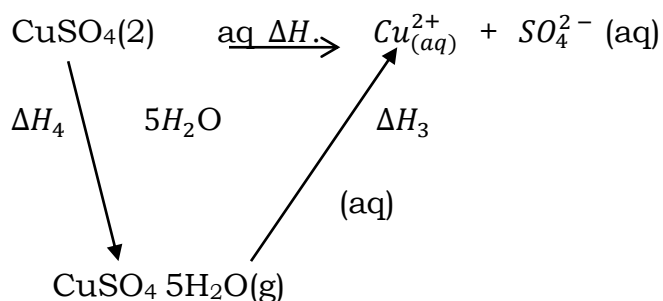
$\Delta H_{solution}$ =   -164kJmol⁻¹

NOTE

The balance between lattice energies and enthalpies of hydration accounts for the observation that certain hydrated cpds dissolve endothermically, where as the corresponding an hydrous 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 outweigh 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. an hydrous copper (ii) sulphate dissolve in form a dilute solution and the enthalpy of solution -66.3 kJmol-1 where as the enthalpy of solution of hydrated copper (iii) solution is +11.4KJmol^{-1}

The following energy cycle can be constructed

$CuSO_4(2)$ aq ΔH $\rightarrow$ $Cu^{2+}_{(aq)}$ + SO_4^{2-} (aq)

ΔH_4 $5H_2O$ ΔH_3

         (aq)

   $CuSO_4\ 5H_2O(g)$

By Hess's law

ΔH_1 = ΔH_3 + ΔH_3

-66.5 + ΔH_2 + 11.4

ΔH_2 = -66.3 - 11.4

-77.7 kJmol^{-1}

$CuSO_4(g)$ + $5H_2O$ $\longrightarrow$ $CuSO_4$ - $5H_2O$ ΔH = -77.7kJmol^{-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 colorimeter which is filled with a striver 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,$°C$

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$_1°C$.

Assumption

The density of the solution is assumed to be equal to that of water = 1gcm3.

The she of a solution is assumed to be equal to that of water = 4.2 1 g^-k^{-1}

Treatment of results

Let ag be the mass of the water.

By be the mass of the all

M be the relative formula mass of salt.

Temp change $\Delta T = (T_{2-}T_1)°C$

Heat absorbed by the solution = M x shc x ΔT
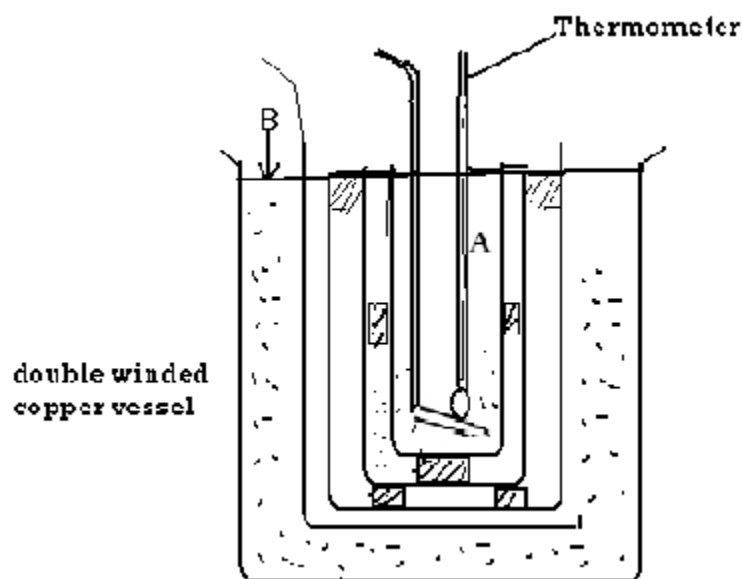
= Cl x 4.2 x $(T_2 - T_1)$

b g of the salt produce a c $(T_2 - T_1)$

Mig of the produce $\frac{ac\ (T_2-T_1)mr}{1000b}$

$\frac{4.2a(T2-T1)mr}{1000b}$

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 abled 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,... or ......by 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 NH_4Cl = 14 + 4 + 35.5 = 53.5

Enthalpy of neutralis Temp change be $(T_1, - T_1)^0C$

Heat absorbed by the solution in Mass x She X DT

   = a x 4 .2   x (T2 – T1)

By of NHaCl produce a x 11.2 x $(T_2 – T_1)$

5353 of NHaCl produce   4.24 (T2 – T1) .55.5

  = $- \frac{4}{b}$ x 224.7 $(T_2 – T_1)$ 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.

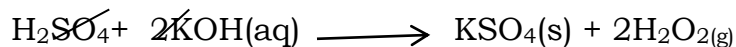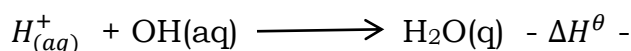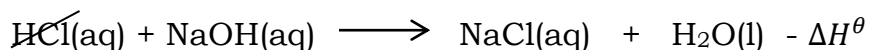$H^+_{(aq)}$ + $\bar{O}H_{(aq)}$ $\longrightarrow$ H2)(1)   . ΔH = - 57.3kJmol^{-1}
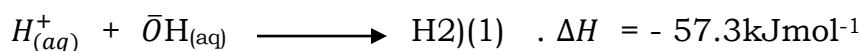
NOTE:

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 .

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) - \Delta H^\theta$

$H^+_{(aq)} + OH(aq) \longrightarrow H_2O(q) - \Delta H^\theta -$

$H_2SO_4 + 2KOH(aq) \longrightarrow KSO_4(s) + 2H_2O_{2(g)}$

$H_2(aq) + 2\bar{O}H \longrightarrow 2H_2O(1)$

The enthalpy of neutralization of a weak acid such as CH_3COOH. HF, hydrogen Propanoil acid (CH3CH2COOH) 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	ΔHneutrralisaiton kJmol^{-1}
Hco	NaOH	-57.4
Hcl	KOH	-57.3
Hno3	NaOH	-57.3
$\frac{1}{2}H_2SO_4$	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 $T_1°C$

A known volume V2cm³ of a strong alkali of known concentration whose initial temp is read and recoded as $T1°C$ 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 $T_2°C$ 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 prolled 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 iexis is the max temp.
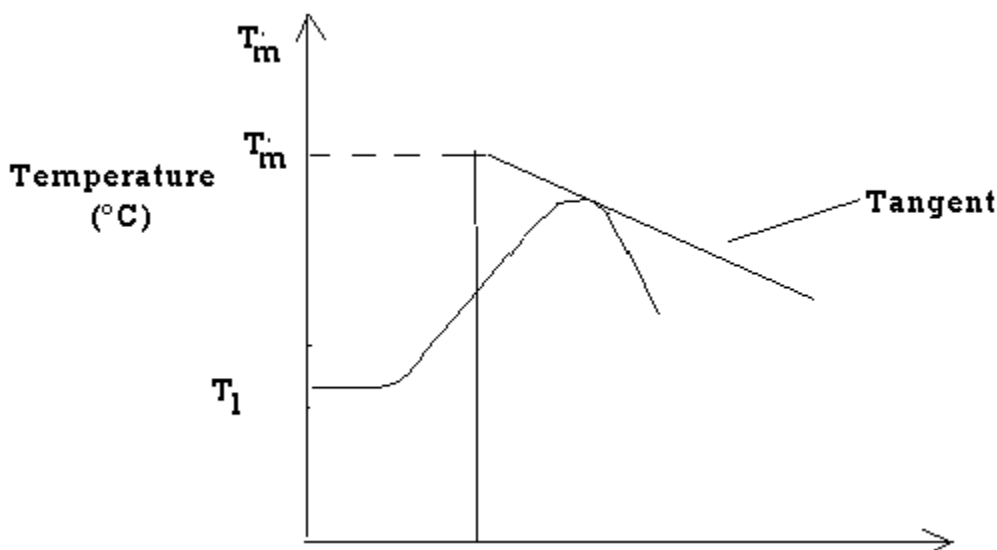
Treatment of results

Initial temp T1 = $\frac{T_0 + T_1}{2}$

Final temperature of the mixture = T_m

Terms change $\Delta T = [T_m = \left(\frac{T_0 + T_1}{2}\right)]$

Let the density of mixture be f

Let the she of the mixture by C

Total volume of the solution = V1 + V2

Mass of the solution = density x volume

$= \int(V_1 + \int V_2)$

Heat absorbed by the solution = $MC\theta$

$= \int(V_1 + V_2) . C . [Tm - (\frac{T_o + T_1}{2})]$

No of moles of the acid $= \frac{M_1 \times V_1}{1000}$

 $= M_1V_1 \times 10^{-3}$

$M_1V_1 \times 10^{-3}$ mole of acid produced $\int(V_1 + V_2 \text{ C.} (T_m - T_o + T_1)$

1 mole of the acid produced $\rho(V_1 + V_2) C (T_m - \frac{T_0 + T_1}{2}$

Enthalpy of neutralization $= \frac{\rho(V_1 + V_2).C.(T_m - \frac{T_0 + T_1}{2})}{M_1 V_1 \, x \, 10^{-3}}$

qns

1. When 25cm³ of 2mHCl were   mixed with 25cm³ of 2M sodium hydroxide solution bot at initial terms of 24.5°C .   The final temp of the mixture was 37.0°C. calculate the enthalpy of neutralization of hydrochloric acid $[Shc \, 2, 4.2 \, Jgk^{-1} \, and \, the \, density \, of \, the \, soluiton \, = 1 \, gem^{-1}]$

$\Delta T = 37 - 24.5 = 12.5°C$

Total volume of the solution = 25 + 25 = 50cm³

Mass of the solution = 1 x 50 = 50g

Heat absorbed by the solution = $MC\theta$

= 50 x 4.2 x 12.5

= 2625J

No of mole of acid 1000cm3 of acid contain 2moles

25cm3 of acid contain $^2/_{1000}$ x 25

 = 0.05 moles

C.C Smoke of acid produced 2625J

1 mole of acid produced $\frac{2625}{005}$ x 1

 = 52500J

∴Enthalpy of neutralization = 52.5kJmol^{-1}

NOTE:

The heat of neutralization determined by the above experiment is less then the theoretical values use some heat is lost to the surrounding .

50cm^3 of 2M H_2SO were mixed with 50cm^{-3} of 2M NaOH solution and the temp of the mixture rose by13.6°C. Calculate the enthalpy of neutralization of Sulphuric acid.

$\Delta T = 136°C$

Total mass of the solution = 50 + 50 = 100cm^3

Mass of solution = 1 x 100 = 100g

Heat absorbed by the solution = MCθ

= 100 x 47 x 13.6

5712 J

100cm^3 of H_2SO_2 contain 2 moles

50cm^3 of $H_2 SO_4$ contain$\frac{2}{1000}$x 50 = 0.1 mole

0.1moles of acid produced 3712 J

1 mole of acid produces $\frac{5711}{0,1}$ = 571205   114.24 kJ

∴ Enthalpy neutralization of H2SO4 = − 114.24   kJmol^{-1}

Thermometric titration Method II

This type of filtration evolves 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 e ach 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 filtration

The graph can be used to determine

(a) Enthalpy of neutralization of the acid or alkal

(b) Stoichrometing of the reaction (reaction mole ratios)
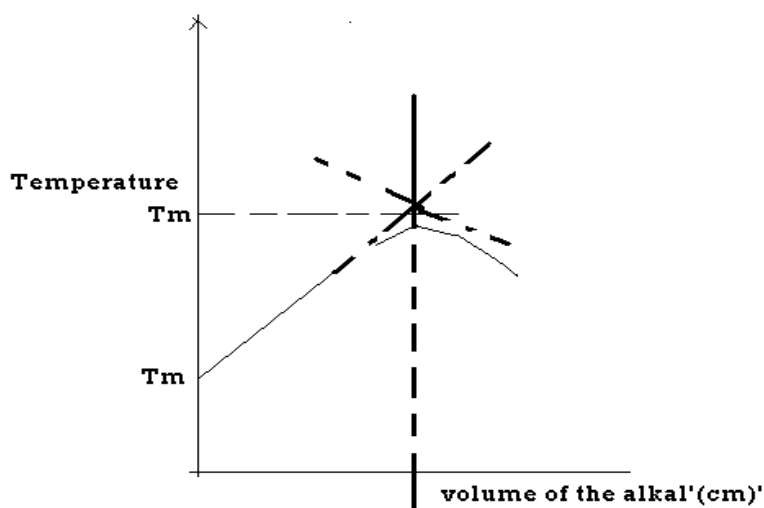
Example

50cm³ of HCl was placed in a plastic beaker and the initial temp read and recorded as 22.5

5cm**3** 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 tale below;

Volume of NaOH/cm³	0	5	10	15	20	25	30	35
Temperature/°C	22	27.5	31.3	34	35	34	32	285

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°C

ΔT = 36.7 − 22.5 = 15.7°C

Total of Neutron = 1 x 85 = ..

Mass of solution 50 x 85 = 85

heat absorbed by the soluiton = mass

55 x 4. 2 x 13.1

4676.TJ

HCl + NaOH   NaCl + H1O

Sodium of NaOH Contain 2m

35cm-3 of NaCH contains $\frac{2}{1000}$ x 35 = 0.07
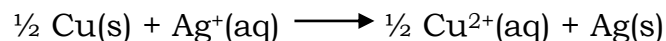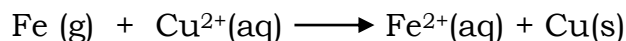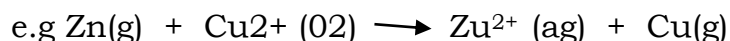
0.07moles produce heat change of 4617 TT

1 mole of HCl produce $\frac{46.0}{0.01}$

= 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 moles

e.g $Zn(g) + Cu2+ (02) \longrightarrow Zu^{2+} (ag) + Cu(g)$

$Fe (g) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s)$

$½ Cu(s) + Ag^{+}(aq) \longrightarrow ½ Cu^{2+}(aq) + Ag(s)$

1. When 0.1 mole of Zinc powder was added to 250cm^3 of 0.2 CuSO$_4$ solution in a plastic cup and the mixture is stirred gently using the thermometer and the temp changed from $19°C$ to 25°C. calculate the moles heat of the displacement reaction.

2. Excess Zn powder was added 25cm^3 of 1m solution of C4SO4 in a plastic beaker and the temp of the solution recorded at regular intervals. Date obtained is shown in the table below;

Time (min)	0	2.5	3	35	5.0	60	7.0
temp$°C$	27.7	66.0	69.5	68.5	68.5	62	59.5

Plot a graph of temp against time.

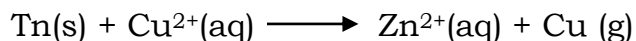Use the graph to determine the moles heat of displacement reaction

$\Delta T - 20 - 19\ 9°C$

Mass of solution 250g

Heat absorbed by solution = $MC\theta$

= 250 x 4.2 x 4

 = 9650J

Tn(s) + Cu²⁺(aq) $\longrightarrow$ Zn²⁺(aq) + Cu (g)

1000cm of Cu^{2-1} Calcium 0.2mole

250cm of $Cu^{2.1}$ calcium $\frac{0.2}{1000}$ x 250 = 0.05mole

Mole of ratio of Zn : Cu^{2+} = 1:1 moles of Zn = 0.05

0.05   ole of Zn 9450J

   1 mole produce $\frac{9450}{0.05}$ = 189 kJmol⁻¹

2. Maximum Temp. = 105°C

ΔT = 70.5 – 27.2 = 43.5

Mass of the solution 1 x 25 = 25g

Heat absorbed by the solution = m.ΔT

   = 25 x 4.2 x 43.3

   4546.5J

1000cm³Cu^{2+} calcium 1 mole

25cm3 of Cu^{2-} contain $\frac{1}{1000}$ x 25 = 0.025 mole

Mole Zn(g) +$Cu^{2+}_{(aq)}Zn \longrightarrow$ + Cu..)Moles of Zinc ions reacted = 0.025 moles

      Moles of Zn ions reated 0.025 moles

      0.025 moles of Zn^{2+} produce 4546kJ

      LM04 of Zn^{2+} Produce $\frac{4546}{0.025}$ 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 standards conditions, of 298k and atmosphere 1994

Determination of heat of preceiptation of AyNo3 measure out 25cm3 of silver Nitrate solution and pour it into the polgethne bottle.

Insort the temp.. filtted with the thermometer and not the temp of the bond to the liquid. Initial temp is 6,°C.

Measure out 25cm3 of 0.5NH4Cl and it to silver nitrate solution in the polythen bottle/

Quickly replace the bung in the bottle and share gents, to allow mixing of solution. Maximum temp = to °C .

Repeat (a) and (b) using 0.5M instead of NH4(1)

Treatment of results

25cm^3 of 0.5M AgNO^3 react with 25cm^3 of NH..(1)

25cm^3 of 0.5M AgNO^3 contain $\frac{0.5 \times 25}{1000}$

= 0.0125 moles Ag^+

25cm^3 of 0.5m NH4Cl or KCl

0.0125 mole of NH_4^+ - k^+ - Na^1

Mass = 1 x 50 = 50g

Heat absorbed = MCθ

= 50 x 4.2 (t$_2$ – t$_1$)

What is meant by the following?

i. standard stat 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 sulphar.

(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
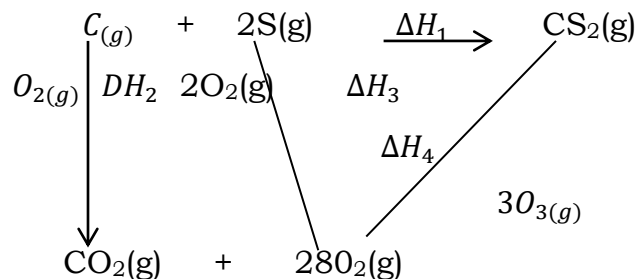
(c) The standard enthalpies of combustion of the first form straight chain alkanes and the first five straight .. alcohols are shown in the table below;

No of carbon atom	1	2	3	4	5
enthalpy of combustion of alkaline (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

$$C_{(g)} \quad + \quad 2S(g) \quad \xrightarrow{\Delta H_1} \quad CS_2(g)$$

$O_{2(g)}$ | DH_2 $2O_2(g)$ $\quad \Delta H_3$

ΔH_4

$3O_{3(g)}$

$$CO_2(g) \quad + \quad 2SO_2(g)$$

$\Delta H_1 + 3\Delta H_4 = \Delta H_2 + 3\Delta H_3$

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