1.0 *TRANSITION METALS.*

1.1.1. Introduction.

Transition metals are d-block elements that have partially filled d-orbital. Or Transition elements are d-block elements that have a partially filled d-orbital in at least one of its oxidation states. Transition elements have their properties transition between the highly reactive s-block elements and less reactive p-block elements.

At this level, the first transition series are covered comprising of elements between scandium to zinc.

Elements	Atomic number	Electronic configuration.
Scadium Sc	21	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^1 4S^2$
Titanium Ti	22	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^2 4S^2$
Vanadium V	23	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^3 4S^2$
Chromium Cr	24	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^5 4S^1$
Manganese Mn	25	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^5 4S^2$
Iron Fe	26	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^6 4S^2$
Cobolt Co	27	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^7 4S^2$
Nickel Ni	28	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^8 4S^2$
Copper Cu	29	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^{10} 4S^1$
Zinc Zn	30	$1S^2 2S^2 2P^6 3S^2 3P^6 3d^{10} 4S^2$

Note:

(a) According to the definition of transition metals Sc^{3+}, Cu, Cu^+, Zn, Zn^{2+} are referred to as non transitional metals.

(i) Sc^{3+} is a non transitional metal because it has empty d-orbital.

$^{18}Sc^{3+}$-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^0 4S^{0.}$

(ii) Cu, Cu^+, Zn, Zn^{2+} are referred to as non transitional elements because they have full d-orbitals.

^{29}Cu-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^{10} 4S^1$

$^{28}Cu^+$-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^{10} 4S^0$

^{30}Zn-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^{10} 4S^{228}Zn^{2+}$-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^{10} 4S^o$

(b) Transition metals which have a full and half filled orbital are thermodynamically stable than those that have a partially filled orbital. Eg.

(i) Copper and chromium are thermodymically stable because of having fully filled and half filled d-orbitals.

^{29}Cu-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^{10} 4S^1$

^{24}Cr-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^5 4S^1$

(ii) Fe^{3+} is more stable than Fe^{2+}because Fe^{3+} forms a half filled d-orbital which is thermodynamically more stable.

$^{24}Fe^{2+}$-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^6 4S^0$

$^{23}Fe^{3+}$-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^5 4S^0$

(iii) Mn^{2+} is more stable than Mn^{3+} because it forms a half filled d-orbital which is thermodynamically more stable.

$^{23}Mn^{2+}$-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^5 4S^0$

$^{22}Mn^{3+}$-$1S^2 2S^2 2P^6 3S^2 3P^6 \underline{3d}^4 4S^0$

(iv) However Cu^{2+} is more stable than Cu^+ yet Cu^+ forms a full d-orbital,because the reaction leading to the formation of Cu^{2+} is more exothermic than that leading to the formation of Cu^+.

1.1.2. Characteristics of transition metals.

(a)They have metallic properties.
(b) They have variable oxidation states.
(c) They form coloured compounds.
(d) They form complexes.
(e) They exhibit magnetic properties.
(f) They can act as catalysts.
(g) They form alloys.

Properties specific to transition metals.

-Variable oxidation states.
-Coloured compounds.
-Form complexes.
-Acts as catalyst.
-Paramagnetism.

(a) Metallic properties.

(i) Have high melting and boiling point because of strong metallic bonds due to formation of a giant metallic structure.
(ii) Conduct electricity and heat due to having free electrons.
(iii) Have a high density.
(iv) Are ductile and malleable becauseelectrons in metals are mobile so the cations in the structure slide over each other upon exertion of a certain force.

(b) Variable oxidation states.

Transition elements are capable of forming many oxidation states because they can loose electrons in the S and d orbitals. E.g

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxidation number	**+3**	**+4**,+3, +2	+5,+4 **+3**,+2	+6,**+3** +2	+7,+6 +4,+3, **+2**	+6,**+3** +2,+4	+4,+3 **+2**	+3, **+2**	+1, **+2**	**+2**

The most stable oxidation states are shown in bold.

Test yourself

Calculate the oxidation state of the transition metal

i. MnO_4^- ii.MnO_2 iii.MnO_4^{2-} iv. $Cr_2O_7^{2-}$ v. VO_3^-

(c) Formation of coloured compounds.

Solution of cation	Colour	Solution of cation	Colour
Sc^{3+}	Colourless	Fe^{2+}	Green

Ti^{3+}	Purple	Fe^{3+}	Yellow/brown
V^{3+}	Green	Co^{2+}	Pink
Cr^{3+}	Green	Ni^{2+}	Green
Mn^{2+}	Pink	Cu^{2+}	Blue
$Mn^{7+}(MnO_4^-)$	Purple	Zn^{2+}	Colourless

Explanation for formation of colour.

Formation of color is associated with the presence of partially filled d-orbitals.

Once light is incident on the d-subshell, there is excitation of electrons which leads to their promotion to the section of the d-orbital which is empty.

However the electrons are unstable in the excited state and they fall back.

As they fall back they emit radiations that fall in the visible region of the spectrum.

These radiations are of a specific colour and wave length.

NB:

Zn^{2+} compounds are colourless because of full d-orbital.

Sc^{3+} compounds are also colourless because of empty d-orbital.

The colour of a particular metal ion depends on:

(i) Nature of the ligand.

(ii) Oxidation state.

(i) Nature of the ligand.

A ligand is an atom, ion or molecule capable of donating lone pair of electrons to an acceptor to form a coordinate bond.

The ligands are anionic like CN^-, Cl^-, I^-, Br^-, SO_4^{2-} or OH^- or neutral molecules like H_2O, NH_3, CO, NO.

A compound shows different colours depending on the ligand bonded to the central metal ion.

$[Cu(H_2O)_4]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons CuCl_4^{2-}{}_{(aq)} + 4H_2O_{(l)}$

blue yellowish-green

$[Cu(H_2O)_4]^{2+}{}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}{}_{(aq)} + 4H_2O_{(l)}$

light blue deep blue

$[Co(H_2O)_4]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 4H_2O_{(l)}$

pink blue

Ligands are also classified as
Monodentate ligands: Ligands that donate one lone pair of electrons e.g.Cl^-, Br^-,NH_3
Polydentate ligands: Ligands that donate more than one lone pair.e.g
bidentate ligands: donate two e.g. $H_2NCH_2CH_2NH_2$, $^-OOCCOO^-$
tridentate ligands: donate three.
tetradentate ligands: donate four.
pentadentate ligands: donate five.
hexadentate ligands: donate six.
NB:complexes with polydentate ligands are called chelates.
complexes with polydentate ligands are more stable because of this chelation.

The above is called **ligand exchange.**

Ligand exchange is process where a ligand which is a stronger lewis base can replace the other from a complex ion.

$[Cu(H_2O)_4]^{2+} \underset{HCL}{\overset{conc}{\rightleftharpoons}} CuCl_4^{2-} \underset{NH_3}{\overset{conc}{\rightleftharpoons}} [Cu(NH_3)_4]^{2+}$

The order of ligand strength is
$CN^- > NH_3 > Cl^- > H_2O$

(ii) Oxidation state.

Compounds also show different colours depending on the oxidation state of the metal cation. e.g $[Cr(H_2O)_6]^{2+}$ - blue. $[Cr(H_2O)_6]^{3+}$ - green. MnO_4^- -purple. MnO_4^{2-} -green.

(d) Complex ion formation.

Complex ion formation is an association between two or more specie each of which is capable of independent existence.

A complex ion is an ion which contains a central metal ion linked to ligands through a dative bond.

The number of ligands bonded to the central metal gives the co-ordination number or the number of co-ordinate bonds.

For example-$[Cu(NH_3)_4]^{2+}$ has co-ordination number of 4.

Reasons why transitional metals form complexes.

- They have a high polarizing power due to their high charge and small ionic radius.
- Because they have empty (d)-orbitals.

Naming complexes.

Rules of naming complexes include.

(a) The anion is always named after the cation.

(b) The ligands are named before the name of the central metal ion.

(c) The oxidation state of the central metal ion is written in roman numerals.

(d) The names of ligands include.

(i) anionic ligands include. N.B. they end with –O.   (ii) Neutral ligands

Ligand	**Names**
CN^-	Cyano CH_3COO acetato
Cl^--	Chloro NO_2^- nitro
Br^--	Bromo
NH_2^-	Ammino
OH	Hydroxo
$C_2O_4^{2—}$	Oxalate
SO_4^{2-}	Sulphato
SCN^-	Thiocynato
$CO_3^{2—}$	Carbonato

Ligand	**Name**
NH_3	ammine
H_2O	aqua
CO	carbonyl

(e) For an anionic complex,

the name of the central metal ion ends with -ate but some use latin names are applied e.g

Centre atom	**Name**
Al	Aluminate
V	Vanadate
Cr	Chromate
Mn	Manganate
Co	Coboltate
Ni	Nickelate
Zn	Zincate

Centre atom	**Name**
Cu	Cuprate
Ag	Argentate
Au	Aurate
Pb	Plumbate
Sn	stannate
Fe	Ferrate

(f) When they are a number of the same ligand, the prefix di, tri, tetra, penta ,hexa for 2,3,4,5,6 respectively. *e.t.c.*

(g) If there is more than one ligand the names are written in alphabetical order.

(h) The name of the complex ion is written as one word.

Examples.

$[Cr(H_2O)_6]^{3+}$ -Hexaaquachromium(III) ions
$[Cu(NH_3)_4]^{2+}$-Tetraamminecopper(III) ions
$[CuCl_4]^{2-}$-Tetrachlorocuprate(III) ions
$[CoCl_4]^{2-}$-Tetrachlorocoboltate(II) ions.
$[Fe(CN)_6]^{3-}$ Hexacyanoferrate(III)
$[Fe(CN)_6]^{4-}$ Hexacyanoferrate(II)
$[Co(SO_4)(NH_3)_5]^{+}$- pentaamminesulphatocobalt(III) ions.
$[Co(NH_3)_4Cl_2]^{+}$- Tetramminedichlorocobalt(II) ions.
$[Fe(OH)(H_2O)_5]^{2+}$- pentaaquahydroxoiron(III) ions.
$Cr(NH_3)_3(H_2O)_3]Cl_3$- triamminetriaquachromium(III) chloride.
$K_4[Fe(CN)_6]$- potassium hexacyanoferrate(II)
$Na_2[NiCl_4]$- sodium tetrachloronickelate(II)

Test yourself

Name the following complexes.
a. $[Ti(H_2O)]_6^{2+}$
b. $[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$
c. $[Co(NH_3)_6]^{2+}$
d.$[Fe(NO)(H_2O)_5]^{2+}$
d. $[CuCl_4\,(H_2\,O)_2]^{2-}$
f. $[FeF_4(H_2O)_2]^{2-}$
g.$[Cr(CN)_5NH_3]^{3-}$
g. $[Pt(NH_3)_2Cl_2]$.

Structure of complexes

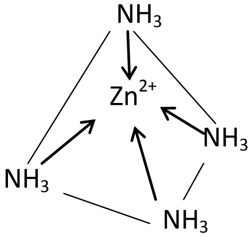
(a) Linear structure.

formed by compounds with coordination number of 2.e.g $[Ag(NH_3)_2]^{+}[Ag(CN)_2]^{-}$ $[Cu(CN)_2]^{-}$

$H_3N \rightarrow Ag \leftarrow NH_3$

(b) Tetrahedral structure.

Usually formed by compounds with coordination number of 4. Common with larger negatively charged ligands. E.g$[Zn(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$

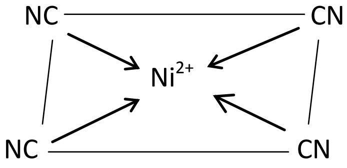


(c) Square planar structure.

Also formed by compounds with coordination number of 4.

It is rare and usually occurs in complexes that have d^8- electron structure.

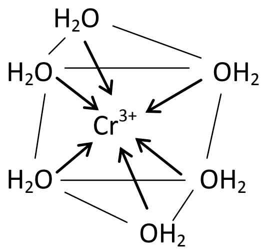
e.g. $[NiCN_4]^{2-}$, $CuCl_4^{2-}$,$[Cu(NH_3)_4]^{2+}$



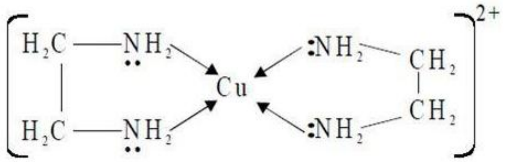
(d) Octahedral structure.

Usually formed by compounds with coordination number of 6.

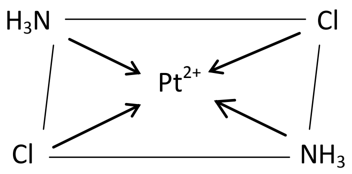
E.g. $[Cr(NH_3)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$



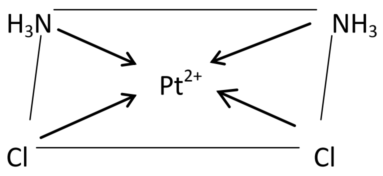
NB: Ligands have the ability to donate two electron pairs are called **bidentate ligands.**
e.g oxalate and 1,2-diaminoethane.
Complexes formed include; $[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$,$[Cr(C_2O_4{}^{2-})_3]^{3-}$ or $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$



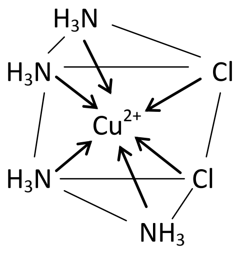
(iv) Isomerism.
It arises due to different arrangement of ligands to the central metal ion.
(a) Geometrical isomerism.
Is the type of stereoisomerism that arises as a result restriction in rotation around the centre atom.
E.g. $[Cu(NH_3)_2Cl_2]$, $[Co(NH_3)_2Cl_2]$. $[Pt(NH_3)_2Cl_2]$.



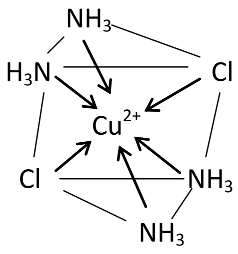
Trans



Cis

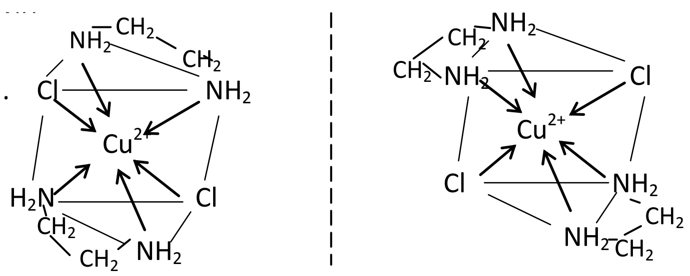


Cis

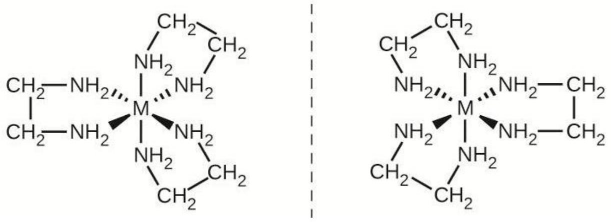


Trans

(b) Opitical Isomerism. Is the type of stereoisomerism that results into formation of non-super imposable mirror images. The cis-geometrical isomer with bidentate ligand forms optical isomers.



Even $[Cr(C_2O_4^{2-})_3]^{3-}$ and $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$ or $[Cr(en)_3]$ form optical isomers



(c) Ionisation isomerism.

This is the type of isomerism that arises due to different arrangement of ligands between those that are directly bonded and those which are not.

E.g. $Co(NH_3)_5BrSO_4$ has two isomers.

$[Co(NH_3)_5Br]^{2+}SO_4^{2-}$

$[Co(NH_3)_2SO_4]^{+}Br^{-}$

(c) Hydration isomerism.

This the type of isomers that differ in the number of water molecules directly bonded to the central metal ion and those which are not.

E.g. $CrCl_3.6H_2O$ has the following isomers.

Structure of the isomer.	No. of moles of Cl^- ions precipitated by silver nitrate(Imole) per isomer	No. of moles of conducting ions per mole of isomer.	Colour
$[Cr(H_2O)_6]^{3+}3Cl^-$	3	4	Violet
$[Cr(H_2O)_5\ Cl^-]^{2+}H_2O2Cl^-$	2	3	Light green
$[Cr(H_2O)_4\ 2Cl^-]^{2+}2H_2OCl^-$	1	2	Dark green

Stability of complexes depends on

. *Nature of ligands*

. *Size of the central metal ion.*

Application of complexes

In haemoglobin iron ii (Fe^{2+}) is complexed and it helps in oxygen transport.

Cis-platin-($[Pt(NH_3)_2Cl_2]$)*.Used in the treatment of some types cancer.*

Vitamin B_{12} which is used to form red blood cells is complexed with Co^{3+}.

Chorophyll in leaves contains a complex of Mg that helps in absorption of sunlight..

(e) Catalysts.

A catalyst is a substance that alters the rate of chemical reaction and remains chemically unchanged at the end of the reaction.

A catalyst may be homogenous or heterogenous.

A *homogenous catalyst* – Catayst with the same physical state as reactants.

eg. esterification of esters using sulphuric acid.

A *heterogenous catalyst*-Catayst with a different physical state from reactants.

e.g. hydrogenation of alkenes using non-metals, Haber process and contact process.

Transition metals are good heterogeneous catalyst.

They are able to behave as catalyst because of.

(i) Presence of 3d electrons which are able to form temporary bonds with reactant molecules.

(ii) Presence of variable oxidation states which provides an alternative reaction pathway with lower activation energy.

For example.

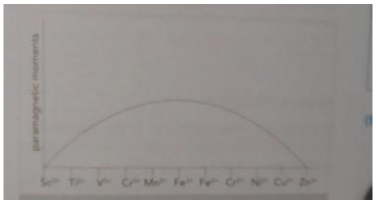
Vanadium (v) oxide used during the manufacture sulphur trioxide and sulphuric acid.

Iron during the manufacture of ammonia.

Maganese (iv) oxide used in the manufacture of oxygen.

Nickel or platinum during hydrogenation of alkenes.

(f) Transitional metals show paramagnetism.



Paramagnetism is the weak attraction of substances in magnetic field.

Transition metals show paramagnetism because of the presence of unpaired electrons in the 3d.

The unpaired electrons spin along their axes which generates electric current.

(g) Transition metals form alloys.

Transitional metals are able to mix together because they have almost the same size.

An alloy is a uniform mixture of two or more elements of which a metal is among. e.g

alloy	elements
Steel	Fe, C,…
Bronze	Cu, Sn
Brass	Cu, Zn

1.1.3 Anomolous behaviour of Sc and Zn.

According to the definition of transition metals Sc^{3+}, Zn, Zn^{2+} are referred to as non transitional metals which explains why they show anomalous behaviour.

(i) Sc^{3+} is a non transitional metal because it has empty d-orbital.

$^{18}Sc^{3+}$-$1S^{2}2S^{2}2P^{6}3S^{2}3P^{6}\underline{3d}^{0}4S^{0.}$

(ii) Zn and Zn^{2+} are referred to as non transitional elements because they have full d-orbitals.

^{30}Zn-$1S^{2}2S^{2}2P^{6}3S^{2}3P^{6}\underline{3d}^{10}4S^{2}{}^{28}Zn^{2+}$-$1S^{2}2S^{2}2P^{6}3S^{2}3P^{6}\underline{3d}^{10}4S^{o}$

1.1.4. Properties in which Sc and Zn show anomolous behaviour.

a. Oxidation states of elements.

Unlike other elements Sc and Zn show one oxidation state.

b. Color of compounds

Unlike other compounds of other transition metals , compounds of Sc and Zn are colorless.

1.1.5. Periodicity of transition metals.

a. atomic size/nm

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0.24	0.20	0.16	0.13	0.14	0.13	0.13	0.13	0.13	0.13

In moving across the series of metals from Sc to Zn,

Nuclear charge increases due to addition of protons.

But, electrons added to the d-orbitals are much more effective at shielding.

Hence, the effective nuclear charge increases only slightly across this period.

Therefore the atomic radii decreases very little.

b. Ionisation energy.(1st Ionisation energy in $kJmol^{-1}$)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+630	+660	+650	+650	+720	+760	+760	+740	+750	+910

In moving across the series of metals from Sc to Zn,

Nuclear charge increases due to addition of protons.

But, electrons added to the d-orbitals are much more effective at shielding.

Hence, the effective nuclear charge increases only slightly across this period.

Hence the ionization energy increases very little.

Exercise.1a

Multiple choice questions.

1. Which of the following metal ions is not a transitional metal cation.

a. Mn^{2+} b. Cu^{+} c. Ti^{2+} d. V^{3+}

2. Identify the element that forms the highest oxidation state.

a. Fe b. Mn c. Co d. Ni

3. Identify the ion that forms a compound with the lowest oxidizing power.

a. VO_3^{-} b. $Cr_2O_7^{2-}$ c. MnO_4^{2-} d. MnO_4^{-}

4. Which of the following ions are blue in solution.

a. Ni^{2+} b. Fe^{2+} c. Cr^{3+} d. Cu^{2+}

5.Formation of colour in transition metals is as a result of

a. having many oxidation states

b. Ligand exchange.

c. Having a partially filled d-orbital that allows absorbs and then emits radiations in the visible region of the spectrum.

d. change in coordination number.

6. Which of the following is a bidentate ligand?

a. NH_3 b. Cl c. SO_4^{2-} d. $C_2O_4^{2-}$

7. One good example of ligand exchange is a solution of copper ii ions is treated concentrated hydrochloric acid and then followed by concentrated ammonia.

what color changes take place.

a. blue to yellow to dark blue b. pale blue to green to dark blue

c. blue to yellow to green d. green to yellow to blue.

8. Which of these properties is not very specific for transitional metals?

a. Variable oxidation states. b. Coloured compounds.

c. Formation of complexes. d. Formation of alloys.

9. Which of these ions will have the least paramagnetism character.

a. Fe b. Zn c. Co d.Mn

Structural questions.

1.a.Define

i. a transition element. ii. d-block element.

b. Explain the following.

i. Zinc is not a transition element. ii. Fe^{2+} is less stable than Fe^{3+}.

iii. Compounds of Cu^{+} are not coloured while those of Cu^{2+} are colored?

c. Briefly state and explain the properties of transition metals.

2. a. Define a complex.

b. Briefly explain why transition metals form complexes.

c. Determine the oxidation states and coordination number of the central metal ion.

Complex	Oxidation state	Coordination number
$Cu(NH_3)_4(OH)_2$		
$[Cr(NH_3)_5Cl]Cl_2$		
$[Co(CN)_6]^{3-}$		
$[Ag(CN)_2]^{-}$		

3.a. Complete the following table.

Complex	Structure of complex	Name of the structure of the complex	Name of the complex
$[Cu(NH_3)_2]^{+}$			
$[Cu(NH_2CH_2CH_2NH_2)_2]^{2+}$			
$[Co(NH_3)_4Cl_2]^{+}$			

b.i. Which type of isomers are found in $[Co(NH_3)_4Cl_2]^{+}$

ii. show the different structures of the above isomers.

4. Explain the following trends in across the 1st transitional series from Sc to Zn.

a. atomic radius. b. Ionisation energy.

5. a. Define a ligand.

b. Explain why ligand is supposed to a lewis base?

c. An hydrous cobolt (ii) chloride is a lewis acid.

i. Explain the meaning of lewis acid?

ii. Give the formula, shape and color of the complex formed when anhydrous cobolt ii chloride is treated separately with water and concentrated hydrochloric acid.

iii. Give the reason for the difference in the shape.

iv. Give the reason for the difference in the color.

6. One of the applications of complexes is cis-platin $[Pt(NH_3)_2Cl_2]$ used in the treatment of some types of cancer.

a. Give the structure and the full name of Cis-platin.

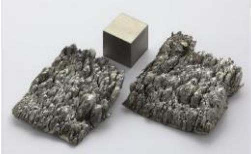
b. What name is given to the structure above.

c. Give the coordination number of the complex.

d. Identify any other two biological applications of complexes

1.2.0.Scandium.

1. 2.1. Introduction.



Sc-silverly white

^{21}Sc- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^1 4S^2$.

Sc has a hexagonal structure and was discovered by Lars Fredrik Nilson in 1879.

(a) Properties. Sc is a soft slivery white metal and slightly yellow when oxidized by air.

(b) Occurence.

Sc is not rare in the earth's crust but the ores of scandium are rare, some of these include:

(i) Thortveitite: $(SC,Y)_2 (Si_2O_7)$

(ii) Kolbeckite: $ScPO_4.2H_2O$

1.2.2. Chemical reactions of Scandium.

(a) Reactions with oxygen.(air)

Sc ignite in air with bright yellow flame to form scandium (iii) oxide.

$4Sc_{(s)} + 3O_{2(g)} \longrightarrow 2Sc_2O_{3(s)}$

(b) Reactions with water.

Sc dissolves in water when finely divided or heated.

$2Sc_{(s)} + 6H_2O_{(g)} \longrightarrow 2Sc(OH)_{3(aq)} + 3H_{2(g)}$

(c) Reactions with acids.

Scandium dissolves readily dilute HCl.

$2Sc_{(s)} + 6HCl_{(aq)} \longrightarrow 2ScCl_{3(s)} + 3H_{2(s)}$

(d) Reactions with halogens.

Sc is very reactive towards halogens to form trihalides.

$2Sc_{(s)} + 3Cl_{2(g)} \xrightarrow{heat} 2ScCl_{3(s)}$

1.2.3. Compounds of Scandium.

Scandium shows compounds in oxidation state of +3

$^{18}Sc^{3+}$- $1S^2 2S^2 2P^6 3S^2 3P^6$

This is the only stable oxidation state of Scandium.

Solutions of Sc^{3+} compounds appear colorless; $[Sc(H_2O)_6]^{3+}$.

(i) Scandium (iii) oxide:

Scandium (iii) oxide is amphoteric oxide.i.e. has both basic and acidic properties.

Scandium (iii) oxide is insoluble in water.

In acids: $Sc_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Sc^{3+}_{(aq)} + 3H_2O_{(l)}$

In bases: $Sc_2O_{3(s)} + 6OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2[Sc(OH)_6]^{3-}_{(aq)}$

(ii) Scandium (iii) hydroxide:

Scandium (iii) hydroxide is an **amphoteric** substance.

With bases: $Sc(OH)_{3(s)} + 3OH^-_{(aq)} \longrightarrow [Sc(OH)_6]^{3-}_{(aq)}$

With acids: $Sc(OH)_{3(s)} + 3H^+_{(aq)} \longrightarrow Sc^{3+}_{(aq)} + 3H_2O_{(l)}$

(iii) Scandium (iii) halides:

The halides of scandium halides include:

Halide	Bond
ScF_3	Ionic bond
$ScCl_3$, $ScBr_3$, ScI_3	covalent

ScF_3 is insoluble in water while other halides are soluble in water.
Like for $AlCl_3$, solutions of Sc^{3+} are acidic**.**

1.2.4. Uses of Scandium.

Sc	Making alloys e.g. Sc-Al alloys used in making Russian MIG fighters planes, bicycle frames base ball bats.

Exercise.1b.

Multiple choice questions.

1. Sc is a transition metal but shows non-transition properties, like showing one oxidation state. Identify the oxidation state.

a. +1 b. +2 c. +3 d. +4

2. Which of the halides is ionic.

a. ScF_3 b. $ScBr_3$ c. ScI_3 d. $ScCl_3$

3. Which group (i) one element has the same flame color as scadium when burnt in oxygen.

a. K b. Na c. Cs d. Rb.

Structural questions.

1. Explain why

a. solutions of Sc^{3+} are acidic.

b. Sc^{3+} compounds show non transitional properties.

c. Scandium (iii) oxide is amphoteric oxide.

2. $[ScF_6]^{3-}$

Given the above complex ion

a. Draw the structure of the complex ion.

b. What is the name of the complex ion.

c. Give the name of the structure of the complex ion.

d. Suggest the co-ordination number in the complex ion.


Ti grey -white

1.3.0. Titanium.

1. 3.1. Introduction.

${}^{22}Ti$- $1S^22S^22P^63S^23P^63d^24S^2$.

Sc has a hexagonal structure and was discovered by William Gregor in 1791.

(a) Properties.-Titanium is a silvery grey-white metallic.

(b) Occurence.

Titanium exists naturally in (ores of Ti)

(i) Rutile, Titanium (IV) oxide, TiO_2.

(ii) ilmenite, $FeTiO_3$ ($FeO.TiO_2$)

(c) Manufacture.

Pure titanium is obtained industrially from the rutile ore,TiO_2

The ore is first converted to titanium (IV) chloride.

$TiO_{2(s)} + 2C_{(s)} + 2Cl_{2(g)} \rightarrow TiCl_{4(g)} + 2CO_{(g)}$

The oxide is the reduced by the Kroll process using Mg.

During this process titanium (IV) chloride and magnesium are heated.

$TiCl_{4(g)} + 2Mg_{(l)} \longrightarrow Ti_{(s)} + 2MgCl_{2(l)}$

1.3.2. Chemical reactions of Titanium.

(a) Reactions with oxygen.(air)

It reacts with oxygen on heating to give titanium (iv) oxide.

$Ti_{(s)} + O_{2(g)} \longrightarrow TiO_{2(s)}$.

(b) Reactions with acids.

Titanium reacts with conc. HCl to give titanium (iii) chloride.

$Ti_{(s)} + 6HCl_{(aq)} \longrightarrow 2TiCl_{3(s)} + 3H_{2(g)}$

Titanium reacts with conc. H_2SO_4 forming titanium (III) sulphate and sulphur dioxide.

$2Ti_{(s)} + 6H_2SO_{4(aq)} \longrightarrow Ti_2(SO_4)_{3(s)} + 6H_2O_{(l)} + 3SO_{2(g)}$

(c) Reactions with halogens.

On passing a current of chlorine over heated titanium, titanium (iv) chloride is formed.

$Ti_{(s)} + 2Cl_{2(g)} \xrightarrow{heat} TiCl_{4(l)}$

1.3.3. Compounds of Titanium.

Chromium shows compounds in its principal oxidation states. E.g +2, +3, +4.

(a) Compounds in the +2 oxidation state.

${}^{20}Ti^{2+}$- $1S^22S^22P^63S^23P^63d^2$Titanium (ii) chloride.

It is obtained by heating titanium (iv) chloride with Ti.

$TiCl_{4(s)} + Ti_{(s)} \longrightarrow 2TiCl_{2(s)}$

(b) Compounds in the +3 oxidation state.

${}^{19}Ti^{3+}$- $1S^22S^22P^63S^23P^63d^1$

Solutions of Ti^{3+} compounds appear violet; $[Ti(H_2O)_6]^{3+}$.

The +3 oxidation state is unstable and is easily oxidized to + 4 oxidation state.


$TiCl_3$ in solution

(i) Titanium (iii) chloride.

It is obtained by heating of titanium reacts with conc. HCl

$Ti_{(s)} + 6HCl_{(aq)} \longrightarrow 2TiCl_{3(aq)} + 3H_{2(g)}$

$TiCl_3$ is ionic.

(c) Compounds in the +4 oxidation state.

$^{18}Ti^{4+}$- $1S^2 2S^2 P^6 3S^2 3P^6$.

This is the most stable oxidation state of Ti.

(i) Titanium (iv) oxide.

It reacts with oxygen on heating to give titanium (iv) oxide.

$Ti_{(s)} + O_{2(g)} \longrightarrow TiO_{2(s)}$

(ii) Titanium (iv) chloride.

It is obtained by heating of titanium with chlorine.

Titanium (iv) oxide

$Ti_{(s)} + 2Cl_{2(g)} \xrightarrow{heat} TiCl_{4(l)}$

$TiCl_4$ is liquid at room temperature proving its covalent character due to a high polarizing power of Ti^{4+}.

$TiCl_4$ hydrolyses vigorously in water giving clouds of titanium (iv) oxide and HCl.

$TiCl_{4(l)} + 2H_2O_{(l)} \rightarrow TiO_{2(g)} + 4HCl_{(g)}$

1.3.4. Uses of titanium and its compounds.

Ti and its alloys (Ti-steel alloy)	Wheel chairs, clutches, making surgical instruments,spectacle frames making body inmplants e.g joint replacement,teeth jewellery(when alloyed with gold) , watches, catalyst-$TiCl_{3/}Al_2(C_2H_5)_6$- in polymerisation fireframes, body of laptops(apple), utensils, cookwares, tennis rockets, golf clubs, cricket stick, hockey sticks, bicycle frames, manufacture of automobile, Making pipes, heat exchangers, tanks, valves used in petrochemical industries.

Ti plates and screws used for repair of fracture.

Exercise.1c.

Multiple choice questions.

1. Identify the most stable oxidation state of Titanium.

a. +2 b. +3 c. +4 d. +5

2. The process of manufacture if titanium is called.

a. Kroll process. b. Haber process. c. Ostwalds process d. Contact process

3. Which of the following compounds shows the highest covalent character.

a. $TiCl_2$ b. $TiCl_3$ c. $TiCl_4$ d. Ti F_3

4. Titanium forms compounds in many oxidation states, in which of the following oxidation states does Ti likely to form compounds showing non-transition properties.

a. +2 b. +3 c. +4 d. +5

5. What is the colour of Ti^{3+} in solution.

a. blue b. violet c. green d. pink

***Structural questions*.**

1. Explain why

a. $TiCl_3$is ionic compound while $TiCl_4$ are covalent.

b. $Ti^{3+}$is easily oxidized to Ti^{4+} c. $TiCl_4$ fumes in moisted air.

d. Like Al, Ti does not react with water. e. Ti^{4+}compounds are colourless.

2.a. Write down the electron configuration of Ti.

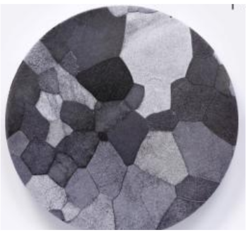
b. With examples give two properties in which Ti is as transition metals.

c. Write down a balanced equation of oxidation Ti using concentrated sulphuric acid.

d. Give two practical applications of titanium metal.

1.4.0. Vanadium.

1. 4.1. Introduction.


V- blue silver-grey

^{23}V- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^3 4S^2$.

V has a body-centred cubic structure and was discovered by Andrs Manuel del Ro in 1801.

(a) Properties.-Vanadium is a blue –silver- grey- metallic.

(b) Occurence.

It is the 20th most abundant element in the earth crust.

Vanadium compounds occur in about 65 minerals but some important ores include(i) patronite, VS_4.

(ii) Vanadinite, $Pb_5(VO_4)_3Cl$

Much of the world's vanadium is obtained from vanadium containing magnetite.

1.4.2. Chemical reactions of vanadium.

(a) Reactions with oxygen.(air)

It reacts with oxygen on heating to give vanadium (v) oxide.

$$4V_{(s)} + 5O_{2(g)} \longrightarrow 2V_2O_{5(s)} \quad .$$

(b) Reactions with halogens.

On heating chlorine with vanadium, vanadium (iv) chloride is formed.

$$V_{(s)} + 2Cl_{2(g)} \xrightarrow{heat} VCl_{4(s)}$$

1.4.3. Compounds of vanadium.

Vanadium shows compounds in its principal oxidation states. E.g +2, +3, +4, +5.

These different oxidation states can shown by shaking a solution of ammonium vanadate with dilute sulphuric acid and zinc amalgam.

The color change from pale yellow to blue, green and finally violet.

Oxidation state	+5	+4	+3	+2
Ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Color	Pale yellow	Blue	Green	Violet

Note: Because of high charge and small ionic radius, of vanadium +5 and +4 exist in the form VO_2^+ and VO^{2+} respectively . They impact a great polarizing effect on water molecules.

(a) Compounds in the +2 oxidation state.

$^{21}V^{2+}$- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^3$.

Hydrated vanadium (II) , $[V(H_2O)_6]^{2+}$ - It is violet.

Vanadium (II) oxide. VO

it is black and basic solid.

(b) Compounds in the +3 oxidation state.

$^{20}V^{3+}$- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^2$

In solution, it exist as $[V(H_2O)_6]^{3+}$ - It is green.

Vanadium (III) oxide. V_2O_3

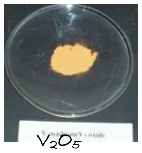
It is black and basic.

(c) Compounds in the +5 oxidation state.

$^{18}V^{5+}$- $1S^2 2S^2 P^6 3S^2 3P^6$

Vanadium (V) oxide. V_2O_5

It is orange and amphoteric.



V_2O_5

1.4.4. Uses of vanadium and its compounds.

V	Making of alloys (steel alloys)	making bicycles,gears,axles,crankshafts.
V_2O_5	Catalysts in manufacture of sulphuric acid. Used in ceramics	

Exercise.1d.

Multiple choice questions.

1 .V_2O_5 is a catalyst for the manufacture of

a. nitric acid b. sulphuric acid c. ammonia d. oxygen.

2. Which of the following ions of vanadium are green in solution.

a. V^{2+} b. V^{3+} c. VO^{2+} d. VO_2^{2+}

***Structural questions*.**

1. Explain why

a. vanadium is a transitional metal.

b. Vanadium in the oxidation state of +4 and +5 exists as $VO^{2+}VO_2^{+}$ in solution.

2. a. Write down the electron configuration of V^{2+}, V^{3+}, V^{4+} (23)

b. With examples, give two properties in which V acts as a transition metal.

c. Give two uses of vanadium.

3. $[V(H_2O)_6]^{3+}$

Given the above complex ion

a. Draw the structure of the complex ion.

b. What is the name of the complex ion.

c. Give the name of the structure of the complex ion.

d. Suggest the co-ordination number in the complex ion.

1.5.0. Chromium.

1. 5.1. Introduction.

Cr-silvery white

^{24}Cr- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^5 4S^1$.

Cr has a body-centred cubic structure and was discovered by Louis Nicolas Vauquelin 1797.

(a) Properties.-Chromium is a lustrous, brittle, hard metal.

-Chromium is a bright shinny metal which forms a transparent protective oxide layer on its surface.

(b) Occurence.

It is the 22nd most abundant element in the earth crust.

Chromium exists naturally in (ores of chromium)

(i) Chromite-$FeCr_2O_4$-($FeO.Cr_2O_3$)(most urbadant)

(ii) Lead chromate $PbCrO_4$

(iii) Chromium(iii)oxide Cr_2O_3

(c) Manufacture.

Pure chromium is obtained from the chromite ore.($FeCr_2O_4$).

The ore is first concentrated and converted to chromium (III) oxide.

The oxide is the reduced by the thermit process.

During this process a powdered mixture of chromium (III) oxide and aluminium are heated.

$Cr_2O_{3(s)} + 2Al_{(s)} \longrightarrow 2Cr_{(s)} + Al_2O_{3(s)}$.

1.5.2. Chemical reactions of chromium.

(a) Reactions with oxygen.(air)

It reacts with oxygen on heating to give a green solid.

$4Cr_{(s)} + 3O_{2(g)} \longrightarrow Cr_2O_{3(s)}$

NB. Chromium is unstable in oxygen; it immediately produces a thin protective oxide layer which prevents further reaction.

(b) Reactions with water.

It reacts with steam at red hot to form chromium (iii) oxide.

$2Cr_{(s)} + 3H_2O_{(g)} \longrightarrow Cr_2O_{3(s)} + 3H_{2(g)}$

(c) Reactions with acids.

Chromium reacts with dilute HCl and H_2SO_4 to give blue solutions of $CrCl_2$ and $CrSO_4$.

$Cr_{(s)} + 2HCl_{(aq)} \longrightarrow CrCl_{2(s)} + H_{2(g)}$

$Cr_{(s)} + H_2SO_{4(aq)} \longrightarrow CrSO_{4(s)} + H_{2(g)}$

(d) Reaction with sodium hydroxide.

Chromium reacts slowly with sodium hydroxide to give sodium chromite and hydrogen gas.

$Cr_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(l)} \longrightarrow Na_2Cr(OH)_{4(aq)} + H_{2(g)}$

(e) Reactions with halogens.

On passing a current of chlorine over heated chromium, chromium (iii) chloride is formed.

$2Cr_{(s)} + 3Cl_{2(g)} \xrightarrow{heat} 2CrCl_{3(s)}$

1.5.3. Compounds of chromium.

Chromium shows compounds in its principal oxidation states. E.g +2, +3, +6.

(a) Compounds in the +2 oxidation state.

(i) Chromium (ii) hydroxide.

It appears as a yellow precipitate obtained by a reaction between sodium hydroxide and a solution of Cr^{2+} ions.

$Cr^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cr(OH)_{2(s)}$

(ii) Chromium (ii) chloride.

It appears as a white solid obtained by reaction of dilute hydrochloric acid with chromium metal as shown above.

(b) Compounds in the +3 oxidation state.

$^{21}Cr^{3+}$- $1S^22S^22P^63S^23P^63d^3$

This is the most stable oxidation state of chromium.

(i) Chromium (iii) oxide: It is a green solid prepared by a reaction between oxygen and chromium or by heating chromium (iii) hydroxide.

$2Cr(OH)_{3(s)} \xrightarrow{heat} Cr_2O_{3(s)} + 3H_2O_{(l)}$

(ii) Chromium (iii) chloride.

It is a reddish violet solid obtained by heating of chromium with chlorine.

$2Cr_{(s)} + 3Cl_{2(g)} \longrightarrow 2CrCl_{3(s)}$.

AnhydrousCrCl3

Note:

(i) like $AlCl_3$, $CrCl_3$is acidic in solution. $CrCl_3 + 3H_2O_{(l)} \longrightarrow Cr(OH)_3 + 3HCl_{(aq)}$

(ii)Hydrated chromium (iii) chloride ($CrCl_3.6H_2O$) undergoes hydration isomerism .i.e .

$[Cr(H_2O)_6]Cl_3$ which is violet.

$[CrCl(H_2O)_5]Cl_2.H_2O$ which is pale green

$CrCl_2(H_2O)_4]Cl.2H_2O$ which is dark green

(iii) Chromium (iii) hydroxide.

It appears as a green gelatinous (solid) precipitate obtained by a reaction between sodium hydroxide (or ammonia solution) and a solution of Cr^{3+} ions.

$Cr^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow Cr(OH)_{3(s)}$ Like $Al(OH)_3$, $Cr(OH)_3$ is amphoteric. I.e it reacts with both acids and bases.

$Cr(OH)_{3(s)} + 3H^+_{(aq)} \longrightarrow Cr^{3+}_{(aq)} + 3H_2O_{(l)}$

$Cr(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow Cr(OH)_4{}^-_{(aq)}$NB. Solutions of Cr^{3+} compounds appear green; $[Cr(H_2O)_6]^{3+}$.

Like solutions of Al^{3+}, the aqueous solutions of Cr^{3+} are also acidic due to high polarizing power (high charge density).

$[Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Cr(H_2O)_3 3OH]_{(aq)} + 3H^+_{(aq)}$

(c) Compounds in the +6 oxidation state.

$^{18}Cr^{6+}$- $1S^22S^2P^63S^23P^6$

(i) Chromium (vi) oxide. It is prepared as a dark (red) precipitate when a concentrated solution of potassium dichromate is acidified with conc. H_2SO_4.

$Cr_2\,O_7{}^{2-}_{(aq)} + 2H^+_{(aq)} \longrightarrow 2CrO_{3(s)} + H_2O_{(l)}$

(ii) Chromates. ($CrO_4{}^{2-}$). Eg. Potassium chromate.

Chromates are yellow in colour and can be obtained when dichromates are reacted with alkali.


Na_2CrO_4

$Cr_2\,O_7{}^{2-}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow 2CrO_4{}^{2-}{}_{(aq)} + H_2O_{(l)}$
In the presence of an acid chromates are converted to orange solution of dichromate.

$2CrO_4{}^{2-}{}_{(aq)} + 2H^+{}_{aq)} \longrightarrow 2Cr_2O_7{}^{2-}{}_{(aq)} + H_2O_{(l)}$
Yelloworange**NB.** This usually confirms the presence of chromate solutions.
(iii) Dichromates. ($Cr_2O_7{}^{2-}$) Dichromates are orange in colour and can be obtained when chromates are reacted with acids.

$2CrO_4{}^{2-}{}_{(aq)} + 2H^+{}_{aq)} \longrightarrow Cr_2O_7{}^{2-}{}_{(aq)} + H_2O_{(l)}$

In the presence of a base dichromates are converted to yellow solution of dichromate.

$Cr_2\,O_7{}^{2-}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow 2CrO_4{}^{2-}{}_{(aq)} + H_2O_{(l)}$
orangeYellowPotassium dichromate.
This is an orange solid obtained by reaction between concentrated solutions of sodium dichromate and potassium chloride.

$2KCl_{(aq)} + Na_2Cr_2O_{7(aq)} \longrightarrow K_2Cr_2O_{7(aq)} + NaCl_{(aq)}$ -
It is a strong oxidizing agent in acidic media.

$Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e \longrightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$
Since it is a less powerful oxidizing agent than potassium permanganate. Its solution can be acidified using hydrochloric acid.

$Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6Fe^{3+}{}_{(aq)} \longrightarrow 2Cr^{3+}{}_{(aq)} + 6Fe^{3+}{}_{(aq)} + 7H_2O_{(l)}$

$Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 3Sn^{2+}{}_{(aq)} \longrightarrow 2Cr^{3+}{}_{(aq)} + 3Sn^{4+}{}_{(aq)} + 7H_2O_{(l)}$

$Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \longrightarrow 3I_{2(aq)} + 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$

-When heated potassium dichromate decomposes on heating to produce potassium chromate, chromium iii oxide and oxygen gas.

$K_2Cr_2O_{7(s)} \xrightarrow{heat} 3K_2Cr_2O_{4(s)} + 2Cr_2O_{3(s)} + 3O_{2(g)}$
1.5.4. Uses of chromium and its compounds.

Cr	Used in the alloys such as Stainless steel-used in the making of untensils. Used as a protective and decorative surface on electroplated steel. Its salts color glass an emerald green. Used to produce synthetic rubies. Used as a catalyst, in dyeing and in the tanning of leather.
CrO_2	Used to manufacture magnetic tape.
$K_2Cr_2O_7$	Used as powerful oxidants and volumetic analysis.
In the body, chromium is involved in the metabolism of glucose and is vital in the breakdown of cholesterol, fats, and proteins.	


Rubies

1.5.5. Qualitative analysis: Cr^{3+}.

Reagent	Observation	Equation
a. NaOH	A green gelatinous precipitate soluble in excess alkali to give a green solution.	$Cr^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Cr(OH)_{3(s)}$ $Cr(OH)_{3(s)} + 3OH^{-}_{(aq)} \rightleftharpoons [Cr(OH)_6]^{3-}_{(aq)}$
b.NH_3	A green gelatenous precipitate slightly dissolves in excess to form a pink or violet solution.	$Cr^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Cr(OH)_{3(s)}$ $Cr(OH)_{3(s)} + 6NH_{3(aq)} \rightleftharpoons [Cr(NH_3)_6]^{3+}_{(aq)} + 3OH^{-}_{(aq)}$
C. Na_2CO_3	A green precipitate of chromium hydroxide and evolution of colourless gas (carbondioxide gas). $2Cr^{3+}_{(aq)} + CO_3{}^{2-}_{(aq)} + 3H_2O_{(l)} \rightarrow Cr(OH)_{3(s)} + 3CO_{2(g)}$ NB: The above reaction shows that chromium (iii) carbonate cannot be obtained. **Reason** : This is because chromium salts e.g $CrCl_3$ are rapidly hydrolysed due to high charge density of Cr^{3+} to release hydrogen ions and chromium (iii) hydroxide. $Cr^{3+}_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Cr(OH)_{3(s)} + 3H^{+}_{(aq)}$ The hydrogen ions now combine with the carbonate to produce carbondioxide gas. $H^{+}_{(aq)} + CO_3{}^{2-}_{(aq)} \longrightarrow H_2O_{(l)} + CO_{2(g)}$ NB: Fe^{3+},Cr^{3+} and Al^{3+} all react with sodium carbonate giving carbondioxide gas. This also explains why the carbonates of Fe^{3+},Cr^{3+} and Al^{3+} cannot be formed.	
(iv) H_2O_2	Add dilute sodium hydroxide solution followed by 2-3 drops of 10% hydrogen peroxide. Observation: A yellow solution of chromate $Cr^{3+}_{(aq)} + 10OH^{-}_{(aq)} + 3H_2O_{2(aq)} \longrightarrow 2CrO_4{}^{2-}_{(aq)} + 8H_2O_{(l)}$ Note: 1. Addition of barium nitrate or barium chloride to the above solution produces a yellow precipitate of barium chromate. $Ba^{2+}_{(aq)} + CrO_4{}^{2-}_{(aq)} \longrightarrow BaCrO_{4(s)}$ 2. Addition of lead nitrate or lead ethanoate to the above solution produces a yellow precipitate of lead chromate. $Pb^{2+}_{(aq)} + CrO_4{}^{2-}_{(aq)} \longrightarrow PbCrO_{4(s)}$ 3. Addition of silver nitrate to the above solution produces a red precipitate of barium chromate. $2Ag^{+}_{(aq)} + CrO_4{}^{2-}_{(aq)} \longrightarrow Ag_2CrO_{4(s)}$ (b) Test of $CrO_4{}^{2-}$ (i) Dilute acids. (a few drops). Observations: The yellow solution turns orange. $2CrO_4{}^{2-}_{(aq)} + 2H^{+}_{aq)} \longrightarrow Cr_2O_7{}^{2-}_{(aq)} + H_2O_{(l)}$ (ii) Concentrated sulphuric acid. Observations: Red precipitate (solute or solid) of CrO_3. $CrO_4{}^{2-}_{(aq)} + 2H^{+}_{aq)} \longrightarrow CrO_{3(aq)} + H_2O_{(l)}$ (iii) Barium nitrate or barium chloride solutions. Observations: Yellow precipitate. $Ba^{2+}_{(aq)} + CrO_4{}^{2-}_{(aq)} \longrightarrow BaCrO_{4(s)}$ (iv) Lead nitrate or lead ethanoate solution. Observations: Yellow precipitate. $Pb^{2+}_{(aq)} + CrO_4{}^{2-}_{(aq)} \longrightarrow PbCrO_{4(s)}$ (v) Silver nitrate solution. Observations: red precipitate.	

	$2Ag^{+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow Ag_2CrO_{4(s)}$ (c) Test of $Cr_2O_7^{2-}$ (i) Dilute sodium hydroxide. (a few drops). Observations: The orange solution turns yellow. $Cr_2O_7^{2-}{}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow CrO_4^{2-}{}_{(aq)} + H_2O_{(l)}$

Exercise.1e.

Multiple choice questions.

1. Name the process of extraction of chromium

a. Kroll process b. Thermit process c. Contact process d. Ostwald's process

2. Which ore is used in extraction of Cr.

a.Heamatite b. bauxite ore c. magnetite d. Chromite

3. What is the most stable oxidation state of chromium.

a. +2 b. +3 c. +4 d. +6

4. Identify the colour of the solution when potassium chromate is mixed with sulphuric acid.

a. yellow b. green c. blue d. orange

5. 0.15g of a sample of iron wire was dissolved indilute sulphuric acid and this solution required $20cm^3$ with 0.02M potassium dichromate during titration.

Calculate the percentage purity of iron in the wire.

a. 89.6% b.74.7% c. 50% d.81.1%

6. $25cm^3$ of portion of iron (II) chloride solution required, after acidification, $15cm^3$ of 0.01M solution of potassium dichromate (VI). Calculate the concentration of the solution.

a. 0.01M b. 0.036M c. 0.024M d. 0.03M

7. 3.34g of a sulphate, $FeSO_4\,nH_2O$ were dissolved in $250cm^3$ of aqueous solution. $25cm^3$ of the above solution of required $20cm^3$ of 0.01M acidified potassium dichromate (VI)in titration.

a.7 b. 8 c.14 d.15

8. State what is observed when sodium hydroxide reacts with Cr^{3+} solution.

a. White precipitate. b. green precipitate. c. brown precipitate d. yellow precipitate.

9. State what is observed when potassium chromate reacts with silver nitrate.

a. White precipitate. b. green precipitate. c. red precipitate d. yellow precipitate

10. Which of the following ions will form a carbonate.

a. Fe^{3+} b. Cr^{3+} c. Al^{3+} d. Fe^{2+}

***Structural questions*.**

1.a. State three properties of chromium as a transition metal.

b. A solution of potassium dichromate (VI) was added to acidified of iron (II) sulphate.

i. State what was observed.

ii. Write the ionic equation for the reaction that took place.

c .i. Write the structural formulae of the isomers of chromium iii chloride, $CrCl_3.6H_2O$.

ii. identify the structure that forms geometrical isomers and show the optical isomers.

ii.i State one of way distinguishing the isomers.

2.a .i. Write down the electron configuration of Cr.

ii. Give all the oxidation states of Cr giving examples of compounds in which chromium has those states.

iii. Explain why the solutions of Cr^{3+} are acidic.

3 .a. State the oxidation states of chromium in

i. Potassium chromate.

ii. Potassium dichromate.

b. Acidified potassium dichromate was reacted with potassium iodide.

i. State what was observed

ii. Write the half equations for reaction.

c. Potassium chromate was added to aqueous lead ii nitrate

i. State what was observed.

ii. Write the equation for reaction.

4. Sodium hydroxide was added drop wise to solution containing Cr^{3+} followed by hydrogen peroxide.

a. State what was first observed before adding hydrogen peroxide and write the equation for reaction.

b. What was finally observed?

c. What will be observed if a few drops of dilute sulphuric acid was added to the above solution.

5.a. Chromium (iii) sulphate solution was dissolved in water and then a few drops of sodium carbonate was added.

i. State what was observed.

ii. Give a reason for your and write the equations for reaction.

b. Potassium chromate was dissolved in water.

i. Draw and name the shape of chromate ion.

ii. To the solution a few drops of sulphuric acid was added followed by sodium hydroxide

State what was observed and write the equations for reaction.

6. A solution of chromate (CrO_4^{2-}) was prepared as follows. Sodium hydroxide solution was added to aqueous Cr^{3+} to give a grey green precipitate. Excess sodium hydroxide was added to dissolve the green precipitate to give a green solution. Aqueous hydrogen peroxide was added and the mixture was warmed to give a yellow solution containing CrO_4^{2-}.

a. Calculate the oxidation number of Cr in CrO_4^{2-}.

b. Write balanced ionic equation to show:

i. the reaction Cr^{3+} to give a grey green precipitate.

ii. the reaction of the grey green precipitate to form a green solution.

c. What is the role the hydrogen peroxide in the above preparation?

d. When an acid is added to CrO_4^{2-}it changes to $Cr_2O_7^{2-}$.

i. State the color of aqueous $Cr_2O_7^{2-}$.

ii. Write an equation for reaction of CrO_4^{2-} with H^+ to form $Cr_2O_7^{2-}$. Is this a redox reaction ?

Give a reason for your answer.

e. Acidified $Cr_2O_7^{2-}$ is commonly used as an oxidizing agent.

The relevant half-equation is

$Cr_2O_7^{2-} + 14H^+_{(aq)} + 6e \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

Write a balanced equation for the reaction between acidified $Cr_2O_7^{2-}$and Fe^{2+}.

f) Chromium is used in the manufacture of steel alloys one such as stainless steel.

i. What is an alloy?

ii. Give one major property of stainless steel.

g. Give the electronic configuration of Chromium(Cr) (Atomic number of Cr: 24)

7.When a conc. NH_3 is added dropwise to a solution of chromium (III) sulphate, a green precipitate **A** forms. **A** dissolves slowly in excess NH_3 to give a purple solution **B**. **A** also dissolves in NaOH to give a green solution, **C**, Addition of hydrogen peroxide to C gives a yellow solution, **D**. when is treated with dil. H_2SO_4, it gives an orange solution E. Identify **A, B ,C, D** and **E**

8. $(NH_4)_2SO_4Fe_2(SO_4)_3.24H_2O$, 5g is dissolved in 250cm^3 of distilled water. 100cm^3 of the solution was boiled with Zn powder until the solution is green. 25cm^3 of this solution was acidified 25cm^3 of 1M H_2SO_4 acid. This solution was titrated with 0.02M potassium dichromate required 24.5cm^3.

a. Write a balanced redox equation between Fe^{2+} and $Cr_2O_7^{2-}$

b. Calculate number

i. moles of potassium dichromate that reacted. ii. moles of Fe^{2+} ion in 25cm^3.

iii. moles of Fe^{2+} ion in 250cm^3. iv. mass Fe^{2+} in 250cm^3 (Fe =56) v. percentage purity of Fe.

c. What is the purpose of Zn.

1.6.0. Manganese.

1.6.1. Introduction


Mn

^{25}Mn- $1S^22S^22P^63S^23P^63d^54S^2$.

Mn has a body-centred cubic structure and was discovered by Torbern Olof Bergman 1770

(a) Properties.

Manganese is a silver metal.

(b) Occurrence.

Manganese is occurs freely in nature. e.g. found in nodules on the ocean floor. Manganese also exists naturally in pyrolusite and in rhodochrosite.


Gahn_Johan_Gottlieb was creditated for the first isolation Mn

(c) Manufacture.

The chief manganese ore is pyrolusite. MnO_2.

The ore is first converted to trimanganese (IV) oxide by heating it strongly.

$$3MnO_{2(s)} \longrightarrow Mn_3O_{4(s)} + O_{2(g)}$$

Pure manganese oxide is obtained from this ore by reduction with aluminium followed by distillation.

$$3Mn_3O_{4(s)} + 8Al_{(s)} \longrightarrow 4Al_2O_{3(s)} + 9Mn_{(s)}$$

1.6.2. Reactions of manganese.

(a) Reactions with oxygen.

It reacts with oxygen on heating to give trimanganese (IV) oxide.

$$3Mn_{(s)} + 2O_{2(g)} \xrightarrow{heat} Mn_3O_{4(s)}$$

(b) Reactions with water.

It does not react with steam or water at room temperature.

(c) Reactions with acids.

Manganese reacts with dilute HCl and H_2SO_4 to produce manganese (II) salts.

$$Mn_{(s)} + 2HCl_{(aq)} \longrightarrow MnCl_{2(s)} + H_{2(g)}$$

$$Mn_{(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_{4(s)} + H_{2(g)}$$

Nitric acid reacts to produce varying products.

(d) Reactions with halogens.

Manganese reacts with chlorine on heating.

$$Mn_{(s)} + Cl_{2(g)} \xrightarrow{heat} MnCl_{2(s)}$$

1.6.3. Compounds of manganese.

Manganese shows compounds in its principal oxidation states. E.g +2, +3,+4,+5 +6 and +7.

(a) Compounds in the +2 oxidation state.

$^{23}Mn^{2+}$- $1S^22S^22P^63S^23P^63d^5$.

This the most stable oxidation state of manganese.

(i) Manganese (ii) oxide.

It is prepared as a green solid by heating manganese (II) carbonate or manganese (ii) hydroxide.

$$MnCO_{3(s)} \xrightarrow{heat} MnO_{(s)} + CO_{2(g)} \ .$$

It is a strongly basic oxide. E.g.

$$MnO_{(s)} + 2H^+_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + H_2O_{(l)}$$

(ii) Manganese (II) hydroxide.

It is prepared as a white precipitate (solid) by addition of Mn^{2+} salts with sodium hydroxide or ammonia.

$Mn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Mn(OH)_{2(s)}$

(iii) Manganese (II) Carbonate.

It appears as a white precipitate by addition of Mn^{2+} salts with sodium carbonate.

$Mn^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow MnCO_{3(s)}$

(iv) Manganese (II) Chloride. It is appears as a pink solid and can be obtained when manganese reacts with HCl.

$Mn_{(s)} + 2HCl_{(aq)} \longrightarrow MnCl_{2(s)} + H_{2(s)}$

$MnCl_2$

NB. Manganese (II) salts appear as a pink in solution. $[Mn(H_2O)_6]^{2+}$

(b) Compounds in the +4 oxidation state. $^{21}Mn^{4+}$- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^3$.

Manganese (iv) oxide. MnO_2

It is a **black** solid formed by heating manganese (ii) nitrate.

$Mn(NO_3)_{2(s)} \xrightarrow{heat} MnO_{2(s)} + 2NO_{2(g)}$

Note:

(i) Manganese (iv) oxide is a strong oxidizing agent. I.e.

It is can be applied in preparation of chlorine gas when it oxidizes hot conc. HCl acid to chlorine.

$MnO_{2(s)} + 4HCl_{(aq)} \longrightarrow MnCl_{2(aq)} + Cl_{2(aq)} + 2H_2O_{(l)}$

(ii) Manganese (iv) oxide also acts as a catalyst in preparation of oxygen gas from hydrogen peroxide.

$2H_2O_{2(aq)} \xrightarrow{MnO_2} 2H_2O_{(l)} + O_{2(g)}$

(c) Compounds in the +6 oxidation state.

$^{19}Mn^{6+}$- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^1$

The most common are maganate(vi) compounds (**MnO_4^{2-}**) e.g potassium manganate(VI) and sodium manganate (VI).

Potassium manganate(VI).

It is a green solid prepared by fusing oxygen MnO_2 and NaOH in the presence of oxygen.

$2MnO_{2(s)} + 4KOH_{(aq)} + O_{2(g)} \longrightarrow 2K_2MnO_{4(l)} + 2H_2O_{(l)}$**Note**:

Potassium manganate(VI) undergoes a disproportionation reaction in the presence of:

$KMnO_4$ solution

(i) an acid: $3MnO_4^{2-}{}_{(aq)} + H^{+}_{(aq)} \longrightarrow 2MnO_4^{-}{}_{(aq)} + MnO_{2(s)} + 4H_2O_{(aq)}$

Observations:Greenpurple black

(ii)Water: $3K_2MnO_{4(aq)} + 2H_2O_{(l)} \longrightarrow 2KMnO_{4(aq)} + MnO_{2(s)} + 4KOH_{(aq)}$

Observations:Green purple black

(d) Compounds in the +7 oxidation state.

$^{18}Mn^{7+}$- $1S^2 2S^2 2P^6 3S^2 3P^6$

Potassium permanganate or potassium manganate (VII). $KMnO_4$.

It is a purple solid and can obtained by using a powerful oxidizing agent such as sodium bismuthate.

$2Mn^{2+}_{(aq)} + 5BiO_3^{-}{}_{(aq)}\ 14H^{+}_{(aq)} \longrightarrow 2MnO_4^{-}{}_{(aq)} + 5Bi^{3+}_{(aq)} + 7H_2O_{(l)}$

Potassium permanganate is a powerful oxidizing agent in acid media and commonly applied in volumetric analysis.

$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$

Note:

Since potassium permanganate is a very strong oxidizing agent it is not acidified using hydrochloric acid. This because it oxidizes HCl to Cl_2 gas.(applied in preparation of chlorine gas)

Examples in which acidified potassium permanganate acts as an oxidizing agent.

$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$

$2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5Sn^{2+}{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 5Sn^{4+}{}_{(aq)}$

$2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(aq)}$

$2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5I^-{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 5I_{2(aq)}$.

During volumetric analysis, acidified potassium permanganate acts as its own indicator when its decolourised.

1.6.4. Uses of Manganese and its compounds.

Mn	used in many alloys. (steel-helmet, duralumin- making beverage cans.) compounds of manganese are used in pigments for colouring ceramics and glass. Biologicaly it is important in bone formation, blood clotting, sex hormones, blood sugar regulation, brain and nerve fuction.
MnO_2	manufacture of dry cells, oxygen and chlorine.
$KMnO_4$	Used in volumetric analysis.

1.6.5. Qualitative analysis:

Reagents	Observation	Equation
(i)NaOH	A white precipitate insoluble in excess alkali and turns brown on standing then to black. The white ppt turns brown then to black due to oxidation by air.	$Mn^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Mn(OH)_{2(s)}$ $Mn(OH)_2$ to Mn_2O_3. XH_2O toMnO_2. XH_2O
(ii)NH_3	A white precipitate insoluble in excess ammonia and turns brown on standing.	$Mn^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Mn(OH)_{2(s)}$
(iii)Na_2CO_3	A white precipitate turns brown on standing.	$Mn^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow MnCO_{3(s)}$
(iv) Sodium bismuthate. ($NaBiO_3$) or lead (iv) oxide. To a solution of Mn^{2+} ions add a little conc. nitric acid followed by Sodium bismuthate or lead (iv) oxide and heat. Observation: Mn^{2+} are oxidized to a purple permanganate. $2Mn^{2+}{}_{(aq)} + 5BiO_3^-{}_{(aq)}\ 14H^+{}_{(aq)} \rightarrow 2MnO_4^-{}_{(aq)} + 5Bi^{3+}{}_{(aq)} + 7H_2O_{(l)}$ purple		

Exercise.1f.

Multiple choice questions.

1. Identify the chief ore of Mn.

a. Bauxite ore b. Sedirite c. pyrolusite d. Heamatite

2. Which of the following elements is used in the reduction during the manufacture Mn.

a. Al b. C c. Mg d. Ca

3. Which of the following acids is best used to acidify potassium permanganate.

a. HCl b. HNO_3 c. H_2SO_4 d. HBr

4. A sample of steel, 0.1646g was dissolved in dilute sulphuric acid and this solution required 27.4cm^3 with 0.02M potassium permanganate during titration.(Fe 56)

Calculate the percentage purity of iron in the wire.

a. 2% b.93.2% c. 50% d.1.7%

5. A sulphate 2.95g of $FeSO_4xH_2O$ were dissolved in 250cm^3 of aqueous solution. 25cm^3 of the above soluition of required 21.2cm^3 of 0.01M acidified potassium manganate (VII)in titration. (Fe 56)

a.7 b. 8 c.14 d.15

6.An iron tablet containing iron (ii) sulphate was analysed using 0.005M $KMnO_4$. The tablet mass o.65g was dissolved in 100cm^3 of dilute suphuric aicd. 10 cm^{3}of the solution required 6cm^3 of $KMnO_4$ to produce a faint pink solution. What is the percentage of theIron in the tablet?(Fe 56)

a. 12.9% b. 15.5% c. 14% d. 20%

7. In the determination of Fe^{2+} and Fe^{3+}salts in the mixture containing both. 25cm^3 of the solution required 15cm^3 of 0.02M acidified potassium permanganate for complete reaction.

After reduction of Fe^{3+} to Fe^{2+} using zinc powder , 25cm^3 of solution required 30cm^3 of 0.02M acidified potassium permanganate for complete reaction .

Determine the mole ratios of Fe^{3+}: Fe^{2+}.

a. 1:1 b. 1:2 c. 2:1 d. 3:1

8. State what is observed when sodium hydroxide reacts with Mn^{2+} solution.

a. dirty white precipitate. b. green precipitate. c. brown precipitate. d. yellow precipitate.

9. Mangenese (ii) chloride is dissolved in water. To a solution of Mn^{2+} ions add a little conc. nitric acid followed by Sodium bismuthate and heat. State the color of the solution which is observed after heating.

a. Pink solution. b. Purple solution. c. yellow solution. d. Green solution.

***Structural questions*.**

1.a.i. Write down the electron configuration of Mn

ii. Give all the oxidation states of manganese giving examples of compounds in which it shows these states.

b. Explain why Mn^{2+} compounds are more stable than those of Mn^{3+}.

2. Potassium permanganate is used as standardising agent in volumetric analysis.

a. Explain why

i. titrations of potassium permanganate do not need indictors.

ii. potassium permanganate is not acidified using hydrochloric acid.

b. Write a balanced equation between

i. acidified potassium permanganate and sodium oxalate.

ii. between acidified $Mn^{2+}$and sodium bismuthate. (state what is observed).

3. A solid X was dissolved in water to give a slightly pink solution. A few drops of sodium hydroxide was added to give a white precipitate which quicky turns to brown the black. when the same pink solution was treated with conc nitric acid followed by sodium bismuthate a purple solution is observed.

a. Identify the cation in X.

b. Write down an ionic equation between the cation and sodium hydroxide.

c. Give the chemical species responsible for then to brown, black and purple colours.

4. In an experiment to find the value of n in $(NH_4)_2SO_4.FeSO_4.nH_2O$, 16.98g of the salt were dissolved in a mixture of the water and dilute sulphuric acid. the solution was made up to 250cm^3 in a volumetric flask. 25.0cm^3 of this

solution was titrated with potassium manganate (VII) of concentration 0.030 mol dm^{-3} . 22.5cm^3 of this solution was required. a.
Calculate the number of moles of potassium permanganate that reacted.
b. Calculate the number of moles of Fe^{2+} that reacted in 25cm^3.
c. Calculate the number of moles of Fe^{2+} that reacted in 250cm^3.
d. Calculate the molar mass of the salt.
e. Find the value of n
f. Explain why Fe^{2+} is less stable than Fe^{3+}
g. What is the color change during titration.
5. An iron iron (ii) salt 10g, was dissolved in water and was made up 200cm^3 . 20 $cm^3$of the solution was acidified with dilH_2SO_4 required 25cm^3 of 0.03M $KMnO_4$.
a. Calculate the number of moles of potassium permanganate that reacted.
b. Calculate the number of moles of Fe^{2+} that reacted in 25cm^3.
c. Calculate the number of moles of Fe^{2+} that reacted in 200cm^3.
d. Calculate the percentage by mass of Fe in the impure salt.

1.7.0. Iron. Fe. (Ferrum – latin name)

1.7.1. Introduction

Fe

^{26}Fe- $1S^22S^22P^63S^2\ 3P^63d^64S^2$.

Fe has a body-centred cubic structure and was discovered before 5000 BC.

(a) Properties.

Iron is brown ductile metal.

(b) Occurrence.

Iron is the fourth most abundant element in the earth crust.Iron exists naturally as

(i) Iron Pyrite (Iron sulphide). FeS_2.

(ii) Haematite. (Iron (iii) oxide). Fe_2O_3.(iii) Magnetite (Triirontetraoxide). Fe_3O_4

(iv) Siderite (iron (ii) carbonate) $FeCO_3$

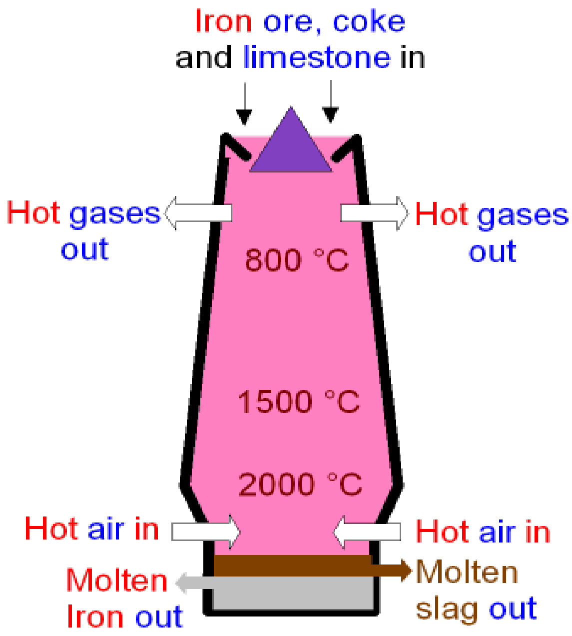
(c) Manufacture.

Iron is commonly extracted from iron (iii) oxide ore.

This done in a blast furnace which is made up of steel lined with fire bricks.

It is lined with fire bricks because they maintain the high temperature.

The blast furnace.



The blast furnace is fed with coke C, limestone $CaCO_3$, heamatite Fe_2O_3& hot air.

At the bottom coke is oxidised to carbondioxide by hot air.

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \Delta H= -392kjmol^{-1}$

The carbondioxide produced reacts with excess coke to produced carbonmonoxide.

$CO_{2(s)} + C_{(g)} \longrightarrow 2CO_{(g)} \Delta H= +172kjmol^{-1}$

The carbonmonoxide produced reduces the iron oxides to iron.

$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(l)} + 3CO_{2(g)} \Delta H= -27kjmol^{-1}$

The iron produced then falls at the bottom of the furnace.

At the same time limestone dissociates to produce quick lime (CaO).

$CaCO_{3(s)} \longrightarrow CaO_{(l)} + CO_{2(g)}$

CaO now combines with impurities in the ore e.g. Silica and aluminium (iii) oxide to form molten **slag.**

$CaO_{(s)} + SiO_{2(s)} \longrightarrow CaSiO_{3(l)}$ or $CaO_{(s)} + Al_2O_{3(s)} \longrightarrow CaAl_2O_{4(l)}$

At the bottom of the furnace slag floats on top of molten iron where it is tapped off separately.

NB:

The molten iron leaving the blast furnace is impure and is referred to as **pig iron.**

It is re-melted, mixed with scrap steel and cooled in moulds to form cast iron or wrought iron.

The slag produced can be used for road making, manufacture of cement and light weight building materials.

Slag in the blast furnace protects iron from further oxidation by air.

1.7.2. Reactions of Iron.

(a) Reactions with oxygen.

It reacts with oxygen on heating to give a black oxide of triirontetraoxide.

$3Fe_{(s)} + 2O_{2(g)} \xrightarrow{heat} Fe_3O_{4(s)}$

(b) Reactions with water.

It reacts with steam when red hot to give triirontetreoxide.

$3Fe_{(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + 4H_{2(g)}$

Note:

In the presence of air and water, Iron forms a brown coating called rust. Rust is hydrated iron (iii) oxide represented as $Fe_2O_3.XH_2O$.

(c) Reactions with acids.

Iron reacts with dilute HCl, H_2SO_4 and HNO_3 to produce iron ii salts.

$Fe_{(s)} + 2HCl_{(aq)} \longrightarrow FeCl_{2(aq)} + H_{2(g)}$

$Fe_{(s)} + H_2SO_{4(aq)} \longrightarrow FeSO_{4(aq)} + H_{2(g)}$

$4Fe_{(s)} + 10HNO_{3(aq)} \longrightarrow 4Fe(NO_3)_{2(aq)} + NH_4NO_{3(aq)} + 3H_2O_{(l)}$

(d) Reactions with halogens.

Iron reacts with chlorine on heating to produce a black solid of iron (iii) chloride.

$2Fe_{(s)} + 3Cl_{2(g)} \xrightarrow{heat} 2FeCl_{3(s)}$

1.7.3. Compounds of Iron.

Iron shows compounds in its principal oxidation states. E.g +2, and +3

(a) Compounds in the +2 oxidation state.

$^{24}Fe^{2+}$- $1S^22S^22P^63S^23P^63d^6$

(i) Iron (ii) oxide

It is prepared as a black solid by heating iron(ii)carbonate.

$FeCO_{3(s)} \xrightarrow{heat} FeO_{(s)} + CO_{2(g)}$.

(ii) Iron (II) hydroxide.

It appears as a dirty green precipitate by addition of Fe^{2+} salts with sodium hydroxide or ammonia.

$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$

(iii) Iron (II) Carbonate.

It appears as a green precipitate by addition of Fe^{2+} salts with sodium carbonate.

$Fe^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)} \longrightarrow FeCO_{3(s)}$

(iv) Iron (II) Chloride.

It is a green solid and is obtained when iron reacts with dilute HCl acid.

$Fe_{(s)} + 2HCl_{(aq)} \longrightarrow FeCl_{2(aq)} + H_{2(g)}$

(iv) Iron (II) Sulphate. $FeSO_4 . 7H_2O$.

It is a green solid and is obtained when iron reacts with dilute H_2SO_4 acid.

$Fe_{(s)} + H_2SO_{4(q)} \longrightarrow FeSO_{4(s)} + H_{2(s)}$**NB.** Iron (II) salts appear green in solution. $[Fe(H_2O)_6]^{2+}$

Hydrated $FeSO_4 . 7H_2O$

(b) Compounds in the +3 oxidation state.

$^{23}Fe^{3+}$- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^5$.

It is the most stable oxidation state of iron.

(i) Iron (III) oxide.

It is prepared as a brown solid by heating iron (iii) sulphate.

$2FeSO_{4(s)} \xrightarrow{heat} Fe_2O_{3(s)} + SO_{2(g)} + SO_{3(g)}$

Fe_2O_3

(ii) Iron (III) hydroxide.

It appears as a brown precipitate by addition of Fe^{3+} salts with sodium hydroxide or ammonia.

$Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \longrightarrow Fe(OH)_{3(s)}$

(iii) Iron (III) Chloride. It is appears as a dark brown solid obtained when iron is heated with chlorine gas.

$2Fe_{(s)} + 3Cl_{2(aq)} \longrightarrow 2FeCl_{3(s)}$.

Anhydrous $FeCl_3$

Like $AlCl_3$, (i) $FeCl_3$is acidic in solution.

$FeCl_3 + 3H_2O_{(l)} \longrightarrow Fe(OH)_3 + 3HCl_{(aq)}$

(ii) $FeCl_3$ sublimes at 300°C, to form covalent dimers. i.e.

Note: Solutions of Fe^{3+} compounds appear brown or yellow; $[Fe(H_2O)_6]^{3+}$.

Like solutions of Al^{3+} , the aqueous solutions of Fe^{3+} are also acidic due to high polarizing power (high charge density).

$[Fe(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Fe(H_2O)_3 3OH]_{(aq)} + 3H^+_{(aq)}$

1.7.4.Uses of iron.

Fe	Alloy(steel)	used to make utensils, machinery, building materials like pipes, gates, doors, windows
	used as a catalysts in manufacture of ammonia	
	Biologically iron is present in heamoglobin for oxygen transport.	

However iron undergoes rusting.

Rusting.

Rust is brown coating on iron referred to as hydrated iron (iii) oxide.

It occurs in the presence of water and oxygen.

How rusting occurs.

Rusting is an electrochemical process in which a cell is made up within a metal.

In a piece of iron, there are areas which tend to give electrons (anodic areas) and areas which tend to accept electrons (Cathodic areas).

This is caused by the presence of impurities and differences in oxygen concentration.

At the anode: $2Fe_{(s)} \longrightarrow 2Fe^{2+}_{(aq)} + 4e$

At the cathode: $O_{2(g)} + H_2O_{(l)} + 4e \longrightarrow 4OH^{-}_{(aq)}$

The Fe^{2+} now reacts with OH^{-} to produce iron (ii) hydroxide.

$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Fe(OH)_{2(s)}$

The iron (ii) hydroxide formed is then oxidised by air and water to a brown solid (rust) $Fe_2O_3.XH_2O$.

$2Fe(OH)_{2(s)} + H_2O_{(l)} + ½\ O_{2(g)} \longrightarrow 2Fe(OH)_{3(s)}$

$Fe(OH)_{3(s)} \longrightarrow Fe_2O_3.3H_2O$.

Prevention of rusting.

-By painting or greasing or oiling

-By alloying e.g. stainless steel.

-By covering iron with other metals. i.e. Tin electroplating and zinc electroplating(galvanizing).

Note:

Metals more reactive than iron prevent rusting because they are oxidised first. E.g. zinc. However tin is less reactive than iron and iron is oxidized first. This explains why iron cans covered with tin rusts rapidly, when they are scratched.

⍰ Test yourself.

Explain why galvanizing may be better than tin platting?

1.7.5. Qualitative analysis.

(a) Test of Fe^{2+}

Reagents	Observation	Equation
(i)NaOH or NH_3	A dirty green precipitate insoluble in excess alkali and turns brown on standing. The green ppt rapidly turns brown due to ariel oxidation of Fe^{2+} to Fe^{3+}	$Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Fe(OH)_{3(s)}$
(ii)Na_2CO_3	A green precipitate.	$Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_{3(s)(s)}$
(iii) Potassium hexacyanoferrate(III) solution. (Potassium ferricyanide solution). **Observation:** A dark blue precipitate (solution). $Fe^{2+}_{(aq)} + K^{+}_{(aq)} + Fe(CN)^{3-}_{6(aq)} \rightarrow KFe_2(CN)_{6(s)}$		

(b) Test of Fe^{3+}

Reagents	Observation	Equation
(i)NaOH or NH_3	A reddish-brown precipitate.	$Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Fe(OH)_{2(s)}$ $Fe(OH)_2$ to Fe_2O_3. XH_2O.
(ii)Na_2CO_3	A reddish-brown precipitate.	$Fe^{3+}_{(aq)} + CO_3^{2-}{}_{(aq)} + 3H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 3CO_{2(g)}$

(iii) Potassium hexacyanoferrate(II) solution. (Potassium ferrocyanide solution).

Observation: A dark blue precipitate (solution).

$Fe^{3+}_{(aq)} + K^{+}_{(aq)} + Fe(CN)^{4-}_{6(aq)} \rightarrow KFe_2(CN)_{6(s)}$

(iv) Potassium thiocyanate solution.

Observation: A blood red coloration.

$Fe^{3+}_{(aq)} + 5H_2O_{(l)} + SCN^{-}_{(aq)} \rightarrow [Fe(SCN)(H_2O)_5]^{2+}$ *Pentaaquathiocynatoiron(III)ions*.

deep red

Exercise.1.g.

Multiple choice questions.

1. Identify the chief ore of Iron.

a. Iron Pyrite b. Haematite. c. Magnetite d. Siderite.

2. State what is observed when sodium hydroxide reacts with Fe^{2+} solution.

a. dirty white precipitate. b. dirty green precipitate. c. brown precipitate d. yellow precipitate.

3. State what is observed when sodium hydroxide reacts with Fe^{3+} solution.

a. dirty white precipitate. b. dirty green precipitate. c. brown precipitate d. yellow precipitate .

4. Which of these metals is best in protection of iron against rusting

a. Sn b. Ag c. Cu d. Zn

5. All these elements are important components in stainless steel except

a. Cr b. Fe c. C d. Cu

***Structural questions*.**

1.a.Using equations outline the process of extraction of iron from iron (iii)oxide (diagram) required.

b. Using equations, briefly explain how iron reacts with the following compounds.

i. Water. ii.chlorine iii.dilute sulphuric acid. iv. dilute nitric acid.

2. a. Which type of bonding is in $FeCl_3$

b. Explain why a solution of $FeCl_3$ has a PH of less than 7.

c. Write the equation and state what will be observed when iron iii chloride solution reacts

i. with sodium hydroxide.

ii with sodium carbonate.

3. Name one reagent that can be used to distinguish between the following pairs of compounds and state what will be observed if each compound is treated with the reagent. Include observations.

a. Ni^{2+} and Cr^{3+}b. Fe^{2+} and Fe^{3+}c. $MnSO_4$ and $FeSO_4$

4. A compound A has 28% Fe, O 48% and S, 24%

a. Calculate its empirical formula.

b. If molecular mass of A is 400. Determine the molecular formula of A.

5.a. Define rust

b. Give the conditions necessary for rusting,

c. Write the equation that occurs during rusting.

i.anode ii. cathode iii. overall equation.

d. Give 4 ways that are used to prevent rusting of iron.

6.a. Write down the electron configuration of Fe^{2+}, Fe^{3+}, Fe^{6+} (26)

b. Explain why $Fe^{2+}$is oxidized to Fe^{3+}

c. With examples, give three properties in which iron acts as a transition metal.

d. Give two practical applications of iron.

7. The addition of iron fillings to the solution of copper (ii) sulphate to give a solution of ion Q and the solid is removed by filtration.

a. Write the ionic equation for reaction.

b. Give two possible observation(s)

c. In solution Q exists as a complex. Give the formula of the complex ion.

d. Addition of sodium hydroxide to Q gives Iron (II) hydroxide and on filtration, it gives a brown solid R on the filter paper.

i. state color of iron hydroxide.

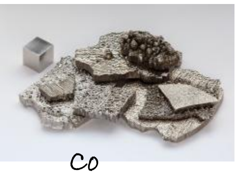
ii. Give the formula of R.

iii. with what does iron (II) hydroxide react with to produce R.

iv. Give the type of reaction that lead to the formation of Q and R?

1.8.0. Cobalt. Co

1.8.1. Introduction.


Co

^{27}Co- $1S^22S^22P^63S^2\,3P^63d^74S^2$.

Co has an hexagonal-close packed structure and was discovered by Georg Brandt 1732

(a) Properties.

Cobalt is a hard ferromagnetic, silver-white, hard, lustrous, ductile element.

(b) Occurrence.

Various cobalt bearing minerals have economic significance include

Cobaltite (CoAsS).

Carrollite ($Cu(Co.Ni)_2S_4$),

Linnaeite (Co_3S_4).

These are often associated with copper minerals and pyrite and pyrrhotite iron sulphides. Cobolt is therefore obtained as a bi product during extraction of copper.

1.8. 2. Reactions of Cobalt

(a) Reactions with oxygen.

It reacts with oxygen on heating to give tricobolttetraoxide however above 900°C cobalt (ii) oxide is obtained.

$$2Co_{(s)} + O_{2(g)} \xrightarrow{above-900^oc} 2CoO_{(s)}$$

$$3Co_{(s)} + 2O_{2(g)} \xrightarrow{heat} Co_3O_{4(s)}$$

(b) Reactions with water.

It reacts with steam when heated strongly to give cobolt (ii) oxide.

$$2Co_{(s)} + H_2O_{(g)} \longrightarrow CoO_{(s)} + H_{2(g)}$$

(c) Reactions with acids.

Cobalt reacts with dilute HCl & H_2SO_4 to produce cobalt ii salts.

$$Co_{(s)} + 2HCl_{(aq)} \longrightarrow CoCl_{2(s)} + H_{2(s)}$$

$$Co_{(s)} + H_2SO_{4(aq)} \longrightarrow CoSO_{4(s)} + H_{2(s)}$$

(d) Reactions with halogens.

Cobolt reacts with chlorine on heating to produce cobalt ii halides.

$Co_{(s)} + Cl_{2(g)} \longrightarrow CoCl_{2(s)}$- blue

$Co_{(s)} + Br_{2(l)} \longrightarrow CoBr_{2(s)}$ –green.

1.8.3. Compounds of cobolt.

Cobalt shows compounds in its principal oxidation states. E.g +2, and +3

(a) Compounds in the +2 oxidation state.

$^{25}Co^{2+}$- $1S^22S^22P^63S^23P^63d^7$

This is the most stable oxidation state of cobalt.

(i) Cobalt (ii) oxide.

It is prepared as a green solid by heating cobalt (ii) carbonate.

$$CoCO_{3(s)} \xrightarrow{heat} CoO_{(s)} + CO_{2(g)} \ .$$

(ii) Cobalt (II) hydroxide.

It appears as a blue precipitate by addition of Co^{2+} salts with sodium hydroxide or ammonia.

$Co^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Co(OH)_{2(s)}$

(iii) Cobalt (II) Carbonate.

It appears as a purple precipitate by addition of Co^{2+} salts with sodium carbonate.

$Co^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow CoCO_{3(s)}$


Hydratedcobolt(ii)chloride

(iv) Cobolt (II) Chloride.

It is a blue solid and is obtained when cobalt reacts with dilute HCl acid.

$Co_{(s)} + 2HCl_{(aq)} \longrightarrow CoCl_{2(aq)} + H_{2(s)}$

(v) Cobalt (II) Sulphate.

It is a green solid and is obtained when iron reacts with dilute H_2SO_4 acid.

$Co_{(s)} + H_2SO_{4(aq)} \longrightarrow CoSO_{4(s)} + H_{2(s)}$**Note:**

i. Cobalt (II) salts appear pink in solution. $[Co(H_2O)_6]^{2+}$

ii. When conc. HCl is added to a solution of Cobolt (ii) ion, the pink solution becomes deep blue.$[Co(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons [CoCl_4]^{2-}{}_{(aq)} + 6H_2O_{(l)}$

This is due to ligand exchange.

(b) Compounds in the +3 oxidation state.

$^{24}Co^{3+}$- $1S^22S^22P^63S^23P^63d^6$.

Cobalt (III) Chloride.

It exists in complex form with other ligands such as ammonia.

E.g.

$CoCl_3.6NH_3$ undergoes hydration isomerism like $CrCl_3.6H_2O$

$[Co(NH_3)_6]^{3+}\ 3Cl^-$ which is a greenish-yellow isomer.

$[Co(NH_3)_5\,Cl^-]^{2+}\ 2Cl^-.NH_3$which is violet.

$[Co(NH_3)_4\,2Cl^-]^+Cl^-.2NH_3$which is green.

1.8.4. Uses of cobalt and its compounds.

Co	Cobolt is used in many Alloys eg. Constantan, nichrome. Cutting tools. Medical treatment as a radioactive source. Manufacture of magnets and and magnetic recording media. Used as catalysts for the petroleum and chemical industries. Used as drying agents for paints and inks. Cobalt blue is used by craft workers in porcelain, pottery, stained glass, tiles and enamel jewellery, rechargeable batteries.


Co blue flask

1.8.5. Qualitative analysis:

Reagents	Observation	Equation
(i)NaOH	A blue precipitate insoluble in excess alkali and turns pink on standing.	$Co^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Co(OH)_{2(s)}$
(ii) NH_3	A blue precipitate insoluble in excess alkali and turns pink on standing.	$Co^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Co(OH)_{2(s)}$

(iii)Na_2CO_3	A pink precipitate..	$Co^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CoCO_{3(s)}$
(iv)KCN	A red-brown precipitate.	$Co^{2+}{}_{(aq)} + 2CN^{-}{}_{(aq)} \rightarrow Co(CN)_{2(aq)}$
(v) Potassium thiocyanate solution. **Observation**: A blue solution. $Co^{2+}{}_{(aq)} + 4KSCN_{(aq)} \rightarrow K_2Co(SCN)_{4(aq)} + 2K^{+}{}_{(aq)}$ Potassium tetrathiocynatocoboltate (II) ions.		
(vi). Hydogen sulphide gas. On passing the gas through a solution cobolt (ii) ions a black precipitate is formed. $Co^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \rightarrow CoS_{(s)}$		

Exercise.1.h.

Multiple choice questions

1. State what is observed when sodium hydroxide reacts with Co^{2+} solution.

a. blue precipitate. b. dirty green precipitate. c. brown precipitate d. yellow precipitate .

2. Which type of isomerism exists in $[Co(NH_3)_4Cl_2]^{+}$

a. ionistion isomers b. hydration isomers c. geometrical isomers d. Tautamerism

***Structural questions*.**

1. Compound R contains cobolt 24.8%, chlorine 29.8% and water 45.4%.

a.i.Calculate the empirical formular of R.

ii. Detemine the molecular formular of R. RFM of 237.9

b. To a solution of Rin water concentrated hydrochloric acid was added dropwise until excess

i. State what was observed.

ii.Write down the equation for reaction that took place.

c.shows optical isomers of $[Co(C_2O_4)_3]^{4-}$.

2. Compound **X** contains Co: 23.8%, N: 27.9%, H:6%, and Cl: 42.5%.

a.i.Calculate the empirical formular of X.

ii. Determine the molecular formular of R. RFM of 264.5. (Co: 59, N:14,H:1, Cl:35.5)

iii. Show all the possible isomers of X and name them.

b. Using the above isomers complete the table below.

Structure of the isomer.	No. of moles of Cl^{-} ions precipitated by $AgNO_3$ per isomer	No. of moles of conducting ions per mole of isomer.

c.i. Which of the above isomers will form geometrical isomers?

ii. Show the geometrical isomers.

1.9.0. Nickel Ni

Ni

1.9.1. Introduction.

^{28}Ni- $1S^2 2S^2 2P^6 3S^2\ 3P^6 3d^8 4S^2$.

Ni has a face centred cubic structure and was discovered by Axel Fredrik Cronstedt 1751

(a) Properties.

Nickel is silvery-white. hard, malleable, and ductile metal.

(b) Occurrence.

Nickel occurs naturally as millerite NiS.

(c) Manufacture.

Purification.

Nickel is produced by reducing Nickel (ii) oxide with carbon.

$$NiO_{(s)} + C_{(s)} \longrightarrow Ni_{(s)} + CO_{(g)}$$

1.9.2. Reactions of nickel.

(a) Reactions with oxygen (air).

It reacts with oxygen on heating to give a green solid of nickel(ii) oxide.

$$2Ni_{(s)} + O_{2(g)} \xrightarrow{heat} 2NiO_{(s)}$$

(b) Reactions with water.

It reacts with steam when heated strongly to give nickel (ii) oxide.

$$2Ni_{(s)} + H_2O_{(g)} \longrightarrow NiO_{(s)} + H_{2(g)}$$

(c) Reactions with acids.

Nickel reacts with dilute HCl, H_2SO_4 and HNO_3 to produce nickel ii salts.

$$Ni_{(s)} + 2HCl_{(aq)} \longrightarrow NiCl_{2(s)} + H_{2(s)}$$

$$Ni_{(s)} + H_2SO_{4(aq)} \longrightarrow NiSO_{4(s)} + H_{2(s)}$$

$$Ni_{(s)} + 2HNO_{3(aq)} \longrightarrow Ni(NO_3)_{2(s)} + H_{2(s)}$$

(d) Reactions with halogens.

Nickel reacts with chlorine on heating to produce nickel (ii) chloride.

$$Ni_{(s)} + Cl_{2(g)} \xrightarrow{heat} NiCl_{2(s)}$$

1.9.3. Compounds of nickel.

Nickel shows compounds in its principal oxidation states. E.g +2, and +3

Compounds in the +2 oxidation state.

$^{26}Ni^{2+}$- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^8$

This is the most stable oxidation state of nickel.

(i) Nickel (II) oxide.

It is prepared as a green solid by heating nickel carbonate, hydroxide or NO_3^{2-}

$$NiCO_{3(s)} \xrightarrow{heat} NiO_{(s)} + CO_{2(g)}.$$

(ii) Nickel (II) hydroxide.

It appears as a green precipitate by addition of Ni^{2+} salts with a solution of sodium hydroxide or ammonia.

$$Ni^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Ni(OH)_{2(s)}$$

(iii) Nickel (II) Carbonate.

It appears as a precipitate by addition of Ni^{2+} salts with aqueous sodium carbonate.

$Ni^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow NiCO_{3(s)}$

(iv) Nickel (II) Chloride.

It is a green solid and is obtained when nickel reacts with dilute HCl acid.

$Ni_{(s)} + 2HCl_{(aq)} \longrightarrow NiCl_{2(aq)} + H_{2(s)}$

(iv) Nickel (II) Sulphate.

It is a blue solid and is obtained when iron reacts with dilute H_2SO_4 acid.

$Ni_{(s)} + H_2SO_{4(aq)} \longrightarrow NiSO_{4(s)} + H_{2(s)}$**Note:**

Nickel (II) salts appear in green solution. $[Ni(H_2O)_6]^{2+}$

1.9.4. Uses of nickel and its compounds.

Ni	Alloys (used to make coins), Magnet(AlNiCo), Cutting tools, Construction, (nichrome(electrical heating elements, utensils)Industrial catalyst e.g hydrogenation of oils (margarine).

Ni-coins

1.9.5. Qualitative analysis:

Test of Ni^{2+}

Reagents	Observation	Equation
(i)NaOH	A green precipitate insoluble in excess alkali.	$Ni^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Ni(OH)_{2(s)}$
(ii)NH_3	A green precipitate soluble in excess ammonia to form a blue solution	$Ni^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Ni(OH)_{2(s)}$ green precipitate. $Ni(OH)_{2(s)} + 6NH_{3(aq)} \longrightarrow [Ni(NH_3)_6]^{2+}_{(aq)} + 2OH-_{(aq)}$
(iii)Na_2CO_3	A green precipitate.	$Ni^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow NiCO_{3(s)}$
(iv) NaCN	: A yellowish-green precipitate that dissolves in excess to give a dark yellow solution.	$Ni^{2+}_{(aq)} + 2CN^{-}_{(aq)} \longrightarrow Ni(CN)_{2(aq)}$ $Ni(CN)_{2(s)} + 2CN^{-}_{(aq)} \longrightarrow [Ni(CN)_4]^{2-}_{(aq)}$
(v)Dimethyl glyoxime.	A red precipitate.	

(vi) Potassium hexacyanoferrate (II) solution. (Potassium ferrocyanide solution).

Observation: A greenish precipitate .

$2Ni^{2+}_{(aq)} + Fe(CN)^{4-}_{6(aq)} \longrightarrow Ni_2[Fe_2(CN)_6]_{(s)}$

(vii) Potassium hexacyanoferrate (III) solution. (Potassium ferricyanide solution).

Observation: A brown precipitate .

$Ni^{2+}_{(aq)} + Fe(CN)^{3-}_{6(aq)} \longrightarrow Ni_3[Fe_2(CN)_6]_{2(s)}$

Exercise.1.i.

Multiple choice questions

1. State what is observed when sodium hydroxide reacts with Ni^{2+} solution.

a. blue precipitate. b. green precipitate. c. brown precipitate d. yellow precipitate .

2. Which type of isomerism exists in $[Ni(NH_3)_2Cl_2]$

a. ionization isomers b. hydration isomers c. geometrical isomers d. Tautamerism

3. What is the oxidation state of nickel in $Ni(CO)_4$

a. +1 b.+2 c.+3 d.O

***Structural questions*.**

1. a. Write down the electron configuration of Ni^{2+}.

b. With examples give four properties in which Ni is as transition metals.

c. Give two practical applications of titanium metal.

2. The table below shows the tests carried out on a solution of substance Z and the observations that were made.

Test	Observation.
i.To the solution of Z was added dilute sodium hydroxide dropwise till excess	Green precipitate insoluble in excess alkali.
ii. To a solution of Z was added dilute ammonia dropwise till excess	Green precipitate dissolves in excess ammonia to a solution.
iii.To a solution Z was added dilute nitric acid followed by silver nitrate solution	White precipitate.

a). i. Identify cation Z .

ii. Identify the anion in Z.

b) Write the ionic equation for the reaction leading to the formation of white precipitate.

c) Name one reagent that can be used to confirm the presence of the cation in Z and state what will be observed if the solution is treated with a reagent.

1.10.0. Copper-(Cuprate-latin name)

1.10.1. Introduction.

^{29}Cu- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^{10} 4S^1$.

Cu has a face centred cubic structure and was discovered around 9000BC.

(a) Properties.

Copper is a soft, malleable, and ductile with a reddish brown colour.

(b) Occurrence.

Copper exists naturally as (ores of copper).

Copper pryrite. $CuFeS_2$. (chief ore).

Copper glance. Cu_2S.

Malachite, $CuCO_3$-$Cu(OH)_2$

(c) Manufacture.(extraction).

The process of extraction of copper from its ore copper pyrite can divided in three stages.

(i) Concentration process.

The copper ore is crushed finely and concentrated by *froth floatation*.

The crushed ore is mixed with water containing a frothing agent (pine oil).

Hot air is then passed through the mixture.

The pyrite ore now floats at the surface where it is removed, filtered and dried.

The earthly material sinks at the bottom due to their high density.

This increases the concentration of the copper in the ore.

(ii) Reduction of the ore.

The concentrated ore is roasted in air to form copper (i) sulphide, iron (ii) oxide and sulphur dioxide gas.

$2CuFeS_{2(s)} + 4O_{2(g)} \longrightarrow Cu_2S_{(s)} + 2FeO_{(s)} + 3SO_{2(g)}$.

The product is then heated with silica in a closed furnace. Iron (ii) oxide reacts with silica to form molten slag which floats on top of molten copper sulphide.

$FeO_{(s)} + SiO_{2(s)} \longrightarrow FeSiO_{3(l)}$ iron (ii) silicate (slag)

Copper (i) sulphide is then heated in air forming copper oxide.

$2Cu_2S_{(s)} + 3O_{2(g)} \longrightarrow 2Cu_2O_{(s)} + 2SO_{2(g)}$

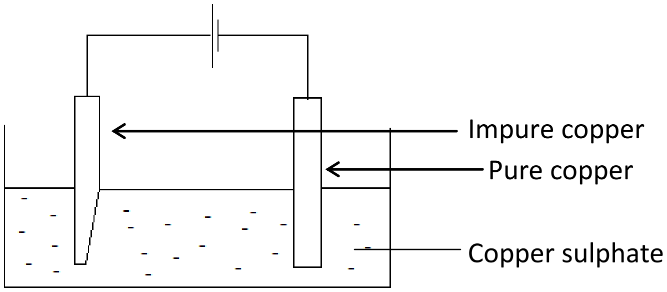
The copper (i) oxide is now mixed with unchanged copper (i) sulphide and are heated strongly in absence of air.

$Cu_2S_{(s)} + 2Cu_2O_{(s)} \longrightarrow 6Cu_{(s)} + SO_{2(g)}$

The copper obtained here is called *blister copper* containing impurities like iron and sulphur.

(iii) Purification.

This is done by electrolysis of copper sulphate solution using pure copper electrode as the cathode and blister copper as the anode.



During electrolysis copper dissolves away from the anode and settles at the anode.

Anode: $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e$

Cathode: $Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)}$

1.10.2. Reactions of Copper.

(a) Reactions with oxygen.

It reacts with oxygen on heating to give copper oxide.

$2Cu_{(s)} + O_{2(g)} \xrightarrow{300^0C} 2CuO_{(s)}$**(b) Reactions with acids.**

Copper does not react with dilute HCl & H_2SO_4.

However copper reacts with concentrated sulphuric acid forming sulphur dioxide.

$Cu_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$

Copper reacts with dilute nitric acid to nitrogen monoxide gas.

$3Cu_{(s)} + 8HNO_{3(aq)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 4H_2O_{(l)} + 2NO_{(g)}$

Copper reacts with concentrated nitric acid to nitrogen dioxide gas.

$Cu_{(s)} + 4HNO_{3(aq)} \longrightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)}$

(c) Reactions with halogens.

When chlorine gas is passed over heated copper, copper chloride is obtained

$Cu_{(s)} + Cl_{2(g)} \xrightarrow{heat} CuCl_{2(s)}$

1.10.3. Compounds of copper.

Copper shows compounds in its principal oxidation states. i.e. +1 and +2.

(a) Compounds in the +1 oxidation state.

$^{28}Cu^{+}$- $1S^22S^22P^63S^23P^63d^{10}$.

(i) Copper (i) Chloride.

It is a white solid prepared heating copper ii chloride at very high temperature.

$2CuCl_{2(s)} \xrightarrow{heat} 2CuCl_{(s)} + Cl_2$

Copper (i) Chloride is unstable and is easily oxidised to copper (ii) chloride.

Copper (i) chloride dissolves in ammonia to give a complex.

$CuCl_{(s)} + 2NH_{3(aq)} \longrightarrow [Cu(NH_3)_2]^+_{(aq)} + Cl^-_{(aq)}$

Note:

This complex (ammoniacal copper(i) chloride is applied organic analysis to test terminal alkynes.

(ii) copper (i) oxide.

It can be obtained by heating oxygen in air also some copper ii oxide is also obtained

It turns easily turns to copper ii oxide

It under goes a disproportination reaction when it reacts with acids.

$Cu_2O_{(s)} + 2HCl_{(aq)} \longrightarrow CuCl_{2(aq)} + Cu_{(s)} + H_2O_{(l)}$

(b) Compounds in the +2 oxidation state.

$^{27}Cu^{2+}$- $1S^2 2S^2 2P^6 3S^2 3P^6 3d^9$

This is the most stable oxidation state of copper.

(i) Copper (ii) oxide.

It is black solid prepared by heating $CuCO_3$ or $Cu(OH)_2$ or $Cu(NO_3)_2$

$CuCO_{3(s)} \xrightarrow{heat} CuO_{(s)} + CO_{2(g)}$.

(ii) Copper (II) hydroxide.

It appears as a pale blue precipitate by addition of Cu^{2+} salts with sodium hydroxide.

$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(s)}$

(iii) Copper (II) Carbonate.

It appears as a green precipitate by addition of Cu^{2+} salts with sodium carbonate.

$Cu^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)} \longrightarrow CuCO_{3(s)}$

(iv) Copper (II) Chloride.

It is a green solid and is obtained when heated copper reacts with chlorine gas.

$Cu_{(s)} + Cl_{2(aq)} \longrightarrow CuCl_{2(aq)}$

(iv) Copper (II) Sulphate.

It is a blue solid and is obtained when copper reacts with conc. H_2SO_4 acid.

$Cu_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$

Note:

i. Copper (II) salts appear blue or green in solution. $[Cu(H_2O)_6]^{2+}$

ii. When conc. HCl is added to a solution of Copper (ii) ions.

the blue solution becomes yellow**.**

$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \longrightarrow [CuCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$

This is due to ligand exchange.

1.10.4. Uses of copper and its compounds.

Cu	Manufacture of electrical wires, building materials, jewellery, coins, water vessels, utensils, coins Alloys. E.g. brass (zinc and copper), Bronze (copper and tin), Manufacture of water pipes.

brass trumpets

1.10.5. Qualitative analysis:

Test of Cu^{2+}

Reagents	Observation	Equation
(i)NaOH	A pale blue precipitate insoluble in excess alkali.	$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(s)}$
(ii)NH_3	A pale blue precipitate soluble in excess to give a deep blue solution	$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(s)}$ $Cu(OH)_{(s)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$
(iii)Na_2CO_3	A blue-green precipitate.	$Cu^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)} \longrightarrow CuCO_{3(s)}$

<table>
<tr><td>(iv) NaCN</td><td>A yellow precipitate which rapidly turns white.</td><td>$Cu^{2+}_{(aq)} + 2CN^{-}_{(aq)} \longrightarrow CuCN_{2(s)}$</td></tr>
<tr><td>(v)KI</td><td>A brown-yellow precipitate or (white precipitate stained brown due to free iodine.)</td><td>$2Cu^{2+}_{(aq)} + 4I^{-}_{(aq)} \longrightarrow 2CuI_{(s)} + I_{2(aq)}$</td></tr>
<tr><td colspan="3">(vi) Potassium hexacyanoferrate(II) solution. (Potassium ferrocyanide solution). Observation: A red-brown precipitate.
$2Cu^{2+}_{(aq)} + [Fe(CN)_6]^{4-}_{(aq)} \longrightarrow Cu_2[Fe(CN)_6]_{(s)}$</td></tr>
</table>

Exercise.1.j.

Multiple choice questions.

1. State what is observed when sodium hydroxide reacts with Cu^{2+} solution.

a. blue precipitate. b. green precipitate. c. brown precipitate d. yellow precipitate .

2. Identify the chief ore of copper.

a. Cu_2S b. $CuFeS_2$ c. Cu_2S d. $Cu(OH)_2$

3. What is observed when copper carbonate is heated strongly?

a. yellow residue b. brown residue c. black residue d. green residue.

4. What is observed when Cu^{2+} ions react ammonia dropwise till excess.

a. a blue precipitate insoluble excess. b. a green precipitate insoluble in excess.

c. a blue precipitate soluble in excess. d. a white precipitate insoluble in excess.

5. Copper reacts with concentrated nitric acid to give a

a. a blue solution and brown gas. b. a green solution and colourless gas.

c. a colorless solution and a brown a gas. d. yellow solution and brown gas.

6. Brass is an alloy of copper and zinc. It reacts with nitric acid to give a solution containing Cu^{2+} ions. The solution was added to excess $KI_{(aq)}$ and titrating the iodine formed against standard thiosulphate solution.

Zinc does not react.

$2Cu^{2+}_{(aq)} + 4I^{-}_{(aq)} \rightarrow 2Cu_{(s)} + I_{2(aq)}$

$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^{-}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

In analysis, 0.2685g used $27.5cm^3$ of 0.1M sodium thiosulphate. Calculate the mass of copper in the specimen of brass.

a. 45% b. 65% c. 35% d. 25%.

***Structural questions*.**

1.a.Write the electron configuration of Copper.

b. State two properties of copper as a transition metal.

c. Hydrated copper (ii) sulphate was dissolved in water.

i. Write the name and the formula of the copper spiecie present.

ii. To the above solution was added concentrated hydrochloric acid.

State what was observed and write down the name of the copper spiece present.

2. a.i. Write down the formula and name of the ore copper.

ii. Outline the process of how pure copper is obtained from the ore above.

b. Write down the equation reactions between copper and

i. Sulphuric acid.

ii. Nitric acid. (include observations and conditions)

c. State what will be observed write the equation of reaction that takes place when the following reagents are added drop wise to the solution of copper ii chloride.

i. Sodium hydroxide solution.

ii. Concentrated hydrochloric acid.

3. A green powder was dissolved in dilute hydrochloric acid to give a green solution.

a. To the first portion a few drops of potassium hexacyanoferrate II.

A brown precipitate was formed. Name the cation in the powder.

b. To the second portion was added was added ammonia solution dropwise till excess.

i. State what was observed

ii. Write the equation for reaction.

c. To the third portion was added potassium iodide.

i. State what was observed   ii. Write the equation for reaction.

4. A solution was prepared by dissolving 2.838g of $CuSO_4 .XH_2O$ to give 250cm^3 of aqueous solution. 25.0cm^3 of this solution was treated with an excess of aqueous KI. The iodine produced was titrated with a solution of $Na_2S_2O_3$ and 23.70 cm^3 of $Na_2S_2O_3$ was required.

Given that 2.976g of $Na_2S_2O_3 .5H_2O$ had been dissolved in water to obtain 250cm^3 of aqueous solution using starch as a suitable indictor. (Cu=63.5, Na= 23, S=32, O=16)

Find the number of moles of water of crystallization x.

Use the following equations in your calculations.

$2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \rightarrow 2Cu_{(s)} + I_{2(aq)}$

$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

1.11.0. Zinc

1.11.1. Introduction.


Zn

^{30}Zn- $1S^22S^22P^63S^23P^63d^{10}4S^2$.

Zn has a hexagonal structure and was discovered around 1000BC

(a) Properties.

Zinc is silver grey.

(b) Occurrence.

Zinc exists naturally as (ores of zinc).

Zinc blende. ZnS (chief ore).

Calamine. $ZnCO_3$

(c) Manufacture.(extraction)

The process of extraction of zinc from its ore zinc blende can divided in 2 stages.

(i) Concentration process.

The zinc ore is crushed finely and concentrated by *froth floatation*.

The crushed ore is mixed with water containing a frothing agent (pine oil).

Hot air is then passed through the mixture.

The zinc ore now floats at the surface where it is removed, filtered and dried.

The earthly material sinks at the bottom due to their high density.

This increases the concentration of the zinc in the ore.

(ii) Roasting of the ore.

The concentrated ore is roasted in air.

$2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2ZnO_{(s)} + 2SO_{2(g)}$.

$2PbS_{(s)} + 3O_{2(g)} \longrightarrow 2PbO_{(s)} + 2SO_{2(g)}$.

The products (ZnO and PbO) are then heated with coke and lime stone in a blast furnace. In a blast furnace coke burns to give CO_2 which is then reduced to CO by unburnt coke.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$CO_{2(g)} + C_{(s)} \longrightarrow 2CO_{(g)}$

The CO produced reduces ZnO and PbO to Zn and Pb respectively.

$ZnO_{(s)} + CO_{(g)} \longrightarrow Zn_{(s)} + CO_{2(g)}$

$PbO_{(s)} + CO_{(g)} \longrightarrow Pb_{(s)} + CO_{2(g)}$

The limestone decomposes to quicklime which combines with impurities such as SiO_2 to produce slag.

$CaCO_3 \longrightarrow CaO_{(s)} + CO_{2(g)}$

$CaO_{(s)} + SiO_{2(s)} \longrightarrow CaSiO_{3(g)}$

Both liquid slag and liquid lead run at the bottom of the furnace and are tapped off separately. Zinc is present as vapour and leaves the furnace at the top which is cooled and tapped off.

1.11.2. Reactions of zinc.

(a) Reactions with oxygen.

It reacts with oxygen to obtain a thin layer of ZnO which prevents further reaction.

$2Zn_{(s)} + O_{2(g)} \longrightarrow 2ZnO_{(s)}$

(b) Reactions with water.

Zinc reacts with steam on strong heating to produce zinc oxide & hydrogen.

$Zn_{(s)} + H_2O_{(g)} \xrightarrow{heat} ZnO_{(s)} + H_{2(g)}$

(c) Reactions with acids.

Zinc reacts with HCl (dil & conc) and dilute H_2SO_4 producing hydrogen.

$Zn_{(s)} + H_2SO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + 2H_{2(g)}$

$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$

However the reaction with conc sulphuric acid is complicated.

(d) Reactions with alkalis.

Zinc reacts with sodium hydroxide to sodium zincate

$Zn_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(l)} \longrightarrow Na_2Zn(OH)_{4(aq)} + H_{2(g)}$

(e) Reactions with halogens.

When chlorine gas is passed over heated zinc, zinc chloride is obtained

$Zn_{(s)} + Cl_{2(g)} \xrightarrow{heat} ZnCl_{2(s)}$

1.11.3. Compounds of Zinc.

Zinc shows compounds in +2 oxidation state.

(a) Compounds in the +2 oxidation state.

$^{28}Zn^{2+}$- $1S^22S^22P^63S^23P^63d^{10}$

Because of the full d-orbital in Zn^{2+}, Its compounds show non transition properties.

(i) Zinc (ii) oxide

It is white solid prepared by heating $ZnCO_3$ or $Zn(OH)_2$ or $Zn(NO_3)_2$.

$ZnCO_{3(s)} \xrightarrow{heat} ZnO_{(s)} + CO_{2(g)}$.

ZnO

(ii) Zinc (II) hydroxide.

It appears as a white precipitate by addition of Zn^{2+} salts with a small amount sodium hydroxide or ammonia.

$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)}$

(iii) Zinc (II) Carbonate.

It appears as a white precipitate by addition of Zn^{2+} salts with sodium carbonate.

$Zn^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow ZnCO_{3(s)}$

Hydrated $ZnCl_2$

(iv) Zinc (II) Chloride.

It is a white deliquescent solid and is obtained by reaction of Zn & HCl.

$Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$

Note:

Zinc(II) salts appear colorless in solution. $[Zn(H_2O)_4]^{2+}$

1.11.4. Uses of zinc and its compounds.

Zn	It is used in the manufacture of alloys like brass and bronze and galvanizing of iron.

1.11.5. Qualitative analysis:

Reagents	Observation	Equation

(i)NaOH	A white precipitate soluble in excess alkali.	$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)}$ White precipitate. $Zn(OH)_2 + 2OH^-_{(aq)} \longrightarrow Zn[OH]_4^-{}_{aq)}$
(ii)NH_3	A white precipitate soluble in excess	$Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)}$ White precipitate. $Zn(OH)_{(s)} + 4NH_{3(aq)} \longrightarrow [Zn(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$
(iii)Na_2CO_3	A white precipitate.	$Zn^{2+}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \longrightarrow ZnCO_{3(s)}$
(iv) Potassium hexacyanoferrate(II) solution. (Potassium ferrocyanide solution). Observation: A white precipitate. $2Zn^{2+}_{(aq)} + [Fe(CN)_6]^{4-}_{(aq)} \longrightarrow Zn_2[Fe(CN)_6]_{(s)}$		

Exercise.1.k.

Multiple choice questions.

1. State what is observed when sodium hydroxide reacts with Zn^{2+} solution.

a. blue precipitate insoluble in excess. b. green precipitate soluble in excess.

c. white precipitate insoluble in excess d. white precipitate soluble in excess.

2. Identify the chief ore of zinc.

a.ZnO b. ZnS c. $ZnCl_2$ d. $ZnSO_4$

3. What is observed when zinc carbonate is heated strongly?

a. yellow residue b. brown residue c. black residue d. green residue.

4. What is observed when Zn^{2+} ions react ammonia dropwise till excess.

a. a blue precipitate insoluble excess. b. a green precipitate insoluble in excess.

c. a white precipitate soluble in excess. d. a white precipitate insoluble in excess.

***Structural questions*.**

1.a.i.Write the name and the formula of the ore of Zinc.

ii. Briefly explain how pure zinc is obtained from its ore above.

b.i. Name one reagent that can differentiate between zinc ions and Aluminium ions.

ii. What will be observed if the above ions are treated separately with reagent.

iii. Write down the equations of reaction.

Trial questions 1

Write true or false?

1. During extraction of copper the anode reduces in size…………………………………………………………

2. Copper (ii) sulphate reacts with ammonia drop wise till excess to give a dark blue solution…….

3. sodium dichromate reacts with sulphuric acid to give an orange solution………………………………

4. Sodium carbonate reacts with a solution of Cr^{3+} to give bubbles of a colourless gas……………….

5. Manganese metal undergoes collosion like iron……………………………………………………………………

Multiple choice questions.

1. Which of the following complex ions will form both optical and geometrical isomers.

a. $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ b. $[Ni(NH_2CH_2CH_2NH_2)_2Cl_2]$

c. $[Ni(H_2O)_4(OH)_2]$ d. $[NiCl_4]^{2-}$

Structured questions.

1. Cr (24) Mn(25) and Fe(26) are d block elements.

a. What is a d block element?

b. Explain why the atomic radii of three elements are similar.

c. Give three properties characteristic of transition elements, with examples from the three elements.

d. Write the electron configuration of Cr^{2+}, Mn^{3+} and Mn^{7+}.

2. Using equation briefly explain the following extraction (s)

a. Iron from haematite.

b. copper from copper pyrite.

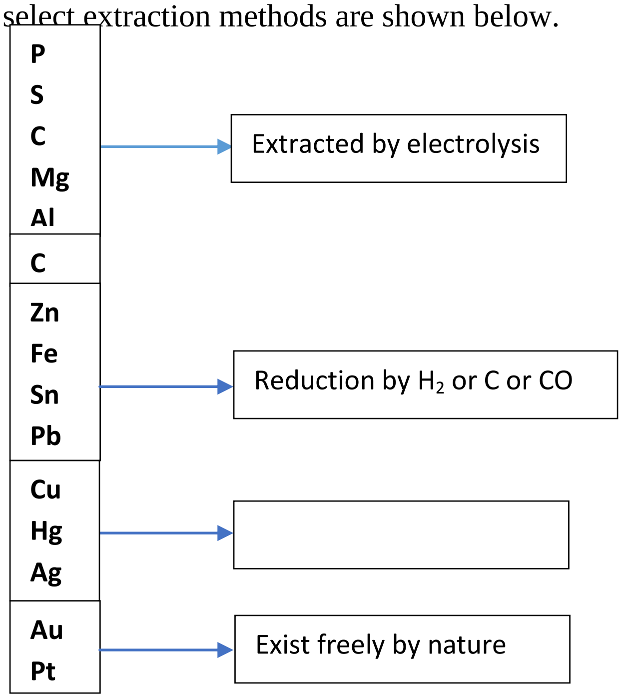
c. Zn from Zinc blende.

2.0. Extraction of metals.

Elements exist naturally as **minerals ores**. The unwanted impurities are called **gangue**.
An ore is a naturally occurring source of a metal that you can economically extract.
The process of extraction of pure metal from impure metal is called **metallurgy**.

2.1. Methods of extraction of a metal.

The method of extraction of metals depends on the number of factor's
These factors include
The reactivity of the metal.
The cost of raw materials.
Weather the metal is required in its most pure form or not.
Amount of energy required.
The effect the method has on the environment.
Health factors.
The quantity that can be made.
But the methods chosen normally depends on the reactivity series.
Some select extraction methods are shown below.



Methods of extraction of the metals.

1. Concentration or Dressing the ore.

Concentration means getting rid of as much of the unwanted rocky material as possible before the ore is converted to a metal.
NB:
It is also important to note that the methods of concentration are methods of extraction to some metals.
These methods of concentration or 'extraction' can be divided into:

A. Physical process.

I. **Mechanical sorting/ Hand picking.**

In this method we use man power to pick the unwanted materials from the ore.

II. **Magnetic separation.**

In this method the magnetic part of the crushed ore is separated from the non -metals or non-magnetic material using a strong magnet.

for example ◦ during extraction Fe from magnetite.

III. **Washing.**

In this method the ore is blasted with a stream of water which carries denser materials and the impurities (gangue) are left floating on the surface.

for example ◦ 1. during extraction Sn from cassiterite.

◦ 2. during extraction Pb from Galena.

IV.**Froth floatation.**

The crushed ore is mixed with water containing a frothing agent like pine oil.

Hot air is blown through the mixture at high pressure.

The earthly material sinks at the bottom and the ore particles combine with the oil to foam a froth which floats on top.

for example ◦ 1. during extraction zinc from zinc blende.

◦ 2. during extraction Pb from Galena.

B. Chemical process

I. **Calcination.**

It is the process of heating the ore in limited supply of oxygen below its melting point.

This process involves removal

-volatile impurities.

-removal of moisture.

-decomposition of carbonates. e.g $ZnCO_{3(s)} \rightarrow ZnO_{(s)} + CO_{2(g)}$

II. **Roasting.**

It is the process of heating the ore in excess supply of oxygen below its melting point.

This process involves removal

-volatile impurities.

-removal of moisture.

-impurities like S,P,As,C …..are removed in form of oxides.

-decomposition of sulphides. e.g. $2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$

III. **Smelting.**

In this process the ore is heated with in presence of an oxidizing agent or reducing agent above its melting point.

$CuO_{(s)} + C_{(s)} \rightarrow Cu_{(l)} + CO_{(g)}$

IV. **Leaching.**

Finely divided ore is treated with a reagent that dissolves in the ore but does not dissolve impurities.

e.g. During extraction of Al the crushed bauxite ore is dissolved in sodium hydroxide which dissolves Al_2O_3 but doesn't dissolve impurities like iron oxides.

V. **Solvent extraction.**Liquid -liquid extraction.

This method involves dissolving the crushed ore in a liquid to form a solution or melting it to liquid.

The resultant solution is shaken with another solvent or liquid in which the metal is more soluble.

This concentrates the ore.

2. Reduction.

I.**Reduction with carbonmonoxide or carbon.**

In this process the roasted ore is mixed with a suitable amount of coke and heated at temperatures above its melting point.

During this reaction an additional reagent like calcium carbonate is added to remove impurities by forming important slag.

e.g.

II. **Reduction with Al.**

Al reduces oxides of Mn and Cr during the extraction of the metals.

$3Mn_3O_{4(s)} + 8Al_{(s)} \rightarrow 4Al_2O_{3(s)} + 9Mn_{(l)}$
$Cr_2O_{3(s)} + 2Al_{(s)} \rightarrow 2Cr_{(l)} + Al_2O_{3(l)}$

III. **Auto reduction.**

Some metals are obtained from the ores by heating without a reducing agent. e.g Cu, Hg

$2Cu_2O_{(s)} + Cu_2S_{(s)} \rightarrow 6Cu_{(s)} + SO_{2(g)}$

3. Electrolysis.

This method extraction of highly reactive elements e.g group I & II elements.

like Na from molten NaCl. Mg from moltenMgCl$_2$.
Anode: $2Cl^- \rightarrow Cl_2 + 2e$ Anode: $2Cl^- \rightarrow Cl_2 + 2e$
Cathode: $Na^+ + e \rightarrow Na$ Cathode: $Mg^{2+} + 2e \rightarrow Mg$

4. Purification

i. Refining.

It is a method of purification where metals are heated beyond their melting point and they melt off and are collected off separating them from impurities.

e.g. Tin is separated from Cu, Fe

ii. electrolysis.

It is a method of purification used to separate impure substances from by carrying out of electrolysis process.

e.g. purification of Cu from impure Cu using copper sulphate.
purification of Zn from impure Zn using zinc sulphate.
purification of Sn from impure Sn using tin sulphate.

Exercise 2a

1.What is an ore?
2. What is the difference between an ore and a mineral?
3.When is carbon used for extraction?
4.Name a metal that could be extracted from its ore using carbon.
5.When is electrolysis used for extraction?
6.What do you understand with dressing of *ore, smelting, froth flotation* and *gangue*?
7.Name two metals that can only be extracted by electrolysis.
8.Suggest a reason why iron is extracted using carbon rather than by electrolysis.
9.State three factors which determine the choice of reduction method used for the extraction of metals from their ores.
10. Why is extraction of iron may be cheaper than extraction of Al.

2.2.0. Metals and how they are extracted.

Al Fe Cu Zn

2.2.1. Extraction of Sn.

Ores of tin.

Cassiterite**,**SnO_2.

Cassiterite. (gasegereti inKinyarwanda)
It is extracted in some regions such as: Rutongo, Rwinkwavu, Gatumba, etc

Properties of tin.

Methods of extraction of Sn from cassiterite.

a.Concentration.

i. Washing.

The mineral is mined from the ground and washed to remove the soil.

ii. Magnetic separation.

Magnetic impurities like wolframite ((Mn,Fe) WO_4) are removed during gravityseparation.

iii. Roasting.

The tin ore is roasted to remove impurities like As and S. Iron pyrites also changes to corresponding oxides and sulphates.

iv. Washing and leaching

The washed ore is treated with water and soluble $CuSO_4$ and $FeSO_4$ are washed away.

The lighter particles like iron oxides are also washed away leaving heavy ore particles containing 60-70% SnO_2 called black tin.

b. Reduction

Then the tin metal is extracted from cassiterite(SnO_2) by carbon reduction using a blast furnace.

$SnO_{2(s)} + C_{(s)} \rightarrow Sn_{(s)} + CO_{2(g)}$

In the furnace limestone is added to remove impurities like SiO_2.

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

$CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(s)}$

The tin produced is drawn into blocks of 99.5% of tin metal called block tin.

c. Purification.

If tin is required in its pure form it is purified by refining or electrolysis.

I.**Refining.**

It is purified by from Cu, Fe by heating beyond its melting point and will melt off at $232^{O}C$.

II.**Electrolysis.**

Tin can be purified by making impure tin as the anode and pure tin as the cathode using tin sulphate as the electrolyte.

Anode: $Sn_{(aq)} \rightarrow Sn^{2+} + 2e$

Cathode: $Sn^{2+} + 2e \rightarrow Sn$

Uses of tin

Electroplating iron and steel.

Making alloys like bronze (Sn,Cu) and solder(Sn, Pb).

Used for food packaging in tin cans mostly made of electroplated steel.

Used make corrosion resistant glass.

Exercise 2b

1.Give the ores of tin.

2.Tin metal is obtained by removing oxygen from the metal oxide.

i. What name do we give to this chemical reaction?

ii. Write down the equation of reaction.

3. Describe the refining method used to have much purer tin.

4. Explain why tin is said to be very useful.

5. State three properties and uses of tin.

2.2.2. Extraction of Na.

Sodium is extracted by the downs process using the **DOWN'S Cell**.

It involves electrolysis of molten sodium chloride.

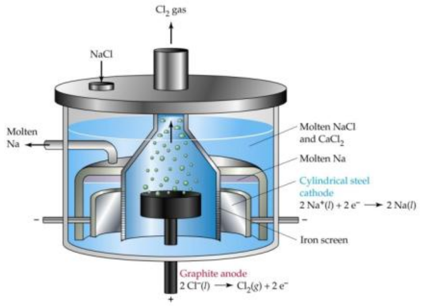
-The downs cell consists of a steel tank lined with fire bricks.

-The anode is a graphite rod.

-The cathode is an iron ring.

-The anode and the cathode are separated from each other using a cylinc

During electrolysis at the anode Chlorine is produced and at the cathode sodium is obtained.



Anode: $2Cl^- \rightarrow Cl_2 + 2e$

Cathode: $Na^+ + e \rightarrow Na$

Uses of Na

Na	Used as a *heat transfer coolant* in certain nuclear reactors because of its excellent heat conduction properties. The energized vapor is orange-yellow and used therefore used in *street lamps*. Used in electrical circuits for special applications.
$NaHCO_3$	

NaCl

Na_2CO_3

Exercise 2c

1. Discuss on the importance of sodium in Chemistry and in the everyday life.
2. Explain why sodium metal does not occur in Free State.
3. Why is sodium not extracted by carbon reduction process? What is the method used?
4. What difficulties arise in the extraction of sodium from its ore?
5. Using equations, briefly explain the process of extraction of sodium metal.

2.2.3. Extraction of Wolfram(tungsten).

Ores

Wolframite [$(Fe,Mn)WO_4$]

Scheelite.$CaWO_4$

Ferberite. $FeWO_4$

Properties

-dull silver

Highest melting point of 3410°C among metals.

More resistant to fracturing than diamond.

It with stands high temperature.i.e.refractory metal.

Harder than steel.

Methods of extraction.

Concentration.

Dissolve in NaOH or Na_2CO_3 in wolframite and scheelite to form sodium tungstate.

Sodium tungstate is then purified by precipitation and filtration.

It is converted to ammonium tungstate solution by solvent extraction and ion exchange resins.

The solution is then crystalized to produce high purity Ammonium paratungstate (APT).

Reduction.

APT can be heated with hydrogen to form tungsten oxide(WO_3).

Powdered WO_3 is heated with hydrogen at 550-850°C in absence of air to avoid explosion risks.

$WO_3 + 3H_2 \rightarrow W + 3H_2O$

NB: W is not reduced by carbon because carbon reacts with W to a carbide.

Uses of tungsten

Tungsten is light bulb filaments.

Tungsten alloys are used in arc welding and as heating elements.

Tungsten carbide is used as an excellent drilling and cutting tools-with new painless dental drill

Used as electrodes, wires, sheets, rods.

Used in microwaves, x-ray tubes, cathode ray tube in computers and TVs, thermocouples.

Exercise 2d

1. Nowadays, there is a special reduction method used to extract Tungsten from its ores.

a. State 2 main ores of tungsten.

b. Write the balanced equation of the reduction reaction of tungsten (Iv) oxide.

2. Suggest the reason why ore concentrating plants are always located in close proximity to the mine.
3. Give 2 widely known physical properties of tungsten and the uses associated to these properties.
4. How wolfram extraction differs from that of zinc in terms of reduction.

2.2.4. Extraction of Tantalum.

Tantalum

Properties

It is hard heavy shinny -grayish- blue metal.

It is very stable ad has a high melting point of 3000°C.

It is found in Rwanda. D.R.C and Brazil, China.

Ores

Pyrochlore
Samarskite. Contains seven metals.
Tantalite[Fe,Mn)$(Ta,Nb)_2O_6$)

Manufacture

It is mined, blasted and crushed**.**

Slurry is a watery mixture of insoluble matter.

Concentration.

Magnetic separation.

It is concentrated through the electromagnetic process to increase the percentage of tantalum oxide and nobium**.**

Leaching.

The concentrate is treated with HF and H_2SO_4 at high temperatures.
This causes the tantalum and niobium to dissolve as fluorides -numerous impurities also dissolve to form a concentrate.
The concentrate is broken down into slurry.

Solvent extraction.

The mixture is filtered and processed by solvent extraction using methyl isobutyl ketone or by liquid ion exchange using amine extractant in kerosene's.

Reduction.

In this way tantalum (iv) oxide is obtained and reduced by Na to tantalum in powder form.

Uses of tantalum

Used to make capacitors, vacuum furnace, filaments, computers, nuclear reactors, surgical appliances, ignite chips in cars, cutting tools, dill bits, teeth drills, bullets, heat shields.
It use evaporate other metals.

Test your understanding.

a. Give 3 uses of tantalum.
b.What is the role of methyl isobutyl ketone (MIBK) in tantalum processing?

2.3.1.Problems associated with extraction of metalsand their possible solutions.

1. Injuries

Metal extraction industry has a higher rate of injuries than most other industries. Sources of these injuries include: splattering and spills of molten metal and slag resulting in burns; gas explosionsand explosions from contact of molten metal with water, falls of heavy objects.

PRECAUTIONS

Adequate training, good storage, housekeeping and equipment maintenance.
Appropriate personal protective equipment (PPE) e.g. hard hats, safety shoes, work gloves and protective clothing.,
Traffic rules for moving equipment like defined routes and an effective signal and warning system.

2. Heat illnesses.

Heat stress illnesses such as heat stroke are a common hazard, primarily due to infrared radiation from furnaces and molten metal.

PRECAUTIONS

Water screens or air curtains in front of furnaces, spot cooling, enclosed air-conditioned booths, heat-protective clothing and air-cooled suits, work breaks in cool areas and an adequate supply of beverages for frequent drinking.

3. Pollutions

Mining operations are major contributors to the pollution of our environment such as: air pollution, water pollution, land pollution, etc.

The carbon dioxide released has more dangers especially the global warming because it is a green house gas.
Acid gases released in atmosphere such as SO_2, SO_3, NO_x are sources of acid rains.

PRECAUTIONS

Dust and fume emissions can be controlled by enclosure, automation of processes, local and dilution exhaust ventilation, wetting down of materials, reduced handling of materials and other process changes. Where these are not adequate, respiratory protection would be needed.

4. Noise.

High noise levels from crushing and grinding ore, gas discharge blowers and high-power electric furnaces can cause hearing loss.

PRECAUTIONS

If the source of the noise cannot be enclosed or isolated, then hearing protectors should be worn. A hearing conservation program including audiometric testing and training should be instituted.

5. Electrical hazards can occur during electrolytic processes.

PRECAUTIONS

Proper electrical maintenance with lockout/tagout procedures; insulated gloves, clothing and tools; and ground fault circuit interrupters where needed.

Trial questions 2

Multiple choice questions.

1. Choose the suitable answer. In sodium extraction, fused (molten) NaCl is used rather than the dissolved (aqueous) NaCl because:
a. Obtaining molten NaCl is easy than obtaining aqueous NaCl.
b. In molten NaCl, the ions are free to move and not in aqueous NaCl.
c. Molten sodium NaCl is an electrolyte and not the aqueous NaCl.
d. Electrolysis of molten NaCl gives Na metal at the cathode but that of aqueous NaCl gives H_2 gas.
2. During extraction of Zn. Zinc is purified by electrolysis, Which of the following is the best electrolyte for the process.
a. $ZnCO_3$ b. $Zn(OH)_2$ c. $ZnSO_4$ d. ZnO
3. Which of the following elements can not be obtained by reduction using carbon.
a. W b. Ta c. Cu d. Zn
4.Which metal is extracted from Bauxite.
a. Tin b. Tantalum c. Copper d. Aluminum
5. Brass is
a. An Element b. A Compound c. A Mixture d. An Alloy
6. Bronze is an alloy of
a. Copper and Zinc b. Lead and Copper c. Copper and Tin d. Barium, Zinc and Iron
7. Which of the following metals is often found in pure state?
a. Copper b. Iron c. Gold d. Aluminum
8. Which metal is extracted from Haematite?
a. Tin b. Iron c. Manganese d. Cadmium
9. Rocks rich in metals with economic value are known as
a. Metalloids b. Ores c. Allotropes d. slag
10. An alloy is a
a. Compound of three elements. b. Solid Solution of two or more metals
c. Heterogeneous mixture. d. Element in impure form
11.If a metal ore is called "pyrites" then it most probably has
a. Chlorine b. Oxygen c. Sulphur d. Nitrogen
12. Often to prevent corrosion, metals are galvanized by covering them with a layer of
a. Copper b. Sodium c. Zinc d.Tin
13. What is not true about Tantalum?
a. It is classified as a "refractory" metal
b. Tantalum oxide is reduced with molten sodium to produce tantalum metal in powder form.
c. Its ore minerals include scheelite
d.It is found in hard rock deposits such as *granites*, *carbonites* and *pegmatites*

Structural questions

1.a. By giving reagents and conditions, state two different methods of extracting metals starting from their oxides. In each case, write equation(s) to illustrate the extraction of an appropriate metal.
b.i. Why are metals more usually extracted from their oxides rather than from any other compound?

ii. State two environmental problems associated with the extraction of metals from their oxides or sulphides and give the chemical responsible for each problem.
2. a. Draw the diagram used in electrolysis during extraction of aluminium
b Write the equations that occur at the anode and carthode
C. Explain why the following are used during extraction
i. cryolite
ii. NaOH.
iii. CO_2.
iv. anode is replaced in intervals.
3.a. Give the ores of iron.
b. Explain the extraction of iron from its ores.
4. Copper is a widely used metal. The main ore of copper contains copper sulphide.
Copper can be extracted from copper sulfide in a three-stage process.
a. In the first stage of extraction the copper sulfide is heated in air.
i. Write down a balanced equation for reaction.
ii. Explain the environmental problem caused by the above reaction.
b. In the second stage copper oxide, CuO, is reduced using carbon.
Describe and explain what happens during this reaction.
c. During the third stage the copper can be purified.
i. What is the name of the type of process used for this purification?
ii. Write down the equation(s) for reaction.
iii. Draw the diagram for the process.
iv. Give one use of purified copper.
d. Copper-rich ores are running out. New ways of extracting copper from low grade ores are being researched. Recycling of copper may be better than extracting copper from its ores. Explain why.
5.a. Give 2 or 3 uses of aluminium, copper, zinc, and iron.
b.Give two reasons why the extraction of aluminium is expensive.
c. Zinc and copper are also extracted in the same way as iron (in blast furnace) but exist as their sulphide ores.
i. How is the sulphide ore converted into an oxide and what is the problem with this process?
(give an equation)
ii. Why can aluminium not be extracted in this way?
iii. Why can tungsten not be extracted in this way? (give an equation
6.Tungsten is prepared in a pure form by high temperature reduction of tungsten (VI) oxide with hydrogen.
a. Construct an equation for this reaction.
b. Suggest why carbon is not used as the reducing agent.
c. Suggest one advantage (other than purity of the product) and one disadvantage of using hydrogen as the reducing agent on an industrial scale

3.0. FERTILISER.

A Fertilizer is any material that is used to supply nutrients to the soil.

3.1.Components of a good fertilizer.

The nutrients of plants are classified into three types namely:

a. Major nutrients.
b. Secondary nutrients
c. Micronutrients

a.Major nutrients

The major nutrients for soil are nitrogen (N), phosphorus (P), and potassium (K).

Role of nutrients N, P, K

N- Stimulates plant growth, Synthesis of proteins and chlorophyll.

P-Promotes early growth, maturity, growth of roots, flowers, fruits and seeds.

It increase resistance to disease and frost.

K- Formation of flowers and fruits, production of sugars, regulates the structures of leaves.

Also, large amounts of limestone($CaCO_3$) isapplied to acidic soils reduce acidity.

b.Secondary nutrients

These include calcium (Ca), magnesium (Mg), and Sulphur (S).

c.Micronutrients

Micronutrients are those elements essential for plant growth which are needed but in only very small (micro) quantities.

These elements are also called **minor** elements or **trace** elements.

These include are boron (B), copper (Cu), iron (Fe), chlorine (Cl), manganese (Mn), molybdenum (Mo) and zinc (Zn).

Recycling organic matter such as grass clippings and tree leaves is an excellent way of providing micro nutrients to growing plants.

3.2.Characteristics of a good fertilizer

A good fertilizer should have the following characteristics:

It should contain the required nutrients, in such a form that they can be assimilated by the plants.
It should be cheap.
It should be soluble in water.
It should be stable, so that it may be available for a long time for the growing plant.
It should not be injurious to the plants.
It should be able to correct the acidity of the soil.

3.3. Types of fertilizers

1. Natural fertilizers or organic fertilizers

These are fertilizers that come from compounds that occur in nature.

They are made from remains of dead plants, wastes from animals or they can be minerals.

Examples of organic fertilizers or manures include.

Farmyard manure: animal manure that consists of feaces.

*Green manure:*plants turned into the soil to improve its overall quality.

*Compost manure:*is organic matter that has been decomposed and recycled as a fertilizer.

*Minerals:*powdered limestone, rock phosphate and sodium nitrate, are inorganic (not of biologic origin) compounds which are energetically intensive to harvest and are approved for usage in organic agriculture in minimal amount.

Advatanges / disadvatanges of use of organic fertilzers

The use of organic fertilizer may have many advantages but also it may have some disadvantages

Advantages

i.They add humus to the soil.
ii.They favours growth of soil organisms.
iii.The release of nutrients is slow and consistent at a natural rate that plants are able use.
iv.They provide a wide range of trace minerals.

v.They do not burn plants.
vi. They are long lasting and do not leach.
vii. It is easier to maintain that level, once a healthy soil condition is reached.
viii. They promotecontrolled growth of plants.

Disadvantages.

i.They produce inconsistent results.
ii.They have low levels of nutrients.
iii.They take a lot of time to prepare.
iv. Cause growth of pests.

2. Artificial or inorganic fertilizers

They are fertilizers which are chemically synthesized. e.g.
Nitrogenous fertilizers. e.g. ammonium sulphate.
Phosphorous fertilizers. e.g.calcium dihydrogen phosphate nitrate
Potassium fertilizers. e.g. Potassium chloride.
Some are mixed
NP fertilisers: e.g.Ammonium dihydrogen phosphate, $(NH_4)(H_2PO_4)$
- calcium dihydrogen phosphate nitrate, $Ca(H_2PO_4)_2 \bullet 2Ca(NO_3)_2$
PK fertilisers:e.g. a mixture of $Ca(H_2PO_4)_2 \bullet 2H_2O$ and K_2SO_4.
KN fertiliser: e.g. KNO_3
NPK fertilisers:e.g. A mixture of $(NH_4)_2SO_4$ (N-type fertiliser), $Ca(H_2PO4)_2.H_2O$(P-type fertiliser), and K_2SO_4(K-type fertiliser).

soil acidity may also be caused by acidic rain.

Advantages / disadvantages of use of inorganic fertilizer

The use of inorganic fertilizers may have many advantages but also it may have some disadvantages.

Advantage

i. They consist of specific nutrientsdesigned to stimulate plant growth.
ii. They predictability and reliability.
iii. Formulations are blended with accuracy.

Disadvantages.

i. They can burn plants
ii. They require a specific timetable of application and watering because of fast release of nutrients.
iii. Increased nitrate levels increase the risks of blue baby syndrome.
iv. Another hazard of chemical fertilizers is that carcinogenic nitrosoamines(yellow oil substance) may be formed in the human digestive track.
v. Repeated use or excess use of the same fertilizer producing acidic ions (NH_4^+). e.g. $(NH_4)_2SO_4$.
vi.Repeated use or excess use of the same fertilizer producing basic ions. e.g. $CaCO_3$.
vii. Excess use of chemical fertilizers causes **eutrophication.**

Eutrophication:

Excessive richness of nutrients in a lake or other body of water frequently dueto run off from the land.
When lake water is enriched with nutrients (e.g.: nitrates and phosphates), algal flourish, and produce an algae bloom, a green scum with an unpleasant smell.
This cuts the oxygen supply leading to death of fish.
Eutrophication can be caused by either of the fertilisers (organic or inorganic), but it is more likely to happen for inorganic fertilizers.
It is also caused excess use detergents.

Exercise 3a

1. Ammonia itself can be used as a fertilizer but has some disadvantages.
Explain the disadvantages of using ammonia as a fertiliser.

2. Which of the following is a better fertilizer? KNO_3 or NH_4NO_3
Give a reason why?

3.Give any two advantages of the use of
a. Natural fertilisers.
b. Artificial fertilisers.

4. Give any two causes of acidic soils?

3.4. Manufacture of fertilizers.

I. Nitrogenous fertilisers: N-type fertilisers.

These fertilisers supply only nitrogen as a major nutrient to the soil. Examples: ammonium sulphate, urea, sodium nitrate (also called chile saltpeter or chilenitre).

a. Ammonium sulphate.

The manufacture of ammonium sulphate is done by reacting ammonia gas with concentrated (60%) sulphuric acid:

$2NH_3(g)+H_2SO_4(aq)\rightarrow \mathbf{(NH_4)_2SO_4}(s)$

b. Ammonium nitrate

The manufacture of ammonium nitrate is done by:

Passing NH_3 gas into 60% HNO_3

$2NH_3 + HNO_3 \rightarrow NH_4NO_3$

Ammonium nitrate is sold as a mixture of calcium carbonate and ammonium nitrate (NH_4NO_3&$CaCO_3$): Calcium ammonium nitrate (nitro-chalk).

c. Urea

Urea is an organic compound used as a fertiliser.

$NH_4^+ CNO^-_{(aq)}\rightarrow H_2N\text{-}CO\text{-}NH_2$(Urea)

Or $Cl\text{-}CO\text{-}Cl+4NH_3 \rightarrow H_2N\text{-}CO\text{-}NH_2+2NH_4Cl$

Or $2NH_3 + CO_2 \rightarrow H_2NCOONH_4 \rightarrow H_2NCONH_2$ (Urea)+ H_2O

Urea is a crystalline solid which melt at 133 °C.
The solid readily dissolves in water.

II. Potassium fertilisers: (K-type fertilisers)

These fertilisers supply only potassium as a major nutrient to the soil. Examples: potassiumchloride, potassiumsulphate.

a.Potassiumsulphate.

It can also be made by heating potassium chloride with concentrated sulphuric acid: $2KCl(s)+ H_2SO_4(conc.)\rightarrow K_2SO_4(s) + 2HCl(g)$

III.Phosphate fertilisers.

Are fertilisers which supply phosphorus as a major nutrient to the soil.

Examples: Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2\cdot H_2O$

Calcium phosphate, $Ca_3(PO_4)_2$, commonly known as rock phosphate or phosphorite.

which are sparingly soluble in water and hence are not able to supply phosphorus to the plants. These minerals are, therefore, converted into soluble materials, by reacting them with phosphoric acid, or sulphuric acid or nitric acid to form as superphosphates, triple superphosphates and nitrophosphosphates.

i. Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2\cdot H_2O$

This compound is prepared in laboratory by dissolving $Ca_3(PO_4)_2$ or $Ca(HPO_4)$ in aqueous solution of H_3PO_4 and evaporating the resulting solution.

$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$

$Ca(OH)_2 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2+ H_2O$

$CaCO_3 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2+ H_2O + CO_2$

ii.Calcium dihydrogen phosphatesulphate, $Ca(H_2PO_4)_2 .2CaSO_4.2H_2O$

(superphosphates of lime or calcium superphosphate)

It is a mixture $Ca(H_2PO_4)_2.2H_2O$ and $CaSO_4.2H_2O$.

It is obtained by treating calcium phosphate**,** $Ca_3(PO_4)_2$ like bone ash with sulphuric acid.

$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4$

iii.Calcium dihydrogen phosphatesulphate nitrate. $Ca(H_2PO_4)_2.2Ca(NO_3)_2$

(calcium superphosphate nitrate or nitrophosphate)

It is a salt containing one molecule of $Ca(H_2PO_4)_2$ and two molecules of 2 $Ca(NO_3)_2$.

It is obtained by treating calcium phosphate**,** $Ca_3(PO_4)_2$ with nitric acid.

$Ca_3(PO_4)_2 + 4HNO_3 \rightarrow Ca(H_2PO_4)_2 + 2Ca(NO_3)_2$

iv. Diammonium hydrogen phosphate, $(NH_4)_2(HPO_4)$

Diammonium hydrogen phosphate is prepared by neutralizing phosphoric (V) acid by excess ammonia. This fertiliser supplies both phosphorus and nitrogen to the soil.

$3NH_3 + H_3PO_{4(aq)} \rightarrow (NH_4)_2(HPO_4)$

3.5. Dangers of substandard fertilizers.

A **sub-standard fertilizer**is a fertilizer which does not conform to the required NPK ratio.A fertilizer may be labelled 16-00-00, while the real NPK ratio isfor example 25-00-00, 10-00-05.

Using these fertilizers can lead to:

i. Soil pollution (basic soil or acidic soil) due to accumulation of ions which are acidic or basic
ii. Poor growth of plants
iii. Poor harvest
iv. Eutrophication
v. Fertilizer burn: leaf scorch resulting from over-fertilization

In order to reduce the effects of substandard fertilizers different measure can be taken;

a. Standardization of the fertilizer before use.
b. Production of fertilizers in Rwanda, as this will help us to choose good minerals(where necessary) in producing fertilizers.
c. Use of chemical fertilizers with coated pellets so that nutrients are released slowly
d. Regular watering.
e.use organic fertilizers
f. burn substandard fertilizers.
g. Teach farmers the use fertilzers.

Exercise.3.

Multiple choice questions.

1.If nitrogen is the main element of fertilisers then fertilisers are classified as
a. NPK fertilisers. b. organic fertilisers. c. Nitrogen fertilisers. d. inorganic fertilisers.
2.Increased ratio of chemical nutrients in ecosystem is classified as watses
a. Triplication b. Eutrophication c. Crystallization d. Distillation
3.Greenhouse gas which can be emitted from storage of nitrogen based fertilisers is
a. Nitrogen monoxide b. Nitrogen dioxide c. Oxygen d. carbondioxide
4.Organic fertilisers can be derived from
a. Animal wastses b. All natural materials. c. plant and animal materials d. plants material only.
5. Which of the following elements is a trace element
a. Ca b. N c. Fe d. Mg.
6. Which of the following compounds a good source of phosphorous for plants.
a. $Ca_3(PO_4)_2$ b. H_3PO_4 c. $Ca_2(HPO_4)$ d. $CaSO_4$
7. Find by calculation, the best source of nitrogen.
a. Sodium nitrate. b. ammonium nitrate

c. ammonium sulphate. d. urea (CH_4N_2O).

8. An (1g) impure sample of ammomiumsulphate was boiled with aqueous sodium hydroxide. The ammonia evolved was nuetraliled by 30cm^3 of 0.1 mol dm^{-3}hydrochloric acid.

Calculate the percentage by mass of nitrogen in the sample of the salt. (N=14).

a. 5.1% b.3.2% c. 4.2% d.6%

Structural questions.

1. The chemical plant for manufacturing ammonia is often on the same site as plantsmanufacturing nitric acid and fertilisers.

a. What advantages will this have for the manufacturing company?

b. Using equation(s) show how ammonium nitrate is obtained from nitrogen gas.

c. i. Describe the environmental impact of such plants on the surrounding area.

ii. Give two ways in which such impact can be reduced

2. Sulphuric acid reacts with ammonia to give ammonium sulphate

a.Write the balanced equation for that reaction

b. What property of ammonia is shown in this reaction?

c. Calculate the maximum mass of ammonium sulphate that can be obtained from 100 g of ammonia. [Ar: H, 1.0;N, 14.0; O, 16.0;S, 32.1)

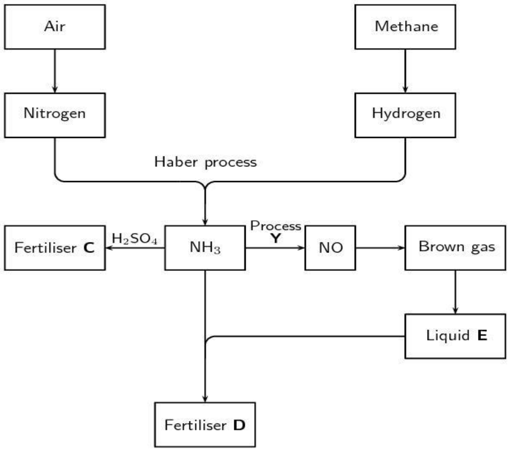
d. State the large scale use of ammonium sulphate.

3. A laboratory method of finding the percentage of ammonia in a fertiliser involves boiling the fertiliser with an excess of aqueous sodium hydroxide until no more ammonia is given off. The excess of sodium hydroxide is found by titration with standard hydrochloric acid.

a.Write an equation for the reaction between ammonium ions and hydroxide ions to give ammonia

b. Say how you could test for ammonia gas.

c. The flow diagram below shows the main steps in the industrial preparation of two importantsolid fertilisers.



4.a. Using advantages and disadvantages give the differences between the action of artificial and natural fetertilzers?

b. Explain the environment impact of excess use of fertilizers?

5. A fertilizer contains ammonium sulphate sample of 0.5g of fertilizer was warmed with sodium hydroxide solution. The ammonia evolved was absorbed in 100 cm^3 of 0.1mol dm^{-3} hydrochloric acid. The excess hydrochloric acid required 55.9cm^{3}of 0.1M sodium hydroxide for neutralization.

a. Write the equation for the reaction between

i. Sodium hydroxide and HCl acid

ii. Ammonium sulphate and sodium hydroxide

iii. Ammonia and HCl acid

b.Calculate

i.moles of base that reacted with excess HCl acid.

ii.total moles of the added HCl acid.

iii. moles of excess acid.
iv. moles of acid that reacted with ammonia.
v. mole of ammonia produced by the fertiliser
vi. moles of $(NH_4)_2SO_4$.
vii. mass of $(NH_4)_2SO_4$
viii. mass of N in the fertiliser
ix. percentage of N in the fertilizer

Experiment

Determination of the percentage by mass of N in$(NH_4)_2SO_4$

You provided with the following

A Solution prepared by mixing 1.0 g of a sample of ammonium sulphate fertilizer which were warmed with sodium hydroxide and the ammonia evolved was absorbed in 20 cm^{3}of 0.5moldm^{-3} sulphuric acid.

1M sodium hydroxide

Procedure

Fill the burette with solution of sodium hydroxide

Pipette 25 cm^3 of solutions of the prepared solution in (1), in conical flask. Add 2-3 drops of methyl orange indicator.

Titrate this solution with sodium hydroxide from the burette until the indicator changes colour (indicator changes from **pink** to **yellow**).

Record the results in the table.

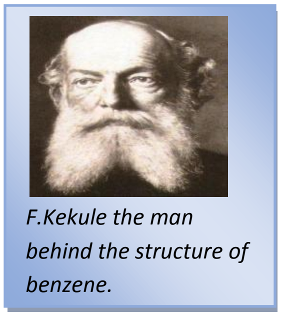
Volume of pipette used: ………………cm^3

ExP	1	2	3
Finalburette reading/cm^3			
Initial burette reading/cm^3			
Volume of NaOH/cm^3			

Questions

a.Titre values: ……………………………………………………….
b.Calculate the average volume of sodium hydroxide used:
c.Write the equation for the reaction between
i. sodium hydroxide and sulphuric acid.
ii. ammonium sulphate and sodium hydroxide.
iii. ammonia and sulphuric acid.
d.Calculate
i.moles of base that reacted with excess sulphuric acid.
ii.moles of excess sulphuric acid.
iii.total moles of the added sulphuric acid.
iv.moles of sulphuric acid that reacted with ammonia.
v. mole of ammonia produced by the fertilizer.
vi.moles of $(NH_4)_2SO_4$.
vii. mass of $(NH_4)_2SO_4$.
viii. mass of N in the fertilizer.
ix. Percentage of N in the fertilizer.

4.0. AROMATIC COMPOUNDS (ARENES)



F.Kekule the man behind the structure of benzene.

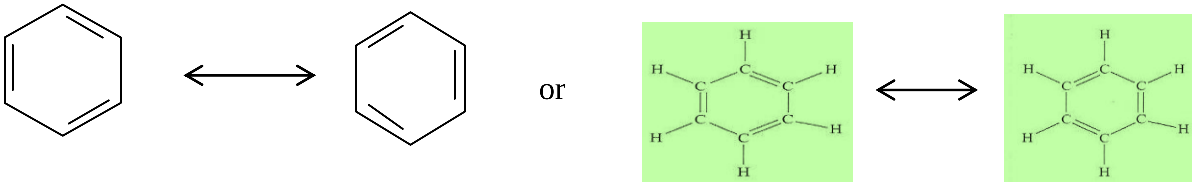
Aromatic compounds are compounds containing the benzene ring.

4.1. Benzene

Benzene is a simplest aromatic compound with molecular formular C_6H_6**.**

Structure of benzene

The structure of benzene was first suggested by Fedrick August kekule in 1865.
He suggested that benzene has two (2) isomeric form



kekule I kekule II

Today benzene has been discovered to have resonance structures.i.e. The three double bond in benzene are untrue, they actually delocalized.

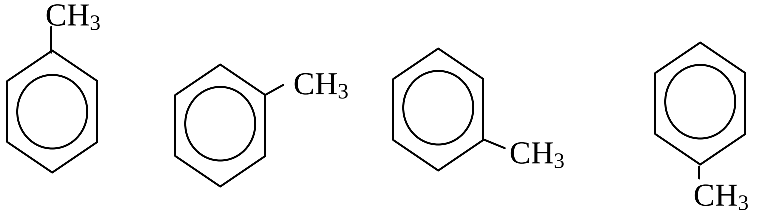
Proofs to show that double bonds in benzene are delocalized i.e they are not real double bonds.

1. Bond length.

Bonds	bond length in nm
C – C (alkane)	0.154
C$\overset{\cdots\cdots}{-}$C (benzene)	0139
C = C (alkene)	0.134

The carbon carbon bond length in benzene is between that of the alkenes and alkanes.

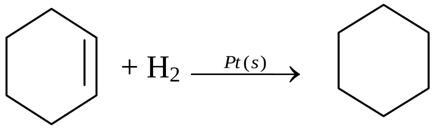
2. The monosubstituted compounds of in benzene show no isomerism



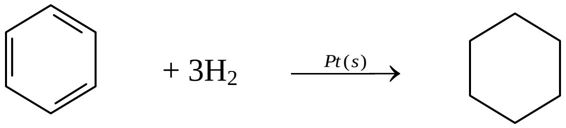
Methyl benzene.

3. Unlike alkenes benzene does not decolorize bromine water or acidified potassium permanganate.

4. Heat of hydrogenation.



$\Delta H = -119$ kJ/mol



$\Delta H = (-119 \times 3)$ kJ/mol

= -357 kJ/mol (calculated value)

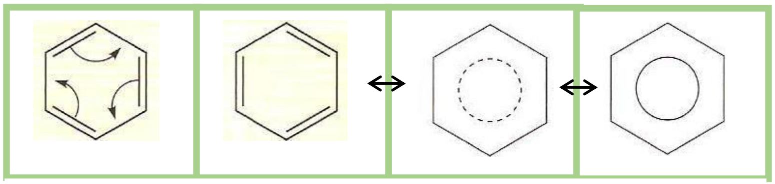
$\Delta H = -207$ kJ/mol (experimental value)

The difference between calculated values and experimental values of enthalpy of hydrogenation of benzene show that the double bonds in benzene are delocalized.

The delocalized electrons in benzene make benzene more stable hence having a higher enthalpy of hydrogenation than expected

Note:

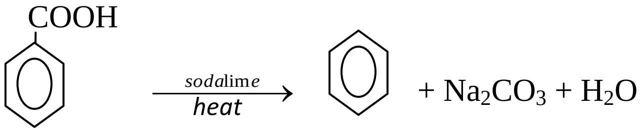
The above evidences show the failure of Kekule structures and today the double bonds in benzene are said to be delocalized.



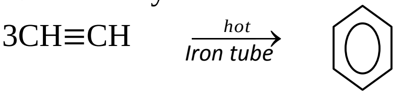
structures of benzene

Preparation of benzene

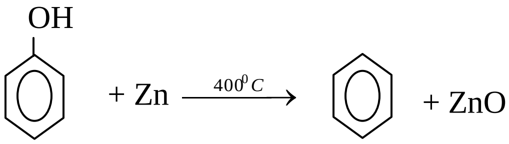
a. From benzoic ac id



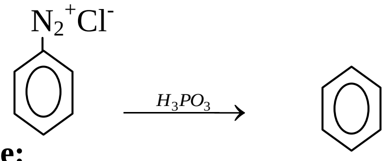
b. From ethyne



c. From phenol



d. From benzene diazonium chloride



Note:

Benzene is also be obtained by fractional distillation in crude oil and from coal.

Physical properties of benzene

Benzene is a colorless liquid with a sweet smell.

Benzene is immiscible with water but soluble in organic solvents.

Benzene has a melting point of 5.5°c and boiling point of 80°C.
However benzene is toxic and should be handled with care.
It is carcinogenic. i.e. causes cancer and anaemia.

Chemical properties of benzene

The chemical properties of benzene can be divided into

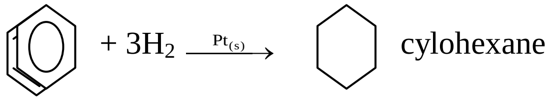
1. Addition reaction
2. Electrophilic substitution reaction.

1. Addition reaction.

It a reaction which involves combination of two or more molecules to form one compound

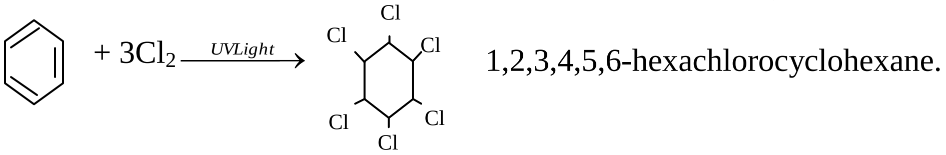
Addition reaction of benzene include.

a. Hydrogenation: Benzene undergoes hydrogenation in presence of catalysts.



b. Halogenation.

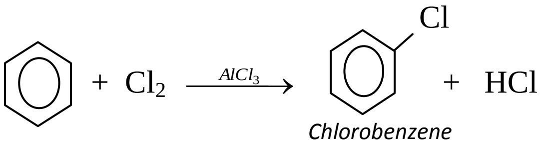
Benzene combines with Cl_2 or Br_2 in presence of ultraviolet lights

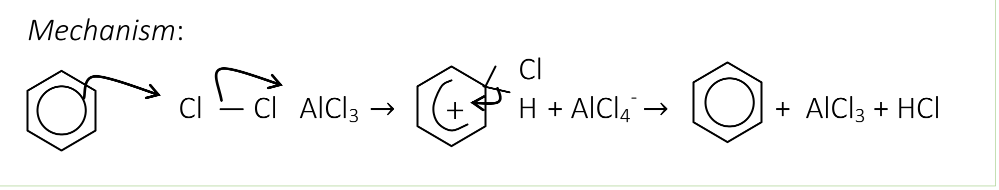


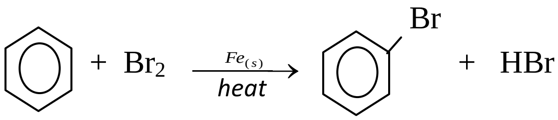
This reaction involves formation of free radicals

2. Electrophilic substitution reaction.

Electrophilie: it is positively charged electron seeking species.
Substitution reaction: a reaction that involves replacement of an atom or group of atoms.
Electrophilic substitution reaction: is a reaction in which a positively charged electron seeking species replaces an atom or group of atoms.
Benzene undergoes electropilic substitution reaction with its delocalized electrons.
Electrohilic substitution reaction of benzene nclude:
a. Hologenation.
Br_2 and Cl_2 react with benzene in the presence of a Friedel Crafts catalyst to produce holobenzenes.
Friedel crafts catalyst (lewis acid or halogen carriers) include $AlCl_3$; $FeCl_3$; $FeBr_3$

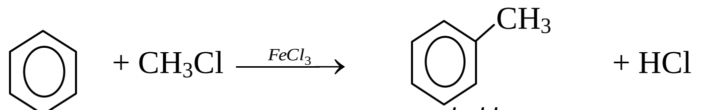






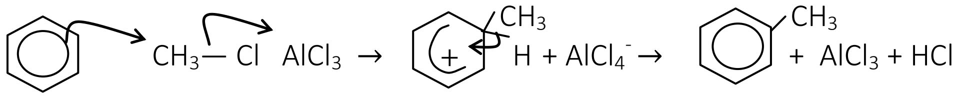
b. Alkylation of benzene.

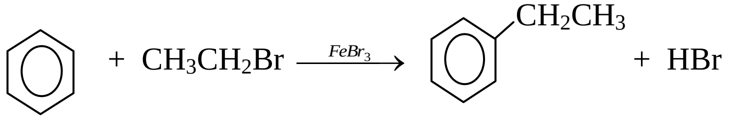
This reaction involves introducion of an alkyl group into the benzene ring. It takes place in the presence of friedel crafts catalysts and alkylhalides.



methyl benzene

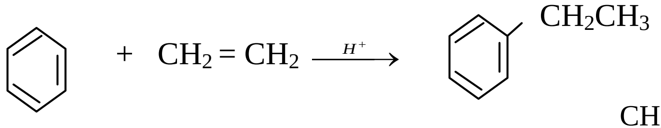
Mechanism:

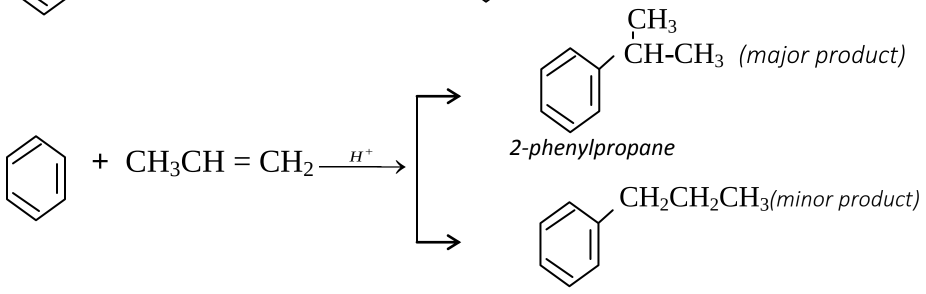




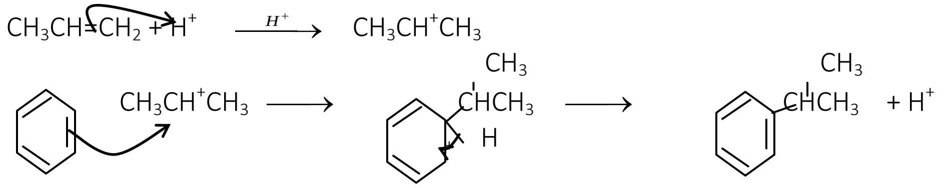
Note:

Alkylation of benzene also take place in the presence of alkenes and small amount of acid





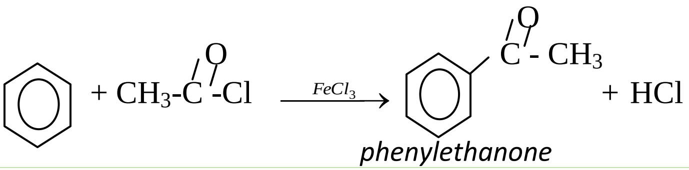
Mechanism:



c. Acylation of benzene

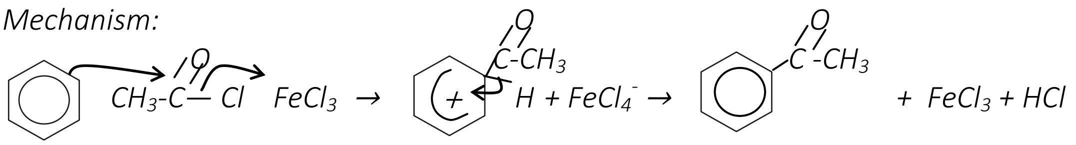
This reaction involves of introduction of the acyl group onto the benzene ring.

It takes place in a presence of acylchloride (acid chloride) and friedel crafts catalyst at 60°C.



phenylethanone

Mechanism:

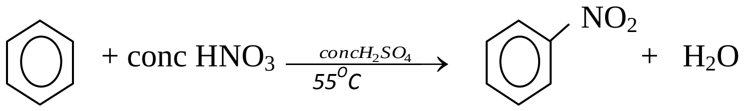


d. Nitration of benzene.

This involves introduction of the nitro group to the benzene ring.

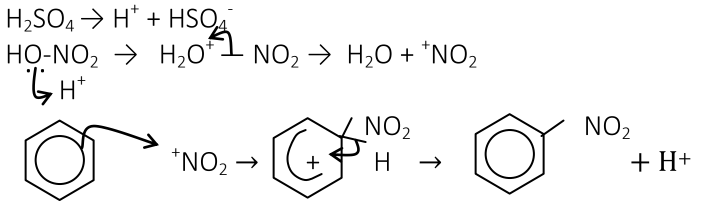
Reagent: concentrated nitric acid

Condition: heat 50–60°c; catalyst conc. H_2SO_4



nitrobenzene

Mechanism:



$H_2SO_4 \rightarrow H^+ + HSO_4^-$

$HO\text{-}NO_2 \rightarrow H_2O^+ - NO_2 \rightarrow H_2O + {}^+NO_2$

H^+

${}^+NO_2 \rightarrow$

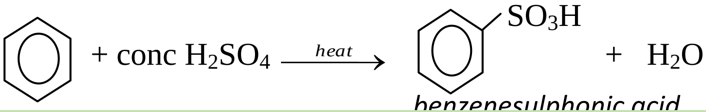
$H^+ + HSO_4^- \rightarrow H_2SO_4$

e. Sulphonation of benzene.

This involves introduction of a sulphonyl group into benzene ring

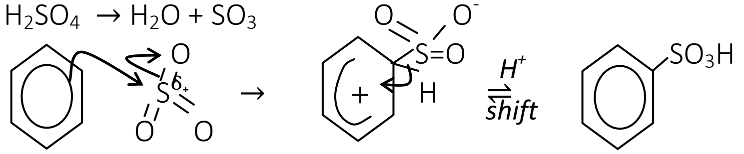
Reagent : fuming H_2SO_4 (conc H_2SO_4)

Condition: reflux (heat)



benzenesulphonic acid

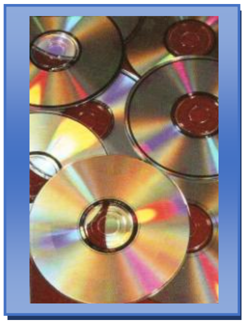
Mechanism:



$H_2SO_4 \rightarrow H_2O + SO_3$

Uses of benzene.

Benezene and its derivatives are used in the manufacture of explosives, CDs, drugs, dyes, plastics, detergents, insecticides.



Trial questions

Multiple choice questions.

1. Which of the following compounds does not decolorise acidified potassium permanganate

a. ethene b. cyclohexane c. benzene d. cyclohex-1,3-diene

2.Benzene undergoes which type of reaction with halogens in presence of a lewis acid.

a. Electrophilic addition reactions.

b. Electrophilic substitution reactions.

c. Nucleophilic addition reactions.

d. Nucleophilic substitution reactions.

3. Calculate the enthalpy of hydrogenation of benzene.

Given enthalpy of formations of benzene and cyclohexane as 49.04kJmol^{-1} and -156kJmol^{-1}

a. +205kJmol^{-1} b. -205kJmol^{-1} c. -107kJmol^{-1} d. 107kJmol^{-1}

4. Benzene reacts with propene to give two products. Identify the product which is the major product.

a. propylbenzene b. Isopropylbenzene. c. methylbenzene d.ethylbenzene

5.What is the hybridization of the ring atoms in an aromatic compound?

a. sp b.sp^2 c.sp^3d.sp^3d

6. How many pi and sigma bonds has benzene.

a. 12 α and 3π b. 6α and 2πc. 12α and 1π d. 6α and3 π

7.What kind of catalyst is essential for halogenation of aromatic compounds with Cl_2 or Br_2?

a. A Lewis acid b. A Lewis base b. a Brönsted acid d. a Brönsted base

8. Why do aromatic compounds undergo electrophilic substitution rather than electrophilic addition?

a. Formation of the substituted benzene is highly exergonic.

b. Aromatic compounds are not very stable.

c. The addition product is much less stable than the substitution product, since it is non-aromatic.

d. Aromatic compounds are not nucleophiles

Structural questions.

1. Given

Enthalpy change of atomization of carbon, C(s): +715kJmol^{-1}
Enthalpy change of atomization of hydrogen, H_2(g): + 218 kJmol^{-1}
Bond energy of C=C (average): +610kJmol^{-1}
Bond energy of C-C (average): +346kJmol^{-1}
Bond energy of C-H (average): +413kJmol^{-1}

a. Work out the enthalpy change of formation of gaseous benzene.

b. Compare your answer with experimental value of +82 kJ mol^{-1}.

Explain the differences in the answers

2. Explain the following observations.

a. The enthalpy of hydrogenation of cyclohexene is -119kJmol^{-1} and that of benzene is -207kJ mol^{-1}.

b. Cyclohexene decolourises bromine water but benzene does not.

3. a. A compound Y contains 47.3% carbon and 7.69% hydrogen. Determine the empirical formulare of Y.

b. B burns with a sooty flame and has a vapour density of 39.

Determine the molecular formula and structural formula of Y

c. Write equation and indicate the mechanism for reactions (include the conditions) when benzene reacts with.

i.nitric acid.

ii. ethanoyl chloride

iii. propene.

4. How can the following organic compounds be differentiated using reagents.

a. ethene and benzene

b. benzene and cyclohexene

5. The nitration of benzene is an important industrial reaction.

a. State the conditions required for the nitration of benzene using nitric acid.

b. Write a balanced equation for the nitration of benzene.

c. i**.** Outline the mechanism for the nitration of benzene.

ii. Explain what curly arrow means in this type of mechanism.

6. Carryout the following organic conversions.

a. ethane to benzene.

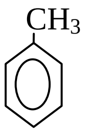
b. ethyne to methyl benzene.

c. benzoic acid to nitrobenzene.

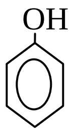
d. benzoic acid to bromobenzene.

7. Discuss the reactions of benzene with chlorine under different conditions. (include equations, names of products indicating the type of reaction)

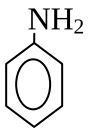
5.0. *Derivatives of benzene*



(1)



(2)



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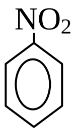

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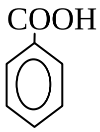

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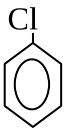


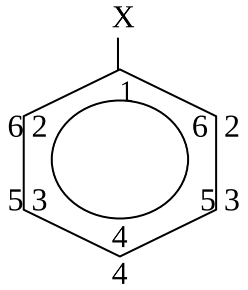
(6)

(1) Methylbenzene (toluene)
(2) Hydroxyl benzene (phenol)
(3) Aminobenzene/ phenyl amine (aniline)
(4) Nitro benzene
(5) Benzoic acid
(6) Chlorobenzene

NB:

When benzene has one substituent it affects the other position of carbon atoms.

Names of the positions



2 or 6 ortho position

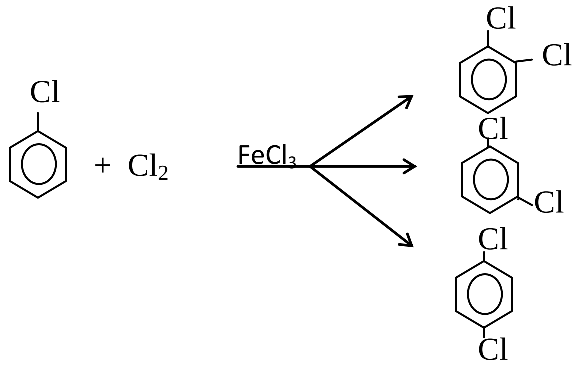
3,5 meta position

4 para position

The group attached to the benzene ring (substituent) either increases the reactivity of the benzene ring or decreases its reactivity.

On addition this group direct the other groups to specific positions of the benzene ring during electrophilic substitution reactions.

Effects of one substituent on electrophilic substitution reactions. E.g.

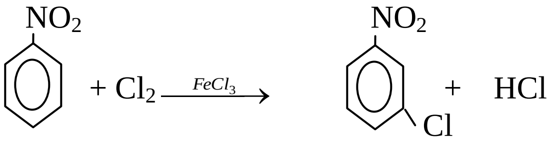


The major and minor compound in the above reactions can be deduced according to vorlander's rule.

1. If the substituent on the benzene ring is an electron withdrawing group or contains double or triple bond, the major product goes in the meta position of the benzene ring.

Examples of electron withdrawing groups. i.e . meta directing groups

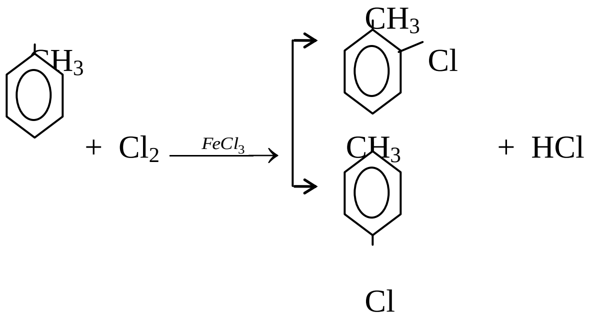
-NO_2; -COOH; -COH; -CO-CH_3; -SO_3H; -CN; -CH=CH_2



2. If the substituent is an electron donating group the major products go in either an ortho or para positions of the benzene ring.

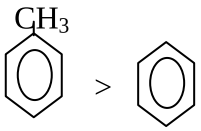
Examples of electron donating groups, ortho–para directing groups.

-CH_3; -NH_2; -OH; -OCH_3, - Cl,- Br, I

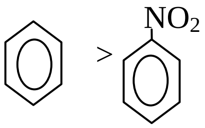


NB:

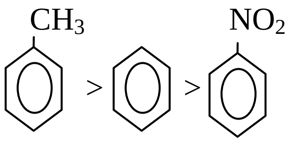
1**.** The presence of electron donating groups increases the reactivity of benzene ring.i.e.order of reactivity is.



2.The presence of electron withdrawing groupsdecreases the reactivity of the benzene ring. i.e order of reactivity.



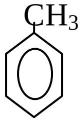
Therefore the following order of reactivity



5.2. *Methyl benzene (toluene)*

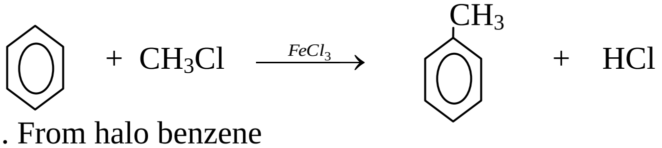
Molecular formula $C_6H_5CH_3$ or C_7H_8

Structural formula

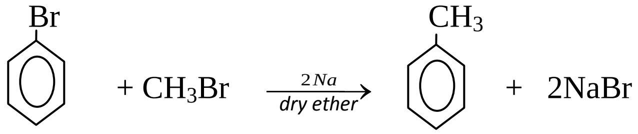


Preparation of methyl benzene

a. From benzene



b. From halo benzene



Physical properties of methyl benzene

Methyl benzene is a colorless liquid at room temperature.

It is insoluble in water but soluble in organic compound/solven and it is also a good organic solvent.

It has a boiling point of 19°C and melting point of -95°C.

> *Note:*
> *Benzene has higher melting point than methylbenzene because the planar molecules of benzene are packed more closely together in a crystal therefore stronger cohesive forces of attraction but the methyl group in methyl benzene prevents such close packing.*

Chemical properties of methyl benzene

The chemical reactions of methyl benzene are divided into:

1.Reactions of the benzene ring.

2. Reactions of the alkyl group.

1. Reaction of the benzene ring.

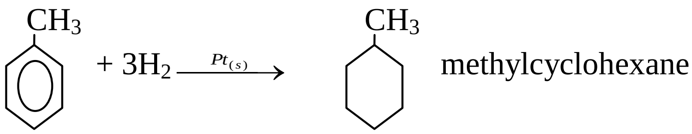
The reactions of benzene ring in methyl benzene are similar to the reactions of benzene and can also be divided into

a. Addition reaction.

b. Electrophilic substitution reaction.

a. Addition reaction

Hydrogenation of methyl benzene

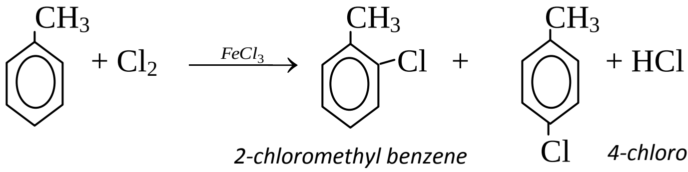


b. Electrophilic substitution reaction.

The electrophilic substitution reactions of methyl benzene are similar to those of benzene, however methylbenzene is more reactive because it possesses an electron donating methyl group.

In methylbenzene substitution is basically in the ortho and para positions. i.e. ortho-para directing or 2,4-directing.

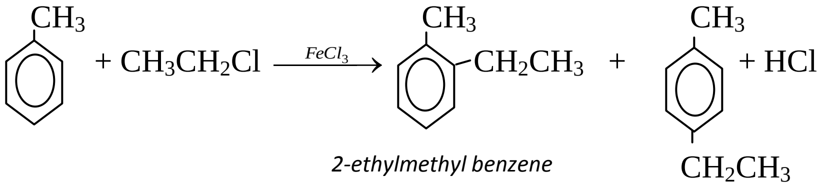
i. Halogenation of methyl benzene.



2-chloromethyl benzene *4-chloromethyl benzene*

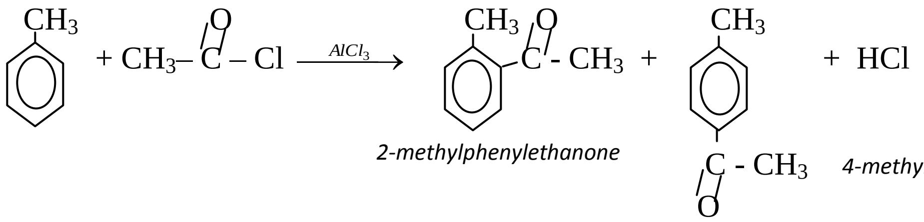
This reaction should takeplace in darkness.

ii. Alkylation of methyl benzene.



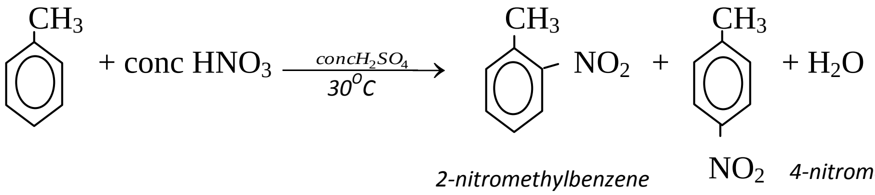
2-ethylmethyl benzene *4-ethylmethyl benzene*

iii. Acylation of methyl benzene



2-methylphenylethanone *4-methylphenylethanone*

iv. Nitration of methyl benzene.

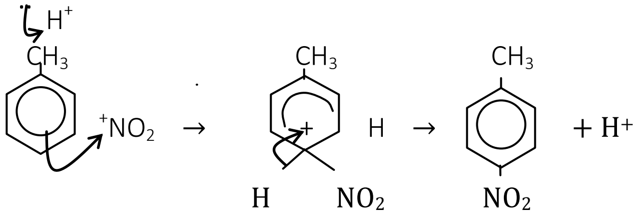


2-nitromethylbenzene *4-nitromethylbenzene*

Mechanism: para product

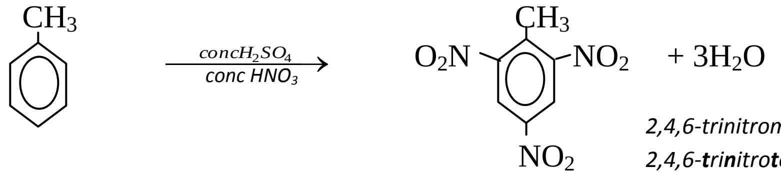
$H_2SO_4 \rightarrow H^+ + HSO_4^-$

$HO\text{-}NO_2 \rightarrow H_2O^+ + NO_2 \rightarrow H_2O + {}^+NO_2$



$H^+ + HSO_4^- \rightarrow H_2SO_4$

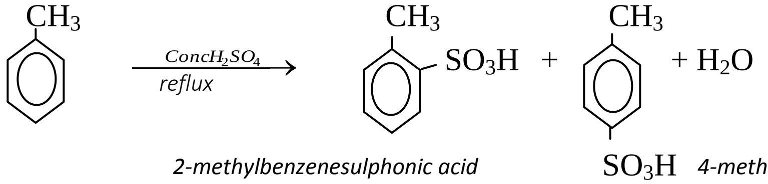
In presence of excess reagents and at higher temperature(50°C) , 2,4,6-trinitromethylbenzene is obtained.



2,4,6-trinitromethylbenzene or
*2,4,6-**t**ri**n**itro**t**oluene.(TNT)*

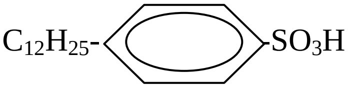
TNT acts as an explosive.

v. Sulphonation of methylbenzene



2-methylbenzenesulphonic acid *4-methylbenzensulphonic acid*

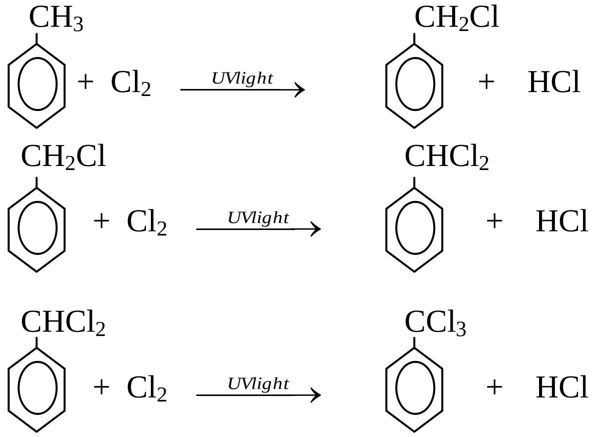
Note:
Long chain benzenesulphonic acid is applied during the manufacture of detergents. e.g.



2. Reactions of the methyl group.

a. Halogenation.

Methyl benzene reacts with halogens (Cl_2 or Br_2) in the presence of ultraviolet light (sun light). This reaction involves formation of free radicals.



Iike alkanes, this reaction undergoes a *free radical substitution reaction mechanism*.

mechanism:

All Alkylbenzenes are oxidized to benzoic acid whatever the length of the alkyl group.

Intiation:

$Br_2 \xrightarrow{UVlight} 2Br^{\cdot}$

propagation:

$C_6H_5CH_3 + Br^{\cdot} \longrightarrow C_6H_5CH_2^{\cdot} + HBr$

$C_6H_5CH_2^{\cdot} + Br_2 \longrightarrow C_6H_5CH_2Br + Br^{\cdot}$

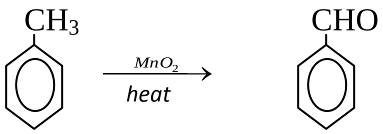
termination:

$C_6H_5CH_2^{\cdot} + Br^{\cdot} \longrightarrow C_6H_5CH_2Br$

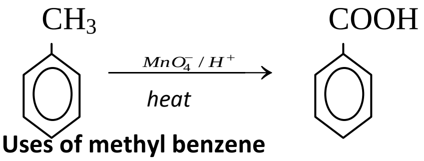
$Br^{\cdot} + Br^{\cdot} \longrightarrow Br_2$

b. Oxidation.

i. Methyl benzene reacts with manganese (iv) oxide or cromyl chloride (CrO_2Cl_2) to give benzaldehyde.



ii. Methyl benzene reacts with acidified potassium permanganate to give benzoic acid.



Uses of methyl benzene

-making explosives, organic solvents, detergents

Exercise 5a

1. An aromatic hydrocarbon D. C_7H_8 is converted into E. $C_9H_{10}O$, on treatment with ethanoyl chloride in the presence of $AlCl_3$. when treated with $NaBH_4$, it is converted in F, $C_9H_{12}O$. Compound G is formed when F is warmed with conc. H_2SO_4.

a. Identify the structure of D.

b. Give all possible isomers of E, F, G

c. Carry out a chemical test to identify the functional group in E, F and G.

2a. Methylbenzene reacts with chlorine to form 2-chloromethylbenzene. State the condition for the reaction.

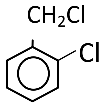
b. Under different conditions the product is phenylchloromethane instead of 2-chloromethylbenzene.

i. State the conditions for reaction

ii. Write the mechanism for reaction.

C. When a compound shown below reacts with aqueous sodium hydroxide, one of chlorine atom is replaced.

.



i. Draw the structure of the product of the reaction above.

ii. Explain the difference in the reactivity of the chlorine atoms.

3. Using equations carry out the following organic conversions.

a. benzene to benzoic acid.

b. Benzene to ethylbenzoate.

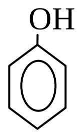
c. benzene to benzaldehyde.

4. Explain why methyl benzene is more reactive than benzene.

5.3. *Phenol (hydroxybenzene)*

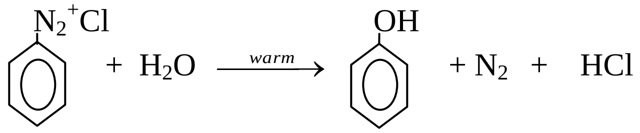
Molecular formula C_6H_5OH or C_6H_6O

Structural formula

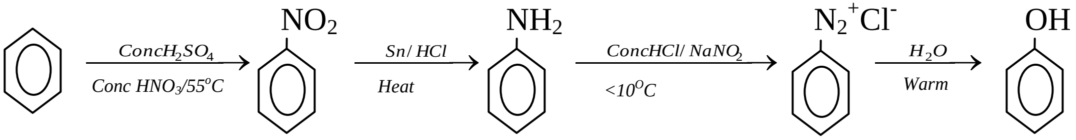


Preparation of phenol

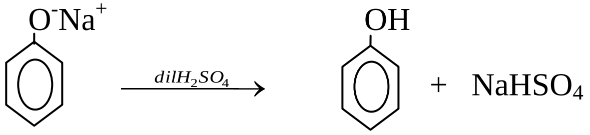
a. From benzene diazonium salt



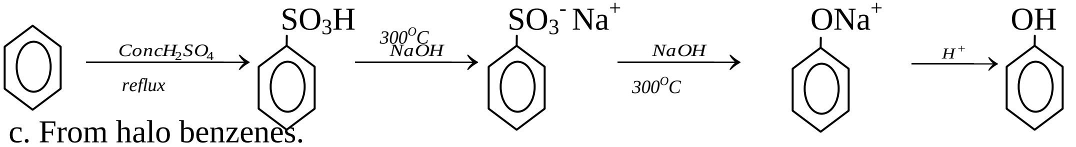
Phenol is obtained from benzene using the following reaction scheme.



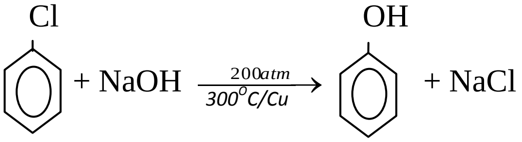
b. From from sodium phenoxide



Phenol is obtained from benzene using the following reaction scheme.



c. From halo benzenes.



Physical properties of phenol

Phenol is a colorless crystalline solid that obtains a red tint on exposure to air and sunlight.

Phenol has a characteristic smell.

It is almost soluble in water to give a solution called ***carbolic acid*** which acts as an antiseptic.

Phenol is readily soluble in organic solvents.

It has a boiling point of 182^oC and melting point of 43^oC.

Phenol is toxic and burns the skin therefore it should be handled with care.

Chemical properties of phenol

The chemical reactions of phenol are divided into

1.Reactions of the benzene ring.

2. Reactions of the hydroxyl group.

1. Reaction of the benzene ring.

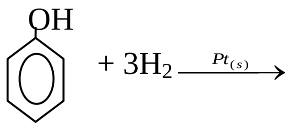
The reactions of benzene ring in phenol are similar to the reactions of benzene and can also be divided into

a. Addition reaction.

b. Electrophilic substitution reaction.

a. Addition reaction

Hydrogenation of phenol



cyclohexanol

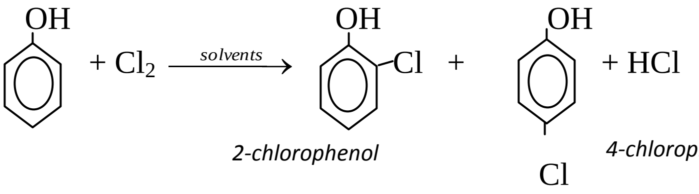
b. Electrophilic substitution reaction.

The electrophilic substitution reactions of phenol are similar to those of benzene, however phenol is more reactive because it possesses an electron activating hydroxyl group.

Like methyl benzene, in phenol substitution is basically in the ortho and para positions. i.e. ortho-para directing or 2,4-directing.

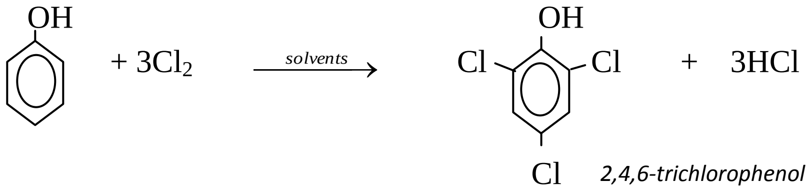
i. Halogenation of phenol

Phenol reacts with halogens (Br_2 and Cl_2) in presence of solvents.

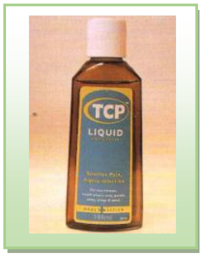


2-chlorophenol *4-chlorophenol*

In presence of excess reagents 2,4,6-trichorophenol is obtained.

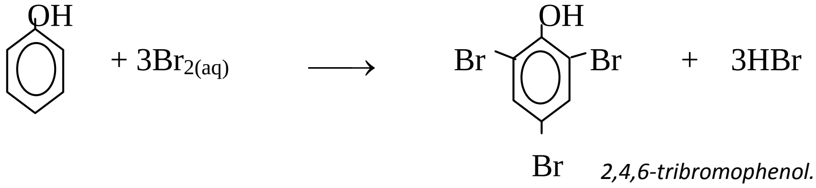


2,4,6-trichlorophenol(TCP)



TCP is used as an antiseptic. It is an additive in soap especially dettol.

Phenol reacts with bromine water to give a 2,4,6-tribromophenol which is a white precipitate.



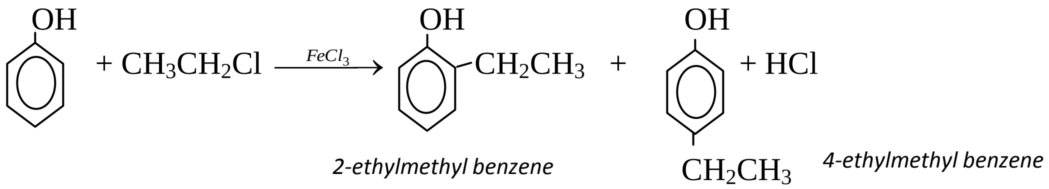
2,4,6-tribromophenol.

Phenol and bromine water

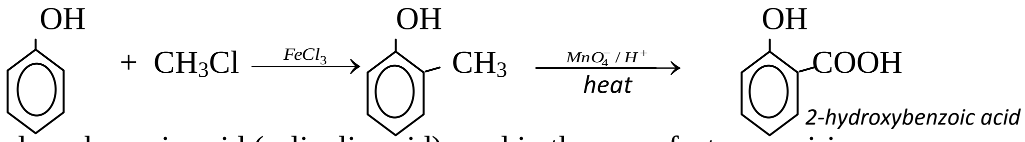
Note: This is a chemical test to show the presence of phenols.

Observation: the brown color of bromine disappears and a white precipitate is formed immediately.

ii. Alkylation of phenol.

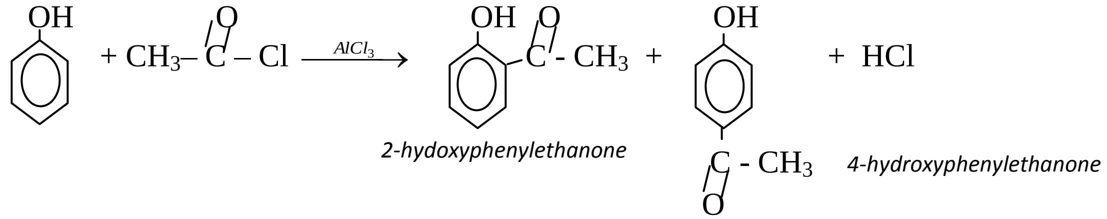


2-ethylphenol is used in the manufacture of surfactants and detergents.

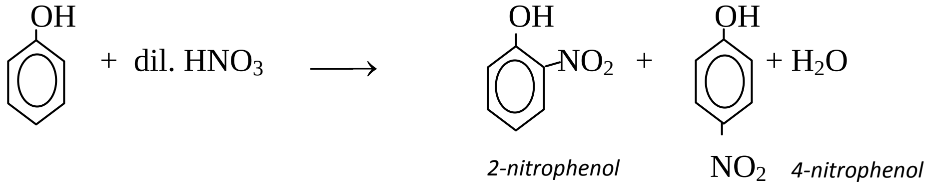


2-hydroxybenzoic acid (salicylic acid) used in the manufacture aspirin.

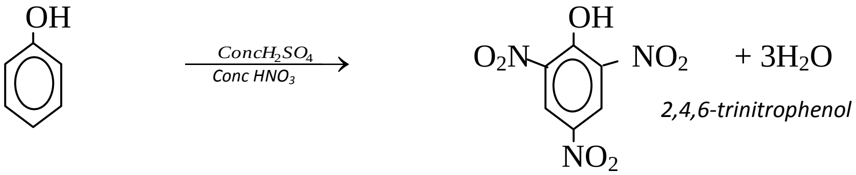
iii. Acylation of methyl benzene



iv. Nitration of phenols. Dilute nitric acid alone is sufficient to nitrate phenol.

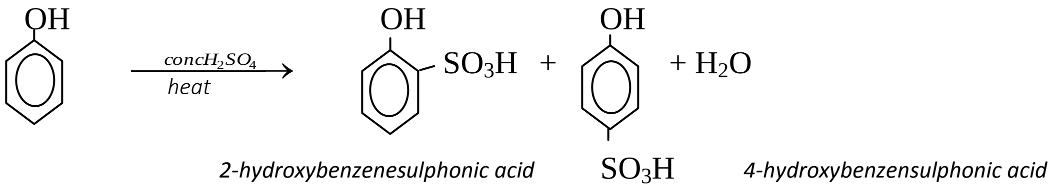


A mixture of conc. HNO_3 and conc. H_2SO_4 forms 2,4,6-trinitrophenol.



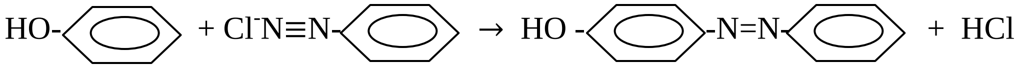
2,4,6-trinitrophenol is a strong acid and is commonly known as picric acid.

v. Sulphonation of phenol



vi. Coupling reaction/diazotization reaction.

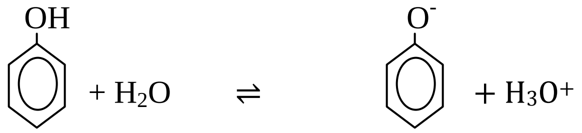
Phenol reacts with benzene diazonium salt to give an azodyes.



2. Reactions of the hydroxy group.

a. Acidity.

Phenol is a weak acid and partially dissolves in solution.



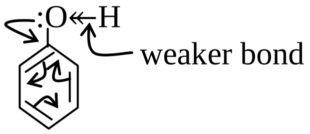
Phenol turns blue litmus red.

Phenol is very soluble in alkaline solutions.

$C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+ + H_2O$

Phenol is a stronger acid than alcohols (phenyl methanol).

because in phenol the lone pairs of elelctrons on the oxygen atom becomes involved with the delocalized electrons of the benzene ring. This weakens the OH bond hence releasing hydrogen ions in solution.



This effect is absent in alcohols.

However phenol is weaker acid than carboxylic acid because it lacks the carbonyl group and unlike carboxylic acids phenol cannot liberate carbon dioxide in the presence of Na_2CO_3 and $NaHCO_3$.

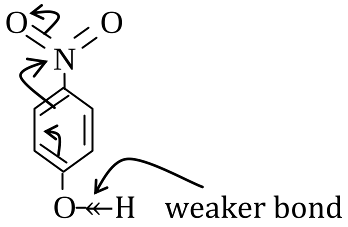
Note:

1. The presence of electron withdrawing group increases the acidity of phenol.

e.g.4 -nitrophenol is a stronger acid than phenol.

4-nitrophenol is a stronger acid because it has an nitro group which is an electron withdrawing group and weakens the O-H bond more, hence releasing more hydrogen ions in solution.

While phenol does not have the nitro group.



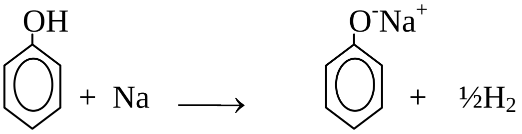
2. The more the electron withdrawing groups the greater the pull (negative inductive effect) , the weaker the OH bond and the more the hydrogen ions are released in solution and hence more acidity.

Therefore the following order of acidity,

2,4,6-trinitrophenol> 2,4-dinitrophenol>2-nitrophenol>phenol

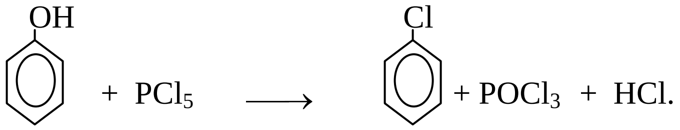
b. Reaction with sodium metal.

Phenol reacts with sodium metal with evolution of hydrogen gas.



c. Reaction with PCl_5

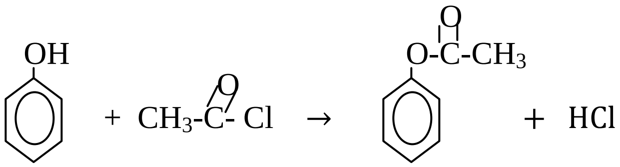
Phenol reacts with phosphorous chloride to give chlorobenzene.



Other phosphorous halides(PBr_5 or PI_5) do not react with phenol due to their bulkness.

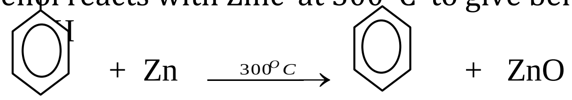
d. Esterification of phenol.

Phenol forms esters with acid chlorides but does react with carboxylic acids.

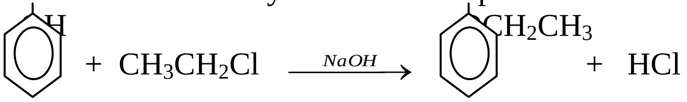


e. Reaction with Zinc.

Phenol reacts with Zinc at 300^0C to give benzene

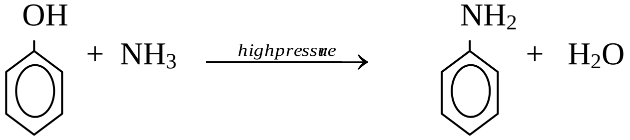


f. Phenol reacts with alkyl halides in the presence of alkali to give ethers.



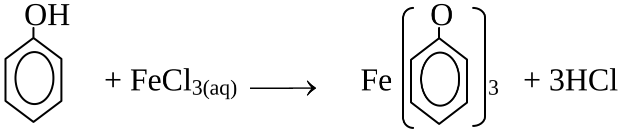
Ethylphenylether.

g. Phenol reacts with ammonia under high pressure or in the presence of $ZnCl_2$ or $CaCl_2$ at 200^0C.



Aminobenzene.

h. Reaction with neutral iron (iii) chloride to violet solutions of phenol complex.



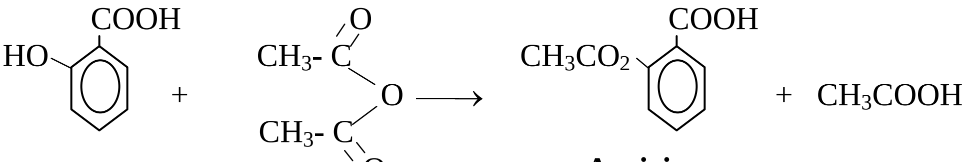
Note: This is a chemical test to confirm the presence of phenols.

Observation: violet solutions.

Uses:

Phenol is used in the manufacture azodyes, pharmaceuticals, detergents, antiseptics, plastics.

e.g .Manufacture of aspirin



Aspirin

Uses of phenols

1. Formation of polymers(plastics) e.g. bakelite used to make pool balls, bags, buttons.
2. Usedin the manufacture of picric acid a yellow dye and other azodyes.
3. Phenols are used to make explosives.
4. Phenol is a starting material for the manufacture of weed killers e.g. 2,4-dichlorophenoxyethanoic acid known as 2,4-D).
5. Phenol is used in the manufacture of phenolphthalein indicator ($C_{20}H_{14}O_4$).
6. Phenol is also used in the manufacture of antiseptics e.g. TCP which is present in "Dettol"
7. Phenol is used as an oral anesthetic/analgesic in the treatment of throat infections.

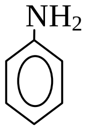
Exercise 5b

1. Explain the following observations.
a. Phenol is a stronger acid than phenylmethanol.
b. 4-nitrophenol is less volatile than 2-nitrophenol
2. How can the following organic compounds be differentiated using reagents.
a. benzyl methanol and phenol.
b. C_6H_5COOH and C_6H_5OH
c. phenol and cyclohexanol
3. Carry out the following organic conversions.
a. Benzene to 2-bromophenol.
b. phenol to 2-aminobenzoic acid.

5.4. Amino benezene (Aniline or phenylmine)

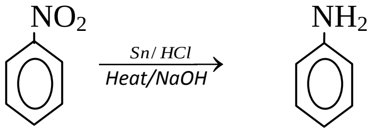
Molecular formula $C_6H_5NH_2$ or C_6H_7N

Structural formula

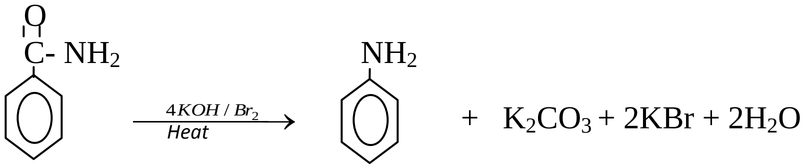


Preparation of aminobenzene.

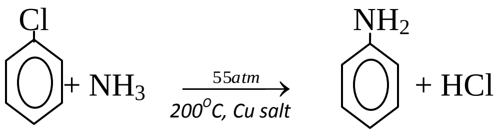
a. Reduction of nitrobenzene.



b. Reduction of benzamide



c. From halo benzenes.



Physical properties of aminobenzene

Aminobenzene is a colorless oily liquid and It turns brown on exposure to sunlight.

Aniline has a characteristic smell.

It is soluble in water and in organic solvents.

It has a boiling point of 184°C and melting point of -6.3°C.

Aniline is poisonous and should handled with care.

Basicity aminobenzene

Amino acid benzene is a very weak base and partially dissolves in water to give a weakly basic solution.

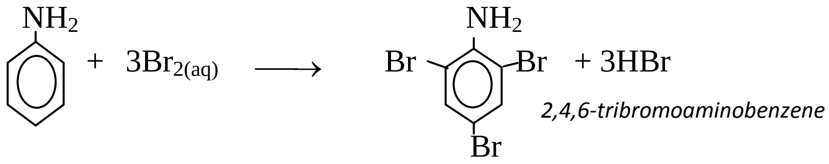
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3 + OH^-$

It reacts with acids

$C_6H_5NH_2 + HCl \rightleftharpoons C_6H_5NH_3Cl^-$

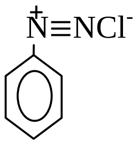
NB:

like phenol, amino benzene gives a white precipitate in the presence of bromine water.



2,4,6-tribromoaminobenzene

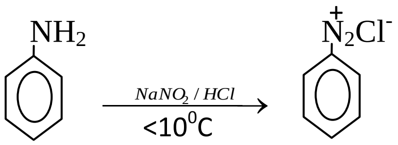
Benzenediazonium chloride.



or $C_6H_5N_2{}^+Cl^-$

Preparation

It is obtained when a mixture of sodium nitrate and hydrochloric acid reacts with aminobenzene at temperature < 10°C.



Chemical reactions.

a. Reaction with warm water.

Benzenediazonium chloride reacts with water at 50°C to give phenols.

$C_6H_5N_2{}^+Cl^- + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$

b. Reaction with HCl acid and copper (i) chlorides

Benzene diazonium chloride reacts HCl in the presence of CuCl to give chlorobenzene.

$C_6H_5N_2{}^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2$

c. Reaction with copper (i) bromide and HBr .

Benzenediazonium chloride reacts HBr in the presence of CuBr to give bromobenzene.

$C_6H_5N_2^+Cl^- \xrightarrow{CuBr/HBr} C_6H_5Br + N_2$

d. Reaction with potassium iodide.

Benzene diazonium chloride reacts with KI to give Iodobenzene.

$C_6H_5N_2^+Cl^- + KI \longrightarrow C_6H_5I + N_2 + KCl$

e. Reaction with copper cyanide.

Benzenediazonium chloride reacts with CuCN to give benzenenitrile

$C_6H_5N_2^+Cl^- + CuCN \longrightarrow C_6H_5CN + N_2$

f. Reaction with phosphoric acid.

Benzenediazonium chloride reacts with phoshophric acid to give benzene.

$C_6H_5N_2^+Cl^- \xrightarrow{H_3PO_3} C_6H_6 + N_2 + HCl$

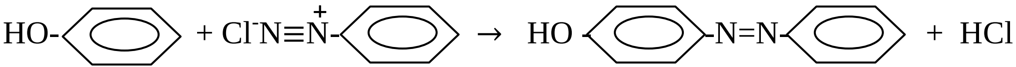
g. *Coupling reaction*.

Benzenediazonium chloride reacts with aromatic compounds to give azo dyes.

In this reaction the nitrogen atoms are mantained.

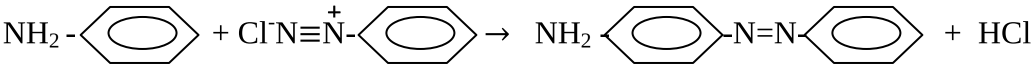
These reactions usually take place in the presence of sodium hydroxide.

i. Phenol reacts to give an orange-yellow azo compound.



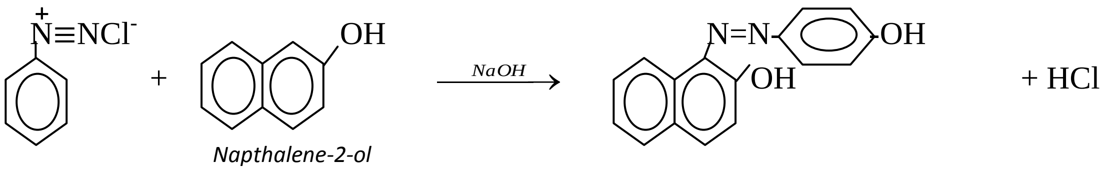
(4-hydroxyphenyl)azobenzene or4-(phenylazo) phenol)

ii. Amino benzene reacts to give a yellow azo compound.



(4-aminophenyl)azobenzene or4-(phenylazo) aniline)

iii. Napthalene-2-ol reacts to give a red azo compound.



Napthalene-2-ol

Note:

i. The azodyes are coloured because of the groups called the chromophores that absorbs light of a specific wavelength.

Chromophores include –N=N-, NO_2, -C=O……

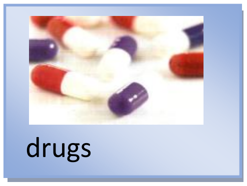
ii. This reaction is applied in industries during the manufacture of dyes.

h) Reaction with sodium hydrogen sulphite.

Benzene diazonium chloride reacts with sodium hydrogen sulphite to phenyl hydrazine.

$C_6H_5N_2^+Cl^- + 2NaHSO_3 \longrightarrow C_6H_5NH_2NH_2 + Na_2SO_3 + HCl$.

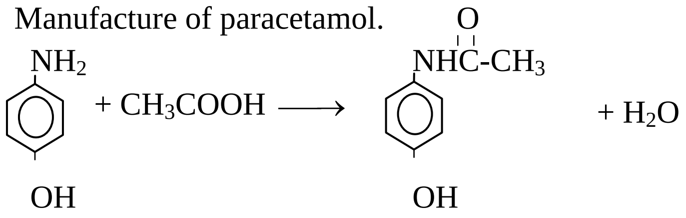
Uses:



drugs

Amino benzene is used in the manufacture of plastics, pharmaceuticals, dyes.

Manufacture of paracetamol.



Exercise 5c

1.a.Write the equation of amino benzene in water and choose the acid base conjugate pair(s)

b.Why is amino benzene referred to as a Bronsted lowry base?

c. Which is more basic Aminobenzene or ammonia?

Explain your answer?

2. Using reagent differentiate between the following pairs of compounds.

a. amino benzene and 1-aminohexane.

b. benzyl amine and methylbenzyl amine.

3. Carryout the following organic synthesis.

a. Nitro benzene to 3-methylphenol

b. amino benzene to benzoic acid.

4. Complete the following equations and outline the mechanism for reaction.

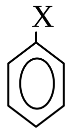
a. $C_6H_5NH_2 + CH_3Cl \xrightarrow{FeCl_3}$

b. $C_6H_5NH_2 + CH_3COCl \rightarrow$

5.5. Halobenzene (s)

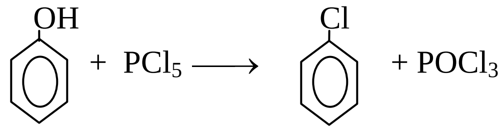
Molecular formula C_6H_5X where X is Cl, Br or I

Structural formula.



Preparation of chlorobenzene.

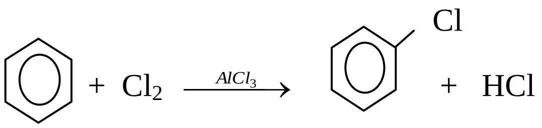
a. from phenol.



b. From benzenediazonium chloride.

$\xrightarrow{CuCl/\ HCl}$

c. from benzene.



Reactivity of halobenzenes.

a. Nucleophilic substitution reactions.

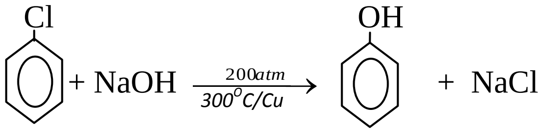
Like halogenoalkanes, halobenzenes undergo nucleophilic substitution reactions.

However, halobenzene are much less reactive than halogenoalkanes because the lone pair of electrons on the halogen atom becomes involved with the delocalized electrons of the benzene ring creating a partial double bond($\pi bond$) .

This adds to the strength of the benzene-hologen bond, and makes it difficult to displace.

This is why nucleophilic substitution reactions of halobenzene need high temperatures, catalyst, pressure…..

e.g. base hydrolysis of halobenzenes needs a temperature of 300^{o}C, pressure and copper catalysts.



This also explains why halobenzenes do not give a positive test in the presence of silver nitrate because the halogen atom can not be easily replaced.

b. Electrophilic substitution reactions.

The benzene ring undergoes usual substitution reactions characteristic to the electron donating group similar to those methylbenzene.

Trial questions:

Multiple choice questions.

1. Which of the following compounds will not decolorise bromine water.

a. $C_6H_5NH_2$ b. C_6H_5OH c. C_6H_{10} d. C_6H_6

2.Which type of reaction type of reaction mechanism does ethylbenzene have with bromine during day.

a. free radical substitution reactions.

b. Electrophilic substitution reactions.

c. Nucleophilic addition reactions.

d. Nucleophilic substitution reactions.

3. Which of the following is the strongest acid.

a. 2-nitrophenol b. 2,4-dinitrophenol c. 2,4,6-trinitrophenol d. phenol

4. Suggest the correct order of increase in basicity.

a. $NH_3 > C_6H_5NH_2 > CH_3NHCH_3 > CH_3CH_2NH_2$.

b. $C_6H_5NH_2 < NH_3 < CH_3CH_2NH_2 < CH_3NHCH_3$

c. $C_6H_5NH_2 > NH_3 > CH_3CH_2NH_2 > CH_3NHCH_3$

d. $NH_3 < C_6H_5NH_2 < CH_3CH_2NH_2 < CH_3NHCH_3$

5. What is observed when bromine water reacts phenol

a. brown solution b. white precipitate c. yellow precipitate d. violet solution.

Structural questions.

1. Complete the following equations and in each case outline the mechanism.

a. $C_6H_6 + CH_3Cl \xrightarrow{FeCl_3}$

b. $C_6H_5CH_3 + Br_2 \xrightarrow{FeBr_3}$

c. $C_6H_5OH + \text{Conc}H_2SO_4 \xrightarrow{heat}$

d. $C_6H_5NO_2 + \text{Conc}HNO_3 \xrightarrow{concH_2SO_4}$

e. $C_6H_5CH_2CH_3 + Cl_2 \xrightarrow{UVlight}$

f. $C_6H_5OH + CH_3Cl \xrightarrow{NaOH}$

g. $C_6H_5NH_2 + CH_3COCl \longrightarrow$

2. Name the reagent that can be used to differentiate between the following pairs of compounds and in each case state what will be observed. Write appropriate equations for reaction

a. cyclohexene and benzene

b. Phenol and benzoic acid.

c. $C_6H_5COCH_3$ and C_6H_5CHO

d. Phenol and Aminobenzene.

e. benzoic acid and benzoyl chloride.

f. C_6H_5Cl and $C_6H_5CH_2Cl$

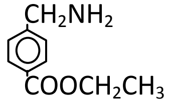
3. Write equation show how the following organic compounds can be synthesized.

a. benzene to benzoic acid.

b. phenol from nitrobenzene.

c. benzoic acid to bromobenzened. cyclohexanol from aminobenzene.

e. benzene to



f. benzene to 3-chloronitrobenzene.

g. Benzoic acid to 3-metylaminobenzene.

4. a. A compound X. $C_8H_{10}Br$ burns with a sooty flame. Write down all the possible structural formulae X.

b. When X was heated under reflux with aqueous sodium hydroxide acompound Q was formed

i. identify X and Q.

ii.Write down and indicate a mechanism for reactionleading to formation of Q from X.

c. Q was converted under one step reaction to an alkene. Write down the equation for reaction and the mechanism for reaction.

d. The alkene in c was polymerized.

i. Write down the structural formula of the polymer.

ii. State the type of polymerization.

5.a. An organic compound M contains C. 80% H. 6.7% the rest being oxygen.

Calculate the empirical formular of M.

b.5g when vapourised at 150^oC and 760mmHg occupies $144.6cm^3$.

Determine the molecular mass of M.

c. M burns with a yellow sooty flame, forms a yellow precipitate with Bradys reagent and iodine in sodium hydroxide. Write the formular of M.

d. Write the equation of reaction between M and bradys reagent.

6. a. Write equations to show how the following compounds can be prepared.

i. phenyl amine.

ii. ethyl amine.

b. Which one of the phenyl amine and ethyl amine is a stronger base?

Explain your answer.

c. Write equations to show how phenyl amine and ethyl amine react with

i. ethanoyl chloride.

ii. acidified solution of sodium nitrite at $5^{\circ}C$.

d. i. Write the mechanism of reaction in C.i.

ii. how can the reaction in C. ii. be used to differentiate phenyl amine and ethyl amine.

c. Phenyl amine can be converted to benzene diazonium chloride.

Writeequations to show how the diazonium salt is converted to

i. iodobenzene.

ii. benzoic acid.

7. Explain the following observations.

a. phenol is more reactive than benzene.

b. 2-nitrophenol is more acidic than phenol.

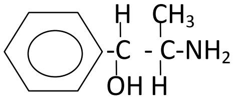
c. Phenol is sparingly soluble in water but soluble in sodium hydroxide.

d. Aminobenzene is a weaker base than ethylamine.

e. 1-bromohexane easily undergoes nucleophilic substitution reaction than bromobenzene.

8. Consider compound A related to the adrenaline hormone.

.



a. Identify the functional groups present in A.

b. Draw the structures of the organic product(s) formed when A reacts.

i. phosphorous pentachloride.

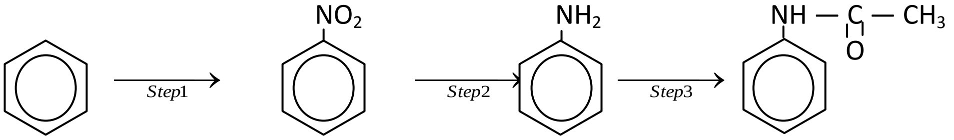
ii. dilute hydrochloric acid.

iii. ethanoyl chloride.

iv. hot alkaline potassium permanganate.

v. hot concentrated sulphuric acid.

9. A reaction scheme is shown below.



a. State the reagents and conditions for step 1.

Name and outline the mechanism for reaction.

b. What type of reaction is involved in step 2 and suitable conditions for reaction.

c. Give the structural formula of the reagents in step 3.

Name and outline the mechanism for reaction.

10. Giving examples explain the following types of reactions including their mechanisms.

a. Electrophilic addition reactions.

b. Electrophilic substitution reactions.

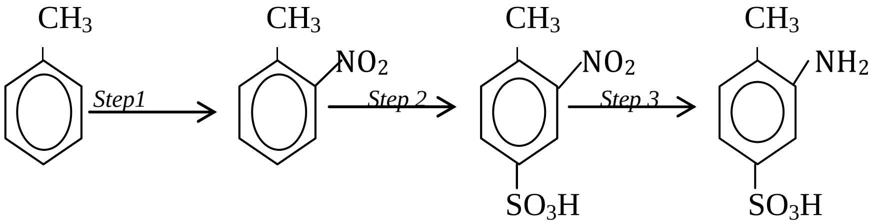
c. Nucleophilic addition reactions.

d. Nucleophilic substitution reactions.

e. Free radical substitution reactions.

f. Elimination reactions.

1



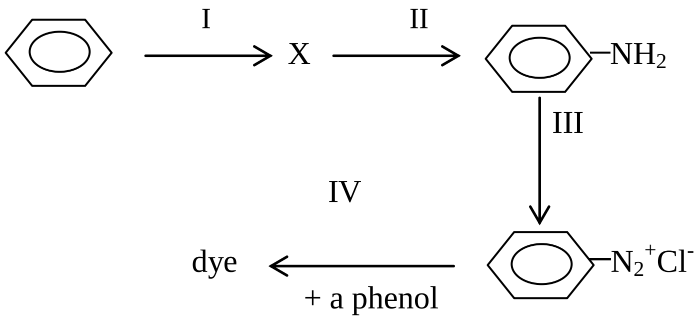
a. What type of reaction is step 2?

b.For each of the steps 1 to 3, state the reagents and conditions needed to carry out the reaction.

c. Outline the mechanism for the reactions in step 2.

12.Dyes can be made from aromatic amines and are widely used in textile industries .

One synthetic route for making a dye is shown as follows.

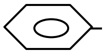


a. Draw the structural formula of the intermediate compound X.

b. State the reagents and conditions for

i. Step I

ii. Step II

c. Phenyl amine  $-NH_2$ is a weak base.

i. Write an equation to show phenylamine acting as a base.

ii. Which one is a stronger base, phenyl amine or ammonia.

Explain your reasoning.

d. State the reagent for step III.

e.Give the structural formular of the dye formed when benzene diazonium chloride reacts with phenol.

13. An aromatic hydrocarbon D. C_7H_8 is converted into E. $C_9H_{10}O$, on treatment with ethanoyl chloride in the presence of $AlCl_3$. when treated with $NaBH_4$, it is converted in F, $C_9H_{12}O$. Compound G is formed when F is warmed with conc. H_2SO_4.

a. Identify the structure of D.

b. Give all possible isomers of E, F, G

c. Carry out a chemical test to identify the functional group In E,F and G.

14.A Compound **A** ($C_{14}H_{12}$) decolorises orange solution of bromine water.

One mole of **A** can react completely with one mole of hydrogen in the presence of nickel at room temperature, its oxidation produces an organic compound benzoic acid only. Indicate all observation made and find possible structure of **A**. A reaction between bromine and **A** ,followed by the action of concentrated sodium hydroxide on the compound formed ,gives **B** ,($C_{14}H_{10}$) **B** react with hydrogen in the presence of palladium to form **C** ($C_{14}H_{12}$)which is different from **A** .

At the end of **A**, **B** and **C**, gives the same compound **D**($C_{14}H_{14}$) by hydrogenation in the presence of nickel.

a.With the complementary information above, write the structures of **A**, **B**, **C** and **D**.(2marks)

b. Name **A**, **B**, **C** and **D** .

6.0 .POLYMERIZATION

Polymerization is the repeated joining of two or more smaller molecular compounds to produce high molecular compounds.

Monomers:

Are simple molecular compounds that combine to produce a polymer

Polymer:

It is a compound formed by repeated joining of two or more simple molecular compounds called monomers.

Polymers are classified as:

a. Addition polymers: polymers formed from monomers having the same functional group.

e.g. polyalkenes such as polyethene, polypropene

*b. Condensation polymers:*polymers formed from monomers having different functional group followed by elimination of small molecules like H_2O, HCl

e.g. polyamides such as nylons, Kevlar.
polyesters such as terylene, Dacron.

Polymers may be classified as:

Homopolymers:- formed from the same monomer units.

$nA \longrightarrow [\ A\ ]_n$

e.g. polyalkenes

*Copolymers:*formed from different monomer units.

$nA + nB \longrightarrow [\ A - B\ ]_n$

e.g. nitrile rubber, ABS rubber, polyesters, polyamides.

Polymers are also classified as:

Natural polymers: Are polymers that exist by nature.e.g.

Proteins from amino acids

Starch from simple glucose molecules.

Cellulose from glucose molecules

Carbohydrates from glucose.

Natural rubber from isoprene.

Artificial polymer(synthetic polymer) Are polymers that are made by man. *e.g.*

polyethene

poly vinyl chloride

Properties of polymers.

a. **Thermosetting** and **Thermosoftening** polymers.

i. Thermosoftening polymers.
These are polymers that soften on heating and can be remoulded into new shapes
e.g Polyethene, polypropene, polyvinylchloride, polystyrene, Nylon 6,6
ii. Thermosetting plastics.
These are plastics that once mouldedcannot soften on heating hence can’t be remoulded
Examples.
Melamine: used to make plates,cups,etc
Polyester resin.
Urea methanol.
Vulcanised rubber.
Phenolic resins eg: bakelite usedto make electrical insulators, bags, buttons, pool balls.
b. Biodegradable and **non-biodegradable** polymers.
Biodegradable polymers.
These are polymers that are decomposed by bacteria.e.g. polyamides like. nylons,
polyesters like terylene
Non-biodegradable plastics.
These are polymers that are not decomposed by bacteria.e.g. polyalkenes

6.1. Types of polymerization

a. Addition polymerization
b. Condensation polymerization

a. Addition polymerization.
This is a process of formation of higher molecular compounds from low molecular compounds having the same functional groups.
These polymers have some empirical formula as the monomer.
This is mainly characteristic of unsaturated compounds.

e.g : Addtion polymer (Polyalkenes) like
i. polyethene
ii. polypropene
iii. polyvinyl chloride(P.V.C)
iv.polytetrafluoroethene (Teflon)
v. polyphenylethene (polystyrene)
vi.polypropenenitrile (orlon)
vii. Poly methyl-2-methylpropanoate (perspex)
viii. polyvinylacetate (P.V.A)

See the polymerization of alkenes.
i. **Polyethene.** (polyethylene)

Additional polymer from ethene as a monomer.

$nCH_2 = CH_2 \longrightarrow [CH_2 - CH_2]_n$

Polyethene includes

Low density polyethene(LDPE) (0.91-0.94) gcm^{-3}

It is made at a pressure of 2000 atm and temperature 200^0C.

uses: making plastic bags, insulators, packing bags.

High density polyethene(HDPE) (0.95-0.97) gcm^{-3}

It is made at a pressure (5-25) atm and temperature (20-50) ^0C.

uses: water tanks, pipes, crates, bottles, trays, bed pans, utensils.

ii. **Polypropene.** (PP)

Additional polymer from propene as a monomer.

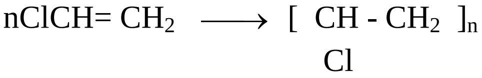
$nCH_3CH{=}CH_2 \longrightarrow [\underset{CH_3}{CH} - CH_2]_n$

It is obtained at a pressure of 40 atm, temperature of 100^oC and catalysts Ziegler-Natta ($TiCl_4$ and $(C_2H_5)_3Al$)

uses: Packing materials, Ropes, Lab wear, toys, bottles, CD cases

iii. **Polyvinylchloride.** (P.V.C) or Polychloroethene.

Additional polymer from chlororoethene as a monomer.



$nClCH{=}CH_2 \longrightarrow [\underset{Cl}{CH} - CH_2]_n$

*uses:*building materials e.g. window flames, pipes, tanks.
footwears, carpets, tablemats, curtains, bottles, tiles.

iv. **Polystyrene.** (PS) (polyphenylethene)

Additional polymer from phenylethene as a monomer.

$n\,CH{=}CH_2 \longrightarrow [CH - CH_2]_n$

uses:

DVD and CD cases

It is colorless and used to make packing materials for foods and utensils.

Disposable cups and plates, Insulation.

-It is the simplest plastic mould. For other polyalkenessee polymerization of alkenes(**pg.32-33**)

b. Condensation polymerization

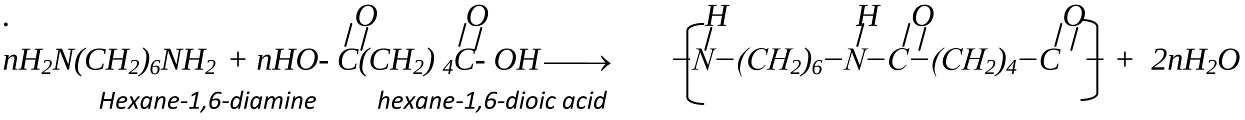
Is the process of formation of polymers from monomers containing different functional groups followed by release of small molecules like water, $HCl_{(g)}$

NB: The composition of the elementary unit is different from the initial monomers. These polymers are formed by addition elimination reaction.

The elimination of the water molecues gives the name of the type of polymerization. i.e. condensation.
These type of polymers are called condensation polymers

e.gi. polyamides like nylon 6,6 and nylon 6,10, Kevlar, nomex.
ii. polyester like Terylene
i. Polyamides

Nylon6,6
It is a polyamide obtained fromhexane-1,6-diamine and hexane-1,6-dioic acid as monomers.
.

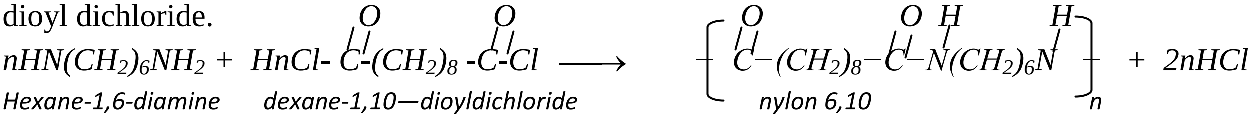


$$nH_2N(CH_2)_6NH_2 + nHO\text{-}\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}\text{-}OH \longrightarrow \left[\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right] + 2nH_2O$$

Hexane-1,6-diamine hexane-1,6-dioic acid

A hexane-1,6-dioyl dichloride can be used instead of a hexane-1,6-dioic acid.
properties.
It is a thermosoftening plastic.
It is tough and strong.
Can be drawn into threads. i.e. forms fibres.
Resistant to chemical attack.
Has a melting point of 263°c
*uses.*To make unlubricated bearings, gears, fishing lines and nets, tyres, bottles, ropes and clothes, tooth brush.

Nylon 6,10
It is a polyamide obtained fromhexane-1,6-diamine and decane-1,10-dioic acid or decane-1,10-dioyl dichloride.

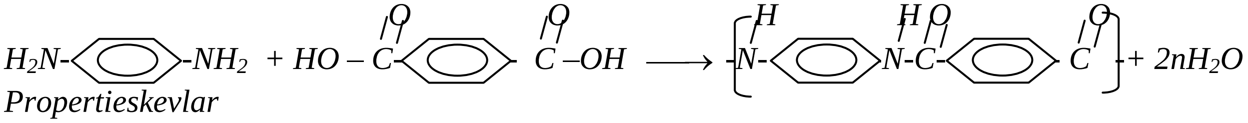


$$nHN(CH_2)_6NH_2 + HnCl\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_8\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl \longrightarrow \left[\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}(CH_2)_6\overset{\overset{H}{|}}{N} \right]_n + 2nHCl$$

Hexane-1,6-diamine dexane-1,10—dioyldichloride nylon 6,10

It is tough and stronger
uses
Used to make surgical gloves, curtains, nets and carpets

kevlar.
It is a polyamide obtained frombenzene-1,4-diamine and benzene-1,4-dioic acid or benzene-1,4-dioyl dichloride.



Propertieskevlar

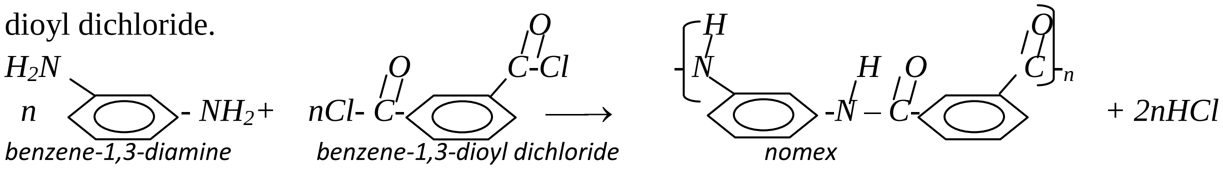
Fire resistant, higher strength steel

uses

Used to make firefighting equipment, bullet proof vests and crash helmets, sports equipment, tyres, ropes

Nomex:

It is a polyamide obtained frombenzene-1,3-diamine and benzene-1,3-dioic acid or benzene-1,3-dioyl dichloride.



Properties.

Heat and fire resistance.

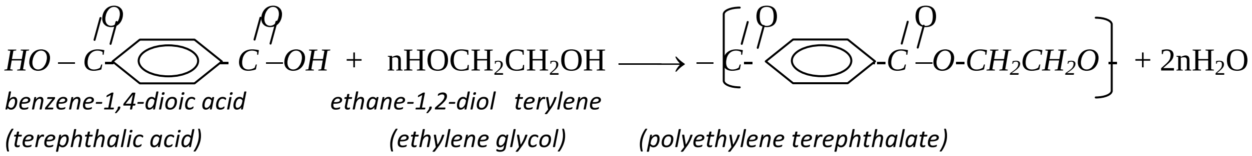
uses.

Used to make fire resistant gloves, jackets, military equipment, garments worn by fire fighters and racing drivers.

ii. Polyesters.

Terylene

It is a polyester obtained from ethane-1,2-diol and benzene-1,4-dioic acid or benzene-1,4-dioyl dichloride.



properties

Good thermal and chemical stability and can be hydrolysed by an alkali at lowest cost.

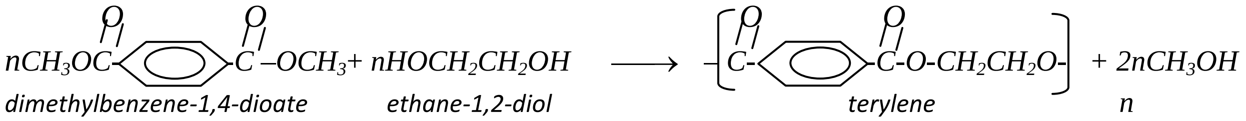
uses.

making clothes, Vehicle repair**,** making of laminates, boats, aircrafts, bottles.

Note:

Terylene(in UK) is traditionally referred to as **PET or PETE** (polyethylene terephthalate,) **dacron** in USA.

During industrial production of PET a dimethyl ester is sometimes used.



Polymers may also be classified as plastics or fibres

6.3. PLASTICS

A plastic is a polymerized organic substance, a solid of high molecular mass which at sometime of its manufacture it is shaped by flow.


Plastics

Plastic include:

- Thermosoftening plastics.
- Thermosetting plastics (thermohardening plastic).

a. Thermosoftening plastics(thermoplastics)
These are plastics that soften on heating and can be remoulded into new shapes
Examples.
Polyethene
Polypropene
Polyvinylchloride
Polystyrene
Nylon 6,6

b. Thermosetting plastics (thermosets)
These are plastics that once mouldedcannot soften on heating hence can't be remoulded
Examples.
Melamine: used to make plates,cups,etc
Polyester resin.
Phenolic resins eg: bakelitean electrical insulator
Urea methanol.
Vulcanised rubber.

limitations of plastics.

Many plastics(like polyalkenes) are non-biodegradable and they cause land pollution, water pollution.

Plastics also cause air pollution when they are burnt.

How to reduce the effect of plastics to the environment.

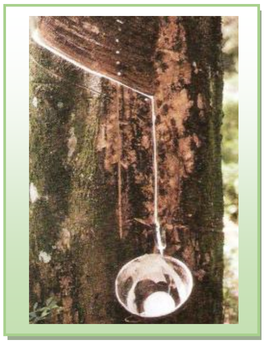
-By recycling.
-Re-using plastics.
-Re-newing plastics.
-Proper disposal of plastics.
-using biodegradable plastics such as polyesters.

6.3.Firbres.

Any thing that can be made in form of threads.

a. Natural fibres: Fibres that exist by nature. e.g. Cotton, wool, silk, thread.

b. Synthetic fibres: Artificially made fibres.e.g.
polyalkenes such as polypropenenitrile(orlon)
Polyamides such as nylon.
Polyester such as terylene.



6.4.Rubber

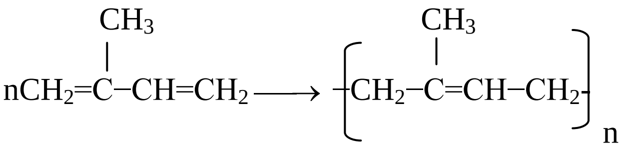
Rubber exists in two forms which include
a. Natural rubber.
b. Synthetic rubber.

a. Natural rubber

It is a plastic hydrocarbon obtained from latex. Latex is a milky emulsion of rubber particles in water obtained from the inner of rubber trees

When a tree is cut latex containing 35% rubber comes out

It is processed and placed into blocks which are dried using a current of dry air.
Natural rubber is a polymer of a monomer 2-methyl buta-1,3-diene

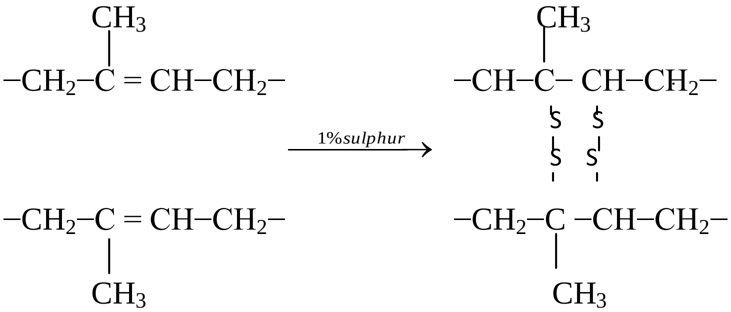


$$nCH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow \left[CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2 \right]_n$$

2-methylbuta-1,3-diene(isoprene) *Poly-2-methylbuta-1,3-diene (natral rubber)*

Rubber is an elastomer ie. can return to its original shape after deformation because of its cis-form hence zigzag structure. This account for its elasticity and poor structure.

To improve on the properties of rubber vulcanization is carried out,
Vulcanization is the heating of crude rubber with sulphur to improve on its strength and elasticity.



$$\begin{array}{l} -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \\ \\ -CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2- \end{array} \xrightarrow{1\% sulphur} \begin{array}{l} -CH-\overset{CH_3}{\overset{|}{C}}-CH-CH_2- \\ \quad\quad S \quad S \\ \quad\quad | \quad\; | \\ \quad\quad S \quad S \\ -CH_2-\underset{CH_3}{\underset{|}{C}}-CH-CH_2- \end{array}$$

car tyres

The sulphur atoms are added between polymer chains across the double bonds.
This sulphur used is about 1%.
Fillers such as carbon black are added to increase hardness.

Uses.

To make car tyres, shoes, clothes, gloves, rubber bands, gum boats, hose pipes.

b. Synthetic rubber.

There are many synthetic rubbers in use and each possesses certain properties.

Synthetic rubber has a series of double bonds in the polymer chains.

eg: polybuta-1,3-diene

Monomer: $CH_2{=}CH{-}CH{=}CH_2$ *buta-1,3-diene*

$$\underset{\textit{buta-1,3-diene}}{nCH_2{=}CH{-}CH{=}CH_2} \longrightarrow \underset{\textit{polybuta-1,3-diene}}{\left[-CH_2{-}CH{=}CH{-}CH_2-\right]_n}$$

- It has good strengths and retains its elasticity at low temperatures

- It can also be vulcanised to increase its strength.

buta-1,3-diene is often copolymerized to give.

Neoprene. (poly-2-chlorobuta-1,3-diene)

Monomer: $CH_2{=}\ CCl{-}CH{=}CH_2$ 2-chlorobuta-1,3-diene.

$$nCH_2{=}CCl{-}CH{=}CH_2 \longrightarrow \left[-CH_2{-}CCl{=}CH{-}CH_2-\right]_n$$

Uses: gloves, gaskets.

Note*:*

Buta-1,3-diene is the simplest form of monomer for making synthetic rubber through copolymerization. E.g.

a. Styrene - buta-1,3-diene rubber.(SBR)

b. Nitrile butadiene rubber (NBR) or nitrile rubber

c. ABS rubber (*acrylonitrile* butadiene styrene rubber)

Exercise 6.

Multiple choice questions.

1. Which of these polymers is a natural polyamide.

a. Kevlar. b. Nomex. c. protein. d. nylon6,6.

2. Identify the polymer which may be biodegradable.

a. Terylene. b. polyethene. c. P.V.C d. polystyrene.

3. Why is nylon 6, 10 called so? because

a. it is a polyamide.

b. It has 16 carbon atoms

c. It is from a dicarboxylic acids with 6 carbon atoms and a diamine with 10 carbon atoms.

d.It is from a diamine with 6 carbon atoms and a diacid chloride with 10 carbonn atoms.

4. Which of these polymers is stronger than steel?

a. nylon 6,6. b. Terylene. c. Kevlar. d. nylon 6,10.

5. Which of these are monomers of natural rubber.

a. Isoprene b. neoprene c. buta-1,2-diene d.buta-1,3-diene.

6. The process of adding sulphurparticles in rubber to improve its properties is called.

a. polymerization. c. reforming.

b. Vulcanisation d. Isomerism.

7. Which of these polymers is artificial, condensation, biodegradable and thermosoftening.
a. polypropene b. nylon6,6 c. polyvinylacetate d. bakelite

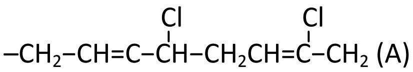
8. These polymers cannot be recycled:
a.Thermoplasts b.Thermosets c.Elastomers. d.All polymers

9. Ingeneral, strongest polymer group is
a. Thermoplasts b.Thermosets c.Elastomers d.All polymers

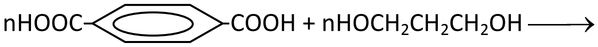
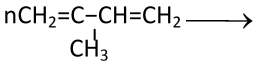
Structural questions

1. i. State what is meant by thermosotftening plastic
ii. Give an example and explain the term synthetic thermosetting plastic
b. i. Write an equation for the formation of nylon 6,6.
ii. State the type of polymerization involved

2. a. Name two types of polymerization.
b. State the structural requirement for the formation of polymer above.
c. Write the names and structural formular of two naturally occurring polymer.
Indicating the names of the monomers

3. 
$-CH_2-CH=C-\underset{}{\overset{Cl}{C}}H-CH_2CH=\overset{Cl}{C}-CH_2$ (A)

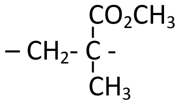
a. i. Name the polymer.
ii. Name the monomer
b.i. Write the equation for the formation of polychloroethene
ii. State one use of polychloroethene
iii. What type of polymer it is?
c. Briefly explain the environmental impact of polychloroethene.

4. a. Complete the equation and state the name of the product and its use
i. $nCH_2=CH_2 \longrightarrow$
ii. 
$nHOOC-C_6H_4-COOH + nHOCH_2CH_2CH_2OH \longrightarrow$
iii. $nH_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow$
iv. 
$nCH_2=\underset{CH_3}{C}-CH=CH_2 \longrightarrow$
b. Give the advantage of the polymer formed in 4.a.ii. over the polymer formed in 4.a.i.
c. Explain why holes form when aqueous sodium hydroxide is dropped on a shirt made of polymer in a.(ii).

5.a. Complete

Polymer	Monomer		Polymer structure	Method of formation
	Name	Structure		
Polystyrene				
Nylon 6,6				
Polyester				

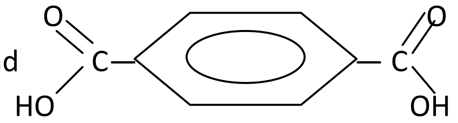
b. Write equation to show how styrene can be obtained from 2-phenyl ethanol

6. a. Explain what is meant by the following
i. addition polymerization
ii. condensation polymerization.
b. 
$-CH_2-\underset{CH_3}{\overset{CO_2CH_3}{C}}-$

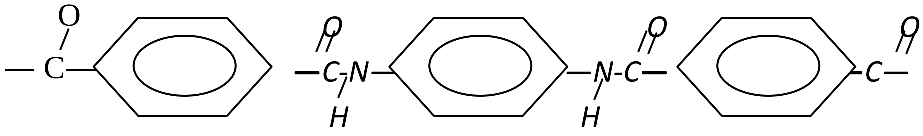
i.write the structural formula of the monomer

ii. Name type of polymerization.
iii. state the use of the polymer.
iv. When 1.25 x 10^{-3} moles of Perspex was heated in the presence of silica as catalyst. 4.85g of monomer was produced. Determine the number of monomer molecules (n)
c. Name and explain the process that makes rubber more useful.
7. Propene was used as a starting material for the manufacture of polypropene
a. write equation to show how propene can be obtained from propanone
b. Outline the mechanism for the formation of propene. [last equation in your conversion]
c. Write the equation for the conversion of propene to polypropene
d. Name type of polymerization
e. What is the structural feature for this type of polymerization.
8. Nomex is a special kind of polymer resistant to high temperatures.
a. Give the structural formula of the monomers of nomex and name them.
b. How are they different from those of Kevlar.
c. Show one repeat unit of nomex.
d. Give one use of nomex as a polymer.
e. Which type of polymer is nomex.
9.Nylon is a condensation polymer formed from two monomers represented by NH_2-X-$NH_2$and HOOC-Y-COOH.
a .Draw a structure to represent the repeat unit of the nylon polymerfrom two monomers and indicate the linkage group by a ring.
b.What is name given to the linkage group in nylon polymer?
10. Nylon 6,6 has a structure containing the followingrepeat unit:
-CO-$(CH_2)_4$-CO-NH-$(CH_2)_6$-NH-
a. What type of polymer is this?
b.Give the structural formulae of the monomers of this polymer.
c. What natural polymerhas the same linkageas Nylon6,6.

11. Terylene is a polymer made from ethane -1,2-diol and benzene-1,4-dicarboxylic acid.
The monomers are

HO - CH_2CH_2 - OH and 

a. Give the structure of terylene showing only one repeat unit.
b. What type of polymer is terylene?
c. Give one advatange of terylene over compared to poly(ethene).
12. Part of the polymer called is shown below:



a. Give the structural formulae of the monomers of the above polymer.
b.What type of polymer is it?
c. Name the polymer

13.a. Rubber is a natural polymer whose monomer is 2-methylbuta-1,3-diene.
i. Write the structure formula of the monomer of rubber and the structure formula of rubber with 3 monomer units.
ii. What is the importance of vulcanization of rubber?
b. There are two type of nylon: nylon 6 and nylon 6/6.
Their monomers are $H_2N-(CH_2)_5-COOH$ for nylon 6 and for nylon 6/6 is $HOOC-(CH_2)_4-COOH$ with $H_2N-(CH_2)_6-NH_2$.
i. Explain why the two polymers are named differently by using the number 6 and 6/6.
(ii) Write the structure formula with 3 monomer units each of the polymers of nylon 6 and nylon 6/6.

7.0.PHYSICAL EQUILIBRIUM

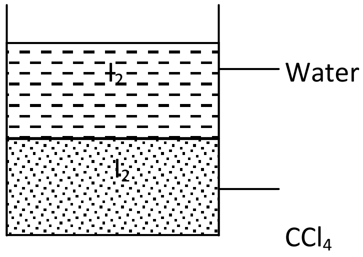
7.1.0. Distribution law and its application.

7.1.1. The distribution law or partition law.

It states that the solute distributes itself in two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

The constant ratio of concentrations of solute in two immiscible liquid is called *the partition co-efficient* or *the distribution constant.*

Consider the distribution of iodine in two immiscible liquids such as Carbon tetrachloride and water.



$$K_D = \frac{concetration\ of\ I_2 in\ CCl_4}{Concetration\ of\ I_2\ in\ water}$$

$$\text{or } K_D = \frac{[I_2]\ CCl_4}{[I_2]aq}$$

Experimental determination of partition coefficient of iodine between Carbon tetrachloride and water.

A known mass of iodine is dissolved in a known volume of water and shaken with known volume of carbon tetrachloride for 5 minutes.

The mixture is left to settle until two completely separated layers are formed.

The two layers are separated using a separating funnel. 25cm^3 of each layer is pipetted and each portion is titrated against the standard solution of sodium thiosulphate.

The moles of iodine in each layer are calculated.

$$2S_2O_{3(aq)}^{2-} + I_{2(aq)} \rightarrow S_4O_{6(aq)}^{2-} + 2I_{(aq)}^{-}$$

The determine the number of moles in each layer in 1dm^3 or litre and obtain the distribution coefficient of iodine between chloromethane and water using.

$$K_D = \frac{concetration\ of\ I_2 in\ CCl_4}{Concetration\ of\ I_2\ in\ water}$$

Limitations of the distribution law.

- temperature should be constant since it affects solubility.
- The liquid (solvent) must be immiscible.
-The solvent should not react with each other.
-The solute and solvent should not react with each other.
- The solute should not associate or dissociate in any of the solvent.

immiscible liquids are liquids when mixed together they form two layers.

7.1.2. Application of the partition law

- Solvent extraction.
- Analysis of compex ions.

-Identification of halides.
-Extraction of crude oil.
-Mining.

Solvent extraction.

It is the removal of a solute from a solvent by shaking with another solvent.

It is a liquid-liquid extraction applied especially during purification of organic compounds, nuclear reprocessing, ore processing, perfume processing and production of vegetable oil and biodiesel.

This liquid-liquid extraction is done in the laboratory using a separating funnel among others.

Worked example

1. When a solution of 1g of X in 100cm^{3}of water was shaken with 10cm^3 of ether, 0.8g of x was transferred to the ether layer.

Calculate the partition coefficient between ether and water.

2. In the experiment 100cm^3 of 0.1M solution of propanoic acid was shaken with 50cm^3 organic solvent immiscible with water. At equilibrium, the aqueous layer required 12cm^{3}of 0.02M NaOH for complete neutralization

a . Calculate the concentration ofpropanoicacid inaqueous layerand in organic layer.

b. Calculate the equilibrium ratio between the concentration of propanoicacid in organic layer and in aqueous layer;

c. What is the name ofthat ratio?

3. 100cm^3 of the solution contain 10g of substances x. calculate the mass of x that can be abstracted (removed) by shaking the solution with

a. 100cm^3 ethoxyethane.

b. two 50cm^3 portion of ethoxyethane.

(K_D of x between ethoxyethane and water is 1.25)

Exercise 7.a

1.A 0.1g sample of phthalic acid was dissolved in 100ml of water. When 25ml of diethylether was used to extract the phthalicacid,0.042grams of phthalic acidwere recovered. What is the distribution coefficient for this extraction?

2. If 0.5g of caffeine is dissolved in 100ml of water, what percentage of caffeine can be separated from the water using a single 40 ml sample of methylene chloride? The distribution coefficient = 4.6

3. Suppose 100cm^3 of benzene is available for extracting 10g of solute x dissolved in 100cm^3 of water and the partition coefficient of x between benzene and water is 5.

How much of x will be extracted when

a. All the 100cm^{3}of benzene is used at once

b. Two portion of 50cm^3 of benzene are used.

4. a. The distribution coefficient of A between ethoxyethane and water is 90 an aqueous solution of A with volume of 500cm^3 contain 5.0g.

i. Calculate the mass of A that will be extracted by 100cm^3 of ethoxyethane.

ii. two successive portions of 50cm^3 of ethoxyethane.

b. State any three conditions under which partition coefficient is valid.

c. State three applications of the distribution law.

5. a. i. Define the term partition co-efficient and state the conditions under which it is valid.

ii. Briefly describe how the partition coefficient for the distribution of iodine between water and trichloromethane can be determined.

b. When 100 cm^3 of aqueous solution containing 30g of ethanoic acid were shown with 50 cm^3 of butanol. 12g of ethanoic acid remained in aqueous layer.

i. Calculate the distribution co-efficient of ethanoic acid between water and butan-1-ol

ii. The aqueous solution of ethanoic acid in (a) was shaken twice with 25cm^3 portion of butan-1-ol. Calculate the mass of ethanoic acid extracted.

6. An aqueous solution contains 5g of X in 100cm^3 of solution. The partition coefficient of X between water and the organic solvent is 0.2. Calculate the mass of X extracted by shaking of 100cm^3 of aqueous solution with two successive 25cm^3 of organic solvent.

7. 2.0. Raoult's law and its application.

7.2.1. Raoult's law.

Raoult's law:

Its states that the partial pressure of a component in an ideal liquid mixture is proportional to its mole fraction at constant temperature.

Raoult's law is true for miscible liquids and for an ideal mixture.

$P \propto X$ where P - Partial pressure.
X – Mole fraction.
$P_A = P^o{}_A X_A$ where P_A - partial pressure of A. $P_B = P^o{}_B X_B$ where P_B- partial pressure of B.
$P^O{}_A$ - saturated vapor pressure. $P^O{}_B$- saturated vapor pressure.
X_A = Mole fraction of A. X_B = Mole fraction of B.
considering a liquid mixture of A and B .
$P_T = P_A + P_B$ where P_T -total pressure.
P_B -partial pressure of B
$P_A = P^O{}_A X_A + P^O{}_B X_B$
$X_A + X_B = 1$

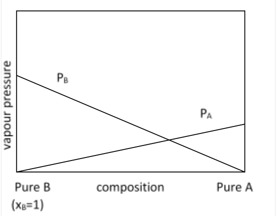


fig: partial vapour pressue ∝ mole fraction.

Partial vapour pressure (P) is directly proportional to to mole fraction (X).

$P_A \propto X_A$
$P_B \propto X_B$

Composition of vapor above an ideal mixture

The composition of vapor above liquid is not the same as the composition of liquid mixture.$P_A \propto X_A$
$P_A = P_T X_A$ where X_A is molar fraction of A in vapour.
P_T is the proportionality constant $X'_A = \frac{P_A}{P_T}$

Worked example.

A mixture containing liquid A and B obeys Raoult's' law, The vapor pressure of A and B are 1kPa and 2.92kPa respectively at 20 ^oC

Calculate the

a. total pressure

b composition of the vapor of a mixture containing 0.5moles of each liquid at 20^{o}C.

c. Which is liquid more volatile and why?

Exercise 7b.

1.Vapour pressure of chloroform and dichloromethane at 25°C are 200mmHg and 415mmHg respectively.

i. Calculate the vapour pressure of the solution prepared by mixing 25.5g of chloroform and 40g of dichloromethaneat 25°C

ii. Calculate themole fraction of eachcomponent invapourphase.

2. a. Heptane and octane form an ideal solution.

Explain the term ideal solution.

b. Calculate the vapour pressure of a solution containing 50g heptanes and 38g of octane at 20^{o}C.(H=1, C=12).

The vapour pressure of heptanes at 20^{o}C =473.2 Pa.

The vapour pressure of octane at 20^{o}C = 139.8 Pa.

3.The vapour pressure of ethanol at 20^{o}C is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg.

The mole fraction of benzene is 0.09 for mixture of benzene and ethanol at 20°C.

a. Calculate the total vapour pressure of the mixture.

b. Calculate the mole fraction of benzene in the vapour phase.

4. Acetone and ethyl acetate are organic liquids that form an ideal mixture and are used as solvents. At 30° c, the vapour pressure of pure acetone is 285mmHg and vapour pressure of pure ethyl acetate is 11 mmHg.

Calculate the vapour pressure at 30°C of a solution prepared by dissolving 25.0g of acetone and 225g of ethyl acetate. (Molar mass: Acetone = 58g mol^{-1}, ethyl acetate = 88g mol^{-1})

Calculations of a solute(solid) in solution.

Worked example

An aqueous solution of glucose is made by dissolving 10g of glucose, $C_6H_{12}O_6$ in 90g of water at 30°C.

If the vapour pressure of pure water at 30°C is 32.8mmHg.What would be the vapour pressure of the solution?

Exercise

1.What is the vapor pressureof an aqueous solution that has a solute mole fraction of0.1000?
Thevapor pressureof water is 25.756 mmHg at 25°C.

2.The vapor pressure of an aqueous solution is found to be 24.90 mmHg at 25 °C. What is the mole fraction ofsolute in this solution? The vapor pressure of water is 25.756 mmHg at 25°C.

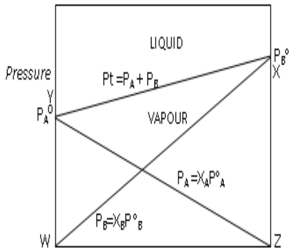
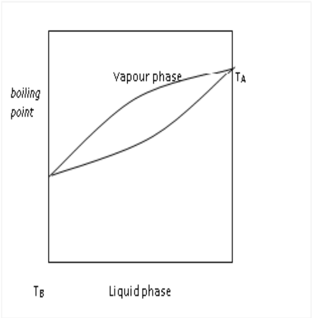
3. How many grams of non volatile compound B (molarmass = 97.8g/mol) would need to be added to 250g of water to produce a solution with a vapor pressureof 23.756 torr? The vapor pressure of water at this temperature is 42.362 torr.

4. At 29.6 °C, pure water has a vapor pressure of 31.1 torr. A solution is prepared by adding 86.8 g of "Y", a non volatile non-electrolyte to 350 g of water. The vapor pressure of the resulting solution is 28.6 torr.
Calculate the molarmass of Y.

5.The vapor pressureof pure water is 23.8 mmHg at 25.0 °C. What is the vapor pressure of 2.50 molal $C_6H_{12}O_6$

7.2.2 Miscible liquid mixture.

Miscible liquids are liquids that dissolves in each other to form uniform layer.

Vapour pressure composition diagram constant temperature	**Boiling point composition diagram constant pressure:**
 P_T–Total pressure P^0_A- vapour pressure of pure component A. P^0_B- vapour pressure of pure component B. ZY-Variation of partial vapour pressure of component A with composition. WX- Variation of partial vapour pressure of component B with composition. YX- Variation of total vapor pressure of solution with composition.	 -The upper curve shows the variation of composition with vapour. -The lower curve shows the variation of composition with liquid.

b. Non-ideal solution or mixture. (real solutions).

Solution made up of 2 or more component whose molecules have unequal magnitude of the intermolecular forces and when mixed heat changes or volume changes occur.

Non-ideal solutions do not obey Raoult's law. i.e. deviate from Raoult's law.(cohesion and adhesive forces are non-uniform).

Deviations from Raoult's law arises from differences in the intermolecular forces of the interaction between molecules of pure components and those of different components hence the vapour pressure composition diagrams are not linear.

They are two types of deviations.

i. **Positive deviations.**

In positive deviations the mixture of liquids show much higher vapour pressure than it is expected from Raoult's law.

This is because there is greater attraction between molecules of pure components than average attraction between molecules of different components(more repulsion between molecules of different components).

i.e. Given that A and B are the components in the mixture, forces of attraction A-A and B-B is greater than those between A-B.

This increases the escaping tendency of liquid molecules hence an observed low boiling point.

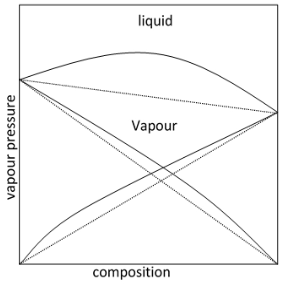
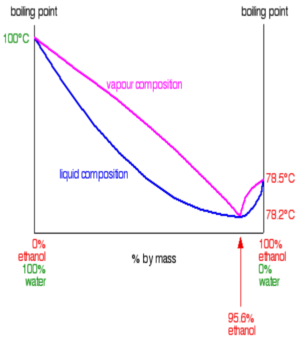
The mixtures that positively deviate from Raoult's law are accompanied by

- Increase in volume of resultant mixtures.
- Endothermic process. i.e. Heat is evolved because when you mix the liquids less heat is evolved when new attractions are formed than was absorbed when original ones are broken.

Examples of mixtures that deviate from Raoult's law.

-water/ethanol - CCl_4/methanol - benzene/cyclohexane -CS_2/acetone -ethanol/acetone

-$CHCl_3$/methanol. -methanol/cyclohexane. -n-butane/n-hexane -CCl_4/benzene ethanol/hexane.

Vapour pressure composition diagram constant temperature	**Boiling point composition diagram constant pressure:**
 Vapour pressure composition diagram ⋯⋯ curve for ideal mixture. —— curve for non- ideal mixture. -The vapour pressure curves of the mixture of two liquids bends up wards with maximum vapour pressure. Hence positve deviation from roaults law.	 **Positve deviation deviation from raoults law** **Boiling point composition diagram of water/ethanol mixture.** Bpt of ethanol: 78.5^{0}C Bpt of water: 100^{0}C Bpt of azetrope: 78.2^{0}C 95.6% ethanol An **azeotrope** is a mixture of components whose composition does not change on distillation.

ii. **Negative deviations.**

In negative deviations the mixture of liquids shows much lower vapour pressure than it is expected from Raoult's law.

This is because there is greater attraction between molecules of different components than average attraction between molecules of pure components.

i.e. Given that A and B are the components in the mixture, forces of attraction A-B is greater than those between A-A and B-B.

This decreases the escaping tendency of liquid molecules.

The mixtures that egatively deviate from Raoult's law are accompanied by

- decrease in volume of resultant mixtures.
- Exothermic process. i.e. Heat is evolved because when you mix the liquids more heat is evolved when new

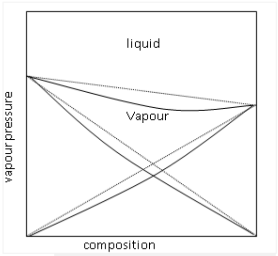
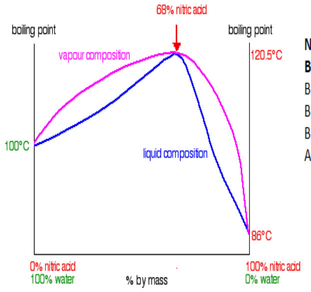
attractions are formed than was absorbed when original ones are broken.

Examples of mixtures that deviate from Raoult’s law.

-water/HCl -water/HNO_3 - water/sulphuric acid

- $CHCl_3$/propanone. -phenol/phenyl amine.

Vapour pressure - composition diagram at constant pressure…

Vapour pressure composition diagram constant temperature	**Boiling point composition diagram constant pressure**
.vapour pressure composition diagram — curve for ideal mixture. — curve for non ideal mixture. - The vapour pressure curves of the mixture of two liquids bends downwards with manimum vapour pressure. - Hence negative deviation from roaults law.	 **Negative deviation from Raoults law.** **Boiling point composition diagram water/nitric acid.** Bpt nitric acid: 86⁰C Bpt water: 100⁰C Bpt of azetrope: 120.5⁰C. Azetrope is at 68% nitric acid.

Exercise 7c.

1. a. Explain the following as related to Raoults law.

i. Positive deviation

ii. Negative deviation

b. Name two pairs of liquids which gives.

i. Positive deviation

ii. Negative deviation

c. Explain the reasons for

i. Positive deviation from Raoult’s law.

ii. Negative deviation from Raoult’s law.

d. Give two properties of mixtures that

i. Positively deviate from Raoult’s law.

ii. Negatively deviate from Raoult’s law.

2. Compound A (b.pt 372^{o}C) and compound B (b.pt 399^{o}C) form an ideal solution.

a. Sketch a labeled diagram to show the variation of vapour pressure with composition.

b. Sketch a labeled boiling point composition diagram for this mixture.

3. a. State Raoult’s law.

b. A mixture of ethanoic acid (b.pt 118^{0}C) and pyridine (b.pt 123^{0}C) show negative deviation from Raoult’s law.

i. Draw the vapour pressure composition curve for a mixture of pydrine and ethanoic acid and indicate the line for ideal gas behaviour.

ii. Explain the shape of the curve in relation to Raoult’s law.

c. Draw the vapour pressure/curve for the mixture of methanol and cyclohexane and explain the shape of the curve with reference to Raoult’s law. (positive deviation).

4. a. Draw diagrams to show how boiling temperature varies with composition for mixtures of

i. methanol T_b=65^{o}C and ethanol T_b=78^{o}C a mixture that obeys Raoult’s law.

ii. Cyclohexane T_b =81^{o}C and ethanol T_b =78^{o}C a mixture that shows positive deviation from Raoult’s law.

b. Explain why one mixture shows an ideal behavior and the other shows positive deviation.

5. a.i. Briefly explain what is meant by negative deviations from Raoult’s law.

ii. A mixture of A and B show negative deviations from Raoult’s law.

Why is that when A and B are mixed the temperature rises.

b. At standard atmospheric, hydrochloric acid and water forms a constant boiling mixture having a boiling point of 110^0C and composition 20% by mass of hydrochloric acid.

i. Define a constant boiling point mixture?

ii. Sketch a labeled diagram of a boiling point –composition for hydrochloric acid and water system.

{The boiling points of water and hydrochloric acid are 100^0C and 85^0C)

c. The boiling points of pure CH_3OH and $CHCl_3$ are 64.7 and 61.2 ^{O}C respectively. If a mixture of 87.4% $CHCl_3$ boils at 53.43^0C.

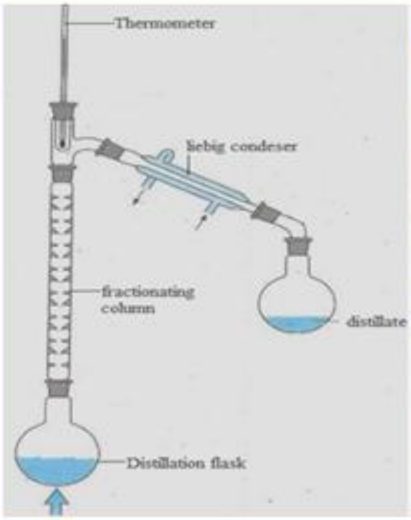
i. Identify the type of deviation.

ii. Draw a labeled diagram showing the variation of boiling point with composition,

7.2. 3. Applications of Raoult's law.

Fractional distillation

Fractional distillation is a principle of separation of two miscible liquids of different boiling points using a fractionating column.



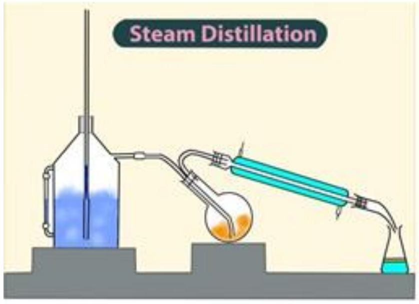
Fractional distillation is carried out in a fractionating column.
The fractionating column consists of discs in short intervals which increase the surface area of separation.
The mixture to be separated in heated in a distillation flask.
On heating, the vapour ascend the column where they condense to form a liquid.
Further heating produces more vapour which in turn heats the condensed liquid in the column.
The condensed liquid vapourises and moves to the cooler parts of column where they condense.
Successive heating finally yield the vapour of more volatile component and the thermometer records its temperature.
The less volatile component will remain in the flask until all the more volatile component comes off.

Applications of fractional distillation.

- refining of crude oil.
- manufacture of oxygen, nitrogen and rare gases from liquid air.
-production of alcoholic drinks e.g. whisky.

7.3.0. Steam distillation.

It is a technique of separating a volatile liquid which is immiscible with water from a non-volatile component at a temperature below its boiling point using steam.

	**Process** During steam distillation, the liquid mixture is heated directly by passing steam through it. A vapour is produced and evaporates is cooled and separates into a solution of two layers. This solution can be separated by using a separating funnel or by filtration if solid is formed. **Principle** The mixture of two liquids boil at a temperature lower than the boiling temperature of one of the volatile substances.(because) In this process, the two liquids contribute its own vapour pressure so that the top vapour pressure is the total vapour pressure of the mixture. This mixture boils at a (low)temperature when the mixture saturated vapour pressure is easily equals to the atmospheric pressure.

Application.

Steam distillation is used to separate a mixture of 2-nitrophenol and 4-nitrophenol.

It applied during purification of phenylamine.

Conditions under which compounds are separated by steam distillation.

-should be immiscible with water.

-Should have a high molecular mas.

Calculating molar mass using a principle of steam distillation.

Vapour pressure of pure component is directly proportional to number of moles.

$P^0 \propto n$

Consider two immiscible liquids.

$P^0_A \propto n_A$

$P^0_B \propto n_B$

$\frac{P_A^o}{P_B^o} = \frac{n_A}{n_B}$ but $n_A = \frac{m_A}{M_A}$ $n_B = \frac{m_B}{M_B}$

$\frac{P_A^o}{P_B^o} = \frac{m_{A/M_A}}{m_{B/M_B}}$ $P_T = P_A + P_B$

Worked example:

1. After distilling at 101kpa pressure for some time the distillate was found to contain 1 g of water and 0.48g of X. Given that the vapour pressure of X is 15kpa.

Calculate a. the Molar mass of X.

b. the composition of distillate by mass.

2. A compound X was steam distillated at 80°C and 760mmHg and the distillate found to contain 90.8% by mass of X. Calculate the formula mass of X? (vapour pressure of water at 80°C is 240mmHg)

3. A mixture of naphthalene $C_{10}H_8$ and water distils at 98.3°C and 753mmHg.

Calculate the composition of the distillate as a percentage by mass. The vapour pressure of water at is 715 mmHg.

A is water and B is $C_{10}H_8$.

Exercise 7c:

1. When a substance Y was distilled at 93°C and 950mmHg, the distillate 55% by mass.

Calculate the relative molecular mass Y.

(the partial pressure of water at 93°C is 654mmHg) (150)

2. a. Define the term steam distillation.

b. When a compound Y was steam distilled at standard atmospheric pressure the distillation temperature was 86°C. The distillate contained 85% by mass of water.

Calculate the relative molecular mass of Y. (118)

3. a. State three conditions which can enable components of a liquid mixture separated by steam distillation.

b. When a mixture of liquids A and B was steam at 96°C at pressure of 774 mmHg. The distillate is 55% by mass of A. (The vapour pressure of water is 634mmHg).

c. Give two examples of compounds separated by steam distillation.

7.4.0. Colligative properties.

A colligative property is a property that depends on the number of non-volatile solute dissolved in a solvent to form a solution independent of their chemical nature.

The properties include*:*

Boiling point elevation.
Freezing point depression.
Osmotic pressure change.
Vapour pressure lowering.

These properties are important in determination of relative molecular mass of a solute dissolved in a solvent but it is possible if the conditions below are meet.

-There should not be any reaction between solvent and solute.
-There should not be association or dissociation of the solute.
-The solution should be very dilute.
- The solute should be non-volatile.

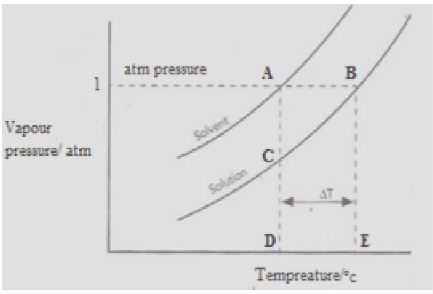
7.4.1. Boiling point elevation.

Boiling point elevation is the increase in boiling point by addition of a non-volatile solute.

Boiling point.

Boiling point is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.

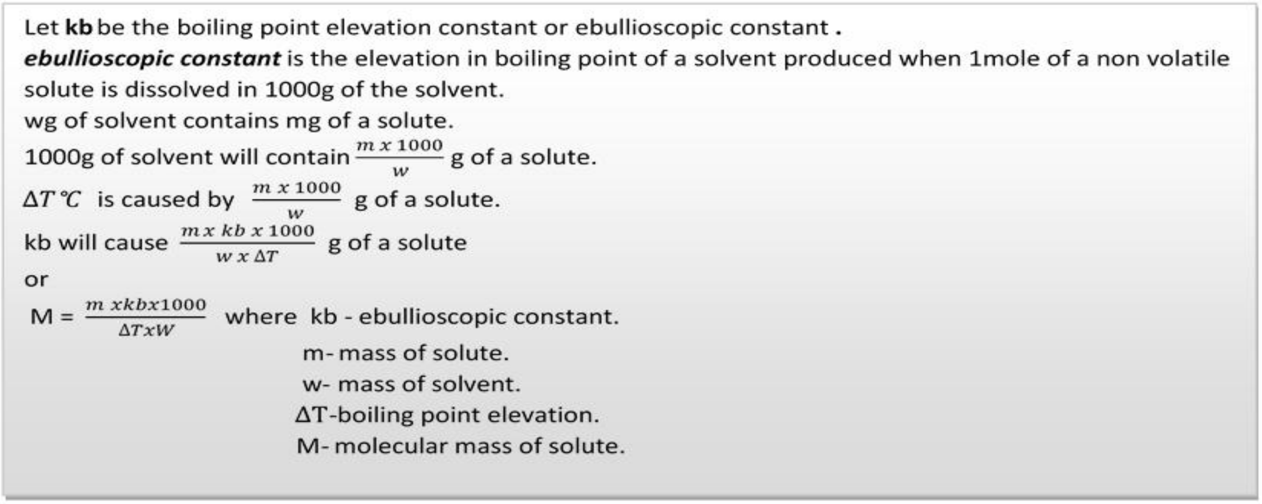
When a solute is dissolved in a solvent, it lowers its vapour pressure so temperature has to be raised to raise the lowered vapour pressure which increases its boiling point.i.e. boiling point elevation.



Variation of vapour pressure with boiling temperature at prevailing atm pressure of 1 atm.

A – vapour pressure of solvent at it's boiling point(atm pressure).
B – vapour pressure of solution at it's boiling point.
C- vapour pressure of solution at it's boiling point of solvent.
D – Temperature at which solvents boils.
E – Temperature at which solution boils.
DE- Elevation in boiling point, ΔT°C.
AC- Vapour pressure lowering,
$\Delta P = P^0 - P$.

Determination of relative molecular mass of a solute using boiling point elevation method.



Let **kb** be the boiling point elevation constant or ebullioscopic constant **.**

ebullioscopic constant is the elevation in boiling point of a solvent produced when 1mole of a non volatile solute is dissolved in 1000g of the solvent.

wg of solvent contains mg of a solute.

1000g of solvent will contain $\frac{m \, x \, 1000}{w}$ g of a solute.

$\Delta T\,℃$ is caused by $\frac{m \, x \, 1000}{w}$ g of a solute.

kb will cause $\frac{m \, x \, kb \, x \, 1000}{w \, x \, \Delta T}$ g of a solute

or

M = $\frac{m \, xkbx1000}{\Delta TxW}$ where kb - ebullioscopic constant.
m- mass of solute.
w- mass of solvent.
ΔT-boiling point elevation.
M- molecular mass of solute.

Worked example:

1. The boiling point of ethanol is 78°C with a boiling point elevation constant of 11.5°C per 1000g. A solution 0.56g of camphor in 16g of ethanol boiled at 78.278°c.
Calculate relative molecular mass of camphor.

2. Calculate the boiling point constant k_b for dichloromethane if 0.4g of champs in 34.5g of dichloromethane raises the boiling point by 0.3°C (champs is $C_{10}H_{16}O$)

3. Calculate the boiling point of a solution of urea, $CO(NH_2)_2$ of concentration 12 gdm^{-3} at a pressure of 101.1kPa of ethanamide.(boiling point elevation constant of water $0.52^0C\ kg^{-1}\ mole^{-1}$).
Assume volume of solute is negligible. (N=14, H=1, O=16, C=12)

Exercise 7.d

1.The boiling point of ethanol is 78°C. Calculate the boiling point of a solution containing 2.7g of ethanamide in 75g of ethanol. (boiling point elevation constant of ethanol 1.15°C per 100g).

2. Explain what is meant by colligative property.

b. A solution was prepared by dissolving 7.5g of propane-1,2,3-triol, $C_3H_8O_3$ in 200g of
water at 25° C. Calculate the boiling point of the solution formed.
(Boiling point constant for water = $0.52^0C\ mol^{-1}kg^{-1}$)

c. Give 2 limitations of the above method.

d. Explain why this method is not suitable for determining molecular mass of ethanoic acid.

3. A solution containing 4.2grams of an organic compound in 50grams of acetone shows an elevation of boiling point by 1.8K. Determine the molar mass of the organic compound.K_b of acetone=1.71 K kg/mol.

4. The boiling point of benzene is 353.23K. when 1.80g of a non-volatile solute was dissolved in 90g of benzene; the boiling point is raised to 354.11K. Calculate the molarmass of the solute. K_b for benzene is 2.53 K kg/mol.

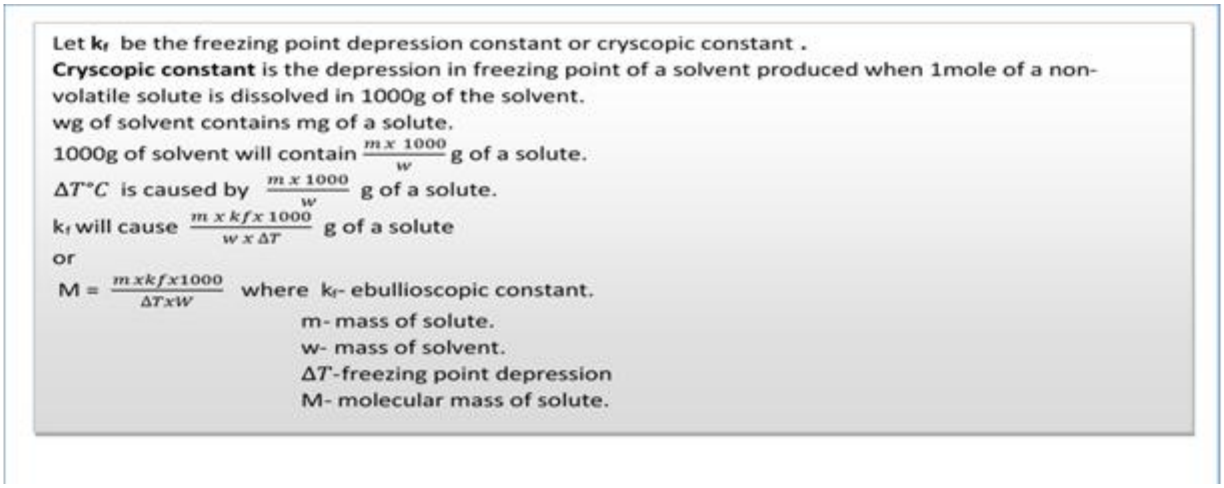
7.4.2. Freezing point depression.

Freezing point depression is the decrease in freezing point by addition of a non-volatile solute.

Freezing point.

Freezing point is the fixed temperature at a given pressure at which a liquid substance turns into solid when two phases are at equilibrium.

Determination of relative molecular mass of solute using freezing point depression method.



Let k_f be the freezing point depression constant or cryscopic constant .
Cryscopic constant is the depression in freezing point of a solvent produced when 1mole of a non-volatile solute is dissolved in 1000g of the solvent.
wg of solvent contains mg of a solute.
1000g of solvent will contain $\frac{m\,x\,1000}{w}$ g of a solute.
$\Delta T°C$ is caused by $\frac{m\,x\,1000}{w}$ g of a solute.
k_f will cause $\frac{m\,x\,kf\,x\,1000}{w\,x\,\Delta T}$ g of a solute
or
$M = \frac{m\,x kf x 1000}{\Delta T x W}$ where k_f- ebullioscopic constant.
m- mass of solute.
w- mass of solvent.
ΔT-freezing point depression
M- molecular mass of solute.

Worked example.

1. Calculate the k_f of nitro benzene if 0.55g of nitro benzene in 22g of ethanoic acid lowers the freezing point of ethanoic acid by 0.78^0C using first principles.

2. The freezing point of cyclohexane is 6.5^0 C, a solution of 0.65g of naphthalene in 19.2g of cyclohexane began to

freeze at 1.2^0C. What is the relative formula mass of naphthalene given that k_f of cyclohexane is 201^0C mol^{-1} per 100g

Exercise 7.e

1. Annon-electrolyte solute1 g dissolved in 50g of benzene lowered the freezing point of benzene by 0.40K.
The freezing point depression constant of benzene is 5.12Kkg/mol. Find the molar mass of the solute.

2. A solution of 2.95g of sulphur (molecules) in 100g cyclohexene has freezing point of 4.18^OC.
Pure cyclohexane has a freezing point of 6.5^OC.

a. Calculate the molecular mass of sulphur.

b. Calculate the molecular formula of sulphur.

(Atomic mass of sulphur = 32, kf =20.2^oC Kg mol^{-1})

3. a. Explain the term colligative property.

b. The freezing point of a sample of pure benzene was found to be 5.481^oC. A solution of 0.321g of a naphthalene, $C_{10}H_8$, in 25g of benzene begins to freeze at 4.91^oC.
Calculate the molar freezing point of benzene.

c. Hence calculate the RMM of benzoic acid given that a solution of 0.305g of benzoic acid in 25g of the same solvent benzene begins to freeze at 5.226^0C.

d. Explain how molecular mass can be obtained using the method of depression in boiling point.

4. An organic liquid C has a freezing pointof 198.5°C and molal depression constant of45.5°C/m. When 0.049 gof a substance A was dissolved in 0.521 gof C, the resultant mixture was found to freeze at 186°C. Calculate the molarmass of A.

5. What mass of ethylene glycol ($C_2H_6O_2$, molarmass = 62.1g/mol), the main component of antifreeze, must be added to 10L of water to produce a solution for use in a car's radiator that freezes at-23.3°C? Assume the density of water is exactly 1g/ml.k_f= 1.86^o*C.Kg/mol*

6. An organic liquid C has a freezing pointof 198.5°C and molal depression constant of 45.5°C/m. When 0.049g of a substance A was dissolved in 0.521 g of C, the resultant mixture was found to freeze at 186°C. Calculate the molarmass ofA.

7. A chemist is trying to identify a human hormone that controls metabolism by determining its molarmass. A sample weighing 0.546g was dissolved in 15.0g benzene, and the freezing point depression was determined to be 0.240°C. Calculate the molar massof the hormone. K_f for benzene is 5. 12°C/Kg/mol.

7.4.3. Osmotic pressure

Osmotic pressure is the pressure which must be applied to stop solvent molecules from diffusing across a semi permeable membrane or this pressure required to prevent osmosis when a solution separated from a pure solvent by a semi permeable membrane.

OSMOSIS

This the process by which solvent molecules move from region of low concentration of solute to a region of higher concentration of solute through a semi permeable membrane.

The passages of solvent molecules from one solution into a more concentrated solution gives rise to a pressure called osmotic pressure.

Osmotic pressure measurements provide a useful way of molar masses determination of large molecules,like protein, polymers and other macromolecules because small pressures can be measured easily and accurately.

Advatanges of osmotic pressure method over other methods.

Pressure measurement is around the room temperature

The molarity of the solution is used instead of molality.

Its magnitude(change) is large even for very dilute solutions.

This technique of osmotic pressure for determination of molarmass of solutes is therefore useful for bio molecules as they are generally not stable at higher temperature and polymers have poor solubility.

Note:

The laws on osmotic pressure are similar to those of ideal gases eg

PV = nRT where P is the osmotic pressure of solution and is denoted by π, i.e

πv=nRT

πv=nRT

$\pi=\frac{n}{v}$RT But $\frac{n}{V}$ concentration C of solution

π=CRT

Also from, πv=nRT

$\pi v=\frac{m}{M}RT$

$M=\frac{mRT}{\pi V}$

Worked example

1. A solution containing 10g dm^{-3} gave an osmotic pressure of 0.703atm at 20^0c.

Calculate the relative molecular mass of the sugar.

2. A sugar solution with concentration 2.5g $dm^{-3,}$ gave an osmotic pressure of 8.3 x10^{-4}atm at 25^0c calculate the relative molecular mass of the solute.

3. A solution of poly vinyl chloride $(CH_2CHCl)_n$ in an organic solvent has a concentration of 4gdm^{-3} and an osmotic pressure of 65Nm^{-2} at 20^0c .

Calculate i. the molecular mass of poly vinyl chloride

ii. the value of n

4. Calculate the osmotic pressure in pascals of 2% of a solution of glucose at 18°C.

Exercise 7.e

1. a**.** The osmotic pressure of solution containing 1.4g of polymer x per 100cm^3 of solution is 1200Nm^{-2} at 25°C.

i. Calculate relative molecular mass of X.

ii. Given that the monomer of X is ethene.

Find the number of monomer units X has.

b. Give any limitations for the above method during determination of molecular mass

2.a. Explain the term osmosis

b. State the conditions under which solutions do not obey laws of osmotic pressure.

c. The osmotic pressure of a solution containing 1.24% of polymer is 3.1 x 10^{-3} atmospheres at 25°C.

Determine the molecular formular of the polymer. (R =0.0821Lmol^{-1}K^{-1})

3. An aqueous solution of 1.10g of a protein in 100ml of a solution has osmotic pressure of 3.93 x 10^{-3}atmospheres at 25^{O}C (298K).
Calculate the molecular mass of the protein. (R= 0.08203 L.atm.mol^{-1}. K^{-1})

4.The osmotic pressure of a queous solution of acertain protein was measured inorder to determine the molarmass of the protein.The solution contained 3.50mg of protein dissolved insufficient water to form 5.00ml of solution.The osmotic pressure of the solution at 25°C was found to be1.54 torr. Calculate the molarmass of the protein.

5. A 50.00mL sampleof an aqueous solution contains 1.08g of human serum albumin, a blood plasma protein.The solution has an osmotic pressure of 5.85torr at 298K.what is the molar mass of the albumin?

6. An organic compound A contains, carbon, hydrogen and oxygen only. On combustion, 0.463g of A gave 1.1g carbon dioxide and 0.563g of water.

a. Determine the empirical formula of A.

b. When 0.1g of A occupies 54.5cm^{3} at 208^{o}C and 98.3kPA.
Determine the molecular formula of A.

c. A reacts with sodium metal with evolution of a gas. Write the structural formulae of possible isomers of A.

d. A reacts with anhydrous zinc chloride and concentrated hydrochloric acid to give a cloudy solution in about 5 minutes.

i. Identify A.

ii. Show how A could be synthesized from but-2-ene.

Reverse Osmosis and Water Purification

Reverse osmosis

Is the process by which a pressure higher than the osmotic pressure is applied to the more concentrated solution side such that the direction of flow of the solvent can be changed.
As a result, the pure solvent flows out of the solution through the semipermeable membrane.

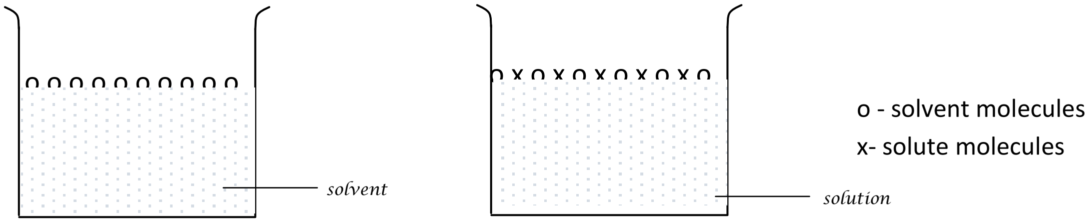
It is of great practical application as it is used for de-salination of seawater to obtain pure water.

When pressure more than osmotic pressure is applied, purewater is squeezed out of the seawater through the membrane.
These days many countries,such as desert Arab countries,use desalination plants based on this technology to meet their potablewater requirements.

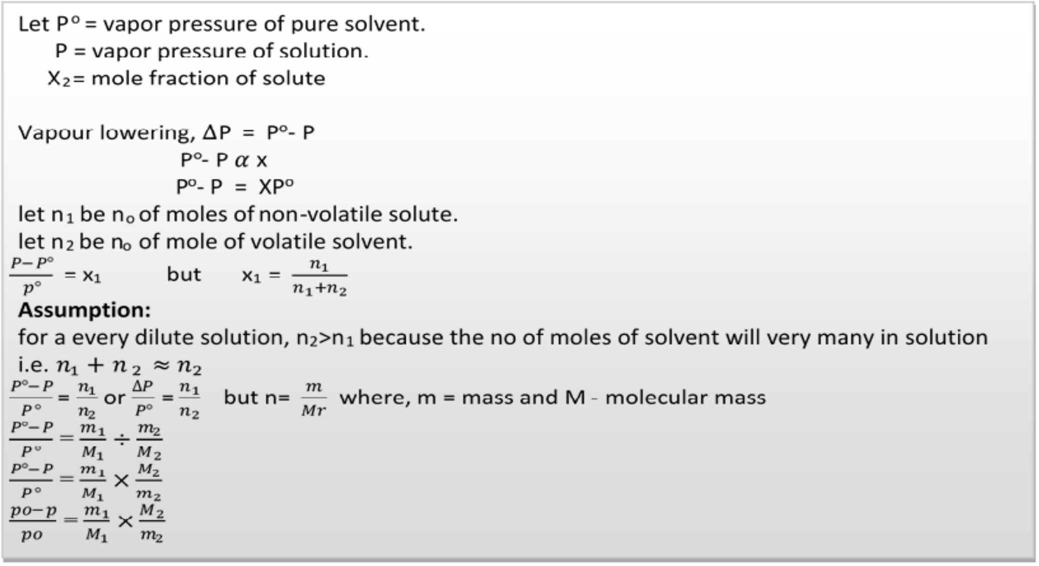
7.4.4. Vapour pressure lowering of the solvent.

Vapour pressure of liquid is the pressure exerted by the vapour when in equilibrium with the liquid.
When a nonvolatile solute is dissolved in solvent, the vapor pressure of the solvent is lowered. i.e. the vapor of a solution containing nonvolatile solute is less than that of the solvent

Explanation



The presence of the non-volatile molecules at the surface of the solution reduces the escaping tendency otherwise volatile solvent molecules.
Since fewer solvent molecules are present at the surface of the solution than that the solvent therefore few solvent molecules can escape and form vapor molecules consequently the vapor pressure will be low.
The lowering of the vapor pressure is given by ***Raoult's law*** is stated that
"*the relative lowering of vapor pressure of a solution containing a non-volatile solute is proportional to the mole fraction of the solute in the solution.*



Let P° = vapor pressure of pure solvent.
P = vapor pressure of solution.
X_2= mole fraction of solute

Vapour lowering, $\Delta P = P° - P$

$P° - P \alpha x$

$P° - P = XP°$

let n_1 be n_o of moles of non-volatile solute.
let n_2 be n_o of mole of volatile solvent.

$\frac{P-P°}{p°} = x_1$ but $x_1 = \frac{n_1}{n_1+n_2}$

Assumption:
for a every dilute solution, $n_2>n_1$ because the no of moles of solvent will very many in solution
i.e. $n_1 + n_2 \approx n_2$

$\frac{P°-P}{P°} = \frac{n_1}{n_2}$ or $\frac{\Delta P}{P°} = \frac{n_1}{n_2}$ but n= $\frac{m}{Mr}$ where, m = mass and M - molecular mass

$$\frac{P°-P}{P°} = \frac{m_1}{M_1} \div \frac{m_2}{M_2}$$

$$\frac{P°-P}{P°} = \frac{m_1}{M_1} \times \frac{M_2}{m_2}$$

$$\frac{po-p}{po} = \frac{m_1}{M_1} \times \frac{M_2}{m_2}$$

Raoult's law can also be stated as:
The vapor pressure of solution p is equal to the product of the mole fraction of solvent and the vapor pressure of the pure solvent at a given temperature.

Worked example.

1. The vapor pressure of water at 20^oc is $1.20 \times 10^4 Nm^{-2}$. if at the same temperature the vapor pressure of a solution of 30g of an non-volatile solute W in 100g of water is $1.10 \times 10^4 Nm^{-2}$.

Calculate the molecular mass of W.

2. The vapor pressure of water at 18 °C is 2.33×10^3pa solution was made by dissolving 33.6g of sucrose $C_{12}H_{22}O_{11}$ in 500g of water calculate :

a. the vapor pressure of the solution at 18^oc

b. the vapor pressure lowering of the solution

Exercise 7.f

1.The vapour pressure of a solvent at 25°C is 3.15×10^3Pa . Calculate the vapour pressure of a solution of 6g of urea $CO(NH_2)_2$ in 100g of water at the same temperature.

2.The relative lowering of vapour pressure roduced by dissolving 7.2g of a substance in 100g of water is 0.00715mmHg. What is the molecularmass of the substance? Vapour pressure water is 760 mmHg

3. Vapourpressure of waterat 293 K is 17.535 mmHg. Calculate the vapour pressure of solution at 293 K when 25g of glucose is dissolved in 450g of water.

4. The vapour pressure of CS_2 at certain temperature is 53330 pascals. At the same temperature, a solution of 5g of sulphur in $63cm^3$ of CS_2 has a vapour pressure of 52340 pascals. The density of CS_2 is $1.27g/cm^3$.

Calculate the

a. the relative formular mass of sulphur.

b. molecular formular of Sulphur.

Trial questions.

Multiple choice questions.

1. a. The distribution coefficient of Y between ethoxyethane and water is 5 an aqueous solution of Y with volume of $5000cm^3$ contain 10g.

Calculate the mass of Y that will be extracted by $100cm^3$ of ethoxyethane?

a. 2.5g b.5g c.7.5g d. 10g e.12.5g

2. An aqueous solution contains 4g of X in $100cm^3$ of solution. The partition coefficient of X between water and diethyl ether is 4. Calculate the mass of X extracted by shaking of $100cm^3$ of aqueous solution with two successive $50cm^3$ of organic solvent.

a. 2.5g b.3.55g c.7.5g d. 10g e.12.5g

3. The constant ratio of concentrations of solute in two immiscible liquid is called

a. kc b. kp c. k_D d. k_f

4. Which of the following metals can be concentrated by solvent extraction.

a. Fe b. W c. Al d.Na

5. Which of the of is not true about the partition coefficient.

a.Ttemperature should be constant.

b. The liquid must be miscible.

c.The solvent should not react with each other.

d.The solute and solvent should not react with each other.

6. X and Y are two miscible liquids which form an ideal mixture. Given that their saturated vapour pressure arep^o_x = 25kpa. P^o_y = 45kpa. Given that the mixture contains 1 mole of x and 4 moles of y. Calculate the total pressure.

a.5kpa b. 36kpa c.41kpa d. 20kpa

7. Liquids A and B have saturated vapour pressure are p^o_A = 15kpa. P^o_y = 40kpa. Calculate the saturated vapour pressure of a mixture that contains 2 moles of x and 3moles of B.

a.6kpa b.30kpa c.24kpa d. 16kpa

8. A solution that deviates positively from Raoult's law because

a. There is greater attraction between molecules of pure components than average attraction between molecules of different components.

b. There is greater attraction between molecules of different components than average attraction between molecules of pure components.

c. There is equal attraction between molecules of pure components than average attraction between molecules of different components.

d. There is less attraction between molecules of pure components than average attraction between molecules of different components.

9. Which of the is not true about the solutions that negative deviate from Raoult's law.

a. ions shows much lower vapour pressure than it is expected from Raoult's law.

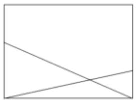
b. e is less attraction between molecules of different components than average attraction between molecules of pure components.

c. The escaping tendency of liquid molecules decreases.

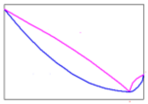
d. The mixtures that negatively deviate from Raoult's law are accompanied by decrease in volume of resultant mixtures.

10.Identify a boiling point-composition diagram for the solution that deviates positively from Raoult's law.

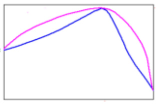
a.



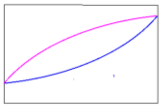
b.



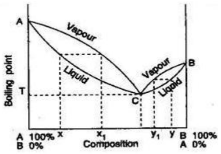
c.



d.



11. Which type of relationship is shown by the following boiling point-composition diagram.



a. positive deviation from Raoult's law. b. negative deviation from Raoult's law.

c. Obeys Raoult's law. d. No deviation from Raoult's law

12. When a compound Y, was steam distilled at atmosphere pressure, the temperature on distillation was 96^{o}C.The vapour pressure of water was 740mmHg and distillate contained 74% of water.

Calculate the RMM of Y.

a. 120 b. 153.89 c. 50 d.140

13. A solution of A g of cane sugar (342g/mol) in 105g of water boiled at 100.06^{0}C. Find the value of A

a. 4g b.3g c. 2g d.1g

14. The freezing point of 3.1g of sucrose $C_{12}H_{22}O_{11}$ in 100g ofwater freezes at -0.204^{O}C. If a solution of 27.3g per dm^{3}of W freezes at-0.282^{0}C. Calculate the mass of compound W.

a. 160g b. 170g c.140g d.182.5g

15. At 25^{0}C, the osmotic pressure of a solution containing 1.35g of protein per 100cm^3 of solution was found to be 1216 Pa. Calculate the relative molecular mass of the protein if the molar volume of s. t.p is 22.4dm^3.

a. 27506 b.2750.6 c.275.06 d.27.506

16. The vapour pressure of a solution of 29g of a substance X in 100g of water at 50^{o}C is 1.12 x10^{4}Pa.If at the same temperature, the vapour pressure f water alone was 1.22 x 10^{4}Pa. Calculate the molecular mass of X.

a.50g b.60g c.52g d. 64g

17. Which of the following is not a colligative property.

a. Boiling point elevation b.Freezing point elevation.

c. Osmotic pressure change. d.Vapour pressure lowering.

18. When a small amount of a non-volatile solute is added to a solvent, there is increase in boiling point because of

a. increase in vapour pressure above the solution. c. decrease in atmospheric pressure.

b. decrease in vapour pressure above the solution. d. Increase in volume.

19. On the basis of information given below, mark the correct option. Information: on adding acetone to methanol some of thehydrogen bondsbetween methanol molecules break.

a.At specific composition methanol-acetone mixture forms minimum boiling azeotropeand will show positive deviation from Raoult‘s law.

b.Atspecific composition methanol-acetone mixture forms maximum boiling azeotrope and will show positive deviation from Raoult‘s law.

c.At specific composition methanol-acetone mixture will form minimum boiling azeotrope and will show negative deviation from Raoult‘s law.

d.At specific composition methanol-acetone mixture will form maximum boiling azeotrope and will show negative deviation from Raoult‘s law.

20. In bromoethane and chloroethane mixture intermolecular interactions of A-Aand B-B type is nearly the sameas A-B type interactions. This solution

a. Obeys Raoult’s law.

b. Deviates positively from Raoult’s law.

c. Deviates negatively from Raoult’s law.

d. Is an immiscible mixture.

21. The vapour pressure of 5% aqueous solution of a non volatile organic substance at 373K is 745 mmHg. Calculate the molar mass of the substance. Vapour of water is 760mmHg.

a.50% b.60% c. 47% d.40%

22.Colligative properties are observed when:

a.anon-volatile solid is dissolved in a volatile liquid

b.anon-volatile liquid is dissolved in anothervolatileliquid

c. agas isdissolved in anon-volatileliquid

d.avolatileliquid is dissolved in anothervolatile liquid

23. Which of the following binary mixtures will have same composition in liquid and vapour phase?

a.Benzene-Toluene

b.Water-Nitricacid

c.Water-Ethanol

d. n-Hexane-n-Heptane

24.Considering the following couples of solvents, predict which mixture will show a positive deviation from Raoult‘s law.

a.Methanol and acetone

b. Chloroform and acetone

c.Nitric acid and water

d.Phenol and aniline

25. Relative lowering of vapour pressure is a colligative property because

a.It depends on the concentration of anon-electrolyte solute in solution and doesnot depend on the nature of the solute molecules.

b.It depends on number of particles of electrolyte solute in solution and doesnot depend on the natureof the solute molecules.

c.It depends on the concentration of a non-electrolyte solute in solution as well as on the nature of thesolute molecules.

d. It depends on the concentration of an electrolyte or a non-electrolyte solute in solution as well as on the nature of solute molecules.

26. If two liquids A and B form minimum boiling azeotrope at some specific composition:

a.A-B interactions are stronger than those between A-A orB-B

b.Vapourpressure of solution increases because more number of molecules of liquids A and B can escape from thesolution.

c.Vapour pressure of solution decreases because less number of molecules of only oneof the escape from the solution.

d. A-B interactions are weaker than those between A-A orB-B

27. Colligative properties depend on

a.The natureof the solute particles dissolved in solution

b.The number of solute particles in solution

c.The physical properties of the solute particles dissolved in solution

d.The natureof the solvent particles.

Structural questions.

1. a. The question concerns the Nernst distribution law as applied to solvent extraction.

a. State the distribution law?

b. Define solvent extraction?

c. A solution of6g of substance X in 50ml of aqueous solution is in equilibrium at room temperature, with a solution of diethyl ether containing 108g of X in 100ml.

Calculate the mass of X extracted by shaking 100ml of an aqueous solution 10g of X with

i. 100cm^3 of ether.

ii. 50cm^3 of ether twice at room temperature and pressure.

d. State the limitations of distribution law.

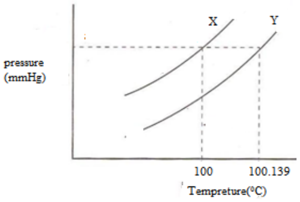
2. The vapour pressure of a solution containing 1 mole of liquid A and 4 moles of liquid B at 1 atm.

The vapour pressure of pure A and pure B are 0.674 and 0.453 atmospheres respectively

a. Calculate the vapour of solution A and B if it obeys ideal law?

b. If the solution deviates from Raoult's law. Give a reason for your answer? 0.4972atm

3. A non-volatile substance 5.5g, B was dissolved in 125g of solvent. The vapour pressure curves are shown below.



a. Identify curves X and Y.

b. Calculate the molecular mass for B.

(boiling point elevation constant of water 0.52^0C per kg mole $^{-1}$)

c. If compound B contains 62% carbon, 10% hydrogen, the rest being oxygen.

i. Determine the empirical formular of B.

ii. Determine the molecular formular of B.

iii. Write down the structural formulae of possible isomers of B.

4.A compound P contains 67.7 % carbon, 11% hydrogen, the rest being oxygen.

a. Determine the empirical formula of P.

b. 7.2 g of organic compound P was dissolved in 250g of water and caused depression in freezing point of 0.744^0C.

(Kf of water is 1.86^0C mol-1 kg^{-1}) find the molecular mass of P and hence determine the molecular formular of P.

c. Write down the structural formulae of possible isomers of P.

d. If P reacts with Tollens reagent. Identify P give the observation for reaction.

5. When 0.155g of an organic compound T was burned in oxygen 0.22g of CO_2 and 0.135g of H_2O was formed.

a. Determine the empirical of T.

b. When 0.225g of T was vapourised at 127^oC and 760mmHg, it occupied a volume of 119.11cm^3.

(molar gas volume at s.t.p is 22.4dm^3)

i. Calculate the molecular mass of T.

ii. Deduce the molecular formular of T.

c.If T reactswith acidified potassium dichromate to form ethane-1,2-dioic acid.

Give the IUPAC name and formular of T

6.a. A solution containing 20g of polymer X in 1lof solvent exerts an osmotic pressure of 1.4mmHg at 25^0C.

i. Explain what is mearnt term osmosis.

ii. Calculate the molecular mass of X.

iii. The molecular formular of the monomer of X is (CH_2=CHCN)

Determine the number of monomer units.

b.i. Calculate the freezing point depression of the solvent in (a) if K_f = 5^0C per litre.

ii. Explain why freezing point depression is not suitable for determining the molecular mas of the polymer.

7. Explain the following

a. Water boils at 100°C at a pressure of 760mmHg. When the pressure is reduced to 660mmHg, water boils at 96°C.explain this observation.

b. The molecular masses of polymers are determined by osmotic pressure method and not by measured other colligative properties.

c. Measurement of molar mass of ethanoic acid using boiling point elevation method,it gives a molar mass twice its original value.

8. Benzoic acid can be separated from water using octanol as the organic solvent. The distribution coefficient for this water/octanol system is P=1.87. Assuming that 1gram of benzoicacid has been dissolved in 100mL of water, how many 20mL extractions must be doneto extract 60+ percent of the benzoic acid from the water.

8.0CHEMICAL EQUILIBRIA.

8.0. Introduction

A dynamic equilibria is developed when chemical reactions take place and this is usually referred to as chemical equilibria.

A chemical equilibrium basically deals with *reversible reactions.*

A reversible reaction is a reaction that proceeds in both direction. i.e. proceeds in the forward and backward reactions.

Some reversible reactions include.

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

$2SO_{2(g)} + 2O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

For chemical equilibria to exist the rate of forward reaction is equal to the rate of backward reaction and this equilibria is said to be dynamic

8.1. The equilibrium constant, K_c and the equilibrium law.

Consider the reversible reaction

$aA + bB \rightleftharpoons cC + dD$

Rate of forward reaction $= K_1[A]^a[B]^b$

Rate of backward reaction $= K_2[C]^c[D]^d$

At equilibrium

Rate of forward reaction = Rate of backward reaction

so, $K_1[A]^a[B]^b = K_2[C]^c[D]^d$

$$\frac{K_1}{K_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \text{ i.e. } \frac{K_1}{K_2} = K_c$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b},$$

Kc is the equilibrium constant and is the ratio of concentration of products raised to appropriate powers to the of concentration of reactants raised to appropriate powers.

The above expression represents equilibrium law or law of chemical equilibrium.

The equilibrium law therefore states that if a reaction is at equilibrium, the ratioof concentration of products raised to appropriate powers to the of concentration of reactants raised to appropriate powers has a constant value called the equilibrium constant, Kc , at a given temperature.

NB:

1.Solids are not included in the expression for equilibrium constant because their concentrations are regarded as constants.

2. When water (in liquid state) is part of reactants, it is not put in the expression for equilibrium because is considered to be in large excess hence a constant.

3. if the K_c value is greater than 1, the forward reaction is favoured.

if the K_c value is less than 1, the backward reaction is favoured.

worked examples.

1. Write down the expression for equilibrium constant, Kc, for the following equations and give its units.

a. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

b. $CH_3COOH_{(l)} + CH_3CH_2OH_{(l)} \rightleftharpoons CH_3COOCH_2CH_{3(l)} + H_2O_{(l)}$ (hint units are in $moldm^{-3}$)

c. $CaCO_{3(s)}$ $CaO_{(s)} + CO_{2(g)}$

d. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

2. $H_{2(g)}$, $I_{2(g)}$ and $HI_{(g)}$ exist in equilibrium. if their equilibrium concentrations are $H_{2(g)}$ 0.14 $moldm^{-3}$, $I_{2(g)}$ 0.04$moldm^{-3}$ and $HI_{(g)}$ 0.32 $moldm^{-3}$.

Calculate the value of equilibrium constant ,Kc.

3. N_2O_4 and NO_2 exist in equilibrium in a closed container of volume $2dm^3$.

$N_2O_{4(g)} \rightleftharpoons 2NO_2(g)$

Calculate the equilibrium constant if moles present at equilibrium are N_2O_4 is 0.4moland NO_2 is 3.2mol.

Exercise 8a

The conversion of sulphur dioxide into sulphur trioxide in the contact process is a reversible reaction.

a. Write a balanced equation for reaction.

b. Write an expression for the equilibrium constant, K_c, for the reaction in(a)

c. Calculate the value of the equilibrium constant, K_c, and state the units given that the amounts present at equilibrium were:

SO_2= 0.4 $moldm^{-3}$; O_2= 0.2 $moldm^{-3}$; SO_3= 1.2 $moldm^{-3}$.

Worked examples 8b

The production of ammonia in the Haber process involves the reaction:

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

a. Write an expression for the equilibrium constant, K_c, for the above reaction.

b. 0.2mol of $N_{2(g)}$ and 0.20mol of $H_{2(g)}$ were reacted in $1dm^3$ closed container until equilibrium was reached. At equilibrium, the concentration of $NH_{3(g)}$ was 0.060 $moldm^{-3}$.

i. Calculate concentrations of $N_{2(g)}$ and $H_{2(g)}$ at equilibrium.

ii. Calculate the value of K_c and state its units.

2. Stochiometric amounts of nitrogen and hydrogen where mixed in $1dm^3$ of vessel.

At equilibrium, 0.8mol of ammonia were present.

Calculate the value of Kc.

Exercise 8b

1. Two gases reacted to form a gaseous product as shown by the following equation:

$2A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$ $\Delta H = -100kJmol^{-1}$

a. Write an expression for the equilibrium constant, K_C, for the above reaction and state its units.

c. 2 mol of a gas A were reacted with 1 mol of gas B to form gas C in a closed vessel of a volume of $1dm^3$. After reaching dynamic equilibrium, it was found that 0.6 mol of A remained in the gaseous mixture.

i. Calculate the number of moles of A that reacted.

ii. Calculate the number of moles of C that were produced. Hence calculate the value of the equilibrium constant, K_c, for the reaction.

2. Given

$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

if 2.0moles of CH_3COOH were mixed with 3.00 moles C_2H_5OH were mixes and allowed to reach equilibrium when 0.43 moles of CH_3COOH had remained.

a. How many moles of CH_3COOH reacted.

b. Find the value of K_C.

3. When 1 mole of hydrogen iodide is allowed to dissociate in1dm^3 vessels at 440^0C, and only 0.78moles of HI are present at equilibrium. What is the equilibrium constant Kc.

4. 1 mole of sulphur trioxide is allowed to dissociate in1dm^3 vessels at 1000K, and only 0.35moles of sulphur trioxide are present at equilibrium. Calculate the equilibrium constant Kc .

Worked example 8c

1. Nitrogen monoxide combines with oxygen to form nitrogen dioxide according to the following equation.

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

a. Write down the expression for K_c.

b. 3mol of $NO_{(g)}$ and 1.50mol of $O_{2(g)}$ were reacted in 1dm^3 closed container until equilibrium was reached . At equilibrium 25% of initial nitrogen monoxide was found to remain.

Calculate the value of K_c.

2. Given the following reaction placed in 1dm^3 reacts to reach equilibrium.

$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$ mk,m,\\\\\\\\\\\\\hjm/]]]]]]]]]

Calculate the value of equilibrium constant Kc of the reaction, given that under an equilibrium pressure of 200atm at a temperature 200^0C, 15% of CO reacted.

Exercise 8c.

1.a. Dinitrogen tetraoxide and nitrogen dioxide exist at equilibrium.

$N_2O_4 \rightleftharpoons 2NO_2$

1 mol of dinitrogen tetraoxide were placed in a vessel of 10dm^3 at a temperature of 70^0C. At equilibrium 50% had dissociated.

Calculate the value of K_c

b . What colour change would you observe if a mixture of dinitrogen tetroxide and nitrogen dioxide is subjected higher pressure?

Explain your answer.

N_2O_4	$\rightleftharpoons$	$2NO_2$
light brown		Dark brown

Worked example 8.d

2 moles of H_2, and 1 mol of I_2 were mixed together in1dm^3 vessel at 440^0C.

Calculate the moles of H_2, I_2 and HI at equilibrium. $K_c = 50$

Exercise 8d

1. What mass of ethyl ethanoate is formed at equilibrium if 90.1g of ethanoic acid is added to 92.1g of ethanol at 100K($K_C = 4$).

2. 6.5cm^3 of CO were heated with 4.8 cm^3 of steam in the closed container of 1dm^3 at 45^0C

4.6cm^3 of carbon dioxide were formed.

$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

Calculate the value of Kc

worked example 8e

Nitrogen monoxide gas (NO) was allowed to react with hydrogen has (H_2) in a 1 litre container according to the eqution:

$2NO_{(g)} + 2H_{2(g)} \rightleftharpoons N_{2(g)} + 2H_2O_{(g)}$

Intially before the reaction started ; the concentration of each gas was $NO_{(g)}$ = 0.10 mole/litre , $H_{2(g)}$ = 0.050mole/litre, $H_2O_{(g)}$ = 0.010 mole /litre , $N_{2(g)}$ = o.oo mole/ litre.

When the reaction reached equilibrium, the concentration of NO gas was equal to 0.062 mole/ litre.

a. Write the mathematical expression for the equilibrium constant , Kc.

b. Calculate the equilibrium constant, KC.

Exercise 8e

1. Given

$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

If 6.0moles of CH_3COOH were mixed with 5.00 moles C_2H_5OH, 6moles of ethyl ethanoate and 4 moles of water and allowed to reach equilibrium when 4 moles of CH_3COOH had remained.

Find the value of K_C.

Degree of dissociation(∝)

This is extent to which a substance dissociates into products.

for example

3.4 moles of SO_3 where decomposed at 60°C in 50dm^3.

$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

When equilibrium was established the amount of SO_2 present at equilibrium were 0.06moles.

Calculate the value of Kc.

Exercise 8f

The degree of dissociation of 3.4moles of Hydrogen iodide is 20% .

Calculate the

a. the number of moles of HI, I_2 and H_2 present at equilibrium.

b. value of K_c.

8.2. The equilibrium constant, K_p .

For gaseous systems the equilibrium constant can be expressed in terms of partial pressures and this equlilibrium constant is called Kp.i.e.

K_C – equilibrium constant in terms of concentrations.

K_p- equilibrium constant interms of partial pressures.

Units of partial pressures in include

atmospheres (atm) or mmHg or Pascals (Pa or NM^{-2})

consider

$aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b},$$

worked examples

1. Write down the equilibrium constant, Kp , for the following equations and give its units.

a. $2SO_{2(g)} + 2O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

b. $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$ partial pressures in atm

2. $H_{2(g)}$, $N_{2(g)}$ and $NH_{3(g)}$ exist in equilibrium. if at equilibrium, the system contains $H_{2(g)}$ 13.5g, $N_{2(g)}$ 60.3g and $NH_{3(g)}$ 24g at a pressure of 10atmospheres

Calculate the value of equilibrium constant , Kp.

3. Hydrogen and iodine react together to give an equilibrium mixture according to the reaction:

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

a. Write an expression for kp for the equilibrium.

b. 0.5mol of I_2 and 0.5 mols of H_2 were reacted in a closed vessel at 450^{0}C and 2 atm.

After attaining equilibrium was found to contain 0.11 mol of I_2.

i. Calculate the number of moles of I_2 which reacted and hence the number of moles of HI.
ii. Calculate the partial pressures I_2, H_2 and HI in the equilibrium mixture.
iii. Calculate the value of Kp at 450^0C.

4. Nitrogen monoxide combines with oxygen to form nitrogen dioxide according to the following equation at 80^0C and 200 atmospheres.

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

a. Write down the expression for K_p
b. At equilibrium 67% of the mixture contained nitrogen dioxide.
Calculate the value of K_p.

5. 2000cm^3 of sulphur dioxide was mixed with 1000cm^3 of oxygen at 300^0C and 10 atmosphers pressure in presence of a catalysts . When equilibrium was attained, it was found that 1333cm^3 of sulphur dioxide remained.
a. Write a balanced equation for reaction between sulphurdioxide and oxygen.
b. State the name of a catalyst.
c. Write an expression for pressure of each of the gasses at equilibrium.
e. Calculate the constant for the reaction.

Exercise 8g

1.Ethane can be cracked at high temperature according to the equation.

$C_2H_{6(g)} \rightleftharpoons C_2H_{4(g)} + H_{2(g)}$

If the standard enthalpy of formation of ethene is positive.

Calculate the value of equilibrium constant Kp of the reaction, given that starting with 1.0 mol ethane under an equilibrium pressure of 180Kpa at a temperature 1000K, 0.36 mol of ethene are produced during cracking.

2. When 10 mol of sulphur dioxide were reacted with 5mol of oxygen at 450^0C. 90% of sulphur dioxide was converted to sulpur trioxide at a pressure of 200kPa.
a. Calculate the moles of SO_2, SO_3 and O_2 present at equilibrium.
b. Calculate the value of K_p.

3. Phoshorous pentacholride dissociates according to the following equation

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

At 430^0 C It was found that the equilibrium mixture contained 36.4% by volume of phosphrous pentachloride at a total pressure of 20,000Pa.
a. Write down the expression for K_p
b. Calculate the value of K_p.

4.In an empty container of 5L, warm until 327^0C, a mixture of 1.2g of H_2 and 50.8g of I_2. When equilibrium is reached, the container has 75% of the initial mass of H_2.
Calculate i. the k_p of reaction
ii. the total pressure of the reaction.

5. Dinitrogen tetraoxide and nitrogen dioxide exist at equilibrium

$N_2O_4 \rightleftharpoons 2NO_2$

When 11.04g of dinitrogen tetraoxide were placed in a vessel of 4.8dm^3 at a fixed temperature , 5.52g of nitrogen dioxide where produced at equilibrium under a pressure of 100kPa.
Calculate the value of i. K_c
ii. K_p

7.4. Relationship between K_p and K_c.

consider

$aA + bB \rightleftharpoons cC + dD$

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ and } K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b},$$

From the ideal gas equation PV = nRT

i.e. $P_A = \frac{n_A RT}{V} = C_A RT = [A]RT$ where C is concentration.

Substituting in the expression for K_p.

$$K_p = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b},$$

$$= \frac{([C]RT)^C([D]RT)^d}{([A]RT)^a([B]RT)^B},$$

$$= \frac{[C]^C[D]^d RT^{c+d}}{[A]^a[B]^b RT^{a+b}} \text{butK}_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$K_p = \frac{K_c (RT)^{(c+d)}}{(RT)^{(a+b)}}$$

$K_p = K_c RT^{(c+d)-(a+b)}$ but $\Delta n = (c+d) - (a+b)$

$K_p = K_c (RT)^{\Delta n}$

worked example

The equilibrium constant K_C for the reaction system below is $2\text{mol}^{-2}\text{dm}^6$. What is the value of K_p for the system at 620K.

$R = 0.82\text{atmdm}^{-3}\text{K}^{-1}\text{mol}^{-1}$

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$K_p = K(RT)^{\Delta n}$

$K_p = 2 \times (0.82 \times 620)^{2-4}$

$= 7.738 \times 10^{-6}\ \text{atm}^{-2}$

2.a. Derivethe relationship between K_p and K_C for the reaction;

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

b. Calculate the K_p for the reaction at 450^0C if K_C is 0.2 M^{-1} ($R = 0.082\ \text{atmdm}^3\text{mol}^{-1}\text{K}^{-1}$)

Trial questions

Multiple choice questions.

1. The following reaction was allowed to reachequilibrium:

$2D_{(aq)} + E_{(aq)} \rightleftharpoons F_{(aq)}$

The initial amounts of the reactants present in 1.00dm^3 of solution were 1 mol D and 0.75mol E .At equilibrium, the amounts were 0.7mol D and 0.6mol E. Calculate the equilibrium constant K_C

a. b. c. d.

2. A gaseous mixture contains 7moles of X, 2moles of Y and 1mole of Z at equilibrium at a total pressure of 100kPa. Calculate the value of K_p for the reaction:

$X_{(g)} + Y_{(g)} \rightleftharpoons 2Z_{(g)}$

a. 0.071Kpa b.0.061Kpa c. 0.071kpa^{-1} d.0.061Kpa^{-1}

3. The gases SO_2, O_2 and SO_3 are allowed to reach the equilibrium. The partial pressures of the gases are 0.025atm. Find the values of K_p for the equilibria. For $2SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3(g)}$

a. b. c. d.

4. A mixture contained 1 mol of ethanoic acid and 5 mol of ethanol. After the system had come to equilibrium, a portion of the mixture was titrated against 0.2moldm^{-3} sodium hydroxide solution and required 289cm^{3} of the alkali. Find the value of K_c.

a. 2.4 b. 3 c. 1.2 d. 3.875

Structural questions.

1. Ammonia is produced by Haber –Bosch process according to following equation:

$N_{2(g)} + 3H_2 \rightleftharpoons 2NH_{3(g)} \Delta H = -92kJ\ mol^{-1}$

Indicate and explain what will happen to the position of the equilibrium if:

a. pressure is decreased. b. Temperature is decreased.

2. The equation below represents an exothermic reaction which is reversible.

$A + B \rightleftharpoons C + 2D \qquad \Delta H = -x\ kJmol^{-1}$

a. Write the expressions for K_c and K_p if.

i. A, B, C and D are all gases.

ii. A, B, C and D are all liquids.

iii. A,B, C are solids and D is a gas.

b. How would an increase in temperature affect the amount of C and D in the equilibrium mixture? Give a reason for your answer.

c. Draw a labeled diagram for the energy profile diagram for this reaction showing: the reactants, products, activation energy and ΔH.

3.a. Equilibrium is established in the reaction.

$A_{(aq)} + B_{(aq)} \rightleftharpoons 2C_{(aq)}$

If the equilibrium concentration are [A]=0.25, [B]=0.40, and C=0.50 mol dm^{-3}.

What is the value of Kc?

b. Hydrogen is used in large quantities in industry to convert nitrogen into ammonia for use in fertilizers. One method of manufacturing hydrogen is to pass methane and steam over a heated nickel catalyst.

$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO + 3H_{2(g)} \qquad \Delta H_1 = +206KJmol^{-1}$

i. Calculate the total bond energy in the carbon monoxide molecule.

(bond energy value C-H=410, O-H=460, H-H=436kJmol^{-1}

ii. Predict and explain the effect of separately increasing the pressure and increasing temperature on the above equilibrium.

4. The manufacture of ammonia in the Haber process is a key in industry that is linked in other useful chemicals.

a. Write a balanced equation for the reaction that occurs in the Haber process and state the conditions of temperature, pressure and catalyst used.

b. Using principles of equilibrium, kinetics and cost, justify the conditions in (a) above.

c. With help of balanced equations, outline the steps involved in manufacture ofnitric acid from ammonia.

5. The reversible reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_3$ is used in the contact process for the manufacture of sulphuric acid ,using V_2O_5 catalyst.

a.i. Calculate the enthalpy of reaction ΔH, of the forward reaction , assuming it goes to completion . You are given enthalpies of formation of $SO_{2(g)}$ and $SO_{3(g)}$ which are -297 and -395 kJmol^{-1} respectively.

ii. State and explain the effect of raising the temperature on the position of equilibrium of this reaction.

iii. The optimum temperature used in this industrial processes reaction is 450^{o}C. Basing your answers on economics and chemical principles, suggest two reasons which determine the choice of operating temperature.

iv. What is the effect of the catalysts on the position of equilibrium in this reaction?

b i.Write the expression for the equilibrium constant Kc for the reaction.

ii. What is the effect of increasing the concentration of oxygen (at the same temperature) on

I: the equilibrium constant, Kc.

II: the position of equilibrium.

9.0*IONIC EQUILIBRIUM.*


Johnnes Bronsted

9.0. Acid –base theory.

Acids and bases are defined according to the following theories.

a. Arrhenuis theory of acids and bases.

Arrhenuis defined acids as substances that dissolve in water to form hydrogen ions.
Arrhenuis bases are substances that dissolve in water to form hydroxide ions.

b. BrØnsted-Lowry theory of acids and bases.

Bronsted and Lowry defined acids as a proton donor.
while a Bronsted - Lowry base is a proton acceptor.
e.g.

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^{+} + OH^{-}_{(aq)}$

A bronsted - Lowry acid- is H_2O , NH_4^+
A bronsted - Lowry base- is NH_3, OH^-

A specie that gives H^+ is called a conjugate acid and a specie formed after release of the H^+ is called it's base conjugate hence an acid-base conjugate pair.

Or:

A specie that receives H^+ is called a conjugate base and a specie formed after gaining of the H^+ is called it's acid conjugate hence an acid-base conjugate pair.

Acid-base conjugate pairs include - H_2O/OH^-
- NH_4^{+}/NH_3
- $H_3PO_4/H_2PO_4^-$

Example

Choose an acid base conjugate pair in the equation below.

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Acid –base conjugate pairs - CH_3COOH/CH_3COO^-
-H_3O^+/-OH

c. Lewis acids and bases.

Lewis acid: lone pair acceptor. e.g. BCl_3
Lewis base: lone pair donor. e.g. NH_3
$H_3N:\rightarrow \square BCl_3$

9.1. Strong and weak electrolytes and Ostwald's law of dilution.

Strong electrolyte: Substances that fully ionizes in solution.
e.g strong acids like HCl, HNO_3, H_2SO_4.
Strong bases like NaOH, KOH
$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Weak electrolyte: Substances that partially ionizes in solution.
e.g weak acids like CH_3COOH, HCOOH, phenol
weak bases like NH_3, $C_6H_5NH_2$
$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Ostwald's law of dilution

It is an attempt on the equilibrium law to electrolytes to obtain a mathematical expression that will accurately relate the equilibrium constant and the degree of ionization of an electrolyte in a given solution.

Relationship between the dissociation constant and degree of dissociation, α

Consider an electrolyte XY that partially ionizes in water.

$$\begin{array}{llll} & XY & \rightleftharpoons & X^{+}_{(aq)} + Y^{-}_{(aq)} \\ \text{initially} & C & & \\ \text{At equilibrium} & C - \alpha C & \alpha C & \alpha C \quad \text{where C is concentration} \end{array}$$

$$k = \frac{[X^{+}][Y^{-}]}{[X][Y]}$$

$$= \frac{\alpha C \alpha C}{C(1-\alpha)}$$

$$= \frac{\alpha^{2} C}{1-\alpha}$$ assumption for a very dilute solution $\alpha <<<<<<< 1$, $(1-\alpha) \simeq 1$

$$k = \alpha^{2} C$$

$$\alpha = \sqrt{\frac{k}{C}}$$ ----- Ostwald's dilution law

It holds for very weak electrolytes very dilute in solution

But dilution $V = \frac{1}{c}$

$$\alpha = \sqrt{kV}$$

9.2. Ionisation of weak acids.

Weak acids partially ionize in solution

Consider ionisation of a weak acid , HA, in water

$HA_{(aq)} \rightleftharpoons H^{+}_{(aq)} + A^{-}_{(aq)}$

$K_a = \frac{[H^{+}][A^{-}]}{[HA]}$ where K_a is the acid dissociation constant.

but $[H^{+}] = [A^{-}]$

$K_a = \frac{[H^{+}]^{2}}{[HA]}$ if $[HA] = C$

$$K_a = \frac{[H^{+}]^{2}}{C}$$

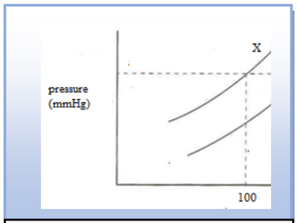
$$[H^{+}]^{2} = CK_a$$

$[H^{+}] = \sqrt{Ck_a}$ but $pH = -\log [H^{+}]$

$$-\log [H^{+}] = -\log\sqrt{Ck_a}$$

$$pH = -\log\sqrt{Ck_a}$$

$$pH = -\tfrac{1}{2}\log Ck_a$$



The pH meter used to measure the pH of solution.

$pH = -\log[H^{+}]$ used to calculate pH values.

Degree of ionization, α, for weak acids.

$$\alpha = \sqrt{\frac{K_a}{C}}$$

worked examples

1. Calculate the pH of 0.1M ethanoic acid whose K_a is $1.75 \times 10^{-5} moldm^{-3}$.

2. A solution of 0.04M methanoic acid has pH of 2.55.

a. Write down the equation for dissociation of methanoic acid.

b. Give the expression for K_a.

c. Calculate the

i. acid dissociation constant Ka for the acid.

ii. degree of dissociation.

3. 0.1M bromoethanoic acid is 18% ionized.

Calculate a. K_a for the acid..

b. pH of the solution.

4. Calculate the pH of a solution made by adding 50cm^3 of 0.1M CH_3 and 49.5cm^3 of 0.1M NaOH.

Exercise 9a

1. Calculate the pH of 0.0125M HClO(K_a =3.2 x 10^{-8}moldm^{-3})
2. Benzoic acid has a pK_a of 3.19

a. Write an equation for dissociation of benzoic acid.

b.Give the expression for K_a.

c. Calculate the pH of 1M benzoic acid.

d. Find its degree of ionisation

3. A solution of 0.01M methanoic acid is1% ionized.

Calculate

a. the ka and Pka values of methanoic acid.

b. the pH of solution.

8.3. Ionisation of water.

$H_2O \rightleftharpoons H^+ + OH^-$

$K_w = [H^+][OH^-]$ where K_w is the ionic product for water at 25^{o}C.

$K_w = 1.4 \times 10^{-14} mol^2dm^{-6}$

The PH of pure water is 7 at 25^{0}C.

i.e $[H^+] = 1x10^{-7}moldm^{-3}$ and $[OH^-] = 1 x10^{-7} moldm^{-3}$

but $pK_w = -\log K_w$

$= -\log(1.4 \times 10^{-14})$

$PK_w = 14$

$K_w =[H^+][OH^-]$

introduce log on both sides of the equation

$-\log K_w = -\log[H^+][OH^-]$

$-\log K_w = -\log[H^+] + -\log [OH^-]$

$pk_w = pH + pOH$

NB:
water is not included in the expression of K_b because it is large excess and regarded constant.

The concentration water is assumed to be in excess and hence not included in the expression for the basic equilibrium

9.4. Ionisation of weak bases.

Weak bases partially ionize in solution

Consider ammonia

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

but $[NH_4^+] = [OH^-]$

$K_b = \frac{[OH^-]^2}{[NH_3]}$ if $[NH_3]$ = Cwhere K_b is the base dissociation constant.

$$K_b = \frac{[OH^-]^2}{C}$$

$[OH^-]^2 = cK_b$

$[OH^-] = \sqrt{Ck_b}$ but $pOH = -\log [OH^-]$

$-\log [OH^-] = -\log\sqrt{Ck_b}$

$pOH = -\log\sqrt{Ck_b}$

$pOH = -½\log Ck_b$

but $pK_w = pH + pOH$

hence , $PH = pK_w - pOH$

Degree of ionization, α, for weak bases.

$$\alpha = \sqrt{\frac{K_b}{C}}$$

worked examples.

1. Calculate the pH of 0.01M ammonia solution whose K_b is 1.6 x 10^{-5}moldm^{-3}.
2. A solution of 0.04M methyl amine has pH of 11.6

a. Write down the equation for dissociation of methylammine.

b. Give the expression for K_b.

c. Calculate the

i. acid dissociation constant Kb for the base and the pK_b

ii. degree of dissociation.

Exercise 9b:

1. Calculate the pH of 0.1M aminomethane (pK_b = 3.4)
2. 0.01M of a solution of phenyl amine is 8% ionized.

Calculate i. K_b for the base.

ii. pH of the solution.

9.5. Use of K_a or pK_a and $K_b$or $pK_b$to explain the strength of acids and bases.

The larger the$K_a$value,the smaller the pK_avalue, and the stronger is the acid.

The larger the value of K_b the higher the level of dissociation and the stronger the base.

For example

1. a. Ethanoic acid has pK_a of 4.77 at 25^{0}C. What is meant by pK_a of the acid?

b. Given the following acids and their corresponding K_a values in the table below.

Acid	Ka/moldm^{-3}
Phenol	1 x 10^{-10}
Ethanoic acid	1.8 x 10^{-5}
Methanoic acid	1.8 x 10^{-4}

State and explain the strongest acid.

2.Complete the table

Base	Kb(Mol / dm^3)	pKb
$C_6H_5NH_2$	4.2 x 10^{-10}	9.38
$CH_3CH_2NH_2$	5.4 x 10^{-4}	3.27
$(CH_3)_2NH$	5.9 x 10^{-4}	3.23
$(CH_3CH_2)_2NH$	8.6 x 10^{-4}	3.07

a. State and explain the strongest base

b. Arrange the compounds in order of increasing basicity

Exercise 9c

1. You are provided with the following acidic solutions and their respective Ka values

1M HF, Ka = 6.3×10^{-4} mol dm^{-3}

1M HCN, Ka = 6.2×10^{-10} mol dm^{-3}

1M $H_2C_2O_4$, Ka = 5.0×10^{-2} mol dm^{-3}

1M CH_3COOH, Ka = 1.25×10^{-3} mol dm-^{3}

a. Calculate the pKa values of each of the acids listed above.

b. State and explain which one is a strongest acid and weakest acid?

c. Rewrite the acids in a decreasing order of their acid strength.

d.Calculate the pH of the resultant solution.

9.6. Ionisation of strong electrolytes.

Strong electrolytes fully ionise in solution. i.e. do not undergo ionic equilibrium.

a. Strong acids

e,g. $HCl \rightarrow H^+ + Cl^-$

worked examples

1. Calculate the pH of solutions of

i. 0.1M HCl.

ii. 0.4M H_2SO_4.

2. Calculate the Molarity of phosphoric acid whose PH is 2.

Strong bases.

$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

worked examples.

1. Calculate the pH of a solution 0.2M NaOH.

2. Find the concentration of $Mg(OH)_2$ in a solution whose pH is 10.41.

3. Calculate the pH of a solution made by adding 50cm^3 of 0.1M HCl and 49.5cm^3 of 0.1M NaOH.

Exercise 9d.

1.Calculate the PH of the following solutions

a. solution containing 0.000001M H^+.

b. solution containing 0.0073M OH^-.

c. 9.8g/l of sulphuric acid.

d. 56g /l of KOH.

2. Calculate the pH of a solution made by adding 35cm^3 of 0.2M HCl and 25cm^3 of 0.2M NaOH.

3. A solution containing 2.3×10^{-3}mol dm^{-3} of aluminium hydroxide ionizes in water(Kw = $1.0 \times 10^{-14} mol^2 dm^{-6}$)

a. Write the equation for the ionization of aluminium hydroxide in water.

b. Calulate the concetration of OH ions.

9.7. Salt hydrolysis.

In ionic equilibrium *salt hydrolysis* is the reaction of water and salts of a weak base or salt of acid.

An ionic hydrolysis equilibrium is set by salts of weak bases and salts of weak acids.

9.7.1. salts of weak acids.

e.g. CH_3COONa, CH_3CH_2COONa, Na_2HPO_4

Condiser hydrolysis of sodium ethanoate

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$ where K_h is the hydrolysis constant.

but $[CH_3\,COOH] = [OH^-]$

$K_h = \frac{[OH^-]^2}{[CH_3COO^-]}$ if $[CH_3COO^-] = C$

$K_h = \frac{[OH^-]^2}{C}$

$[OH^-]^2 = cK_h$

$[OH^-] = \sqrt{Ck_h}$ but pOH = -log $[OH^-]$

-log $[OH^-]$ = -log$\sqrt{Ck_h}$

pOH = -log$\sqrt{Ck_h}$

pOH = -½logCk_h

but pK_w = pH + pOH

hence , PH = pK_w –pOH

Degree of hydrolysis, α, for weak acids.

$\alpha = \sqrt{\frac{K_h}{C}}$

Relationship between K_h , K_w and K_a

$K_h = \frac{[CH_3COOH][OH]}{[CH_3COO^-]} \times \frac{[H^+]}{[H^+]}$ but $K_w = [H^+][OH^-]$ and $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$K_h = \frac{K_w}{K_a}$

worked examples.

1. Calculate the PH of a solution of sodium ethanoate made by dissolving 8.2g of the ethanoate in one litre of solution. ($K_h = 5.5 \times 10^{-10}$moldm^{-3}).

2. A solution of was made by dissolving 1.7g of sodium methanoate to 250cm^3 of solution.

a. Write

i. an equation for hydrolysis of sodium methanoate in water.

ii. the expression for the hydrolysis constant, Kh of sodium methanoate.

b. Calculate

i. the hydrolysis constant K_h for the salt. (Pk_a of methanoic acid = 3.75, PKw = 14)

ii. the PH of the solution.

iii. degree of hydrolysis of the salt.

iv. state the assumptions made.

Exercise. 9.e.

1. a. Write an equation for the hydrolysis of sodium ethanoate in water.

b. Write an expression forthe hydrolysis constant, K_h of sodium ethanoate.

(c) Calculate

i. the value of Kh of sodium ethanoate and indicate its units

(K_a for CH3COOH is 1.8 x10^{-5}MK_W=1 x10 $^{-14}$)

ii. The pH of a 0.1M sodium ethanoate solution.

2.a. Write

i. an equation for hydrolysis of sodium benzoate in water.

ii. the expression for the hydrolysis constant, Kh of sodium benzoate.

b. A solution contains 0.2 moles sodium benzoate per litre at 25^0C.

i. Calculate the PH of the solution. (hydrolysis constant of sodium benzoate is 1.6×10^{-10} mol dm^{-3} PKw = 14)

ii. State the assumptions made.

3. What is the hydrolysis constant, K_h of 0.1mol dm^{-3} aqueous solution of sodium propanoate of pH 8.9 giventhat $K_w$is$1.0 \times 10^{-14} mol^2 dm^{-6}$?

9.7.2. Salts of weak bases

e.g. NH_4Cl, CH_3NH_3Cl , $C_6H_5NH_3Cl$

Condiser hydrolysis of sodium ethanoate

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$ where K_h is the hydrolysis constant.

but $[NH_4OH] = [H^+]$

$K_h = \frac{[H^+]^2}{[NH_4^+]}$ if $[NH_4^+] = C$

$K_h = \frac{[H^+]^2}{C}$

$[H^+]^2 = cK_h$

$[H^+] = \sqrt{Ck_h}$ but $pH = -\log [H^+]$

$-\log [H^+] = -\log\sqrt{Ck_h}$

$pH = -\log\sqrt{Ck_h}$

$pH = -½\log Ck_h$

Degree of hydrolysis, α, for weak bases.

$\alpha = \sqrt{\frac{K_h}{C}}$

Relationship between K_h , K_w and K_b

$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \times \frac{[OH]}{[OH]}$ but $K_w = [H^+][OH^-]$ and $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

$K_h = \frac{K_w}{K_b}$

worked example

1. Calulate the pH the of 0.1M solution of ammonia chloride ($K_h = 5.56 \times 10^{-10}$ $moldm^{-3}$)

$pH = -\log\sqrt{Ck_h}$

$= -\log\sqrt{0.1 \times 5.56 \times 10^{-10}}$

$= 5.13$

Exercise 9f:

1. Ethyl ammonium chloride undergoes hydrolysis when dissolved in water .

a. Write the equation of its hydrolysis

b. Give the expression for the hydrolysis constant

c. If the pH of 0.1M aqueous solution of ethylammonium chloride is 3.4.

Calculate its hydrolysis constant, K_h.

2. Calculate the hydrolysis constant, K_h and pH of a 0.01M ammonium chloride solution at 25 ^{0}C. (K_w is $1.0 \times 10^{-14} mol^2 dm^{6}$ and $K_b = 1.8 \times 10^{-6}$ mol dm^{-3})

9.8. Buffer solutions.

A buffer solution is a solution that resists change in pH when a small amount of acid or base is added. Buffer solutions include acidic buffers and basic buffers

9.8.1. Acidic buffers

An acidic buffer is formed by weak acids and their salts.

e.g. CH_3COOH/CH_3COONa, C_6H_5COOH/C_6H_5COONa

H_3PO_4/NaH_2PO_4, $NaHPO_4/NaH_2PO_4$,

Consider an buffer of CH_3COOH/CH_3COONa

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ introducing -log on both sides of the equation

$$-\log K_a = -\log \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$-\log K_a = -\log \frac{[CH_3COO^-]}{[CH_3COOH]} + -\log [H^+]$$

$$pka = -\log \frac{[CH_3COO^-]}{[CH_3COOH]} + PH$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

*Action of an acidic buffer***.**

Using CH_3COOH/CH_3COONa buffer

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

When a small amount of acid is added it is removed by excess CH_3COO^- from the salt to form CH_3COOH, the PH is maintained.

$CH_3COO^- + H^+ \rightarrow CH_3COOH$

When a small amount of base is added it is removed by excess CH_3COOH in the buffer mixture the PH is maintained.

$H^+ + OH^- \rightarrow H_2O$

worked example

1. A buffer solution contains 0.2 mol dm^{-3} propanoic acid and 0.5 mol dm^{-3} sodium propanoate.

a. What is meant by the term 'buffer solution'?

b. i. Calculate the PH of the buffer solution.

(Ka of propanoic acid = 1.35×10^{-5} $moldm^{-3}$

c. Calculate the change in pH change on addition of

i. 1cm^3 0.1M HCl.

ii. 1 cm^3 1M NaOH.

d. Using relevant equations, explain how a buffer reacts when a small amount of

i.hydrochloric acid is added.

ii. Sodium hydroxide.

2. The pKa of phosphoric acid (H_3PO_4) is 2.1. Given a 0.1M solution of H_3PO_4 and you are required to obtain a buffer solution of PH = 2 by adding a solution of NaH_2PO_4) .

What should be the concentration of the salt (NaH_2PO_4) in gl^{-1}? (Atomic mass: H=1, O=16, Na=23, P=31).

3. Calculate the pH of the resultant solution when 10cm^3 of a 0.1M NaOH was added to 25cm^{3}of 0.1M ethanoic acid (K_a = 1.8 x10^{-5}M).

Exercise 9g:

1. Calculate the PH of the buffer solution that contains 0.2 mol dm^{-3} benzoic acid and 0.5 mol dm^{-3} sodium benzoate. (Ka of benzoic acid = 6.3 x 10^{-5} moldm^{-3}.

2.a. Define a buffer solution

b. Calculate the mass of sodium ethanoate the should be added to 0.1M ethanoic acid in order to produce a PH of 4. (ka = 1.75 X 10^{-5} M, Na=23, O=16, C=12, H=1)

c. Explain what will happen to the PH of the above solution if a small amount of the following is added.

i. NaOH.

ii. HCl.

3.a. What is the pH of a solution containing 7.2g of sodium benzoate in 1dm^3 of 0.02M benzoic acid.

b. By how much will the pH change if 1cm^3 of 1M NaOH was added. (K_a = 6.4 x10^{-5}moldm^{-3})

4. 50cm^3 of 0.1M ethanoic acid was mixed with 25cm^3 of 0.1 sodium hydroxide.

Calculate the pH of the resultant solution. (K_a = 1.8 x10^{-5}M).

9.8.2. Basic buffers.

An basic buffer is formed by weak bases and their salts.

e.g. NH_3/NH_4Cl, $C_6H_5NH_2/C_6H_5NH_3Cl$, CH_3NH_2/CH_3NH_3Cl,

Consider an buffer of NH_3/NH_4Cl

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$ introducing -log on both sides of the equation

$$-\log K_b = -\log \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$-\log K_b = -\log \frac{[NH_4^+]}{[NH_3]} + {}^-\log [OH^-]$$

$$pK_b = -\log \frac{[NH_4^+]}{[NH_3]} + POH$$

$$pH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

Action of a basic buffer

Using NH_3/NH_4Cl buffer

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

When a small amount of acid is added it is removed by excess NH_3 from the salt, the PH is maintained.

$NH_3 + H^+ \rightarrow NH_4^+$

When a small amount of base is added it is removed by excess NH_4^+ in the buffer mixture the PH is maintained.

$NH_4^+ + OH^- \rightarrow NH_4OH$

worked example.

A solution of 0.01M ammonia solution and 2.13g of ammonium chloride

Calculate the pH of the resultant solution. K_b for ammonia = 1.2 x 10^{-5}M

Exercise 9h:

Calculate the pH of a solution made by addition of 30cm^3 of 0.1MHCl and 80cm^3 of 0.1M ammonia solution. K_b for ammonia = 1.2 x 10^{-5}M.

Calculate pH change on addition of 1 cm^3 of 1MHCl.

Applications of buffer solution.

It helps to maintain the pH of blood when intravenous injections are applied.

Buffer solutions are used in food and drink preservations.

Skin care products are buffered to maintain their pH.

Most fermentation processes are buffered to avoid small changes in pH which may cause death of fermenting organisms.

Trail questions

Multiple choice questions

1.In Bronsted-Lowry definition of acids and bases, an acid

a. Is a proton donor b.is a proton acceptor c. Forms stable hydrogen bonds d. Breaks stable hydrogen bonds?

2.In the following reaction in aqueous solution,the acid reactant is…… a2nd its conjugate base product is …….

$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$

a. CH_3COOH, CH_3COO^- b. NH_3, NH_4^+ c. CH_3COOH, NH_4^+ d. NH_3, CH_3COO^-

3. Which one of the following is a conjugate acid of the hydrogen phosphate ion, HPO_4^{2-}?

a. H_3PO_4 b. PO_4^{3-} c. $H_2PO_4^-$ d. HPO_4^{2-}

4. Which one of the following is a strong acid?

a. HNO_2 b. H_2SO_3 c. H_2CO_3 d. $HClO_4$

5. Which one of the following is basic?

a. Cl^- b. HSO_4^- c. NO_3^- d. SO_4^{2-}

6. What is the hydroxonium ion concentration of a 0.2M solution of ammonia?

The K_b value of ammonia is 1.8 x10 $^{-5}$mol dm^{-3}

a. 2.8 x10^{-10} b. 5.2 x10^{-12} c. 1.8 x10^{-5} d. 1.9 x 10^{-3}

7.A cup of coffee has a hydroxide ion concentration of 1.0 x 10^{-10}M.

What is the pH of this coffee?

a. 10 b. 4 c. 7 d. 1.

8. A solution of a weak acid, HA contains 0.25M, given the concentration of H^+ as 0.001 moldm^{-3}

Determine the degree of ionization of this acid in 1M solution?

a. 0.02 b. 0.2% c. 0.02% d. 0.0002

9. How would you calculate K_b for the formate ion, given that the K_a for formic acid is 1.8 x 10^{-4}M

(K_W = 1.0 x 10 $^{-14}$)

a. $K_b = K_a \times K_W$ b. $K_b = K_W + K_a$ c. $K_b = K_W/K_a$ d. $K_b = K_a/K_W$

10.In anionic hydrolysis, the pH of the resultant solution is

a. Greater than 7 b. Less than 7 c. Equal to 7 d. Less than zero

11.When a salt of strong acid and weak base is dissolved in water,…………occurs to give………solution.

a. Ionization, basic b. Ionization, acidic c. Hydrolysis, acidic d. Hydrolysis, basic

12. A solution with pH of 9.5 has a pOH of……….?

a. 9.50 b. 0.50 b. 4.50 d. 19.0

13. The pH of a popular soft drink is 3.4. What is its hydroxoniumion concentration?

a. 5.0 x 10^{-4}M b. 4.0 x 10^{-4}M c. 2.5 x 10^{-3}M d. 5.0 x 10^{-4}M

14. A solution with a [OH^-]of 1.20 x 10^{-7}M has a pOH…… and a pH of …...

a. 6.92 and 7.08 b. 7.08 and 6.92

c. 5.94 and 8.06 d. 5.35 and 8.75

15. Which of the solutions may form a buffer?

a. HCl and NaBr b. NaOH and NH_3 c. H_2SO_4 and H_3PO_4 d. CH_3COOH and NaOH

15. Which of the following pairs of compounds forms buffer solution when equal amounts are mixed?

a. HCl and NaCl b. $HCHO_2$ and $NaCHO_2$ c. HCl and HBr d. KOH and NH_3

Structural questions.

1. a. What is meant by a Bronsted-Lowry acid?

Give one equation to show that ethanoic acid is a Bronsted – Lowry acid.

b. A buffer solution contains ethanoic acid and sodium ethanoate.

Using equations, explain how this buffer solution resists change in PH when small amounts of acid or base are added.

c. Calculate the PH of a buffer solution which consists of 0.200 mol dm^{-3} of ethanoic acid and 0.250 mol dm^{-3} of sodium ethanoate.

2. Ammonia reacts with water as shown by below:

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

a. Identify acid base conjugate pairs in the reaction.

b. The base dissociation constant (K_b) for ammonia is $1.2x10^{-5}$ $moldm^{-3}$.

i. Write an expression for k_b of ammonia.

ii. Calculate the concentration of OH^- ions in $0.1moldm^{-3}$ $NH_{3(aq)}$ and hence the pH of ammonia solution. (K_w= 1.0 x 10^{-14} mol^2dm^{-6} at 25^0C).

3. Some foodstuffs contain acidityregulators which have a buffering action on the pH. Mixtures of citric acid and its sodium salt are often used for this purpose.

$C_5H_7O_4COOH \rightleftharpoons C_5H_7O_4COO^- + H^+$ citric acid K_a = 7.4 x 10^{-4} mol dm^{-3}

a. The concentration of citric acid in lemon juice is 0.23 $moldm^{-3}$

Assuming that no other acid is present. Calculate the pH of lemon juice.

b.Write equations to show how citric acid and sodium citrate buffer system regulates the acidity on addition of:

i. H^+ions ii.OH^-ions

c. Calculate the pH of the solution containing 0.20 mol dm^{-3} citric acid and 0.3 mol dm^{-3} sodium citrate.

10.0 Indicators and titration curves

10.1. Acid- base indicator.

These are weak organic acids which change in color according to the concentration of hydrogen ions in solution.

Indicators are used to test the acidity and basicity of solution .

acid-base indictors include

•Methyl orange indicator. •Phenolpthalein indicator. •litmus paper.

Action of indicators.

An indicator changes colour depending on the number of undissociated and dissociated ions present in solution.

Commonly used indicators are weak acids that partially ionize in solution

Consider using phenolphthalein indicator (HI_n)

$HI_n \rightleftharpoons H^+ + I_n^-$

colorless pink

When a small amount of acid is added the equilibrium will shift to the left to reduce the amount acid added and maintain the indicator constant .

Hence, phenolphthalein indicators is colourless in acidic medium.

When a small amount of base is added it reacts with H^+present. The equilibrium will shift to the right to replace the removed H^+.

Hence phenolphthalein indicators is pink in basic medium.

Indicator constant, K_i

$HI_n \rightleftharpoons H^+ + I_n^-$

$K_i = \frac{[H^+][I^-]}{[HI_n]}$

Color changes when $[HI_n] = [I_n^-]$

hence $K_i = [H^+]$

Therefore at the point of color change

$K_i = [H^+]$

$Pk_i = PH$

PH range at which indicators change color.

Indicators change colour over a given pH range as shown in the table below.

Within this range indicators show a given color change as shown below.

Indicator	**Colour**		**pH range**
	Acidic medium	Basic medium	
Phenolpthalein	Colourless	Pink	8.2-10
Methyl orange	Red	Yellow	3.2-4.4

Litmus	Red	Blue	5 – 8
Methyl red	Yellow	Red	4.8-6.0
Thymol blue	Yellow	Blue	8.0-9.6

Choice of indicator

The indictor chosen during titration is in such a way that the pH at the end point lies within the working range. (pH range).

End point is reached when addition of small amount of acid or base causes a sharp increase in pH.

10.1. PH titration curves.

Titration can be carried by measuring pH changes at addition of a given volume of acid or base.

Graphs of pH against volume of acid or base added are drawn.

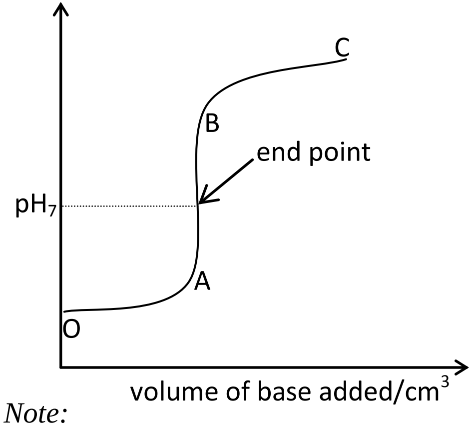
These graphs are referred to as titration curves and are specific for a depending in the strength of acids or bases.

a. Strong-base - strong acid titration.

e.g. NaOH and HCl.

Consider base added to acid.

<u>A graph of pH against volume of base added</u>



At O: pH is low because high concentration of hydrogen ions from a strong acid.

Along OA: pH increases because of addition of OH^- ions from a strong base.

Along AB: There is a sharp increase because end point has been attained.

$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

pH at end point is 7.

Along BC: The pH gradually rises because of addition of excess base.

Note:

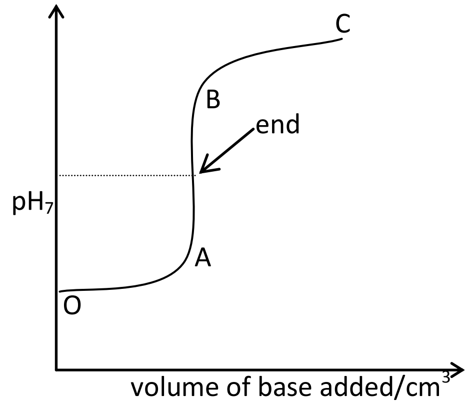
In practice methyl orange indicator and phenolphthalein indicators can be used for this titration

.b. Strong base- against weak acid titration.

e.g. NaOH and CH_3COOH.

Consider base added to acid

<u>A graph of pH against volume of base added</u>



At O: pH is low because high $[H^+]$ from a weak acid.

Along OA: pH gradually increases because of addition of OH^- ions from a strong base.

Along AB: There is a sharp increase because end point has been attained

$NaOH_{(aq)} + CH_3COOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$

pH at end point is above 7 because of hydrolysis of the salt.

$CH_3COONa_{(aq)} \rightarrow CH_3COO^- + Na^+_{(aq)}$

$CH_3COO^-_{(aq)} + H_2O \rightarrow CH_3COOH_{(aq)} + OH^-_{(l)}$

Along BC: The pH gradually rises because of addition of excess base.

Note:

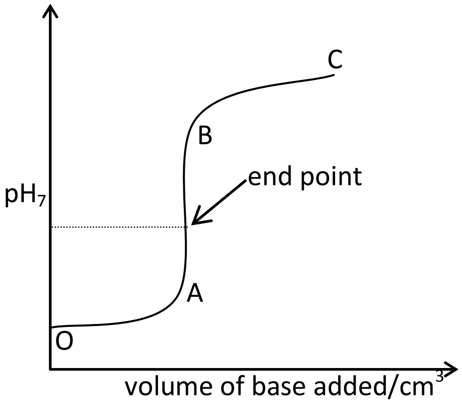
In practice phenolphthalein indicator is more suitable for this titration because its pH at end point is above 7.

c. Weak base- against strong acid titration.

e.g. NH_4OH and HCl

Consider base added to acid

<u>A graph of pH against volume of base added</u>



At O: pH is very low because high $[H^+]$ from a strong acid.

Along OA: pH graduallyincreases because of addition of OH^- ions from a weak base.

Along AB: There is a sharp increase because end point has been attained

$NH_4OH_{(aq)}+HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O_{(l)}$

pH at end point is below 7 because of hydrolysis of the salt.

$NH_4Cl_{aq)} \rightarrow NH_4^+ + Cl^-_{(aq)}$

$NH_4^+{}_{(aq)} + H_2O \rightarrow NH_4OH_{(aq)} + H^+_{(l)}$

Along BC: The pH gradually rises because of addition of excess base.

Note:

In practice methyl orange indicator is more suitable for this titration because it's pH at end point is below 7.

worked example.

1.Sodium hydroxide solution was added to 25cm^3 of 0.1M ethanoic acid and PH of the solution was measured at intervals of time.

The results are tabled below.

Volume of NaOH(cm^3)	0	4	8	12	16	20	22	22.5	23	24	28
P^H of the mixture	2.8	3.5	4.0	4.5	5.1	5.8	7.0	9.0	10.5	11.4	12.3

a.Plot a graph P^H (yaxis) against volume of NaOH.

b. Explain the shape of the graph.

c. Using the graph , determine the volume of the of NaOH required to neutralise the acid and hence calculate the molarity of NaOH.

d. Calulate the ka for ethanoic acid and hence its degree of ionization.

Mutiple choice questions.

1. What is the color of phenolphthalein in acid solution?

a. colourless b. yellow c. pink d. red

2. What is the colour of a solution of HCl and NaOH containing excess base and a few drop of methyl orange indicator.

a. colourless b. yellow c. pink d. red

Structural questions.

1. To study a titration curve, 10ml of 1M NaOH solution were titrated with 1M HCl.

(a) Copy and complete the table below.

Volume of HCl added during the titration	**pH of the solution in the titrated solution**
0.0ml	
2.00ml	
5.00ml	
8.00ml	
9.90ml	
9.99ml	
10.00ml	
10.01ml	
10.10m	
15.00ml	
18,00ml	
20.00ml	

(b) Plot the titration curve(added volume of HCl: x-axis, pH: y-axis) (3marks)

(c) The following are indicators with their pH change range

Indicator	**pH change range**
A	1.2-2.8
B	5.8-7.8
C	8.3-10.0

(i) Which one of these indicators must not be used in the titration of NaOH (strong base) with HCl (strong acid) ?

(ii) Explain your choice.

2. A 20ml aliquot of 0.1M HNO_2 is titrated with 0.1N NaOh ($K_a = 4 \times 10^{-4}$)

a. What is the pH before the titration ?

b. What is the pH of solution after 15mL of NaOH has been added?

c. What is the pH at equivalent point(after 20mL of NaOH is added)

d. What is the pH of solution after 25mL of NaOH has been added?

11.0. Solubility and Solubility product of a sparingly soluble salt.

11.1. Introduction.

Solubility.

It is the measure of the maximum amount of solute dissolved in a solvent in a saturated solution.

Molar solubility (molarity, solubility in moles per litre).

It is the amount of a solute in moles dissolved in one litre of solution.

Mass solubility (solubility in g/l)

It is the amount of a solute in grams dissolved in one litre of solution.

Unsaturated, saturated and super saturated solution.

Unsaturated solution. It is a solution which can dissolve more solute.

Saturated solution. It is a solution which cannot dissolve any more solute at a given temperature.

Super saturated solution. It is a solution which contains more solute than it can dissolve at a given temperature.

11.2. Solubility product.

This is the product of molar concentration of products raised to appropriate powers contained of a saturated solution of a sparingly soluble salt.

For example

$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$K_{sp} = [Pb^{2+}][SO_4^{2-}]$

$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

$K_{sp} = [Ag^+]^2[CO_3^{2-}]$

solids are not included in the expression of solubility product.

11.3. Factors affecting solubility of salts

a. Common ion effect.

This the reduction in solubility by addition of a solution containing a common ion.

For example:

Explain the effect on solubility of silver chloride after adding hydrochloric acid.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

The solubility of silver chloride decreases.

Explanation:

Hydrochloric acid contains Cl^- ions which is a common ion and the equilibrium will shift to the left so as decrease the amount of chloride ions added and maintain the value of K_{sp}.

Hence more silver chloride precipitates which leads to decrease in the solubility of silver chloride.

The idea of common ion effect can be used to explain industrial processes such as

- Salting out soap during soap manufacture.
- Purification of common salt from its impure salt using HCl gas.

Common ion effect also explains precipitation of salts during qualitative analysis.

b.Complex ion formation.

Addition of a solution that contains an ion which forms a complex with one the ions in the sparingly soluble salt leads to an increase in solubility

For example:

1.Explain the effect on solubility of silver chloride after adding ammonia solution.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

The solubility of silver chloride increases.

Explanation:

$Ag^{+}_{(aq)} + 2NH_{3(aq)} \rightarrow [Ag(NH_3)_2]^{+}$

Ammonia forms a complex with silver ions and therefore the equilibrium will shift to the right to replace the sliver ions removed so as to maintain the value of K_{sp}.

Hence more silver chloride dissolves which means increase in solubility.

Note:

The above explanation can also be used to explain why

i.Copper (ii) hydroxide is more soluble in ammonia than in water.

ii.Aluminum (iii) hydroxide is more soluble in sodium hydroxide than in water.

iii. iodine is sparingly soluble in water but soluble potassium iodide.

2. Lead (ii) chloride is more soluble in concentrated hydrochloric acid than in dilute hydrochloric acid.

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

Concentrated hydrochloric acid forms a complex with Pb^{2+} (due to high concentration of chloride ions) which leads to an increase in solubility (more soluble).

$Pb^{2+}_{(aq)} + 4Cl^{-}_{(aq)} \rightarrow PbCl_4^{2-}{}_{(aq)}$

while dilute hydrochloric acid causes a common ion effect (unable to form a complex with Pb^{2+} due to low concentration of chloride ions) which to decrease in soluble (less soluble).

c. Addition of a solution of soluble salt containing an ion that reacts with one of the ions in the sparingly soluble salt.

For example:

1. Calcium phosphate is sparingly soluble in water but it dissolves in a solution of nitric acid.

$Ca_3(PO_4)_{2(s)} \overset{aq}{\rightleftharpoons} 3Ca^{2+}_{(aq)} + 2PO_4^{3-}{}_{(aq)}$

The H^{+} from nitric acid reacts with PO_4^{3-}ions to give phosphoric acid.

$3H^{+}_{(aq)} + PO_4^{3-}{}_{(aq)} \rightarrow H_3PO_{4(aq)}$

This reduces the concentration of PO_4^{3-} ions and hence to restore K_{sp} more calcium phosphate dissolves. Hence calcium phosphate is more soluble in HNO_3 than in water.

Note:

The above explanation can also be used to explain why

i. Silver chromate is more soluble in nitric acid than in water.

ii. Calcium oxalate is more soluble in acid than in water.

PH change and solubility

The pH of a solution can change by addition of a base or acid this affects the solubility of sparingly solube salts.

Addition of an acid.

Addition of a base.

11.4. Calculations involving Solubility and solubility product.

worked example 11a

Calculations of K_{sp} from solubility.

1. The solubility of silver carbonate at 290K is 1.16×10^{-4}M.

a. Write the equation of solubility of silver carbonate in water.

b. Give the expression for K_{sp}.

c. Calculate the solubility product of silver carbonate.

Exercise 11 a

1.The solubility of calcium carbonate $CaCO_3$, at 298K is 6.9×10^{-4} mol dm^{-3}.Calculate the solubility product at this temperature.

2.Given that the molar solubility of Ag_2CO_3 is equal to 1.27×10^{-4} M. Calculate its solubility product.

3.The solubility of calcium sulphate $CaSO_4$ at 298K is 0.67g/dm^3.Calculate the solubility product at this temperature.

(O=16, S=32, Ca=40)

3.The solubility of calcium phosphate,$Ca_3(PO_4)_2$ is 7.7×10^{-4} g/dm^3 at 25^{0}C.

Calculate the solubility product at this temperature. (O =16, P =31, Ca=40)

Worked example. 11b.

Calculations of solubility from K_{sp}.

2. The solubility product of silver chloride at 25^{0}C is 1.44×10^{-10} mol^2 dm^{-6}.

a. Calculate its solubility in mol/dm^3 at 25^{0}C in mol dm$^{-3.}$

b. Calculate its solubility in g/dm^3 at 25^{0}c. (atomic masses Ag = 108, Cl = 35.5)

Exercise 11 b

1. Calculate the molar solubility of $PbSO_4$ (lead II sulphate), given its solubility product equal to 1.6×10^{-8}

2.Calculate the solubility in mol/dm^3 of silver (i) sulphide, Ag_2S at 298K if its solubility product is 6.3×10^{-31} mol^{3}dm^{-9}

3. Calculate the solubilityi in gdm^{-3} of chromium III hydroxide, $Cr(OH)_3$ at 25^{0}C if its solubility product is 1×10^{-33}mol^{4}dm^{-12} (H=1, O=16,Cr=52)

4. Calculate the molar solubility of $Sr_3(AsO_4)_2$ given its solubility product equal 4.29×10^{-19}

Worked example. 11c.

Calculations involving change in solubility after adding a common ion.

1.A saturated solution of barium sulphate ($BaSO_4$) contains 2.563×10^{-3}g/l of the salt.

a. Calculate the solubility product of $BaSO_4$.

b. Calculate the solubility of barium sulphate in moles\dm^3 in one litre 0.1M barium chloride.

c. Explain the effect of barium chloride solution on the solubility of barium sulphate.

2.a. The solubility product of calcium iodate, $Ca(IO_3)_2$ is 1.69×10^{-9} mol^{-3}l^{-3}.

Calculate the concentration of iodate ions in the solution.

b. if 0.1mole of calcium nitrate is added to a one litre of the solution above.

Calculate the mass of calcium iodate that was precipitated. (state any assumptions made)

d. Triphosphate forms complexes with calcium ions.

Explain what happens to the solubility of calcium iodate if triphosphate ions are added to it.

e. Give any three factors that affect the value of solubility product.

f. Give two applications of solubility products.

Exercise 11.c

1.a. Define Solubility product.

b. A saturated solution of calcium hydroxide contains 1.1×10^{-5} g/dm^3 of the salt.

i. Calculate the solubility product of $Ca(OH)_2$.

ii. Calculate the solubility of calcium hydroxide in moles\dm^3 in one litre 0.1M NaOH.

iii. Explain the effect of addition sodium hydroxide solution on the solubility of calcium hydroxide.

2.Silver chromate is sparingly soluble in water. Given the solubility product of silver chromate at room temperature. 5.6×10^{-12} mol^{3}dm^{-9}.

a. Write

i. an equation for the solubility of silver chromate at in water.

ii. the expression for the solubility product of silver chromate at room temperature.

b. Calculate the solubility in moldm^{-3} of silver chromate in

i. water.

ii. 0.1M potassium chromate.

iii.0.01M silver nitrate.

c. Explain the effect of addition of potassium chromate and silver nitrate on the solubility of silver chromate.

3.a. Calcium fluoride is sparingly soluble in water.

i. Write the equation of solubility of calcium fluoride in water.

ii. Give its expression for K_{sp}.

b. Calculate the solubility of Calcium fluoride in a solution containing $0.35moll^{-1}$ of fluorides ions.

(K_{sp} =1.7 $x10^{-10}$)

4 a. Lead sulphate is sparingly soluble in water.

i. Write the equation of solubility of calcium fluoride in water.

ii. Give its expression for K_{sp}.

b. 5g of lead (ii) sulphate was shaken with $1dm^3$ of water.

(K_{sp} = 1.6 $x10^{-8}$, Pb=207, S=32, O=16)

Determine the percentage of lead(ii) sulphate that dissolves.

c. If 0.05M of sulphuric acid was used instead of water.

Calculate the percentage of lead ii sulphate that dissolved.

11.5. Comparing solubility and solubility products.

The compound with lower value of solubility precipitates first

worked examples.

The solubility products of AgCl is 1.78 x $10^{-10}$and that of Ag_3PO_4 is 1.8 x 10^{-18}

Which one the salts is more soluble?

Exercise 11d

1. The solubility product

Given K_{sp} values of

AgCl = 1.78 x 10^{-10}, AgBr = 5 x 10^{-13} and AgI = 8.5 x 10^{-17}

Which of the following is more soluble?

2. A solution contains 1 x 10^{-2} M $Ag^+$and 2 x 10^{-2} M Pb^{2+} When Cl^- ion is added to the solution, both AgCl (Ksp = 1.8 x 10^{-10}) and $PbCl_2$ (Ksp = 1.7 x 10^{-3}) precipitate from the solution.

What concentration of Cl^- ions is necessary to begin the precipitation of each salt,and which salt precipitates first?

11.6. Ionic product and solubility product

Ionic product. (Q_{sp})

It is the product of concentrations of ions of a salt in a solution raised to appropriate powers.

Solubility product.(K_{sp})

This is the product of molar concentration of products raised to appropriate powers contained of a saturated solution of a sparingly soluble salt.

Note:

The solubility product is a special form of an ionic product because the solution is supposed saturated. i.e. solids and liquids are supposed to be in equilibrium.

Ionic product	Solubility product
concentrations of ions should not be necessary from a saturated solution.	concentrations of ions should necessary from a saturated solution.

11.7. Predicting precipitation.

The values of ionic product and solubility product are used

If

$Q_{sp} > K_{sp}$ There is precipitation.

$Q_{sp} < K_{sp}$ There is no precipitation.

$Q_{sp} = K_{sp}$ The solution is just saturated**.**

For a solution to be insoluble, the ionic product should be greater than solubility product.

Worked example.

Will a precipitate of lead II chloride be formed if $10cm^3$of 0.1mol dm^{-3} lead II nitrate solution,$Pb(NO_3)_2$ is mixed with $10cm^3$of $0.2moldm^{-3}$ hydrochloric acid, HCl? Ksp ($PbCl_2$) = 1.6 × 10^{-5} mol^3dm^{-9}at 298K.

Exercise 11e.

1. Will a precipitate of calcium hydroxide; $Ca(OH)_2$ form if $5.0cm^3$ of $0.05moldm^{-3}$ sodium hydroxide solution; NaOH,

is added to 5.0cm^3 of 0.05moldm^{-3} calcium chloride solution. $CaCl_2$? Ksp(Ca(OH)2) =5.5 ×10^{-6}mol^{3}dm^{-9} at 298K

2. Will a precipitate of calcium hydroxide form if 5.0 cm^3 of ammonia solution containing OH$^-$ ions with concentration of 2 ×10^{-3}mol/dm^3 is added to 5.0cm^3 of 0.05moldm^{-3} is added to 5.0cm^3 of 0.05moldm^{-3} calcium chloride solution. $CaCl_2$? Ksp (Ca(OH)2) = 5.5 × 10^{-9} mol^{3}dm^{-9}at 298K.

If the ionic product obtained is less than the known K_{sp} value there is no precipitation.

Applications of the concept of solubility products.

•Selective precipitation of compounds especially sulphides.

This concept is important in separation of a mixture of substances.

If the K_{sp} values are known, selective precipitation is carried out to separate the substances.

•Predicting precipitation during qualitative analysis.

If the ionic product obtained is less than the known K_{sp} value there is no precipitation.

Trial questions

Multiple choice questions.

1. When finding the value solubility product of a sparingly solution should be

a. saturated. b. Unsaturated. c. super saturated.

2. The solubility of lead II chloride,$PbCl_2$ is 0.016moldm^{-3}at 298K. Calculate the solubility product at this temperature.

a.1.6 x 10^{-3}mol^{-3}dm^{-9} b. 1.6 x 10^{-4}mol^{-3}dm^{-9} c. 1.6 x 10^{-5}mol^{-3}dm^{-9} d. 1.6 x 10^{-6}mol^{-3}dm^{-9}

3. Calculate the solubility in gdm^{-3} of chromium III hydroxide, $Cr(OH)_3$ at 25^{o}C.

if It's solubility product is 1.0×10^{-33}mol ^{4}dm^{-12}(H=1, O=16,Cr=52)

a.2.47 x 10^{-9}moldm^{-3} b. 2.47 x 10^{-8}moldm^{-3}

c. 2.5 x 10^{-6} gdm^{-3} d. 2.5 x 10^{-7}gdm^{-3}

4. Calculate the solubility of calcium sulphate in moldm^{-3} in dilute sulphuric acid of concentration 0.50 moldm^{-3}

Ksp =2.4 x 10^{-5} mol^{2}dm^{-6}

a. 4.8 x 10^{-4}moldm^{-3} b. 4.8x 10^{-5}moldm^{-3} c. 4.8 x 10^{-6} moldm^{-3}d. 4.8 x 10^{-7}moldm^{-3}

Structural questions.

1.a. What is meant by the term acid according to the Bronsted-Lowry theory of acids and bases?

b. Identify two substances acting as acids in the following reaction:

$CH_3NH_2 + H_2O \rightleftharpoons CH_3\overset{+}{N}H_3 + OH^-$

c. Write an expression for solubility product(K_{sp}) of calcium hydroxide.

d. A 20.0cm^3 sample of saturated, aqueous calcium hydroxide required 18.2cm^3 of 0.050 mol dm^{-3} hydrochloric acid for neutralisation.

Calculate

i. the concentration of OH$^-$ in the saturated solution.

ii. A value of the solubility product of calcium hydroxide stating units.

e. Explain why calcium hydroxide is more soluble in water than in potassium hydroxide.

2. The Ksp of $Mg(OH)_2$ is 1.8 x 10^{-11}

a. Calculate the solubility of $Mg(OH)_2$in pure water.

b. Calculate the molar solubility of $Mg(OH)_2$ in a solution of pH of 11. 22.

3. The solubility of calcium phosphate $Ca_3(PO_4)_2$ is 0.0011g per 100g of water at 25^{0}C.

a. Caculate the solubility product of calcium phosphate.

(Ca=40, P=31, O=16)

b. What would be the effect on the solubility of calcium phosphate when a solution of sodium phosphate is added to a saturated solution of calcuim phosphate?

12.0. Electrochemical cells.

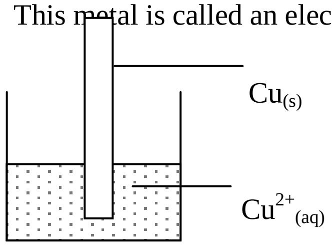
An electrochemical cell is a device that gives electric current as result of chemical reactions.

An electrochemical cell is made up of two half cell connected to each other.

12.1. Half cells.

Consists of an electrode placed in a solution of ions.

This metal is called an electrode.



On one half cell there is oxidation.

$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$

Cu^{2+}/Cu

On the other half cell there is reduction.

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e$

Cu/Cu^{2+}

A reaction in which there is both oxidation and reduction is called a redox reaction.

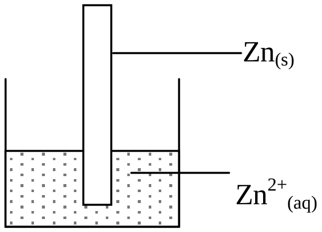
When the two processes take place at the same time an electrode potential is developed between them and current flows.

Types of half cells.

a. Metal-metal ion half cell.

This is a half cell made of a metal placed in a solution of its ions.

e.g. zinc placed in a solution of Zn^{2+} ions.

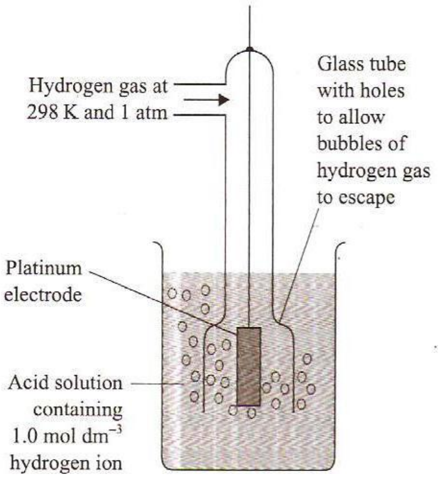


Half cell. Zn^{2+}/Zn

b. Non metal ion half cell.

It is made from a non-metal and its aqueous ions.

eg: a hydrogen half cell consists of hydrogen gas; hydrogen in contact with H^+ ion.



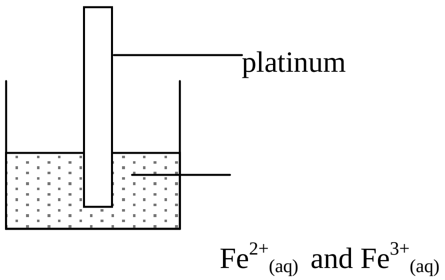
Hydrogen half cell is refer as $Pt/H_{2\,(aq)}/H^+_{(aq)}$ if Pt is anodes

Or $H^+_{(aq)}/H_2/Pt$ if Pt is cathodes

The platinum is inserted in the solvent to allow transfer of electrons into and out of the half cell via connecting wire.

c. ion-ion half cell.
This type of half cell consists of an inert electrode dipped into a solvent containing ions of the same metal in two different oxidation states.

e.g:half cell containing Fe^{2+} ,Fe^{3+} ions



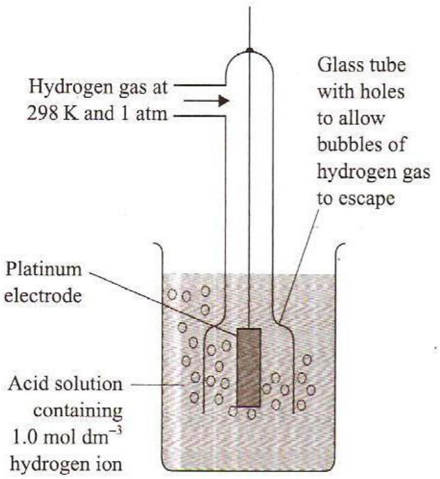
It can be represented as $pt/Fe^{2+}Fe^{3+}_{(aq)}$

as $Fe^{3+}_{(aq)}$,Fe^{2+}/pt
$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)}$ +é

12.2. Measurement of standard electrode potential values.
Standard electrode potential E^θ is the value of the electrode potential of an electrode at 298K when the metal is dipped in a solution of the metal ion at unit concentration measured with respect to the standard hydrogen electrode.
Standard electrode potential is measured with reference with the standard hydrogen electrode.

The standard hydrogen electrode.

The S.H.E consists if H_2 gas at 1 atm ,pressure,bubbling on a platinised/platinum electrode dipping in a solution of 1.0M H^+ ions



Cell notation

$Pt/H_{2\,(aq)}/H^{+}_{(aq)}$ $E^{\theta} = 0.0V$

A potential develops on the surface of the platinum, it is assigned a value of zero volts.i.e its given an arbitrary value of 0.0 volts at $25^{0}C$.

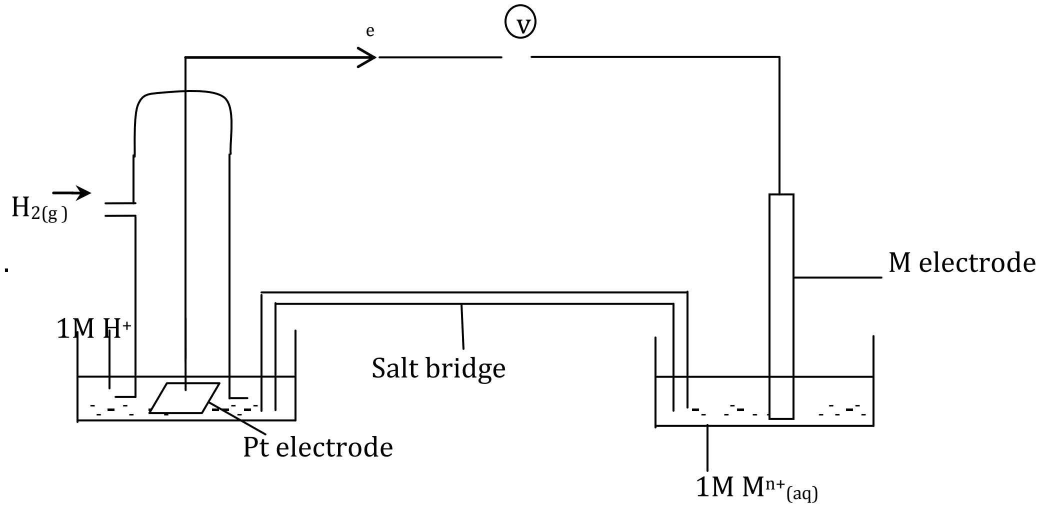
This fixes a scale against which other relative electrode potentials can be measured.

Measurement of standard electrode potential of a electrode.

The standard hydrogen electrode is joined to the metalelectrode placed in a solution of its ions of unit concentration.

The two electrodes are joined using a salt bridge.

The potential of the whole cell is assigned to the half cell as measured by the voltmeter or potentiometer.



Reaction

LHE- left hand electrode

$H_{2(g)} \rightarrow 2H^{+}_{(aq)} + 2e$ } $Pt_{(s)}/H_2/2H^{+}$

RHE- right hand electrode

$Mn^{n+}_{(aq)} + ne \rightarrow M_{(s)}$} $M^{n+}_{(aq)}/M_{(s)}$

Cell notation

$Pt_{(s)}/H_2/2H^{+} // M^{n+}_{(aq)}/M_{(s)}$

If hydrogen gas is evolved the E^{θ} for the metal is negative.

If hydrogen gas is dissolves the E^{θ} for the metal is positive

A ***salt bridge*** is a glass tubing or filter paper containing a saturated solution of potassium chloride or potassium nitrate.

Purpose:

To allow current flow from one half cell to another.

The double lines in the cell notation show represent a salt bridge.

A porous partion may be used to instead of a salt bridge and this time dotted lines are used.

$Zn/Zn^{2+}\ \vdots\ Cu^{2+}/Cu_{(s)}$

Foctors that affect the magnitude of electrode potential values.

a. Atomisation energy.

b. Ionisation energy.

c. Hydration energy.

12.3. Construction of emf cells and calculation of cell voltage.

An emf cell is constructed depending on the values of the electron potential values.

The more positive electrode is put on the right hand side and the less positive is put on the leftt hand side.
On the right hand electrode there is reduction.i.e the cathode.
On the left hand electrode there is oxidation. i.e. the anode.
emf of the cell = $E^{\theta}_{cathode} - E^{\theta}_{anode}$

$= E^{\theta}_{reduction} - E^{\theta}_{oxidation}$
$= E^{\theta}_{RHE} - E^{\theta}_{LHE}$

Worked example.
1. Given the electrode potentials of the following half cells

Zn^{2+}/Zn E^0=-0.76V

Ni^{2+}/Ni E^0=-0.25V

a. Determine

i. the standard cell emf

ii. overall cell equation

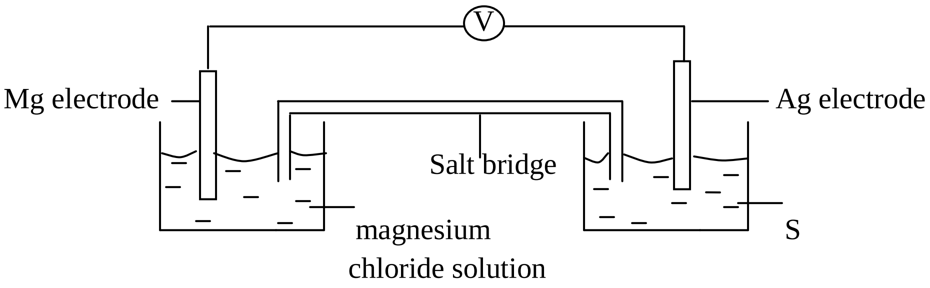
iii. the cell diagram (cell notation)

iv. whether the reaction is feasible or not give a reason for your answers.
b. Draw a labelled diagram to show the cell set up.
On your diagram show the direction of electron flow, flow of current, the anode and the cathode.

2. The standard electrode potentials for some sytems are given below.
Mn^{3+}/Mn^{2+} E^{θ} = +1.5V
V^{3+}/V^{2+} E^{θ} = -0.26V
a. aWrite the cell convetion for the cell above.
b. Write down the overall equation.
c. Calculate the emf of the cell.

←

Exercise 12.a
1. A electrochemical cell (Voltaic cell) was set up using two electrodes systems shown below:
$Fe^{2+}_{(aq)} + 2e \rightleftharpoons Fe_{(s)}$, E^{θ} = -0.45V
$Ag^{+}_{(aq)} + e \rightleftharpoons Ag_{(s)}$, E^{θ} = +0.8V
a. Draw a labelled diagram to show the cell set up. On your diagram show the direction of electron flow.
b. Calculate the cell e.m.f (cell voltage) and write a balanced equation for the cell reaction that occurs.
2. A cell consists of magnesium and silver electrodes as shown below.



a. What is solution S.

b. Given the cell potentials of half cells

Mg^{2+}/Mg $E^\theta = -2.37V$
Ag^+/Ag $E^\theta = 0.8V$
i. Write the half cell equations and hence the overall equation
ii. Give the cell diagram for the cell.
iii. Calculate the cell voltage.
iv. Label the anode and the cathode on the cell and show the diagram for the flow of current.
3.Nickel- cadmium cells are used to power electrical equipment such as drills and shavers.
The electrode reactions are shown below:
$NiO_2 + 2H_2O + 2e \rightarrow Ni(OH)_2 + 2OH^-$ $E^\theta = +0.52V$
$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e$ $E^\theta = +0.88V$
(a) Calculate the standard e.m.f of a Nickel-cadmium cell.
(b) Deduce the overall equation for the reaction that occurs in the cell when it is used.

12.4. Applications of standard electrode potential values.

1.To choose the suitable oxidizing and reducing agent.
The more negative the electrode potential value the stronger the reducing agent and the more positive the E^θ value stronger the oxidizing power.
2. To choose an element for protection of iron.
3. To predict the feasibility of reaction.
For the reaction to be feasible (spontaneous) the E^θ value should be positive and the ΔG should be negative.
Standard of Gibbs free energy (ΔG^θ)

Gibbs free energy ΔG^θ(entropy) is the measure of the randomous of a system

Gibbs free energy is given by:

$\Delta G^\theta = -nF E^\theta$
where F=Faraday's constant

E^θ =emf of cell

n =number of electrons transferred
If the E^θ is negative and ΔG^θ is positive the reaction is not feasible.
4. To determine the equilibrium constant $k_c$for reaction.
$\Delta G = RT\ln K_C$ where R – is universal gas consant.
T- Temperature
K_c – equilibrium constant.

Exercise 12b.

1. Given the following electrode potentials.
$Na^+_{(aq)} + e \rightarrow Na_{(s)}$ E = -2.71V
$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$ E = +0.34V
$Zn^{2+}_{(aq)} + 2e \rightarrow Zn_{(s)}$ E = -0.76V
$Ag^+_{(aq)} + e \rightarrow Ag_{(s)}$ E = +0.80V
a. Arrange the electrodes in order of reducing power starting with the most reducing.
b. Calculate the E.M.F of a cell formed between zinc and silver electrodes.
c. Write the overall cell reaction.
d. State the direction of the current when the two electrodes are connected by a conductor.

12.5. Nernst's law.

Nernst's equation

The equation helps us to show how the cell voltage depends on the concentration of reactants and products of the cell reaction.

$\Delta G = \Delta G^{\theta} + RT\ln Q$
ΔG –Gibbs free energy.

Q= reaction quotient of concentration products and reactants.

$-nFE = -nFE^{\theta} + RT\ln Q$
$E = E^{\theta} - \frac{RT}{nF}\ln Q$
Consider:
$Zn_{(s)} + Ni^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Ni_{(s)}$
$E = E^{\theta} - \frac{RT}{nF}\ln \frac{[Zn^{2+}]}{[Ni]^{2+}}$

$E = E^{\theta} - \frac{RT}{nF}\ln \frac{[ox]^{a}}{[red]^{b}}$ or $E = E^{\theta} + \frac{RT}{nF}\ln \frac{[red]^{a}}{[ox]^{b}}$

Or $E = E^{\theta} - \frac{RT}{nF}\ln \frac{[anode]^{a}}{[Cathode]^{b}}$
Where n =number of electrons

[ox]=concentration of the system has been oxidized.

[red]=concentration of the system has been reduced**.**

Note:
If the concentrations of reactants is increased emf of the cell increases.
If the concentrations of products is increased emf of the cell decreases.

Worked example:
1. Given that
$Zn^{2+} + 2e \rightarrow Zn$ $E^{\Theta} = -0.76V$
$Cu^{2+} + 2e \rightarrow Cu$ $E^{\Theta} = +0.34V$
a. Calculate the e.m.f of the cell.
b.i. Write down the overall equation for reaction.
ii. Calculate the e.m.f of the above equation given cell at $[Cu^{2+}] = 0.02M$ and $[Fe^{2+}] = 0.01M$.
2.a. The following equation shows the reduction of manganese ions in acidic solution.
$MnO_4^{-} + 8H^{+} + 5e \rightarrow Mn^{2+} + 4H_2O$
i. Write the expression of the redox potential (E) of the reaction above.
ii. if the concentration of MnO_4^{-} and Mn^{2+} is 0.1mole/dm^3 each, and the pH is 6, calculate the redox potential(E) of the reaction above.
E^0 $MnO_4^{-}/Mn^{2+} = 1.510V$

Exercise 12c.

1 . Calculate the emf at 298K generated by the cell described by the redox equation between acidified dichromate and iodine ion
when $[Cr_2O_7^{2-}]=2.0$ *M*,$[H^+]= 1.0$*M*,$[I^-] =1.0$ *M*,and $[Cr^{3+}]= 1.0 \times 10^{-5}$*M:* $Cr_2O_7^{2-}/Cr^{3+} = +1.33V$, $I_2/I^- = +0.54v$

2. If the voltage of a Zn—H^+cell 0is 0.45V at 25°C when $[Zn^{2+}] = 1.0$*M* and P_{H2}= 1.0 atm. What is the concentration of H^+?$E°$= +0.76 V.

12.6. Corrosion

Rusting.

Rust is brown coating on iron referred to as hydrated iron (iii) oxide.

It occurs in the presence of water and oxygen.

How rusting occurs.

Rusting is an electrochemical process in which a cell is made up within a metal.

In a piece of iron, there are areas which tend to give electrons (anodic areas) and areas which tend to accept electrons (Cathodic areas).

This is caused by the presence of impurities and differences in oxygen concentration.

At the anode: $2Fe_{(s)} \longrightarrow 2Fe^{2+}_{(aq)} + 4e$

At the cathode: $O_{2(g)} + H_2O_{(l)} + 4e \longrightarrow 4OH^-_{(aq)}$

The Fe^{2+} now reacts with OH^- to produce iron (ii) hydroxide.

$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$

The iron (ii) hydroxide formed is then oxidised by air and water to a brown solid (rust) $Fe_2O_3.XH_2O$.

$2Fe(OH)_{2(s)} + H_2O_{(l)} + ½ O_{2(g)} \longrightarrow 2Fe(OH)_{3(s)}$

$Fe(OH)_{3(s)} \longrightarrow Fe_2O_3.3H_2O$.

Prevention of rusting.

-By painting or greasing.

-By alloying e.g. stainless steel.

-By covering iron with other metals. i.e. Tin electroplating and zinc electroplating(galvanizing).

Worked example

Exercise 12.d.

1. Using the electrode potentials

$Zn^{2+} + 2e \rightarrow Zn \quad E^{\Theta} = -0.76V$

$Fe^{2+} + 2e \rightarrow Fe \quad E^{\Theta} = -0.44V$

$Sn^{2+} + 2e \rightarrow Sn \quad E^{\Theta} = -0.14V$

Explain briefly why Zn is better at protection of Fe against rusting than Sn.

2.a. Define rust

b. Give the conditions necessary for rusting,

c. Write the equation that occurs during rusting.

i.anode ii. cathode iii. overall equation.

d. Give 4 ways that are used to prevent rusting of iron.

3.a. Can 1M $Fe_2(SO_4)_3$ solution be stored in a container made of nickel metal?

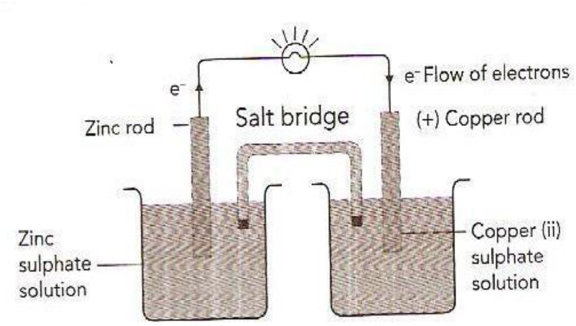
Explain your answer. (E^0Fe^{3+}/Fe= -0.040V; E^0Ni^{2+}/Ni = -0.231V)

b. Dentist know that it is not acceptable to put dentures of different metal in the mouth of a patient. Give an explanation for this phenomenon.

12.7. Cells

1. Daniel cell.

A Daniell cell consists of a zinc rod immersed in a solution of zinc sulphate and copper rod immersed in a solution of copper sulphate joined by a salt bridge.



Electric current is generated.
Equations:
Anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e$
Cathode: $Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$
Cell notation
$Zn_{(s)}/Zn^{2+}_{(aq)} // Cu^{2+}_{(aq)}/Cu_{(s)}$

2. The leclanche dry cell

This is a primary (voltaic) cell consisting of zinc as the anode (negative terminal) and carbon as the cathode (the positive terminal) dipped into aqueous ammonium chloride electrolyte(NH_4Cl)

The carbon rod allows conversion of NH_4^+ ions to NH_3, H_2 the rod is surrounded by a mixture of powdered charcoal + manganese (IV) .

Manganese IV oxide helps to oxidize H_2 produced to H_2O to avoid polarizing the cell.

The ammonium produced at the anode then dissolves in the NH_4Cl paste surrounds the mixture

of charcoal of MnO_2

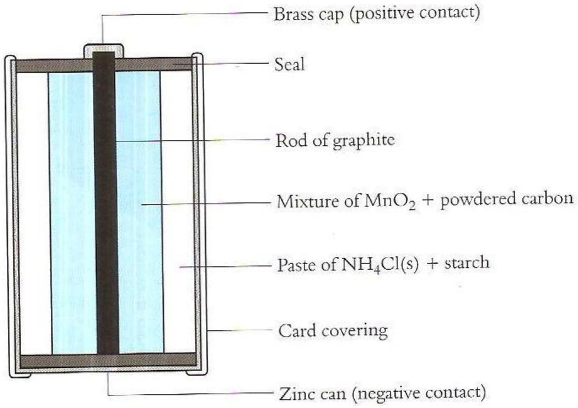
$Mn^{4+} + H_2 + 2OH^- \rightarrow 2Mn^{2+} + 2H_20$

Cell reaction

At Anode: $Zn \rightarrow Zn^{2+} + 2é$

At cathode: $2NH_4^+ + 2é \rightarrow 2NH_3 + H_2$

Cell notation : $Zn/Zn^{2+} // 2NH_4^+/2NH_{3,}H_2$



4.Lead acid accumulator.
This consists of 3 or 6 lead cells in series giving a total pd of 6V or 12V respectively.
It is a secondary cell. i.e. can be recharged after being used.
The electrolyte is aqueous sulphuric acid.

The anode is made of lead-plate and at the anode lead dissolves into solution.
At anode: $Pb \rightarrow Pb^{2+} + 2é$ 0.36V

The cathode is made of lead IV oxide reactions with the H^+ from sulphuric acid.
At cathode: $PbO_2 + 4H^+ + 2e \rightarrow Pb^{2+} + 2H_2O$ 1.69V

Overall equation

$Pb + PbO_2 + 4H^+ \rightarrow 2Pb^{2+} + 2H_2O$

The Pb^{2+} ions produced then reacts with SO_4^{2-} ions from H_2SO_4 to form valuable insoluble $PbSO_4$.

i.e: $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

At discharge the cell yields electrical energy by the reactions

The cell can be recharged by passing electricity in the opposite direction to that of the cell produces.

The anode becomes the cathode and vice verses.

At cathode: $Pb^{2+} + 2é \rightarrow Pb$

At anode: $Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2é$

Overall eqn: $Pb^{2+} + 2H_2O \rightarrow Pb + PbO_2 + 4H^+$

5. Nickel-cadmiumstorage cell

It is another rechargeable cell. The anode is made of ***nickel(IV)oxide coated by*** $Ni(OH)_2$ and the cathode of ***iron or cadmium-covered by*** $Fe(OH)_2$ ***or*** $Cd(OH)_2$ respectively. The electrolyte is aconcentrated solution ofKOH.

The reactions occurring are:

Operation during discharge:

Anode: $Fe + 2OH^- - 2e^- \rightarrow Fe(OH)_2$

or: $Cd + 2OH^- - 2e^- \rightarrow Cd(OH)_2$

Cathode: $NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$

While charging, the opposite phenomena take place**.**

These batteries provide an emf:**1.42 V**(Fe-Ni) or **1.31V** (Ni-Cd). The cell is also called **nicadcell**.

The products formed adhere to the electrodes and can be reconverted by recharging process since no gaseous products are produced.This cell is becoming more popular these days and finds use in electronic watches and calculators.

Fuel cells

Fuelcells worklike batteries but they do not run down or need recharging. They produce electricity and heat as long as fuel is supplied. Afuel cell consists of **two electrodes:** a negative electrode (or anode) and a positive electrode(orcathode) sandwiched around an **electrolyte.** A***fuel, such as hydrogen, is fed to the anode,*** and ***air is fed to the cathode.***

In a hydrogen fuel cell, a catalyst at the anode separates hydrogen molecules into protons and electrons, which take different paths to the cathode. The electrons go through an external circuit, creatinga flow of electricity. The protons migrate through the electrolyte to the cathode, where they unite with oxygen and the electronsto produce waterand heat.

The reaction in a single fuel cell typically produces only about 0.7 volts. Therefore, fuel cells are usually stacked or connected in some way to form a fuel cell system that can be used in cars, generators, orother products that require power.

The reactions involved in a fuel cell are as follows:

- ► **Anode** side (an oxidation reaction): $2H_2 \rightarrow 4H^+ + 4e^-$

► **Cathode** side (are reduction reaction): $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

► **Net reaction** (the"redox"reaction):$2H_2 + O_2 \rightarrow 2H_2O$

Differences between electrolytic and electrochemical cell

ElectrochemicalCell	Electrolytic Cell
It converts chemical energy into electrical energy.	It converts electrical energy into chemicalenergy.
Electrical energy is produced.	Electrical energy is consumed.
It is based upon the redox reactions which are spontaneous.	The redox reactions are non-spontaneous and take place onlywhen energy is supplied.
The chemical changes occurringin the two beakers are different.	Onlyone chemical compound undergoes decomposition.
Anode (-ve)-Oxidation takesplace.	Anode (+ve)-Oxidation takesplace.
Cathode(+ve)-Reduction takesplace.	Cathode(-ve)-Reduction takesplace
Anode is negative and cathode is positive.	Anode is positive and cathode is negative.
The electrons move from anode to cathode in External circuit.	The electrons are supplied by the external source.They enter through cathode and come out through anode.
Thetwo halfcells are setup in different Containers and are connected through salt bridge orporous partition.	Both the electrodes are placed in the solution or molten Electrolyte I nthe same container.

Trial questions.

Multiple choice questions.

1. Identify a primary cell

a. laclanche b. Lead acid accumulator c.Nicad cell d. lithium ion cells.

2. The type of reaction in a voltaic cell is best described as

a. spontaneous oxidation.

b. non spontaneous oxidation.

c. spontaneous oxidation and reduction.

d. non spontaneous oxidation-reduction.

3. In an electrochemical cell

a. The anode is positively charged.

b. The cathode is negatively charged.

c. The Cathode is positively charged.

d. The anode is negatively charged

4. Given

$2H^+ + 2e^- \rightarrow H_2$ $E^\Theta = 0.00V$

$Cd^{2+} + 2e^- \rightarrow Cd$ $E^\Theta = -0.4V$

$Sn^{2+} + 2e^- \rightarrow Sn$ $E^\Theta = -0.140V$

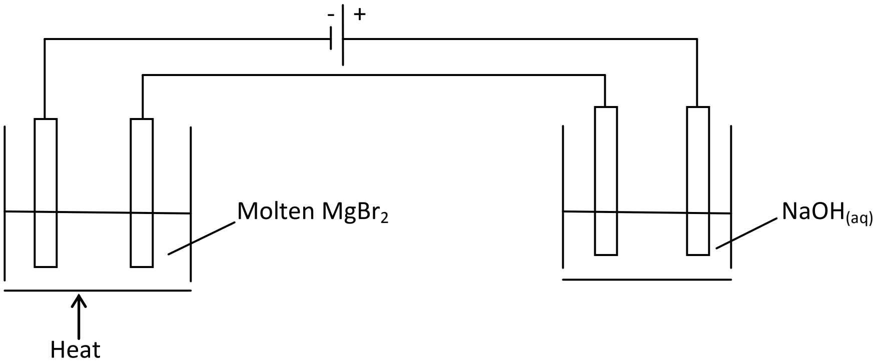
Which pair of substances will react spontaneously

a. Sn and Cd^{2+} b. Sn and H^+ c. Cd and H_2 a. Cd and Sn^{2+}

Structural questions

1.a. With the help of equations of reactions which occur at each electrode, outline what happens during the electrolysis of dilute aqueous sodium chloride. What happens to the PH of the solution as electrolysis continues.

b. Two electrolytic cells containing molten magnesium bromide and dilute sodium hydroxide respectively are connected in series as shown in the diagram below.



The electrodes in both cells are inert 6.0g of magnesium is produced in the first cell

i. Identify the products produced in the second cell.

ii. Calculate the mass of each product in the second cell.

(Mg=24,Br=80, Na=23,H=1, O=16)

c. Briefly outline the method of purifying copper using electrolysis.

2. Use the data below to answer the questions that follow:

$Ag^+ + e \rightleftharpoons Ag$ $E^\ominus = +0.8V$

$Fe^{2+} + 2e \rightleftharpoons Fe$ $E^\ominus = -0.44V$

Draw a labeled diagram to show a electrochemical cell consisting of silver and iron half-cells/electrodes

In the diagram show.

i. A salt bridge

ii. The direction of electron flow by using an arrow(→).

b. Calculate the standard cell voltage for the above electrochemical cell.

c. Write a balanced equation for the cell reaction.

d. On which electrode does oxidation occur.

e. A constant current is passed through an electrolyte of copper (II) sulphate using copper electrodes. After one hour, the mass of copper cathode increased by 15.24g. Calculate the current in amperes. [F = 96500Cmol^{-1}, Cu=63.5]

3. a. Acidified solution of copper (II) sulphate, $CuSO_{4(aq)}$, was electrolyzed using platinum electrodes. Use the standard electrode potentials below to answer the following questions.

$2H^+ + 2e^- \rightarrow H_2$ $E^\ominus = 0.00V$

$Cu^{2+} + 2e^- \rightarrow Cu$ $E^\ominus = +0.34V$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ $E^\ominus = +0.40V$

i. Sketch and label an apparatus that can be used in such an experiment.

ii. Write an equation for the reaction that occurs at the cathode.

iii. Write an equation for reaction at the anode.

iv. What happens to the PH of the solution as electrolysis proceeds?

Explain why

b. The platinum electrodes are replaced by copper electrodes.

State and explain two differences in the observations that would be made.

4. The following list gives standard electrode potentials for various half-cell.

	E^{Θ}/volts
$I_{2(aq)} + 2e^- \rightarrow 2I^-_{(aq))}$	+0.54
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	+0.80
$F_{2(aq)} + 2e^- \rightarrow 2F^-_{(aq)}$	+2.87
$O_{2(aq)} + 4H^+_{(aq)} + 4e \rightleftharpoons 2H_2O_{(l)}$	+1.23
$Mg^{2+}_{(aq)} + 2e \rightarrow Mg_{(s)}$	- 2.36
$Cu^{2+}_{(aq)} + 2e \rightarrow Cu_{(s)}$	+0.34

a. Draw a labeled diagram of a cell which can be used to measure the standard electrode potential of Cu^{2+}/Cu half cell.

b. From the list above, identify the.

i. Strongest reducing agent.

ii. Strongest oxidizing agent.

c. Calculate the standard cell e.m.f (E^{Θ} cell) corresponding to the cell reactions.

$2Cu^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow 2Cu_{(s)} + O_{2(g)} + 4H^+_{(aq)}$

d. When a constant current was passed through an aqueous solution of copper (ii) nitrate for one hour the mass of the copper cathode increased by 15.24g.

Calculate the current in amperes which was used.

(F=96500C mol^{-1}, Cu=63.5)

5.(a) The leclanche dry cells used in a wide range of appliances such as torches, bicycle lamps ,radio… it is composed of a zinc container filled with a thick moist paste of manganese (IV) oxide (MnO_2), zinc chloride ($ZnCl_2$) ,ammonium chloride (NH_4Cl)and water. A graphite (carbon) rod is embedded in the paste.

(i) State the role of the zinc container and the graphite rod.

(ii) State the role of the thick moist paste.

(iii) Write the oxidation and reduction reactions during the discharge of the cell.

(b) A lead acid accumulator or a lead storage battery is a cell that is connected to appliances to generate electricity. It is used in automobiles. The following are the reaction that occur on the electrodes:

oxidation: $Pb + SO4^{2-} \rightarrow PbSO_4 + 2e$

reduction: $PbO_2 + 4H^+ + SO_4^{2-} + 2e \rightarrow PbSO_4 + 2H_2O$

(i) Indicate where (on anode or cathode)oxidation and reduction take place.

(ii) Write the overall redox reaction in the battery.

(iii) The reaction in (b) ii) is a reaction that occur when the battery discharges.

Deduce the reaction of the recharging of the battery.

6. The table below shows standard electrode potentials of some ions of group 7 elements in the periodic table.

$Cl_2 + 2e \longrightarrow 2Cl^-$	+1.36V
$2IO_3^- + 12H^+ + 10e^- \longrightarrow I_2 + 6H_2O$	+1.19V
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54V

a) Calculate the oxidation number of I in IO_3^-.

b) Write a balanced ionic equation for the reaction between IO_3^- and I^- in the presence of acid. Calculate the standard cell e.m.f (E^{Θ} cell) for reaction.

c) Would you expect a reaction between I_2 and Cl^-? Give a reason for your answer.

13.0 CHEMICAL KINETICS.

13.0. Introduction

Chemical kinetics is the study of the rate of reaction and the factors affecting the rate of reaction.

Reaction rate

A rate of reaction or speed of reaction is the change in concentration of reactant or product per unit time.

Units $moldm^{-3}s^{-1}$ or MS^{-1}

The rate of reaction is expressed as the

i. The rate of appearance of products.

ii. The rate of disappearance of reactants.

Consider

$aA + bB \rightarrow cC$

Rate of appearance of products $= \frac{d[C]}{dt}$

Rate of disappearance of reactants $= \frac{-d[A]}{dt} = \frac{-d[B]}{dt}$

The rate law.

The rate of a chemical reaction is directly proportional to the product of concentration of reactants raised to appropriate powers.

The rate equation.

This is a mathematical expression that relates the concentration of the reactants to the reaction rate.

Order of reaction

This refers to the power to which the concentration of reactants are raised in an experimentally determined rate equation.

The order of reaction is zero, 1st or 2nd order.

The order of reaction with respect to the reactant is obtained from the experimental data and not from the coefficients of reactant in a balanced equation and this makes this topic an experimental topic.

Consider a reaction : $A + 2B + C \longrightarrow$ products

If the rate equation from experimental data is;

Rate $= k[A][B]^2$ where k-rate constant, [A]- concentration of A

Rate constant, k, is the constant that links the rate of reaction and to the product concentration of reactants raised to appropriate powers.

From the rate of equation of reaction

- first order with respect to A.
- second order with respect to B.
- zero order with respect to C.

overall order $= 1+2+0$

$= 3$

Overall order is the sum of all the orders with respect to reactants.

worked example.

A reaction between A and B is represented by the equation

$2A + B \longrightarrow 2C+D$

The reaction is known to be a second order with respect to A and first order with respect to B.

a. Write a rate expression or rate equation for the above reaction.

b. State the overall order of reaction.

c. If the [A] = $6x10^{-3}moldm^{-3}$ and [B] =$3x10^{-3}moldm^{-3}$with initial rate as $4.5moldm^{-3}S^{-1}$.

Find the value for the rate constant and state its units

d. If the concentration of both A and B are doubled by what factor does the rate change?

Exercise 13.a.

1.The rate equation for a certain reaction is

Rate = $K[P][Q]^{2}[R]$

a. State what will happen to the rate of reaction if

i. the concentration of P and Q are kept constant but that of R is doubled.

ii the concentration of all species are halved.

iii.The concentration of all species are tripled.

b. Deduce the units for the rate constant, if units of [] is M and those rate are MS^{-1}.

2.A reaction between A and B is represented by the equation

$2A + B \longrightarrow 2C+D$

The reaction is known to be a second order with respect to A and first order with respect to B.

a) Write a rate expression or rate equation for the above reaction.

b) State the overall order of reaction.

c) Deduce the units of the rate constant.

d) If the concentration of both A and B are doubled by what factor does the rate change?

13.1. Orders of reaction.

a. Zero order reaction.

A zero order reaction with respect reaction implies the rate of reaction is independent of the concentration of that reactant. i.e. The rate of reaction remains constant.

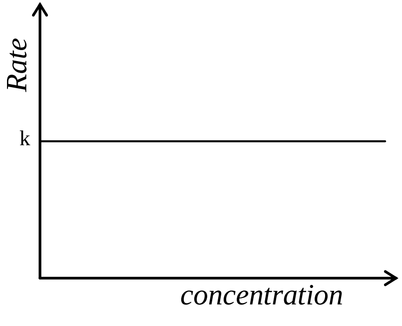
Consider a zero order reaction

$A \rightarrow$ products.

Rate = $k[A]^0$

Rate= k

A graph of rate versus concentration for zero order reaction.



•The rate is unaffected by the concentration.

Rate = k = $\frac{-dA}{dt}$

$\frac{dA}{dt}$ = -K ,where [A] is concentration of A, K is rate constant and t is time.

-dA = -Kdt

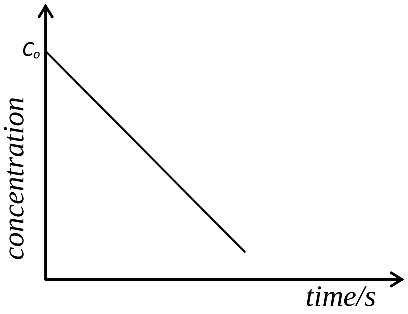
$\int_{C_o}^{C_t} dA$ = -$\int_0^t kt$, when t=o, [A] =C_0 and when t=t, [A]=C_t

(C_t –C_o)= -k (t-0)

C_t – C_o = -kt

C_t = C_o - kt………….Intergrated form of zero order.

A graph of concentration (C_t) against time



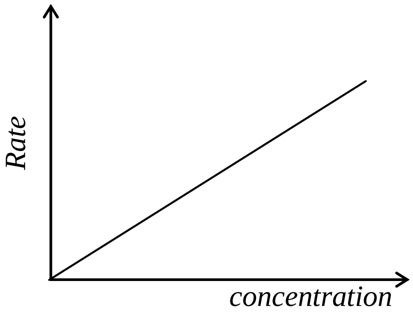
b. First order reaction

Consider a first order reaction

A → products.

Rate = K[A]

A graph of rate versus concentration for first order reaction.



- When the concetration increases 2 times, the rate also increases 2 times.
- When the concentraion increases 3 times, the rate also increases 3 times.

Rate = k[A] = $\frac{-dA}{dt}$

$\frac{-dA}{dt}$ = K[A] ,where [A] is concentration of A, K is rate constant and t is time.

$\frac{dA}{[A]}$ = -Kdt

$\int_{C_o}^{C_t}\frac{dA}{[A]}$ = -K$\int_0^t dt$, when t=o, [A] =C_0 and when t=t, [A]=C_t

lnC_t – lnC_0 = -k (t-0)

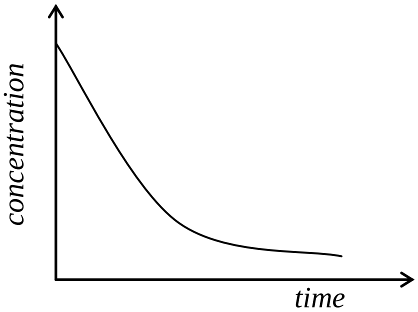
ln$\frac{C_t}{C_o}$ = -kt ....x_1

ln$\frac{C_o}{C_t}$ = kt............x_2- Intergrated form of first order.

i.e. $C_t = C_oe^{-kt}$ ....x_3 from x_1

Using equation x_3(. $C_t = C_oe^{-kt}$)

A graph of concentration (C_t) against time



Half life ($t_{½}$)

Time taken for the concentration of a substance to decrease to half the original value.

$\ln\frac{Co}{Ct}$ = kt . Where t = t½, $C_t = \frac{Co}{2}$

$\ln\frac{Co}{\frac{Co}{2}}$ = kt½

ln2 = kt½

$t½ = \frac{ln2}{k}$ i.e. $t½ = \frac{0.693}{k}$

worked examples

The half life of a first order reaction is 100s.

Calculate the rate constant.

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

Exercise 13b.

1.The half life of radium is 15.90 yrs .how long will it take for a sample of decay to 10% of its original radioactivity

2.a radioactive element decays with a rate constant of $2.0x10^{-4}s^{-1}$. How long will it takes for 0.5g of the substance to decay to 0.1 g?

3.If the half life of a radioactive element is 150 s,what percentage of the isotope will remain after 600 seconds.

4.if a radioisotope loses 75% of this activity in 10 minutes.what is its half life.

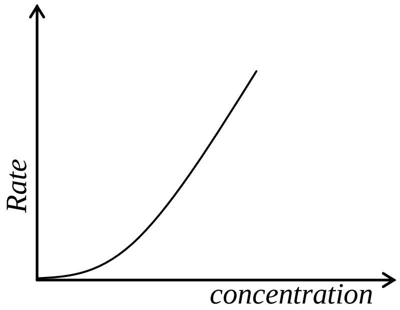
c. Second order reaction

consider a second order reaction

$$2A \rightarrow B$$

Rate = $K[A]^2$

A graph of rate versus concentration for second order reaction.



- When the concentration increases 2 times the rate also increases 2^2 times (4 times)
- When the concentration increases 3 times the rate also increases 3^2 times (9times)

consider

$$A \rightarrow B$$

initially C_o

At time, t C_o- x x

Rate = $K[A]^2$

Intergraded form of second order.

$\frac{x}{C_o(C_o - X)}$ = kt where C_o – original concentration X- concentration of at time t

Half life for second order reaction.

$t_{½}= \frac{1}{KC_o}$

13.2. Determining order of reactions.

6.1.1. Using inspection method or calculation method (intial rate method)

The order of reactions can be determined by inspecting experimental data.

worked examples.

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

Experiment	[A] moldm^{-3}	[B] moldm^{-3}	Intial rate of reaction in moldm^{-3}s^{-1}
1.	0.50	0.50	2.0×10^{-2}
2.	1.00	0.50	8.0×10^{-2}
3.	1.00	1.00	16.0×10^{-2}

a. Determine the overall order of reaction.

b. Calculate the rate constant indicating clearly the units.

2. A rection between A and B was investigated to determine its rate equation. The results of the investigation are shown in the following table. The temperature was kept constant during the investigation.

[A] (moldm^{-3})	[B] (moldm^{-3})	[intial rate] (moldm^{-3}S^{-1})
0.2	0.2	3.2×10^{-4}
0.4	0.2	1.3×10^{-3}
0.4	0.4	1.3×10^{-3}

a. Deduce the order of reaction with respect to

i. A ii. B

b. Write the rate equation for reaction.

solution:

The inspection method.

a. i. Using experiment 1 and 2.

[B] is kept constant

[A] doubles and the rate multiplies by 4 , order of reaction with respect to A is 2.

ii. Using experiment 2and 3.

[A] is constant.

[B] doubles and the rate is constant i.e. does not have any effect on rate , order of reaction with respect to B is 0.

b . $R=K[A]^2[B]^0$ where R is rate and k is rate constant.

$R= K[A]^2$

Exercise 13c.

1. In an experiment to determine the order of a reaction between substance A and B, the following results are obtained.

Experiment	[A]/moldm^{-3}	[B]/moldm^{-3}	Rate of reaction moldm^{-3}min^{-1}
1	1.0 x10^{-3}	1.0 x10^{-3}	2.0 x10^{-4}
2	2.0 x10^{-3}	1.0 x10^{-3}	4.0 x10^{-4}
3	2.0 x10^{-3}	2.0 x10^{-3}	8.0 x10^{-4}

a. State the order of reaction with respect to A and B.

b. Write the rate expression for reaction.

c. Calculate the rate constant for reaction showing clearly the units.

2. In an experiment to determine the order of a reaction between substance A and B, the following results are obtained.

Experiment	[A]/moldm^{-3}	[B]/moldm^{-3}	Rate of reaction moldm^{-3}min^{-1}
1	0.1	0.1	1.0 x10^{-4}
2	0.1	0.3	9.0 x10^{-4}
3	0.3	0.3	2.7 x10^{-3}

a. State the order of reaction with respect to A and B.

b. Write the rate expression for reaction.

c. Calculate the rate constant for reaction showing clearly the units.

d. If the intial concentrations of both A and B were 0.4M.

Calculate the intial rate of formation of C.

3. A reaction between X and Y was investigated in order to determine its rate equation.
The results below were obtained:

Experiment Number	[X] (mol dm^{-3})	[Y] (mol dm^{-3})	Intial Rate (mol dm^{-3} s^{-1})
1	0.5	1.0	2
2	0.5	2.0	8
3	0.5	3.0	18
4	1.0	3.0	36
5	2.0	3.0	72

a. Deduce the order of reaction with respect to X and Y.
Explain your reasoning.
b. Write the rate equation or rate expression for the reaction.
c. Calculate a value for the rate constant and give its units.
4.The initial rate of reaction between substance P and Q was measured in a series of experiments and the following rate equation was deduced:
Rate = $k[P]^2[Q]^1$

Experiment	Initial [P](moldm^{-3})	Initial [Q](moldm^{-3})	Initial rate (moldm^{-3} S^{-1})
1	0.20	0.30	4.8×10^{-3}
2	0.10	0.10	**X**
3	0.40	**Y**	9.6×10^{-3}
4	**Z**	0.60	19.2×10^{-3}

(a)Using the data from the above table, calculate the value of the rate constant K, and deduce its units.
(b) Find the value of **X,Y** and **Z** in the table.
(c) Indicate a change in the reaction conditions that will cause the value of rate constant to change.

Worked example 13.d.

According to the data given below in relation to the reaction.

$[I^-]$ (mol/dm^3)	$[BrO_3^-]$ (mol/dm^3)	$[H^+]$ (mol/dm^3)	Rate(moldm^{-3}S^{-1})
0.10	0.10	0.10	3.0×10^{-4}
0.14	0.18	0.10	7.56×10^{-4}
0.10	0.18	0.10	5.40×10^{-4}
0.31	0.18	0.20	1.67×10^{-3}

<u>Equation:</u>

$BrO_{3(aq)}^- + 9I^-_{(aq)} + 6H^+_{(aq)} \longrightarrow 3I_{2(aq)} + Br^-_{(aq)} + 3H_2O_{(l)}$

a. Find the order of reaction with respect to
BrO_3^-, I^-, H^+
b. Find the overall order of reaction.
c. Find the rate constant K for the reaction.

Exercise 13d.

1. According to the data given below in relation to the reaction.

[P] (mol/dm^3)	[Q] (mol/dm^3)	[R] (mol/dm^3)	Rate(moldm^{-3}S^{-1})

0.001	0.002	0.003	4.56×10^{-4}
0.001	0.004	0.003	9.12×10^{-4}
0.0005	0.004	0.003	2.28×10^{-4}
0.0005	0.012	0.006	6.84×10^{-4}

a. Find the order of reaction with respect to

P, R, S

b. Find the overall order of reaction.

c. Find the rate constant K for the reaction.

2. Nitrogen monoxide react with carbon monoxide and oxygen to form nitrogen dioxide and carbon dioxide .

$NO_{(g)}+CO_{(g)}+O_{2(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$ The results from a series experiments for this reaction are shown below:

Experiment	[NO] /	[CO] /	[O2] /	initial rate /
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3} S^{-1}	
1	1.00×10^{-3}	1.00×10^{-3}	1.00×10^{-1}	4.4×10^{-4}
2	2.00×10^{-3}	1.00×10^{-3}	1.00×10^{-1}	1.76×10^{-3}
3	2.00×10^{-3}	2.00×10^{-3}	1.00×10^{-1}	1.76×10^{-3}
4	4.00×10^{-3}	1.00×10^{-3}	2.00×10^{-1}	7.04×10^{-3}

Use the above results to deduce the order with respect to

i. No

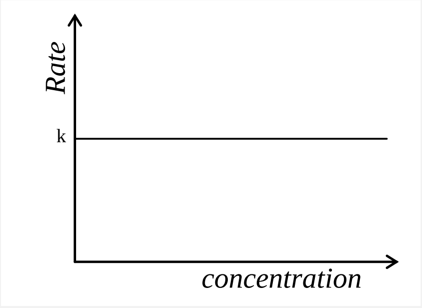
ii. CO

iii. O_2 Give reasons in each case. Write an expression for the rate equation.

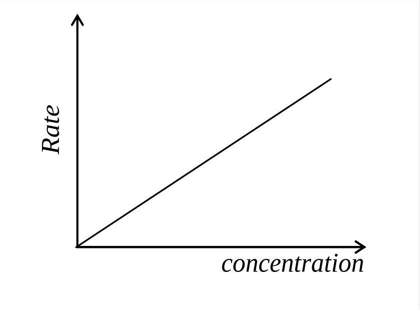
13.2. Using the graphical method.

The order of reaction can be determined using the graphical method by knowing the kind of graph for a given order of reaction.

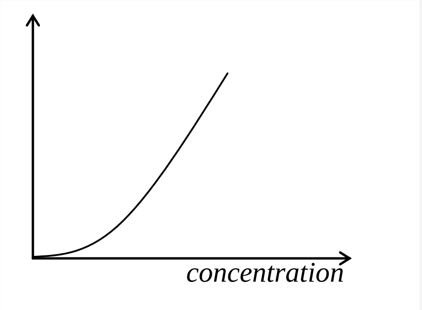
Rate-concentration graphs include:



zero order

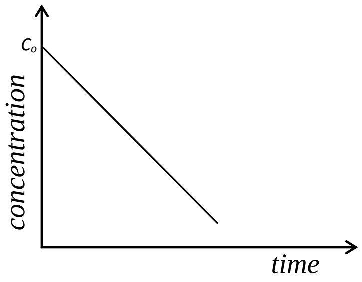
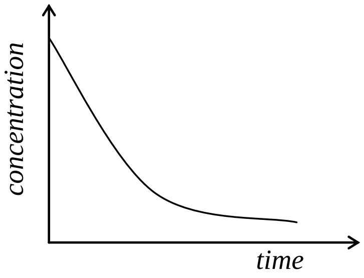
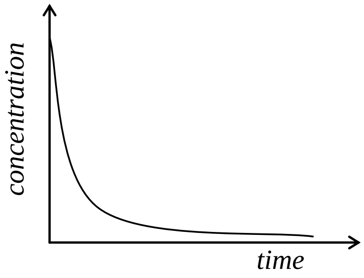


first order



second order

Concentration-time graphs

		
zero order	1st order	2nd order

worked examples.

1. The table below shows the kinetic data for decomposition of hydrogen peroxide

$[H_2O_2]$/moldm^{-3}	Rate / moldm^{-3}s^{-1} x 10^{-4}
0.1	0.593
0.175	1.04
0.25	1.48
0.3	1.80

Plot a graph of initial rate against concentration and hence determine the order of reaction.

2. The table below shows the kinetic data for decomposition of compound Y.

Time/min	Concentration/ moldm^{-3}x10^{-4}
0	2.9
18	2.3
30	2.0
54	1.6
80	1.3
120	1.0
160	0.725

a. Plot a graph of concentration of y against time.

b. Determine the order of reaction and the half life of reaction.

Exercise 13e.

1. Plot a graph and use it to determine the order of reaction.

[A]/moldm^{-3}	Rate / moldm^{-3}s^{-1}
0.1	0.0001
0.2	0.0004
0.3	0.0009
0.4	0.0016

2. The table below shows the kinetic data for decomposition of compound A.

Time/min	Concentration/ moldm^{-3}x10^{-4}
0	100
7.2	91
18	79
36	63
72	40
108	25

a. Plot a graph of concentration of A against time.

b. Determine the order of reaction.

c. Determine the half life of reaction and hence the rate constant.

3. Explain what is meant by the following terms

i. rate of reaction.

ii. Order of reaction.

iii. molecularity

b. The table below shows the kinetic data for the reaction between a bromoalkane and hot alkali.

Time/s	O	9	18	27	40	54	75	105
[RBr] x10^{-2} moldm^{-3}	10.6	9.6	8.6	6.5	-	5.4	4.3	3.0

a. Plot a graph of concentration of [RBr] against time.

b. Determine the order of reaction.

c. Determine the half life of reaction and hence the rate constant.

d. Find the concentration of [RBr] at 40s.

4.The table below shows the kinetic data for the reaction between a bromine and methanoic acid

Time/s	O	30	60	90	120	180	240	360	480	600

$[Br_2]$ moldm^{-3}	0.01	0.009	0.0081	0.0073	0.0066	0.0053	0.0044	0.0028	0.0020	0.0013

a. Plot a graph of concentration of $[Br_2]$ against time.

b. Determine the order of reaction.

c. Determine the half life of reaction and hence the rate constant.

13.3. Molecularity and mechanism of reactions.

Molecularity is the number of reactant molecules taking part in the rate determining step.

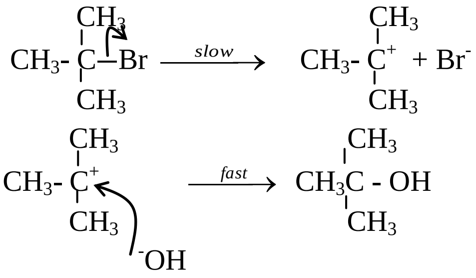
•If it is only one reactant taking part in the rate determining step, the reaction is called *unimolecular* (1st order)

$(CH_3)_3C\text{-}Br + NaOH \xrightarrow{heat} (CH_3)_3C\text{-}OH + NaBr$

Rate = $K[(CH_3)_3C\text{-}Br]$

mechanism:

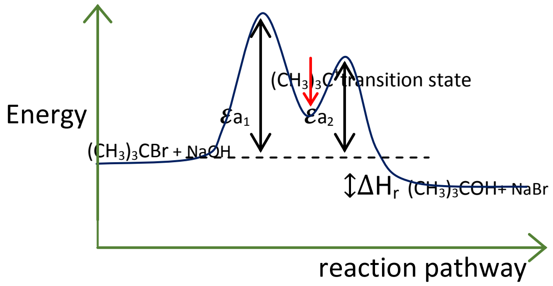
$NaOH \longrightarrow Na^+ + OH^-$



$CH_3\text{-}C(CH_3)_2\text{-}Br \xrightarrow{slow} CH_3\text{-}C^+(CH_3)_2 + Br^-$

$CH_3\text{-}C^+(CH_3)_2 + {}^-OH \xrightarrow{fast} CH_3C(CH_3)_2\text{-}OH$

Energy profile diagram(SN_1)



$\mathcal{E}$a-activation energy

$\updownarrow\Delta H_r$ -heat change for reaction.

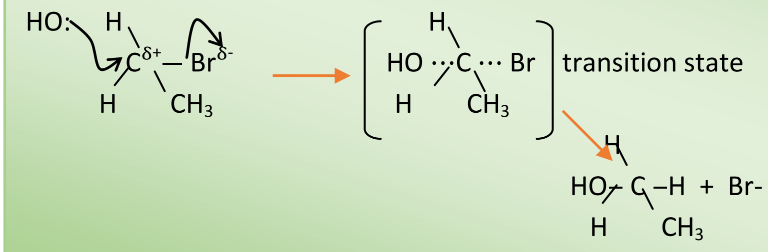
For example Alkaline hydrolysis of tertialy alkyl halides.

• If there two reactants taking part in the rate determining step, the reaction is called *bimolecular*(2nd order).

For example Alkaline hydrolysis of primary alkyl halides.

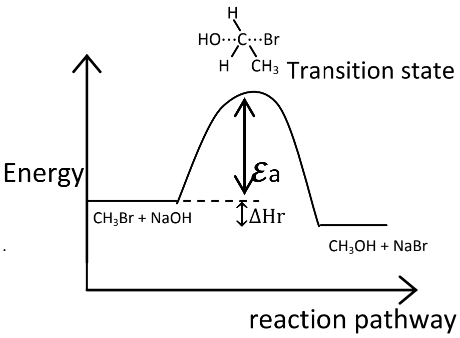
The above reaction involves transition state.

$NaOH \rightarrow Na^+ + {}^-OH$



$Na^+ + Br^- \rightarrow NaBr$

Energy profile diagram(SN_2).



Experiment Number	[RBr] (mol dm^{-3})	[OH] (mol dm^{-3})	Intial Rate (mol dm^{-3} s^{-1})

1	0.1	0.5	0.002
2	0.1	0.25	0.002
3	0.05	0.25	0.001
4	0.025	0.25	0.0005

a. Deduce the order of reaction with respect to RBr and sodium hydroxide.

b. Write the rate equation for or rate expression for the reaction.

c. Calculate a value for the rate constant and give its units.

d. Suggest the class of the bromo alkane.

e. Outline the possible mechanism of reaction.

f. Draw a well labeled energy level diagram.

2.a. Differentiate between molecularity and order of reaction.

b. The results of hydrolysis of a bromoalkane by sodium hydroxide at 25^{o} C are given below.

Experiment Number	[RBr] (mol dm^{-3})	[OH] (mol dm^{-3})	Intial Rate (mol dm^{-3} s^{-1})
1	1.0×10^{-2}	2.8×10^{-3}	2.1
2	5.0×10^{-3}	2.8×10^{-3}	1.1
3	1.0×10^{-2}	5.6×10^{-3}	4.3

a. Deduce the order of reaction with respect to RBr and sodium hydroxide.

b. Write the rate equation for or rate expression for the reaction.

c. Calculate a value for the rate constant and give its units.

d. Suggest the class of the bromo alkane.

e. Outline the possible mechanism of reaction.

f. Draw a well labeled energy level diagram.

13.4. Factors affecting the rate of chemical reactions.

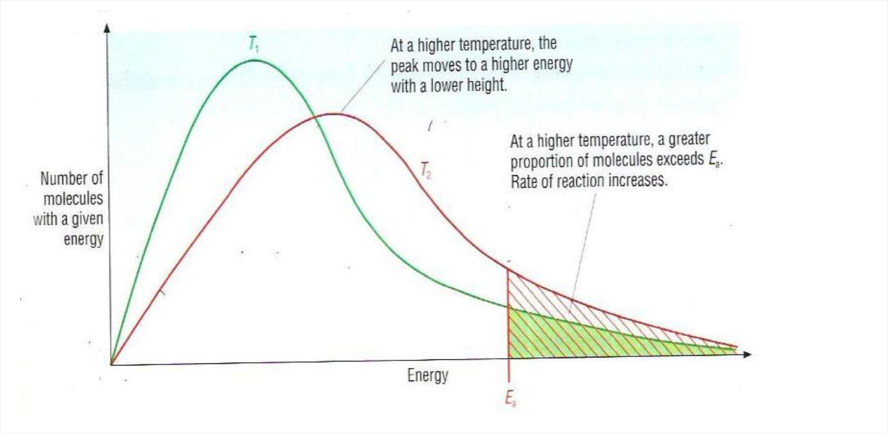
a. Concentration.

The rate of reaction is directly proportion to the concentration of reactions.
Therefore the rate of reaction increases with increase in the concentration of reactants because,
As the concentration increases, the number of reactant molecules come closer together ,
the greater the collisions and the faster the reaction.

b. Temperature.

The rate of a chemical reaction increases as temperature because
as temperature rises ,the number of reactant molecules the kinetic energy of molecules increases, the amount of collisions increases hence the number of molecules that gain necessary activation energy increases which leads to an increase in rate of reaction.
This can be demonstrated by Boltz mann -Maxwell distribution curve,

Distribution of molecular kinetic energies at different temperature.



Boltzmann distribution curve.

Boltzmann
(1984-1906)
Remebered for his
work in kinectics

Relationship between temeperature(T) and the rate constant(K)

This is demonstrated using Arrehenius expressions

$K= Ae^{-Ea/RT}$………………$*_1$

A-is the exponential factor.

e - exponential

E_a- activation energy

R-molar gas constant.

introducing ln in equation $*_1$

$\ln K = \ln A\ e^{-Ea/RT}$

$\ln K = \ln A - \frac{E_a}{RT}$

Given T_1&T_2

$\ln K_1 = \ln A - \frac{E_a}{RT_1}$………………$*_2$

$\ln K_2 = \ln A - \frac{E_a}{RT_2}$ ………………$*_3$

equations $*_2$-$*_3$

$\ln\frac{K_1}{k_2} = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})$………………$*_4$

From the arrehenius expression it comfirms that temperature affects both the rate and the rate constant.

Activation energy- The energy required to start a chemical reaction.

Worked example.

1. For a reaction with activation energy of 55 KJ/mol, by what factor will the rate constant go up witha rise in temperature from 300 K to 310K.

solution.

$\ln\frac{K_1}{k_2} = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})$

$\ln\frac{K_1}{k_2} = \frac{55}{8.314}(\frac{1}{300} - \frac{1}{310})$

Exercise. 13.g.

1.The rate constants of reaction at 700K and 760K are 0.011$M^{-1}s^{-1}$and 0.105$M^{-1}s^{-1}$respectively. What are the values of 'A'and 'Ea'?

2. What is the activation energy of a reaction whose rate quadruples when the temperature is raised from

293 K to 313 K.

3.Find the value of activation given.

Temp/k	Rate constant/dm^{-3}mol^{-1}s^{-1}
313	3.95 x 10^{-3}
323	8.63 x 10^{-3}

c. Catalyst.

A catalyst is a substance that alters the rate of chemical reaction and remains chemically unchanged at the end of the reaction.

A catalyst may be positive or negative.

A *positive catalyst*- speeds up the rate of chemical reaction.

A *negative catalyst* –lowers the rate of chemical reaction.e.g.

A catalyst may be homogenous or heterogenous.

A *homogenous catalyst* – Catayst with the same physical state as reactants.

eg. esterification of esters using sulphuric acid.

A *heterogenous catalyst*-Catayst with a different physical state from reactants.

e.g. hydrogenation of alkenes using non-metals, haber process and contact process.

Catalyst poisoning.

Catalyst poisoning is inhibiting the effectiveness of a catalyst.

Impurites added or in reactants cause catalyst poisoning by forming strong bonds with reactants in active sites on the surface of reactants . e.g

- Barium sulphate during Resenmund – reduction.

Auto catalysis.

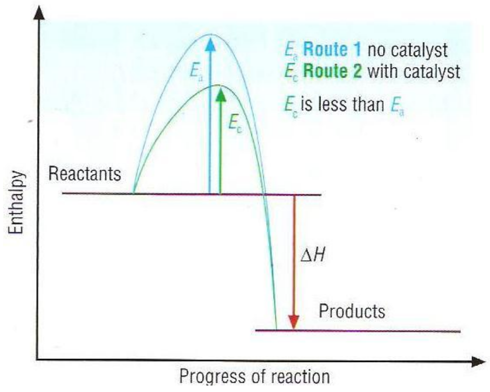
This occurs when one of the products acts as a catalyst.

For example during reduction of manganate(VII) ions using oxalate , the Mn^{2+} produced acts as a catalyst of reaction.

Effect of a catalyst on the rate of reaction and activation energy.

A positive catalyst increases the rate of reaction by providing an alternative pathway with lower activation energy.

Because catalyst lowers the activation energy, the amount of reactant molecules with necessary activation energy increases.



Reaction path way showing how a catalyst lowers activation energy.

Note:

A negative catalyst will increase activation energy hence slows down the rate.

d. Pressure.

When pressure is increase the rate of the chemical reaction increases because the collision of molecules increases hence a greater proportion of reactant molecules gain necessary activation energy.

e. light.

Light has an effect on some reactions which are sensitive to it like photochemical reactions.

e.g. -Free radical reactions like halogenations of alkanes and benzene.

-Photosynthesis.

i.e. In the presence of light (sun light) these reactions are possible hence it increases their speed.

f. Physical state or particle size.

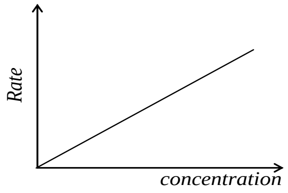
By changing the physical state (like from solid to liquid) it increases the surface area required for reaction which increases the rate of reaction.

For solids if they are broken down into small particles, the rate of reaction increases because increase in the surface area for reaction.

Trial questions.

Multiple choice questions

1. Given



Which order of reaction is shown by a graph above.

a. 1st order b. 2nd order c.3rd order d. zero order

2. The radioactive active isotope $^{24}Na^+$ is injected into an animal. If the half life is 15hours, how long will it take before the radioactivity has fallen to 25% of the original value

a. 30 hours b. 20 hours c. 30 days d.25 hours

3. A radioactive isotope decays from intial count of 160cpm to 20cpm in 27days. What is the half life?

a.7days b. 6days c. 7days d. 9days

4.Given thereaction $PCl_3+Cl_2 \rightarrow PCl_5$

Thefollowingrate data were obtained atconstanttemperature:

Experiment Number	InitialconcentrationofPCl$_3$/ moldm^{-3}	InitialconcentrationofCl$_2$/ moldm^{-3}	Initial rate/ moldm^{-3}s^{-1}
1	0.2	0.1	0.0004
2	0.4	0.1	0.0008
3	0.8	0.2	0.0064

What is the overall order of reaction

a.1 b. 2 c.3 d.4

5.The results were obtained for the rate of hydrolysis of methylmethanoate at 298K

$[HCO_2CH_3]$	$[H^+]$	Initial rate x 10^3 $moldm^{-3}$
0.5	1	0.56
1	1	1.11
2	1	2.24
2	0.5	1.13
2	22	4.49

Calculate the value of the rate constant.

a.0.112$moldm^{-3}$ S^{-1} b. 1.12 $mol^{-1}dm^3S^{-1}$ c. 0.112$mol^{-1}dm^3S^{-1}$ d. 1.12 $moldm^{-3}S^{-1}$

6. Given

Exp	$[S_2O_8^{2-}]$/$moldm^{-3}$	[I]/$moldm^{-3}$	Initial rate /$moldm^{-3}S^{-1}$
1	0.040	0.04	9.6×10^{-6}
2	0.08	0.04	1.92×10^{-5}
3	0.08	0.02	9.6×10^{-6}

What is the is initial rate when $[S_2O_8^{2-}]$ = 0.12M [I] =0.015M

a. $1.08 \times 10^{-4}MS^{-1}$ b. $1.08 \times 10^{-3}MS^{-1}$ c. $1.08 \times 10^{-5}MS^{-1}$ d. $1.08 \times 10^{-6}MS^{-1}$

7. Which type of catalysis is observed during the Haber process.

a. Heterogenous catalysis b. Homogenous catalysis c. Autocatalysis.

8. Given

A →

Identify a rate equation that corresponds to a zero order reaction with respect to A.

a. Rate = K[A] b. Rate = $k[A]^2$ c. Rate = k d. Rate = $k[A]^3$

9. For the reaction: $2A + B \rightarrow C$

Which statement is correct.

a. The rate of disappearance of B is twice of A.

b. C appears the rate equal to the sum of the rates of the disappearanceof A nad B.

C. The rate of appearance of Cequals the rate of disappearance of A.

d. The rate of disappearance ofA is twice of B.

10.A radionuclide has half life of 62min. What is the rate constant.

a. 89min^{-1} b. 0.011S^{-1} c. 0.0011S^{-1} d. 89S^{-1}

11.The half of Rn is 3.8days. After 15.2days, 5.6mol remained. What was the intial amount of Rn?

a.0.9mol b.0.45mol c. 0.09mol d. 0.045mol

12. The decomposition rate dimethyl at 504^{0}C is first order with half life of 1570yrs. What fraction of the initial amount will remain after 4710S.

a. $1/3$ b. $1/6$ c.$1/8$ d. $1/16$ e. $1/32$

Structural questions

1.a.The reaction between oxygen and nitrogen monoxide:

$O_2 + 2NO_{(g)} \longrightarrow 2NO_{2(g)}$

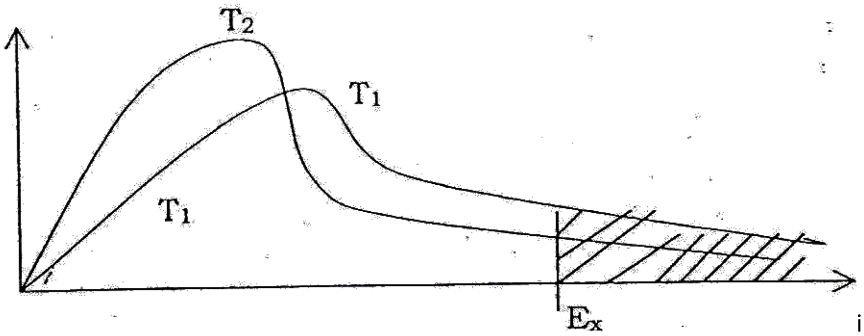
is known to be first order with respectto oxygen and second order with respect to nitrogen monoxide.

i. Write an expression for the rate equation for the reaction.

ii. What are the units of the rate constant?

iii. When the initial $[O_2] = 1.0\times10^{-2}$ moldm^{-3} and $[NO] = 3.0\times10^{-2}$ mol dm^{-3} , the initial rate is 6.3×10^{-4} mol dm^{-3} S^{-1} Calculate the numerical values of the rate constant.

b. The graph below shows the Boltzmann distribution curve for the same amount of a gas sample at two different temperatures.



i. State what you would label on X and Yaxis.

ii.What does the shaded part represent.

iii. Explain why a small increase in temperature increases the rate of a chemical reaction tremendously.

2. Nitrogen monoxide reacts with bromine as shown by equation below.

$2NO_{(g)} + Br_{2(g)} \longrightarrow 2NOBr_{(g)}$

The variations of concentration of reactants and rate at a constant temperature and pressure are shown in the table below.

Experiment	Intial [NO] in mol dm^{-3}	Intial [Br] in mol dm^{-3}	Intial rate in mol dm^{-3}s^{-1}
1	2.00×10^{-2}	2.50×10^{-3}	1.60×10^{-3}
2	2.00×10^{-2}	5.00×10^{-3}	3.20×10^{-3}
3	4.00×10^{-2}	5.00×10^{-3}	1.30×10^{-2}

a) Deduce the order of reaction with respect NO and the order of reaction with respect to Br_2. Give reasons for your answers.

(b) Write an expression for the rate equation for the above reaction.

c) Calculate the rate constant using experiment 1 and give its units.

d) Briefly explain the effect of temperature on the rate of reaction.

e) Using the concept of activation energy briefly explain how a catalyst affects the rate of reaction.

14.0Radioactivity

Radio activity is the spontaneous disintegration of heavier particles to produce lighter particles accompanied by release of energy and active rays without any external force applied.

Each radioactive element has got its own way of disintegration and may lead to release emission of $\alpha, \beta and \gamma$ rays.

14.1. Radioactive emissions

***Alpha particles** (α-particles)*

These are helium nuclei ions $^{4}_{2}He$.

They are heavy.

Alpha particles are positively charged ($^{4}_{2}He^{2+}$).

Thespeed ofα-particleis of the orderof10^{7} *m/s.*

They are deflected by both electric and magnetic field.

They have a poor penetrating power.

Theyhave large kinetic energy.

They affect a photographic plate.

They destroy living cells and cause biological damage.

***Beta particles**(β-particles)*

β*-particles are*$_{-1}^{o}e$.

They affect photographic plates.

They are very light

Are negatively charged.

Its speed is oftheorderof10^{8}*m/s.*

They are deflected by both electric and magnetic field.

They have a high penetrating power.

They cause greater radiation damage as they can easily pass through the skin of the body.

***Gamma rays** (γ-rays)*

Are electromagnetic waves and not particles.

They affect photographic plates.

Have no charge. ($^{o}_{o}\gamma$). *Zero charge.*

Thespeed is the same as the speed of light.

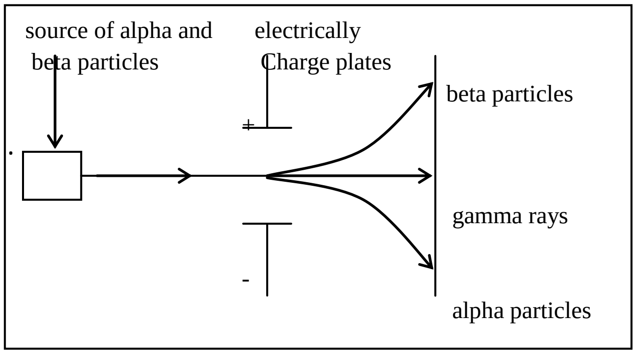
They are not deflected by both electric and magnetic field.

They have the highest penetrating power.

γ*-rays or radiations simply represent energy lost during radioactivity*

They can easily pass through the human body and cause immense biologicaldamage.

They are veryuseful in thetreatmentofcancer.



14.2. Stability of the nucleus and radioactive isotopes.

Radioactivity occurs in radioactive isotopes and is as a result of instability of the nucleus.

Stability of the nucleus

Stability of the nucleus is attained when the number of protons is approximately equal to the number of neutrons.

A Stable nuclear usually contain an adequate number of neutrons in order to dilute the concentration of positive charges (protons) which strongly repel one another and cause instability of the nucleus.

Therefore the atoms whose nuclei contain high number of protons than neutrons undergo radioactivity in order to attain stability. This is process is accompanied by loss of mass which is converted to large amount of energy.e.g.

consider a radioactive isotope radium

$^{226}_{88}Ra \longrightarrow ^{222}_{86}Rn + ^{4}_{2}He$ + energy

The mass of radium nucleus and helium atom formed is less than the mass of radium and the difference is converted to large amounts of energy.

Thus attaining stability of the nucleus.

Factors affecting the stability of the nucleus.

***a.* Binding energy per nucleon.**

This is the energy required to separate the nucleus of the atom into protons and neutrons.

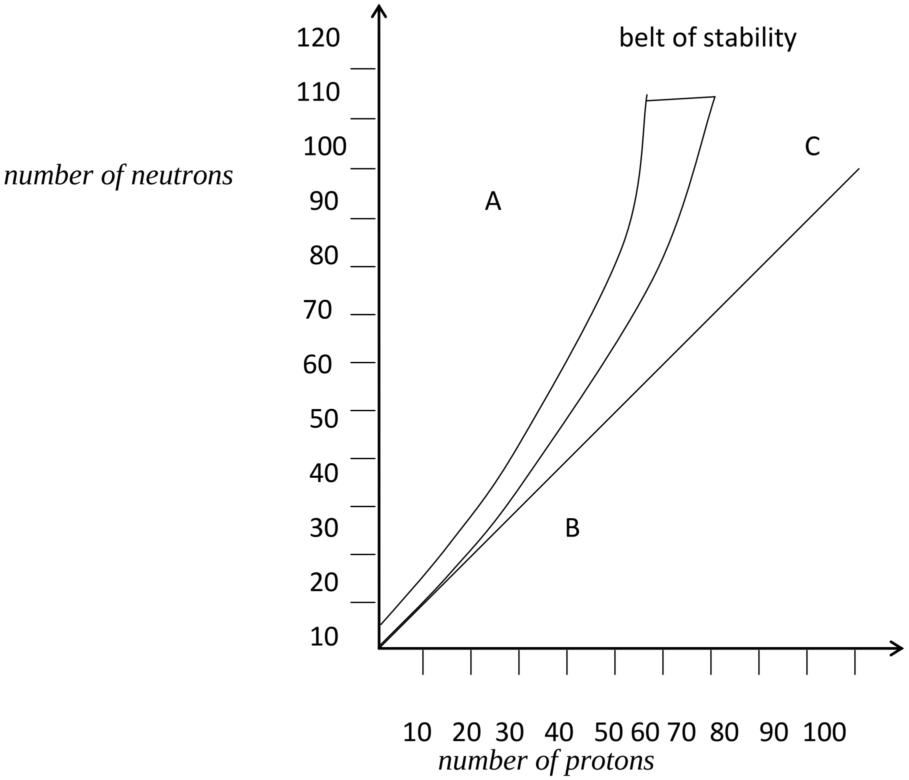
The higher the binding energy per nucleon the higher the stability of a given nucleus.

b. Ratio of neutrons to protons.

When the n:p≃1, the nucleus is stable this is true especially true for light nuclei.

When n:p>1, the nucleus is unstable for heavy isotopes.

The graphs below shows a plot of number of neutrons versus number of protons with a belt of stability



A. represents nuclei above the belt of stability (nuclei with high neutron to proton ratios)

The nuclei gains stability by emission of β particle.

In this process a neutron is converted to a proton and an electron which is a β particle.

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

This decreases the number of neutrons and increases the number of protons.

B. represents nuclei below the belt of stability (nuclei with high proton to neutron ratios)

The nuclei gain stability by electron capture.

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

This increases the number of neutrons and decreases the number of protons.

C: Represents nuclei with exceeding large number of protons (above 84) .

The nuclei gains stability by emission of α -particles.

$^{212}_{84}Po \longrightarrow {}^{208}_{82}Pb \ + {}^{4}_{2}He$

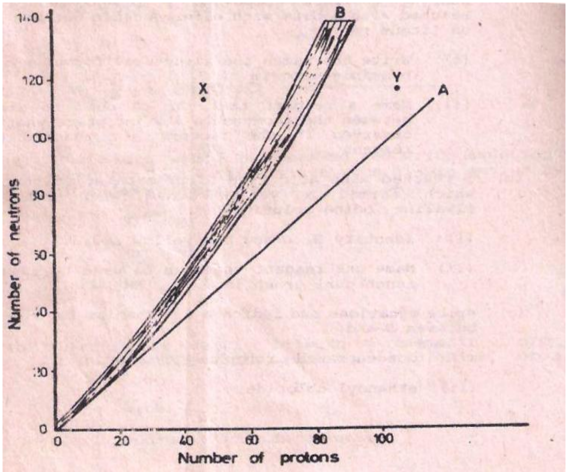
This reduces the number of neutrons and protons moving the nucleus diagonally to the belt of stability.

Exercise 14 a

1.a.i. Explain the term nuclear stability

ii. Explain the factors that determine the stability of the nucleus

b. The graph shows a plot of a graph of number of neutrons against number of protons in a stable nuclei.



i.State what line A and B represent.

ii. Briefly explain how the nuclei x and y gain stability.

14.3. Radioactive equations

Radioactive equations are nuclear equations and these include:

Radioactive equations by emission of beta particles.

$^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa \ + \ {}^{o}_{-1}e$

$^{222}_{86}Rn \longrightarrow {}^{222}_{87}Fr \ + \ {}^{o}_{-1}e$

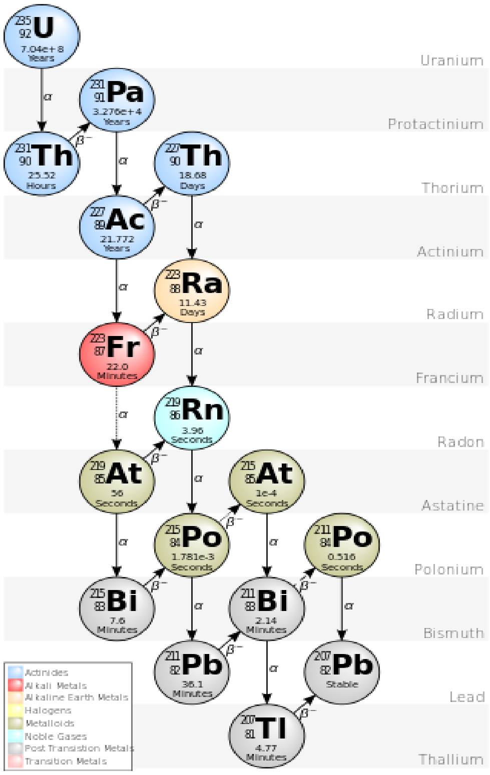
Radioactive equations by emission of alpha particles.

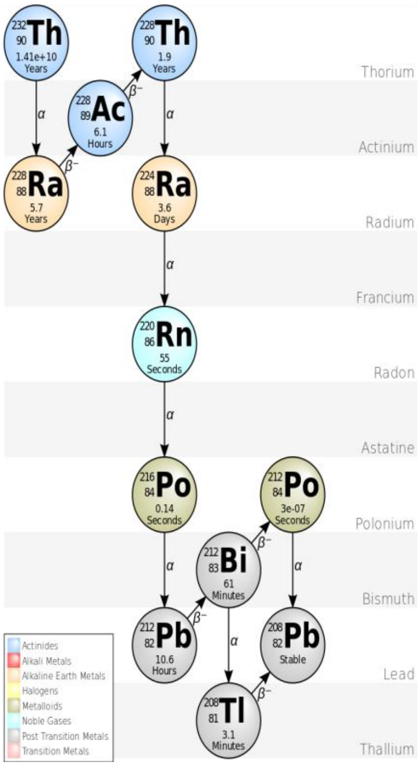
$^{218}_{92}U \longrightarrow {}^{214}_{90}Th \ + {}^{4}_{2}He$

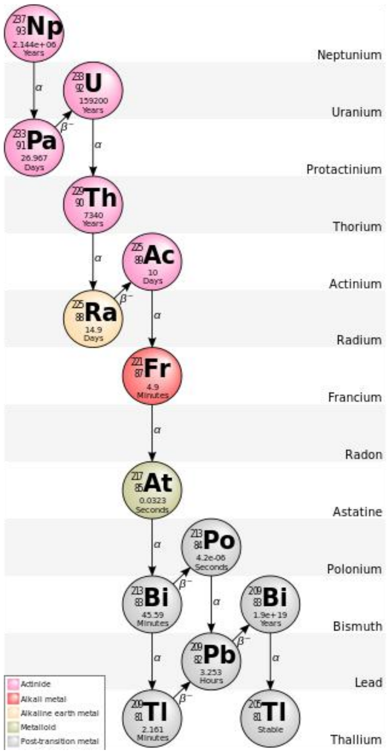
$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn \ + {}^{4}_{2}He$

14.4. Radioactive and Nuclear decay series.

Radioactive DecaySeriesis the seriesofsteps bywhich aradioactive nucleus decays into a non-radioactive nucleus







14.5. Nuclear fission and fusion.

Nuclear fission.

It is the disintegration of heavier nuclei to form lighter particles.

This happens when the heavy nuclei bombarded with other particles (neutrons).

The heavier nuclei splits into new nuclei (elements) followed by release of a lot of energy.

Neutrons are used in this purpose because they have a high penetrating power and have no charge. e.g.

$^{235}_{92}U+^{1}_{0}n \longrightarrow ^{95}_{42}Mo + ^{139}_{50}Te + 2^{1}_{0}n$ + energy.

The process of fission emits neutrons and these are available to collide with uranium atoms to produce new fissions which lead to a chain reaction.

These chain reactions are what happen in *atomic bombs*.

Applications of nuclear fission.

The lots of energy produced during nuclear fission in important and dangerous to mankind.

-Under controlled conditions it is used in nuclear power plants as a source of electricity.

-Nuclear fission is also applied during the manufacture of atomic bombs.

Nuclear fusion.

It is the joining of lighter nuclei to produce heavier nuclei.

It was discovered by Rutherford and is an example of *nuclear transmutations.*

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

Greater energy is generated during nuclear fusion and is a source of energy

This energy used to make a fusion bomb (thermonuclear bomb), The **hydrogen bomb** which derives its energy from combination of hydrogen atoms.

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

14.5.Comparison between chemical and nuclear reactions.

Nuclearreaction	Chemical reaction
Takesplace within the nucleus and involves neutrons and protons.	Takesplace on the outer energylevels containing the valence electrons.Doesnot involve protons and neutrons.
Releases large amounts of heat energy	The heat energy released is much less
Not affected by environmental factors such as temperatures, pressure and do not involve catalysts	Are affected byenvironmental factors such as Temperature and pressure and can or not involve catalysts.
One element maybe converted into another.	No new element can be produced.

14.6.Balancing nuclear equations and predicting modes of decay.

To balance a nuclear equation or radioactive equation the mass numbers and atomic numbers must balance on both sides of the equations.

Worked example

Balance the following equations and identify elements X, Y and Z.

a. $^{35}_{17}Cl + ^{1}_{0}n \longrightarrow ^{a}_{b}X + ^{1}_{1}H$

b. $^{234}_{90}Th \longrightarrow ^{a}_{b}Y + ^{4}_{2}He$

c. $^{7}_{3}Li + 2^{2}_{1}H \longrightarrow ^{a}_{b}Z + ^{1}_{0}n$

Exercise 14b.

1.a. Complete the following equations for the nuclear reactions.

i. $^{239}_{94}Pu + ^{1}_{0}n \longrightarrow ^{91}_{39}Y + ^{146}_{55}Cs$ + ……………………

ii. $^{239}_{92}U \longrightarrow ^{239}_{93}Np$ + ……………………

iii. $^{226}_{88}Ra \longrightarrow ^{4}_{2}He$ + …………………

b. The isotope $^{230}_{90}Th$ is formed by decay invoving loss of 2α and 2β particles. Write down the equation for the decay process.

2. A series of radioactive decays can be represented as

$^{232}_{90}Th \xrightarrow{\alpha-emission} X \xrightarrow{\beta-emission} Y \xrightarrow{\beta-emission} Z$

State the mass and atomic number of Y and Z

3. $^{238}_{92}U \xrightarrow{\alpha-emission} A \xrightarrow{\beta-emission} B \xrightarrow{\beta-emission} X \xrightarrow{\alpha-emission} Y$

Calculate the mass number and atomic numberof element Y.

4. Complete this radioactive series:

$^{233}_{88}Ra \xrightarrow{\alpha} Rn \xrightarrow{\alpha} Po \xrightarrow{\alpha} Pb \xrightarrow{\beta^-} Bi \xrightarrow{\alpha} Tl \xrightarrow{\beta^-} Pb$

5.Write a balanced nuclear equation for each disintegration process.

a. An known element emits ϒ rays plus particles that are readily blocked by paper.

The yield contains also substantial quantity of tin-104.

b. Bombarding $^{253}_{99}Es$ with an alpha particle produces one neutron plus another transuranium isotope.

c. Carbon -14 is generated on bombardment of nitrogen -14 by a neutron.

6. After a series of nuclear transformations, the $^{238}_{92}U$ finally ends as $^{206}_{82}Pb$

a. Why does the series stop at this isotope?

b. Calculate the number of ∝-particles and **β**- particles for that transformation.

14.7. Rates of decay

The rate of decay is directly proportional to the number of atoms present.

It is a first order reaction and is represented by

$\ln\frac{No}{Nt}$ = kt .Where t = t½, $N_t = \frac{No}{2}$

$\ln\frac{No}{\frac{No}{2}}$ = kt½

ln2 = kt½

t½ = $\frac{ln2}{k}$ i.e. t½ = $\frac{0.693}{k}$

Half life ($t_{½}$)

Time taken for a radioactive substance to decay to half the original value.

$\frac{-dN}{dt}$ = KN ,where N is the number of radioactive atoms , K is the decay constant and t is time.

$\frac{dN}{N}$ = -Kdt

$\int_{No}^{Nt}\frac{dN}{N} = -K\int_0^t kt$, when t=o, N =N_0 and when t=t, N=N_t

$\ln N_t - \ln N_0 = -k\,(t-0)$

$\ln\frac{Nt}{No}$ = -kt

$\ln\frac{No}{Nt}$ = kt

The instruments used to measure radioactivity are ***the Geiger muller counter, the scintillation counter and cloud chamber.***

Worked example 14 b

1. A radioactive count rate of living matter due to the decay of carbon 14 is approximately 16 minutes per gram. A wooden stuff was found to have a count rate of 4 minute per gram of carbon. How old is the wood. (take half life of carbon 14 to be 5600 years)

Exercise 14 b.

1. It has been estimated that carbon -14 isotope in the atmosphere is responsible for producing 60 atoms of nitrogen -14 and 60 electrons every hour for each gram of atom of carbon this disintegration rate is 60 counts hour^{-1}g^{-1}.A sample of a sea shell was found to have a count rate of 4 counts hour $^{-1}$g^{-1}.

Calculate the age of the shell.(half life of carbon -14 is 5730 years)

2.a. The initial count of a radioactive nucleus was 680 per second. After 350 seconds, the count rate is 125 per second.

Calculate the

i. decay constant.
ii. half life of the nucleus
3.Assuming that the half life of element X is 400 years, how long does it take 50g of X to change to 3.125g.
4. The half – life of $^{238}_{92}U$ is 4.5 x 10^9 years.
How many years would be required for 1000 atoms of $^{238}_{92}U$ to decay to 250 atoms?

worked examples 14 c.

A radioactive isotope decays at a rate such that after 84 days only $\frac{1}{8}^{th}$ of the original substance remains. Calculate
i. decay constant
ii. half life.

Exercise 14 c

1.A radioactive isotope X decays by emitting beta particles. It was found that only $\frac{1}{32}$ of the original isotope remained after 100 days,
Calculate the half-life of the radioactive isotope.
2a. What is meant by the term half-life of a radioactive isotope.
b. The half-life of carbon-14 is 5600 years. Analysis of a fossil from the historical site Showed that 6.25% of carbon-14 was present compared to living materials.
Calculate the age in years of the fossil.
3.The half-life of cobolt -60 ($^{60}_{27}Co$) is 5.2 years What fraction of cobolt-60 will remain after 26 years?
4. A radioactive isotope has a half life of 15 days. What fraction of the original amount of the isotope would remain after 75days?
5.The disintegration rate constant of conversion of radioactive sodium to magnesium is 2.85 x$10^{-3}S^{-1}$. Calculate the percentage of the original sample left after 150 S.

Worked example14 d

The half life of bismuth is 19.7 minutes.
Determine the time taken for 43% by mass of bismuth to decay.

Exercise 14 d.

1. If the radio active decay of Ni to Cu has a half life of 120 years , how long will it take for three-quarters of ni to change to Cu.
2. a. Calculate the rate ofdecayconstantfor U-238 ifits half-life is 4.468 × 10^9years.

b. Calculate how long it will take forn25% of a U-238 sample to radioactively decay.

3. a. i. Define half life.
ii. Using 2.303 log $\frac{No}{Nt}$ = kt , derive an expression for half life.
b. The half life of a radioactive decay is 100s.
Determine the percentage of radioactive sample that decays after 250S.
3. A radioactive sample contains 1000 units and its half life is 1.3 minutes. If allowed to decay for 6.7 minutes.
Determine i. the units remaining
ii. the percentage that has decayed

Worked example

A Geiger Muller count is filled with each sample of carbon dioxide and the following counts are recorded.

Carbondioxide from back ground gives 10.775 counts per 90 minutes.

Carbondioxide from fresh wood gives 26393 counts per 200 minutes.

Carbondioxide from a sample to be dated gives 10788 counts per 400 minutes.

What is the age of the sample. (half life of the sample is 5570 years).

$t½ = \frac{ln2}{k}$

$k = \frac{ln2}{t½}$

$k = \frac{ln2}{5570} = 1.244\ 3x\ 10^{4}\ yr^{-1}$

$ln\frac{No}{Nt} = kt$

back ground $\frac{10775}{90} = 11.97$ C/min

fresh wood $\frac{26393}{200} = 131.97$ C/min

sample to be dated $\frac{10788}{400} = 26.97$C/min

No =131.97-11.97=120c/min

Nt = 26.97-11.97 =15 c/min

$ln\frac{120}{15} = 1.2443 \text{ X } 10^{-4}t$

t =16711.8 min.

14.7. Applications and dangers of radioactive substances.

Applications

Used in treatment of cancer.

Used in detection of brain tumors and circulatory disorders.

Used to analyse the mechanism of complex reaction especially in organic chemistry

Used in food preservation.

Applied in dating of specimens.

Sterilizing surgical instruments.

Dangers.

Causes cancers e.g. leukemia.

It also causes damage of body cell.

Trial questions.

Multiple choice questions.

1. Which is always true when a nucleus undergo radioactivity decay

a. an alpha particle is always emitted.

b. A beta particle is always emitted.

c. the nucleus loses energy.

d. a new nucleus is always formed.

2. The process of determining the age of the sample is

a. Carbon dating

b. smoke detecting

c.radioactive dating

d.irradiation

3. In the following reaction. Identify the missing atom.

$^{249}_{95}Am \longrightarrow {}^{A}_{Z}Y + {}^{4}_{2}He$

a.Th b. Pa c. U d. Np

4. Which of the following metals can shield against radioactive emissions

a. Pb c. U c. Au d. Ra

5. Select the correct of increase in penetrating power.

a. Alpha, beta, gamma

b. gamma, beta, alpha

c.alpha, gamma, beta

d. beta , gamma, alpha

6. Which of the particles has the speed as the speed of light?

a. $\propto$ b. **β** c. γ d. n

7.Which of the correcty balances the nuclear reaction below?

$^{230}_{90}Th \longrightarrow {}^{230}_{91}Pa$ + ………….

a. $\propto$ b. **β** c. γ d. n

8. The radioactive isotope Z has a half life of 12hours. After 2 days, the fraction of the original that remains is

a.½ b. ¼ c.$^1/_8$ d .$^1/_{16}$

9. Which of the following is most likely to be attracted to the positive plate?

a. $\propto$ b. **β** c. γ d. n

10. A radioactive decays series will continue until it forms a stable isotope of ….

a. Uranium b. Lead c. bismuth d.Lawrencium

11. U(238) is most likely to release a particle of

a. $\propto$ b. **β** c. γ d. n

12. C(14) has a half life of 5730year.

How many years would it take for 4g to change to 0.25g.

a. 4 b. 5730. c. 11700 d. 17200

13. Identify the particles that can be blocked the paper.

a. $\propto$ b. **β** c. γ d. n

14. Which of the elements are used in treatment of cancer

a. U b. Pb c. Po d. Co

Structural questions.

1. **(**a) How many alpha particles and beta particles are there from this conversion $^{237}_{93}Np$ to $^{207}_{82}Pb$

(b) A stable nuclide absorbs a neutrons, emits an electron, and then splits into two $\propto$ particles. Identify the nuclide.

(c)(i) One can produce sodium -24 by exposing stable sodium $^{23}_{11}Na$ to a flux of neutrons . Write down the formation reaction of sodium -24

(ii) Sodium -24 is radioactive by emission of $\boldsymbol{\beta}^-$ and its half- life is 15 hours, Write down the equation for the decay of sodium -24.

(iii) One injects into the blood of an individual 10 cm3 of a solution initially containing sodium -24 with a concentration of 10mol.l-1. What is the number of moles of sodium -24 that have been injected into the blood? How much of it will remain after 6 hours?

The Periodic Table of Elements

Group																	
I	II											III	IV	V	VI	VII	VIII
				Key			1 H hydrogen 1										2 He helium 4
3 Li lithium 7	4 Be beryllium 9			atomic number atomic symbol name relative atomic mass								5 B boron 11	6 C carbon 12	7 N nitrogen 14	8 O oxygen 16	9 F fluorine 19	10 Ne neon 20
11 Na sodium 23	12 Mg magnesium 24											13 Al aluminium 27	14 Si silicon 28	15 P phosphorus 31	16 S sulfur 32	17 Cl chlorine 35.5	18 Ar argon 40
19 K potassium 39	20 Ca calcium 40	21 Sc scandium 45	22 Ti titanium 48	23 V vanadium 51	24 Cr chromium 52	25 Mn manganese 55	26 Fe iron 56	27 Co cobalt 59	28 Ni nickel 59	29 Cu copper 64	30 Zn zinc 65	31 Ga gallium 70	32 Ge germanium 73	33 As arsenic 75	34 Se selenium 79	35 Br bromine 80	36 Kr krypton 84
37 Rb rubidium 85	38 Sr strontium 88	39 Y yttrium 89	40 Zr zirconium 91	41 Nb niobium 93	42 Mo molybdenum 96	43 Tc technetium –	44 Ru ruthenium 101	45 Rh rhodium 103	46 Pd palladium 106	47 Ag silver 108	48 Cd cadmium 112	49 In indium 115	50 Sn tin 119	51 Sb antimony 122	52 Te tellurium 128	53 I iodine 127	54 Xe xenon 131
55 Cs caesium 133	56 Ba barium 137	57–71 lanthanoids	72 Hf hafnium 178	73 Ta tantalum 181	74 W tungsten 184	75 Re rhenium 186	76 Os osmium 190	77 Ir iridium 192	78 Pt platinum 195	79 Au gold 197	80 Hg mercury 201	81 Tl thallium 204	82 Pb lead 207	83 Bi bismuth 209	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 Fl flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 139	58 Ce cerium 140	59 Pr praseodymium 141	60 Nd neodymium 144	61 Pm promethium –	62 Sm samarium 150	63 Eu europium 152	64 Gd gadolinium 157	65 Tb terbium 159	66 Dy dysprosium 163	67 Ho holmium 165	68 Er erbium 167	69 Tm thulium 169	70 Yb ytterbium 173	71 Lu lutetium 175
actinoids	89 Ac actinium –	90 Th thorium 232	91 Pa protactinium 231	92 U uranium 238	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –