

Introduction

Inorganic chemistry is the study of substances other than carbon compounds through a few of the latter are, conventionally included in inorganic chemistry

Early studies in inorganic chemistry were directed towards solving analytical and mineralogical problems. There is, too, a mass of relatively factual information concerning the preparation, manufacture, properties factual and uses of inorganic chemicals

Periodic Table

The original form of the periodic table was first put forward by Mendeleef in 1869 when he arranged the known elements in the order of their relative atomic masses.

The elements fall into 8 vertical groups numbered from I-VIII and horizontal rows of elements are known as periods which are 7 numbered 1-7.

Those periods containing 8 elements are known as short periods and the others as long periods

The elements in any one vertical group have similar chemical and physical properties

Therefore the properties of elements are periodic function of their atomic number *which is periodic table*

Electronic configuration

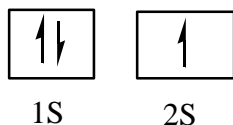
Describes how the electrons of an atom are arranged in the energy levels, subshells and orbitals. The term normally applies to an atom in their ground states

Rules for filling electrons

Rule 1: Aufbau Principle

The electrons in the ground state occupy orbital's in order of the orbital energy levels. The lowest energy orbital's are always filled first

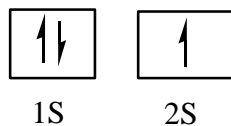
e.g. for ${}_3\text{Li}$



Rule 2: Pauli Exclusion Principle

This states that an orbital can not contain more than two electrons and then only if they have opposite spins

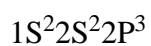
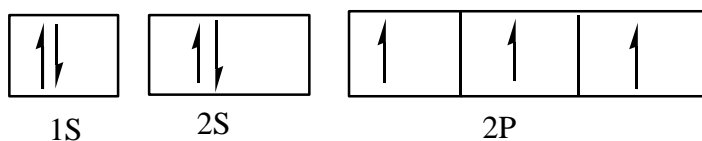
e.g. ${}_3\text{Li}$



Rule 3: Hund's Rule

This states that the orbital's of a subshell must be occupied singly first and with parallel spins before they can be occupied in pairs

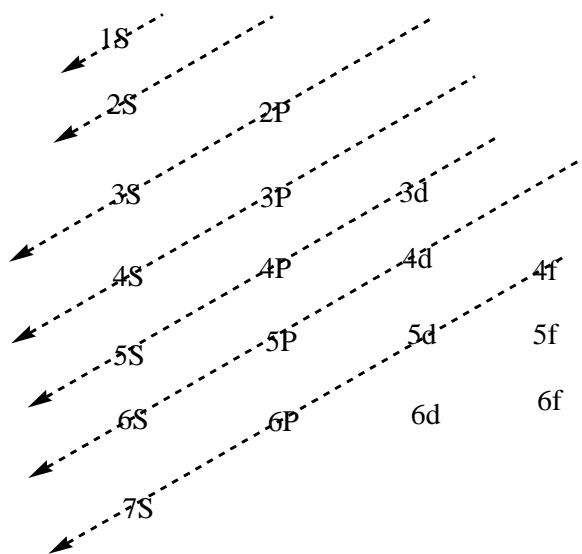
e.g. ${}_7\text{N}$



Rule 4:

Electrons in degenerate orbital's which are singly occupied have parallel spins

The order of filling in the electrons in atoms is



Principal quantum number , n where n= 1,2,3,4 etc

This denotes the principal quantum energy shell in which the electron in an atom is found. Within the principal quantum energy shell there are shells but the total number of electrons that can occupy any principal quantum shell is given by $2n^2$

The inner most orbital i.e. the one nearest to the nucleus has principal quantum number of 1 and the number of electrons in each energy level is shown as

n	1	2	3	4	5
Max. no. of electrons	2	8	18	32	50

Subsidiary quantum number

Within the principal quantum energy shell there are subshells which are denoted as **s, p, d and f** and the number of electron that an orbital can accommodate is shown as

orbital	S	P	d	f
No. of electron	2	6	10	14

Question

Write the electronic configuration of the following elements with their respective atomic number

- (i) Aluminium (Z=13) (ii) Phosphorous (Z=15) (iii) Calcium (Z=20) (iv) Chlorine (Z=17)
(v) Vanadium (Z=23) (vi) Selenium (Z=34) (vii) Nickel (Z=28) (viii) Copper (Z=29)

N.B. Fully filled and half filled orbital's are regarded as thermodynamically more stable therefore the electronic configuration of Chromium (Z=24) and Copper (Z=29) follow this.

Determination of Block of an element

The block to which an element belongs is determined by the orbital's which are in the process of filling up. E.g.

${}_{11}\text{Na} - 1s^2 2s^2 2p^6 3s^1$ Belongs to the S- block

N.B. Electronic configuration can be used to determine the period and group of the element.

PERIODIC PROPERTIES

1. Atomic radius/ covalent radius

Atomic radius is half the internuclear distance between two atoms of the same element joined by the singly covalent bond.

The covalent radius depends on:

- ❖ **Nuclear charge.** This is the attraction of the positively charged nucleus for the outermost electron. Increase in nuclear charge, decrease in atomic radius
- ❖ **Screening effect/ shielding effect.** This is tendency of inner electrons to shield outer electrons from nuclear attraction. Increase in screening effect results into increase in atomic radius.

Variation across the period

Atomic radius decreases across the period. This is because the nuclear charge increases due to the addition of protons to the nucleus. For every proton added, an electron is added to the same energy level and almost screening effect almost remains constant. The effective nuclear charge increases thus the electrons become more strongly attracted and closer to the nucleus

Example of the period variation is that of period 3

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic radius(nm)	0.156	0.136	0.125	0.117	0.110	0.104	0.09	0.094

N.B. In the transition metal series the decrease is gradual

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
At. Radius (°A)	1.44	1.32	1.22	1.17	1.17	1.16	1.16	1.15	1.17	1.25

The metallic radius decreases from scandium to nickel and it slightly increases from nickel to Zinc.

As atomic number increases, the nuclear charge increases. However, the electrons are being added to inner 3d-subshell therefore these electrons are poorly shielded from the nuclear charge hence the nuclear attraction for the outer for the most electron increases resulting into increase in atomic radius/ metallic radius.

The slightly increase from nickel to Copper is because the 3d-subenergy level in copper is fully filled with electrons and this increases the shielding of the outer electrons from the nuclear charge hence atomic radius increases.

The decrease in radius coupled with increasing atomic mass causes an increase in the density and decrease in atomic volume in passing from Scandium to Nickel.

Variation down the group

Atomic radius increases down the group. Both nuclear charge and screening effect increases. However the increase in screening effect outweighs the increase in nuclear charge due to addition of extra energy level of electrons thus the effective nuclear charge decreases such that the outermost electrons are less strongly attracted towards the

Example of such variation is in group 1:

Element	Li	Na	K	Rb	Cs
At. Radius (nm)	0.123	0.157	0.203	0.216	0.235

Ionic radius

(a) Positive ions

These are formed by removing one or two electrons from the outer most energy level. The nuclear attraction for the remaining electrons increases thus the radius of the cation is smaller than that of the atom from which it is formed.

Examples include

species	Mg	Mg ²⁺	Fe	Fe ²⁺
radius	0.136	0.065	0.116	0.076

(b) Negative ions / Anion

Formed by addition of one or more electrons to a neutral gaseous atom . The effective nuclear charge is reduced and hence the electron cloud expands. Therefore the anions are larger than corresponding atoms .e.g.

Species	Cl	Cl ⁻	O	O ²⁻
Radius (nm)	0.09	0.18	0.066	0.140

2. Ionisation energy/ Potential

The first ionization energy is minimum amount of energy required to remove one mole of electrons from one mole of free gaseous atoms to form one mole of unipositively charged gaseous cations.

Successive ionization energies refer to loss of a second, third, , nth electron. Thus the second ionization energy of X is the first ionization energy of X^+ and sum of the first n ionization energies gives the energy change for the formation of the X^{n+} ion

The magnitude of ionization energy depends:

- ❖ **Nuclear Charge**; ionization energy increases with increasing nuclear charge.
- ❖ **Screening effect**: increase in screening effect decreases the magnitude of ionization energy
- ❖ **Nature of orbital**: Electrons being removed from fully filled and half filled energy levels require more energy because such electronic structure are stable.
- ❖ **Type of orbital**: S, P, d and f orbital have different shapes. In energy level the S- orbital penetrate closer to the nucleus therefore the penetrating trend is $S > P > d > f$ hence an orbital of higher penetrating power requires more energy
- ❖ **Atomic radius**: Atoms with small radius the electrons are strongly bound by the nuclear attraction and thus require more energy to be removed.

Variation across the period

Element	Li	Be	B	C	N	O	F	Ne
I.E (KJmol ⁻¹)	520	899	801	1086	1403	1310	1681	2080

Across a period, ionization energy increases with increase in atomic number. Electrons are added to the same main energy level as nuclear charge increases. These electrons shield each other poorly from the increasing nuclear charge therefore atomic radius decreases resulting into increase in ionization energy along the period

However, beryllium, neon and nitrogen have abnormally high ionization energy because the electrons are removed from $2S^2, 2P^6$ and $2P^3$ which are fully filled and half filled respectively and are regarded as thermodynamically stable

Qn: The table below shows the elements in period 3 of the periodic table

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Z	11	12	13	14	15	16	17	18
1 st I.E	502	745	587	791	1020	1000	1260	1530

(a) Plot a graph of first ionization energy against atomic number

(b) Explain the shape of your graph in (a)

Variation down the group

Ionisation energy decreases down the group. Both nuclear charge and screening effect increase down the group. Due to extra energy level of electrons being added, the increase in screening effect exceeds the increase in nuclear charge. Effective nuclear charge decreases such that the outer most electrons become less strongly attracted hence less energy is required

The values of ionization energy can be used to deduce:

- ❖ Atomic number of an element. The number of successive ionization energy indicates the number of electrons present. *E.g. Mg has 12 successive ionization energies.*
- ❖ Arrangement of electrons and distribution of energy levels
- ❖ Metallic character. *Elements which easily lose electrons have low values of ionization energy and are electropositive. The 1st ionization energy is usually below 800KJmol⁻¹*

Qn: The data given below are for the elements A, B, C and D which belong to the same period in the periodic table

Element	A	B	C	D
1 st I.E	495	580	790	1255
Melting point of oxide	2300	1610	-20

- (a) Which ones of the elements A,B, C and D is a metal? Explain your answer
- (b) State the type of bonding and structure of the oxides of elements A and D
- (c) The 2nd, 3rd, and 4th ionization energy of element B are 1500, 7700 and 10500KJmol⁻¹ respectively. To what group in the periodic table does B belong? Give reason for your answer

ELECTRON AFFINITY (E.A.)

This is the energy released when an electron is gained by one mole of an isolated neutral gaseous atom to form a uninegative gaseous ion

Electron affinity values are negative i.e exothermic process even for highly electropositive elements. The more exothermic the E.A, the easier an atom gains electron hence the more stable the ion is.

The second E.A is accompanied by absorption of energy i.e. endothermic. This is because the incoming electron experiences greater repulsion from both outermost electron and the negative ion. In addition, the increased radius of the ion decreases the nuclear attraction for the incoming electron.

E.A. Values are not experimental and thus inaccurate. They are determined directly from Born-haber cycle

Variation across the period

Across the period, E.A increases. This is due to decrease in atomic radius and increase ineffective nuclear charge which increases the nuclear attraction for the incoming electron thus more energy is evolved.

N.B. E.A. of Beryllium and Magnesium are less exothermic because the electron is added to completely filled S-orbital which is stable

Variation down the group

Down the group, E.A decreases due to decrease in effective nuclear charge caused by addition of an extra energy level of electrons. The nuclear charge decreases and ability of the nucleus to attract electrons is reduced hence less energy is given out.

ELECTRONEGATIVITY

This is the tendency of an element to attract bonding electrons towards itself in a covalent compound.

The magnitude electronegativity depends on:

- ❖ Nuclear charge
- ❖ Atomic radius
- ❖ Screening effect

Variation across the period

Across the period, electronegativity increases because the atoms become smaller and the effective nuclear charge increases therefore the electron attractive power increases

Variation down the group

Down the group, electronegativity decreases due to increasing atomic radius and decrease in effective nuclear charge.

Example of such variation is;

Element	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

ELECTROPOSITIVITY

This is the ability to lose outermost electrons to form a positively charged ion. This is basically a property of a metallic elements because they have few electrons in the outermost energy level with low ionization energy.

Down the group, Electropositivity increases because:

- ❖ The shielding of outer most electrons from nuclear attraction increases as more completed energy levels are added.
- ❖ Atomic radius increases

The most reactive metals are therefore found at the bottom of the group e.g. Lithium in group I reacts slowly with cold water due to low Electropositivity value

CHARGE DENSITY

This is the ratio of charge of a given ion to its radius.

According to Fajan, polarization is favoured by:

- ❖ High charge. Highly charged positive ions greatly polarize anions with large negative charge
- ❖ Small radius of the Cation
- ❖ Large anions. Anions with large radius are more polarisable

Polarisation affects both the chemical and physical properties of ionic compounds

Examples include:

The melting point of chlorides of Sodium, Magnesium and Aluminium are shown below

Chloride	NaCl	MgCl ₂	AlCl ₃
Melting point	801	746	sublimes

DIAGONAL RELATIONSHIP

This is the similarity in chemical properties between elements in period two to their diagonal neighbours in period three and adjacent groups.

The pairs of elements with similarity in chemical properties include:

- Lithium and Magnesium
- Beryllium and Aluminium
- Boron and Silicon

The similarity in chemical properties is due to following reasons:

- Similar polarizing power or charge density
- Similar electronegativity
- Similar electropositivity
- Similar electrode potential

N.B. The similarity in Chemical properties between the pairs See S- block elements.

ATOMIC STRUCTURE

Evidence for Sub-atomic particles

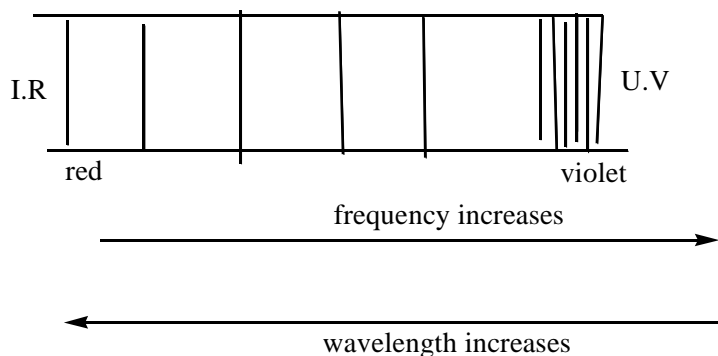
See physical chemistry notes

Hydrogen Spectrum

The hydrogen spectrum consists of a series of lines both in the visible and invisible region of the electromagnetic spectrum i.e. line spectrum.

In each series, the spacing between the adjacent lines decreases towards the continuum i.e. converge into continuous spectrum.

For the visible spectrum, each line has a different colour and represents a radiation of definite wavelength and frequency



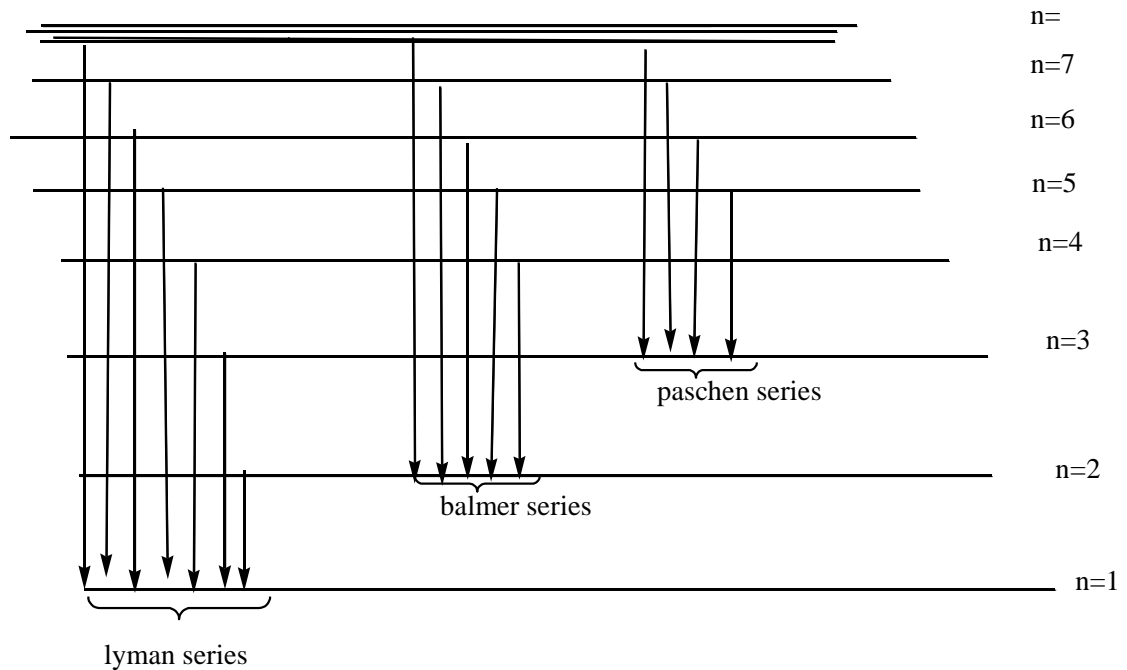
Explanation of the line Spectrum

When an electric discharge is passed through hydrogen gas at low pressure, the gas molecules break down to form gaseous atoms. The hydrogen atoms absorb energy in discrete units quanta.

The electron in each hydrogen atom becomes excited and gets promoted from levels of lowest energy (ground state) to higher energy levels far away from the nucleus.

The electron in higher permissible state is unstable and falls back towards the ground state emitting light/ radiations with definite frequencies.

When the radiations are resolved by the spectrometer, an emission spectrum develops.



Each series represent a transition from a higher energy level to a given level of lower energy.

The wavelength of each line is by;

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \text{Where } R_H \text{ is Rydberg's constant}$$

The energy given out when an electron falls back to lower energy level is given by:

$$\Delta E = hf \quad \text{Where } h \text{ -Planck's constant and } f \text{-frequency of radiation}$$

Since $f = \frac{c}{\lambda}$, the expression can be written as $\Delta E = \frac{hc}{\lambda}$ where c is speed of light

When an electron is removed from n_∞ , it is removed from the influence of the nucleus .i.e .ionisation

Qn: The diagram below shows some energy levels in the hydrogen atom



- (a) If an electron is in ground state, what is the minimum energy for ionisation
- (b) What is the significance of the shaded area?
- (c) If an electron is in energy level 4 what is the frequency of the lowest energy it can emit ($h=3.99 \times 10^{-13}$)

Evidence for existence of energy levels

- ❖ Hydrogen atoms has one electron but produces a spectrum containing a series of lines
- ❖ The lines in each series have definite frequency and wavelength.
- ❖ The spacing between the adjacent lines in each series differs and converges into a continuum.
- ❖ The number of lines in spectro-series increases with an increase in the resolving power of the spectrometer prism used. hence atom has got an infinite number of energy levels

Qn: The atomic spectrum of hydrogen can be divided into a number of series

- (a) Why does the spectrum consist of line?
- (b) Explain why each series converge
- (c) Explain how ionisation energy of an element can be calculated from spectro-measurement
- (d) Explain the term convergence limit
- (e) What is meant by the term principal quantum number?

BONDING AND STRUCTURE

BONDING

(a) Covalent bond

These are bonds formed by equal sharing of two or more electrons between two atoms in a molecule.

Each atom contributes equal numbers of electrons so that the atomic orbital overlap. The shared electrons must be unpaired with opposite spin.

Covalent bonds are usually formed between non-metal atoms due to their high electronegativity. e.g. Ammonia, Chlorine, carbon dioxide, methane etc

Polar and Non-polar covalent compounds

When a covalent bond is formed between atoms of different electronegativity, the more electronegative atom attracts bonding electrons towards itself leading to slight charge separation.

Examples include:

- ❖ Carbon dioxide and tetrachloromethane have polar bonds due to difference in electronegativity but the bond polarity cancels out because the molecule is symmetrical therefore they are called non-polar covalent compounds.
- ❖ Trichloromethane the bonds are polar but the molecule is unsymmetrical therefore it is a polar covalent compound

Properties of covalent compounds

- ❖ They contain simple discrete molecules held by weak van der Waals forces in simple molecular structure e.g. Sulphur, carbon dioxide and giant atomic structure e.g. Silicon (IV) oxide, Diamond
- ❖ They are soluble in non-polar solvents e.g. benzene
- ❖ They are non-electrolyte
- ❖ They have low melting and boiling points

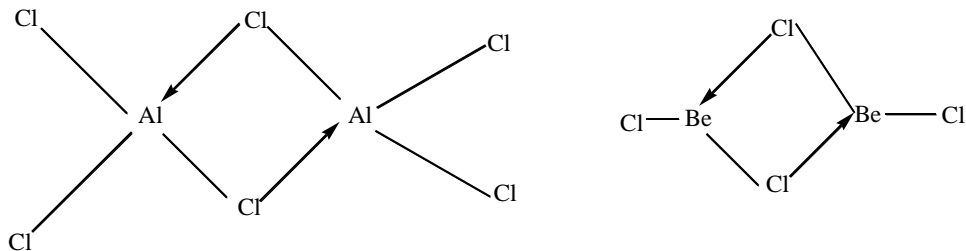
(b) Co-ordinate/ Dative bond

This is a weak covalent bond formed between an electron rich atom and an electron deficient atom/ion.

The atom with lone pairs of electrons donates an electron pair therefore it is called donor atom and the atom receiving the electrons is acceptor.

Examples include:

Hydroxonium, ammonium and dimerised AlCl_3 and BeCl_2 i.e. in the vapour phase Aluminium Chloride and Beryllium chloride exist as



Qn: A compound contains 79.78% chlorine and rest Aluminium. The vapour of this compound has a density of $2.28 \times 10^3 \text{ gm}^{-3}$ at 1427K and $1.013 \times 10^5 \text{ Pa}$

- Calculate the molecular formula Q and draw its structure.
- State the conditions under which the above structure exists

(c) Ionic bond

Ionic bond is bond formed by electron transfer from electropositive element to another electronegative atom.

The electropositive _{atom} loses electrons to become positively charged while the electronegative atom gains the electrons to become negatively charged.

There is a total separation of charges held by strong electrostatic forces of attraction which constitute a large continuous arrangement of oppositely charged ions resulting into a giant ionic lattice.

The strength of the ionic bond depends on the magnitude of the forces which depends on:

- ❖ Charge of the ion. Electrostatic forces of attraction increases with increase in the magnitude of the charge on the ions.
- ❖ Ionic radius. Electrostatic attraction decreases with increase in ionic radius.

(c) Metallic bond

This is an electrostatic attraction between the delocalized electrons of the metal atoms and positive nucleus.

The strength of the metallic bond increases with increase in the number of delocalized electrons

Qn: The melting points of group I metals decreases down the group

Soln: The metallic radius increases therefore the delocalized electrons are held by weak forces hence decrease in melting point.

Qn: The table below shows the melting points of elements in period 3

Element	Na	Mg	Al	Si	P	S	Cl
At.No.	11	12	13	14	15	16	17
Melting point($^{\circ}$ C)	98	650	660	1410	44	119	-101

(a) Plot a graph of melting point against atomic number

(b) Explain the shape of graph

(d) Hydrogen bonding

It is a permanent bond formed by dipole-dipole attraction between the hydrogen atom and a highly electronegative atom in a molecule with at least a lone pair of electron

Compounds of Nitrogen, Oxygen and Fluorine form hydrogen bonds

Effects of hydrogen bonding on the physical properties

1. Solubility in water

Organic compounds with polar functional groups such as Alcohols, Amines and Carboxylic acids are soluble due to association of the molecule with water through hydrogen bond

2. Boiling and Melting points

Hydrogen bonds in molecule elevate the boiling points due to extra energy required to overcome the bonds before molecule vapourise

The effects of hydrogen bonding on boiling point depend on:

- ❖ Number of hydrogen bond formed
- ❖ Electronegativity of the atom

Examples include:

$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2NH_2$	H_2O	HF	NH_3
98	49	100	24	-33

Since oxygen is more electronegative than nitrogen, the b.p. of $CH_3CH_2CH_2OH$ is greater than $CH_3CH_2CH_2NH_2$.

Water molecule forms more hydrogen bond although the electronegativity of Fluorine is higher hence a higher b.p.

3. Density and Volume

Hydrogen bonds increases the volume and lowers the density e.g. Ice floats on water

Each oxygen atom is tetrahedrally attached to four hydrogen atoms i.e two are normal covalent bonds and the other are longer hydrogen bond. This arrangement gives ice a more open structure hence an increased volume therefore a fixed mass for water, the density decreases and it freezes.

Qn:

- (a) Explain what is meant by the term Melting point
- (b) State the factors that affect the melting point of:
 - (i) Metal
 - (ii) Molecular substances
- (c) Explain the trend in the melting points of the elements in group II and group IV of the periodic Table
- (d) Why are transition metals of period 4 having higher melting point than non-transition metals of the same period.
- (e) Explain why
 - (i) The melting point of Aluminium chloride is abnormally low compared to that Aluminium Oxide
 - (ii) The melting point of Calcium oxide is higher than of Calcium chloride

S-BLOCK ELEMENTS (Group I and II)

The elements in this block have their valence placed in the S-orbital. The outer most configurations are:

Group I (Alkali metals) - nS^1

Group II (Alkaline earth metals)- nS^2 where n is principal quantum number .

The physical properties include:

Group I (Table 1)

Element	Li	Na	K	Rb	Cs
1 st I.E (KJmol ⁻¹)	520	500	420	400	380
2 nd I.E(KJmol ⁻¹)	7300	4600	3100	2700	2400
Atomic radius(nm)	0.15	0.19	0.23	0.25	0.26
Melting point (°C)	180	98	63	39	29
Density(gm ⁻³)	0.53	0.97	0.86	1.53	1.87
Hydration energy(KJmol ⁻¹)	-499	-390	-305	-281	-248
Electrode potential(V)	-3.05	-2.71	-2.92	-2.93	-3.02

Group II (Table 2)

Element	Be	Mg	Ca	Sr	Ba
1 st I.E (KJmol ⁻¹)	900	740	590	550	500
2 nd I.E(KJmol ⁻¹)	1800	1460	1150	1060	970
Atomic radius(nm)	0.11	0.16	0.20	0.21	0.22
Melting point (°C)	1280	650	838	768	714
Density(gm ⁻³)	1.86	1.74	1.55	2.60	3.50
Hydration energy(KJmol ⁻¹)	-2385	-1897	-1561	-1414	-1274
Electrode potential(V)	-1.85	-2.37	-2.87	-2.89	-2.91

Melting point

Group II elements have higher melting point than group I because they contribute two electrons for delocalization unlike group I which contributes only one electron. Therefore the metallic radius of group II elements is smaller than those for group making the metallic bond to be stronger.

Density

The alkali metals are less dense due to larger atomic radius and weaker metallic lattice

Oxidation state

This is the net charge that can be created on an atom when all other atoms bonded to it have been removed as ions with a noble gas configuration.

The elements easily lose their valence electron to form positively charged ions therefore the oxidation state of group I and II is +1 and +2 respectively.

Qn: Explain why group II elements are divalent

Hydration energy

This is the evolved when one mole of a gaseous ion is completely surrounded by water molecules to form an infinitely dilute solution.

The magnitude of hydration energy depends on:

- Ionic charge
- Ionic radius

The lower the charge density, the weaker the attraction for the water molecules hence the lower the hydration energy

Down the group hydration energy decreases due to an increase in ionic radius

The hydration energy of group II elements is more negative than those of group I because of higher charge and smaller ionic radius.

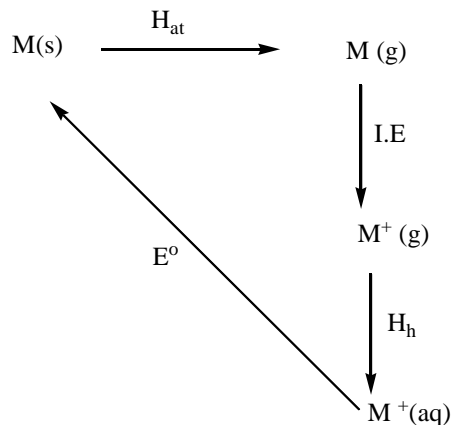
Electrode potential (E^θ)

The standard electrode potentials values increase down the group. This is due to decrease ionization energy and atomization energy (endothermic processes) which is exceeded by hydration energy (exothermic process) i.e. becomes more negative.

However, the standard electrode potential of lithium is higher than expected due to high hydration energy caused by high charge density of lithium ions.

The electrode potential of group II elements are more negative despite hydration energy because endothermic processes (atomization and ionization energy) have low value which is exceeded by exothermic process (hydration energy).

Born- harber cycle relating the energy changes is:



Qn: Draw the born- harber cycle for relating standard electrode, E^{θ} , atomization energy, ΔH_{at} , ionization energy, $I.E$ and Hydration energy, ΔH_{h}

The standard electrode potential for conversion of each metal to its ion is positive (endothermic) thus S- block elements are reducing agents.

Group I elements are stronger reducing elements than Group II and the tendency increases as you move down the group.

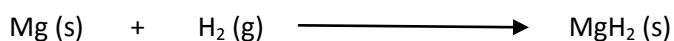
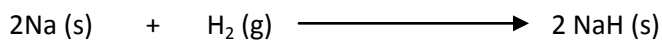
Qns: (a) State three energy factors which make group I elements stronger reducing agent than Group II elements.

(b) Explain briefly why Potassium is a stronger reducing agent than Sodium.

CHEMICAL PROPERTIES OF S-BLOCK ELEMENTS

1. HYDROGEN

The hot metals react with dry hydrogen gas to form ionic hydrides i.e.

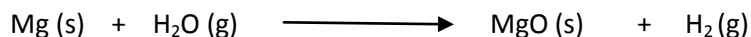


Since the metals are electropositive, the oxidation state of hydrogen in the hydrides is **-1**.

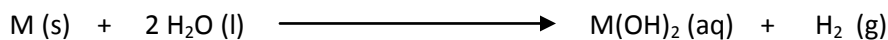
2. WATER

All the elements except Beryllium react with water with increasing vigour down the group to liberate hydrogen gas.

Magnesium reacts slowly with cold water but vigorously with steam

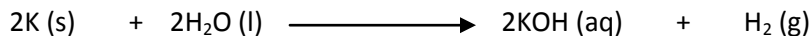


Calcium, Barium Strontium react readily with water to form the hydroxide and hydrogen gas.



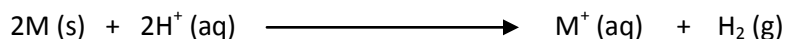
Where M= Ca, Ba and Sr.

All group I elements readily react with cold water to form strong alkaline solution e.g.

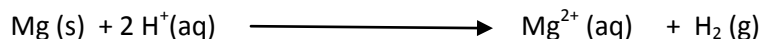


3. ACIDS

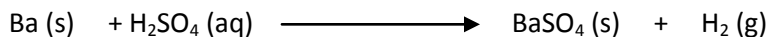
Group I elements react violently with dilute mineral acids to form salt and hydrogen gas.



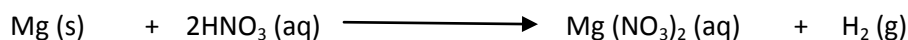
Group II elements react but the reaction becomes more vigorous down the group except with dilute sulphuric acid. e.g.



Calcium, Strontium and Barium react slowly with dilute sulphuric acid due to formation of sparingly soluble salt which prevent further reaction e.g.



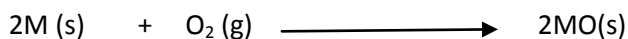
Magnesium, Calcium and Barium react with very dilute nitric acid to liberate hydrogen gas e.g.



Qn: Compare the reaction of beryllium and barium with sulphuric acid

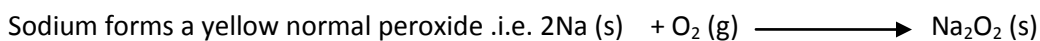
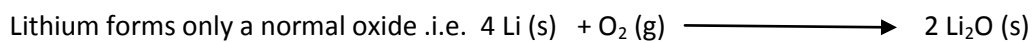
4. OXYGEN

Group II elements form normal oxides .i.e.

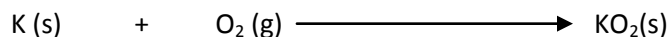


However barium and Strontium can form peroxides when the normal oxide is heated in more oxygen .e.g. $2\text{BaO (s)} + \text{O}_2\text{(g)} \longrightarrow 2\text{BaO}_2\text{(s)}$

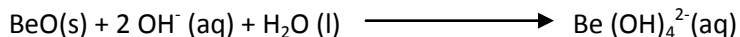
Group I elements burn in excess oxygen to form variable oxides .i.e.



Potassium, Caesium and Rubidium form super oxides when burnt in excess in oxygen e.g.



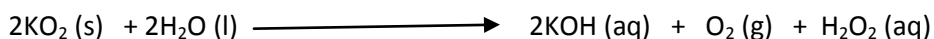
All the oxides are basic except beryllium oxide which is amphoteric .i.e.



The peroxides form hydroxides and hydrogen peroxides when dissolved in water



The super oxides liberate oxygen gas, hydrogen peroxide and the hydroxide when dissolved in water.



Qn: (a) Be, Mg, Ca and Ba belong to group II of the periodic table. Describe the reactions of the elements with;

(i) Water

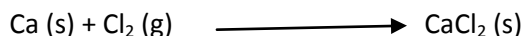
(ii) Air

(b) Explain why Lithium doesn't form peroxide or superoxide when burn in oxygen.

(c) State what is observed when potassium super oxide is dropped in water. Write the equation of reaction.

5. CHLORINE (HALOGENS)

The hot metals directly combine with chlorine to form ionic halides except beryllium i.e.



The anhydrous chlorides are ionic except beryllium chloride which is covalent

NOTE: Beryllium behaves differently from the rest of the elements due:

- Small atomic radius
- High charge density
- Low electropositivity
- High polarizing power

COMPOUNDS OF S-BLOCK ELEMENTS

Group I compounds are more ionic than the corresponding compounds of group II. This is due to high charge density.

The salts of group II elements are less soluble in water than group I. Solubility of ionic compounds in water is affected by lattice energy and hydration energy i.e.

$$\Delta H_s = \Delta H_h + U \quad \text{Where } \Delta H_s \text{ is enthalpy of solution}$$

ΔH_h is hydration energy

U is lattice energy

Soluble salts have negative enthalpy of solution. The more negative the enthalpy of solution the more soluble the salt.

Qn: Given the following thermo chemical data

Salt	Hydration energy (KJmol ⁻¹)	Lattice energy (KJmol ⁻¹)
AX	880	860
BX	790	800

State which salt is more soluble and explain your answer

1. HYDROXIDES

The hydroxides of Group I elements are all white solids and deliquescent except lithium hydroxide. They dissolve in water exothermically to form strong alkaline solution.

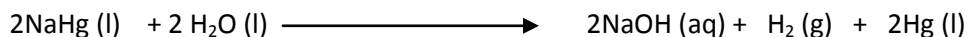
The hydroxides become more soluble down the group due to increasing ionic radius of the cation which decreases the lattice energy.

Qn: (a) Describe how sodium hydroxide is prepared on a large scale.

(b) Explain how sodium hydroxide pellets react with air.

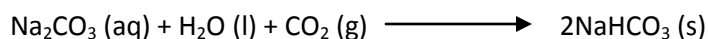
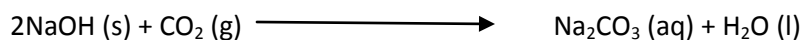
Soln: (a) It is prepared by electrolysis of brine using Mercury cathode.

At the cathode, Na⁺ ions are discharged instead of H⁺ ions because of the high concentration of the Brine. The sodium thus formed dissolves in the mercury surface to form Sodium amalgam. The sodium amalgam then flows out and mixes with water to form a mixture of hydrogen gas, sodium hydroxide and mercury.

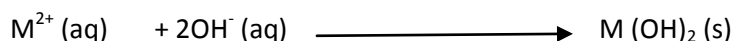


The mixture is then heated and sodium hydroxide is then stable at high temperatures hence it is formed.

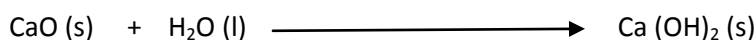
- (b) It is deliquescent hence absorbs water to form sodium hydroxide solution which reacts with carbon dioxide to form sodium carbonate and in excess a white crystal of sodium hydrogen carbonate is formed . I.e.



Group II hydroxides are sparingly soluble and are prepared by precipitation method. i.e.



They can also be prepared by dissolving a normal oxide of the metal in water. e.g.



Qn: Explain why beryllium hydroxide cannot be prepared by precipitation method.

Soln : Because Beryllium hydroxide is amphoteric and therefore it forms complex .



The table below shows the solubility of the hydroxides of group II elements

Hydroxide	Solubility at 25°C
Be(OH) ₂	0.00
Mg(OH) ₂	0.01
Ca(OH) ₂	0.015
Sr(OH) ₂	0.89
Ba(OH) ₂	3.32

The solubility generally increases down the group. This is because the radius of the cations increases while charge remains constant therefore both hydration and lattice energy decrease. However due to small size of the hydroxide ion, the lattice energy decreases more rapidly than the hydration energy therefore the enthalpy of solution becomes more negative.

N.B. The trend is similar for fluoride ions (**F**)

The table below shows the solubility of sulphates of group II elements

Sulphates	Solubility
BeSO ₄	4095.24
MgSO ₄	3600
CaSO ₄	11.0
SrSO ₄	0.62
BaSO ₄	0.009

The solubility decreases. Both lattice energy and hydration energy decrease due decrease in ionic radius of the cation. Since the sulphate ion is large, the hydration energy decreases more rapidly than the lattice energy therefore the enthalpy of solution become less exothermic.

N B. The trend is similar for CO₃²⁻, CrO₄²⁻, PO₄³⁻, and Cl⁻

2. CARBONATES AND HYDROGEN CARBONATES

Group I elements form soluble carbonates except lithium carbonate.

The carbonates are prepared by bubbling carbon dioxide through the hydroxide solution to precipitate the less soluble hydrogen carbonate which on heating decomposes to anhydrous carbonate.

Qn: Explain why Lithium carbonate is insoluble in water.

Soln: Due to high charge density of lithium ions which greatly polarize the carbonate ion thus Lithium carbonate is covalent.

Qn: Describe how sodium carbonate is prepared by solvay process on a large scale.

Soln: See *A New Certificate of Chemistry, 6th edition (1987), Holderness and Lambert, page331.*

Group II carbonates are insoluble in water and undergo thermo decomposition to form oxide and carbondioxide gas.

The carbonates are prepared by addition of sodium carbonate solution to the solution containing the metal ion i.e. precipitation e.g.



THERMOSTABILITY OF CARBONATES, NITRATES AND HYDROXIDE

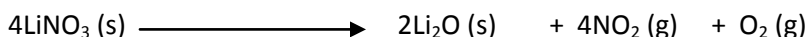
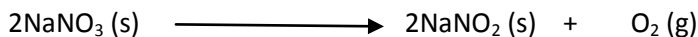
The stability of the ionic compound depends on the standard lattice energy.

Lattice energy is affected by:

- Ionic charge, the greater the charge on the ion, the greater the stronger the attraction between the ions thus lattice energy increases with ionic charge.
- Ionic radius, Smaller ions closely approach each other in the lattice thus increasing the lattice energy.

NITRATES:

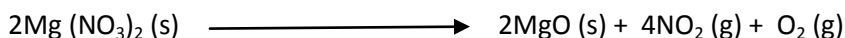
The nitrates of group II decompose to nitrites and oxygen gas except lithium nitrate i.e.



Qn : Explain why Sodium nitrite is more stable than Sodium nitrate

Soln: Because in Sodium nitrite, the nitrite ion has a smaller relative to the nitrate thus it forms a stable lattice.

However, for group II nitrates, the oxide ion is smaller and more highly charged than nitrites therefore the nitrates of group II elements decompose to metal oxide, nitrogen dioxide and oxygen gas. e.g.



CARBONATES

The carbonates of Potassium, Sodium, Rubidium and Caesium are stable and do not decompose.

Qn: Explain why Lithium carbonate decomposes while other carbonates of group I do not

Soln: It is because the Lithium ions have a high charge density hence easily polarize the carbonate ions to form a covalent compound which is held by weak vanderwaals forces which makes it easily decompose

Qn:

- Explain why Sodium carbonate is used as a base in acid-base titration
- State and Explain what is observed when sodium carbonate solution is added to aluminium chloride solution
 - Write the equation of reaction in b (i)

The table below shows the decomposition temperatures for group II carbonates

Carbonate	Temperature (°C)
BeCO ₃	100
MgCO ₃	350
CaCO ₃	900
SrCO ₃	1290
BaCO ₃	1350

The thermal stability increases due to increasing ionic character i.e. Lattice enthalpy. The larger the metal ion, the less the polarizing power thus the carbonates become ionic and the stronger the electrostatic forces of attraction.

Group I metal carbonates are more stable than group II metal carbonates. This is because M²⁺ ions have higher charge density than M⁺ ions therefore they polarize the large carbonates more than M⁺

COMPLEX FORMATION

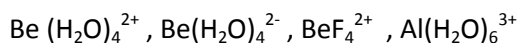
Complex formation is favoured by:

- High charge density of the cations i.e. Small and highly charged cations easily attract the lone pair of electrons in the ligand (donor atom)
- Presence of suitable vacant orbital to accommodate the lone pairs of electrons from ligand to form a dative bond

Down the group, the tendency to form complexes decreases due to decrease in charge density.

The Be²⁺ ion has the highest charge density in the group and thus forms complex ions.

Examples of complexes formed include:



HYDROLYSIS OF SALTS

Hydrolysis is the reaction of salts with water molecules which results in change P^h.

The large group I and II metals are hydrated in solution and their salts don't undergo hydrolysis.

However the carbonates and hydrogen carbonate of Sodium and potassium undergo hydrolysis to form alkaline solution.

Qn: Explain why sodium carbonate is use in acid-base titration.

Salts containing cations of high charge density undergo hydrolysis e.g. Soluble beryllium alt exist as $\text{Be}(\text{H}_2\text{O})_4^{2+}$ in aqueous solution which hydrolyses to release a proton which causes the solution to be acidic.



Qn : Explain why Magnesium chloride solution has a P^{H} less than seven.

DIAGONAL RELATIONSHIP

This is the similarity in chemical properties between elements in period two to their diagonal neighbours in period three and adjacent groups.

The pairs of elements with similarity in chemical properties include:

- Lithium and Magnesium
- Beryllium and Aluminium
- Boron and Silicon

The similarity in chemical properties is due to following reasons:

- Similar polarizing power or charge density
- Similar electronegativity
- Similar electropositivity
- Similar electrode potential

Similarities in chemical properties include:

Li and Mg	Be and Al	B and Si
Both react with nitrogen on heating to form nitrides.	Oxides and hydroxides are amphoteric. $\text{Be}(\text{OH})_2 (\text{s}) + 2\text{OH}^- (\text{aq}) \longrightarrow \text{Be}(\text{OH})_4^{2-} (\text{aq})$ $\text{Al}(\text{OH})_3 (\text{s}) + \text{OH}^- (\text{aq}) \rightarrow \text{Al}(\text{OH})_4^- (\text{aq})$	Both form acidic oxide as B_2O_3 and SiO_2
Their hydrogen carbonates exist in solution	Both react with Conc. Sodium hydroxide solution to form a complex and hydrogen gas. $\text{Be}(\text{s}) + 2\text{OH}^- (\text{aq}) + 2\text{H}_2\text{O} (\text{l}) \longrightarrow \text{Be}(\text{OH})_4^{2-} (\text{aq}) + \text{H}_2 (\text{g})$ $2\text{Al}(\text{s}) + 2\text{OH}^- (\text{aq}) + 6\text{H}_2\text{O} (\text{l}) \longrightarrow 2\text{Al}(\text{OH})_4^- (\text{aq}) + 3\text{H}_2 (\text{g})$	Both form series of covalent hydrides.
Both form normal oxides when heated in oxygen (air)	Their chlorides and bromides are covalent and dimerize in vapour phase as Be_2Cl_4 and Al_2Cl_6 . $2\text{AlCl}_3 (\text{s}) \rightleftharpoons \text{Al}_2\text{Cl}_6 (\text{g})$	Both form chlorides which hydrolyze readily.

Their hydroxides and carbonates are sparingly soluble in water	Both form ionic carbides which hydrolyze to form methane. $\text{Be}_2\text{C (s)} + 4\text{H}_2\text{O(l)} \longrightarrow \text{CH}_4\text{(g)} + 2\text{Be(OH)}_2\text{(aq)}$ $\text{Al}_4\text{C}_3\text{(s)} + 12\text{H}_2\text{O(l)} \longrightarrow 3\text{CH}_4\text{(g)} + 4\text{Al(OH)}_3\text{(aq)}$	Form covalent compounds.
Carbonates, hydroxides, peroxide decompose on heating to give an oxide.	Both are rendered passive concentrated nitric acid.	Form borides and silicides with metals.
Nitrates decompose on heating to give an oxide, nitrendioxide and oxygen.	Both form fluoro complexes.e.g. BeF_4^{2-}	
Halides (except fluorides) and chlorates (VII) are soluble in organic solvent.		

Qn . State three properties in which:

- (a) Lithium differs from the rest of group I elements.
- (b) Beryllium differs from the rest of group II elements.
- (c) Boron differs from the rest of group III elements.

QUALITATIVE ANALYSIS OF Ca^{2+} , Mg^{2+} and Ba^{2+}

Dilute Sodium hydroxide Solution until in excess:

A white precipitate insoluble in excess is observed by Ca^{2+} , Mg^{2+} and Ba^{2+}

Dilute Ammonia solution until in excess

Mg^{2+} - White precipitate insoluble in excess.

Ca^{2+} and Ba^{2+} - No observable change

Dilute Sulphuric acid / Sodium Sulphate solution

Mg^{2+} - No observable change

Ca^{2+} and Ba^{2+} - White precipitate

Potassium Chromate solution

Ba^{2+} - Yellow precipitate insoluble in Ethanoic acid

Ca^{2+} - Yellow precipitate soluble in Ethanoic acid

Ammonium Oxalate followed by Ammonia Solution

Ca^{2+} - white precipitate

Mg^{2+} and Ca^{2+} - No observable change

Disodium Hydrogen Phosphate

Mg^{2+} - A white precipitate insoluble in excess Ammonia solution

N.B. Zn^{2+} - forms a white precipitate soluble in excess ammonia solution

GROUP VII ELEMENTS (HALOGENS)

Elements	nature	Boiling point	Bond energy	Electron Affinity	Electronegativity	Electrode potential
Fluorine	Gas (Yellow)	-188	37	-322.6	4.0	+2.87
Chlorine	Gas (Greenish-Yellow)	-34	57.2	-364	3.0	+1.39
Bromine	Liquid (Red-brown)	58	45.4	-342	2.8	+1.07
Iodine	Solid (Purple)	183	35.6	-295.4	2.5	+0.54
Astatine	RADIOACTIVE ELEMENT					

1. The diatomic molecules have simple molecular structure with molecules held by weak vanderwaals forces whose magnitude depends on molecular mass of the molecule.

2. **Boiling point / melting point.**

Boiling point increases down the group. This is because the simple molecules are held by weak vanderwaals forces whose magnitude increases with increase in magnitude molecular mass.

3. **Bond Energy**

The bond energy decreases from Chlorine down the group. This is due to increase in atomic radius which decreases the nuclear attraction for the bond pairs thus increasing the bond length.

However, the bond energy of fluorine is lower than expected due to small radius which makes the lone pairs of electrons easily approach other thus the further repulsion.

4. **Electron affinity**

Down the group, electron affinity decreases from chlorine to iodine due to the reduction in nuclear attraction for the incoming electron caused by the addition of extra energy levels of electrons therefore the incoming electron experiences greater repulsion hence less energy is evolved.

However, the electron affinity of fluorine is lower than expected due to small atomic radius which gives a higher electron density hence extra repulsion of the incoming electron.

5. **Electrode Potential**

The reduction potential becomes less positive down the group therefore fluorine is the most powerful oxidizing agent.

The most negative electrode potential represents the strongest reducing agent and the most positive electrode represents the strongest oxidizing agent.

The high oxidizing strength of fluorine is favoured by:

- Low bond dissociation energy
- High enthalpy of hydration
- Absence of enthalpy of fusion and vaporization

Fluorine behaves differently from the rest of the members due:

- High electronegativity
- Small atomic radius
- Low bond energy
- High electrode potential

Special properties of fluorine which indicate how it behaves differently:

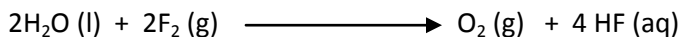
- It combines directly with carbon at room temperature to form carbon tetra fluoride.
- Hydrogen fluoride has a very high boiling point due to formation hydrogen bonding.
- Hydrofluoric acid is the weakest acid compared to other halogen acid.
- Silver fluoride is soluble in water while the chloride, bromide and iodide of silver are insoluble in water. This is because the small fluoride ions have high hydration energy which exceeds lattice energy hence the enthalpy of solution is negative.
- Fluorine has only one oxidation state.
- Fluorine does not form oxo-acids.
- Calcium fluoride is insoluble in water while the other halides are soluble in water.

Qn: Describe briefly how fluorine, Bromine and chlorine can be prepared in the laboratory.

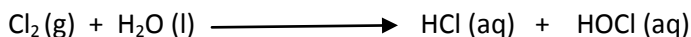
REACTIONS OF HALOGENS

(a) **Water**

Fluorine oxidizes water vigorously to oxygen. Hydrofluoric acid is also formed.



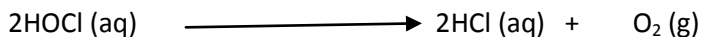
Chlorine and bromine reacts with water to form halic (I) acids



Iodine is sparingly soluble in water but highly soluble in potassium iodide solution due formation of potassium tri-iodide which is a complex salt I.e.



N.B. In the presence of Sunlight, the halic (I) acid decompose to oxygen.



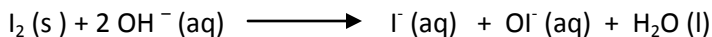
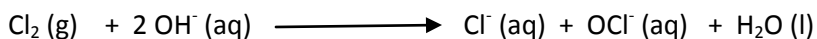
(b) **Alkalis**

(i) **Cold dilute Alkalis:**

Fluorine forms oxygen difluoride, fluoride and water

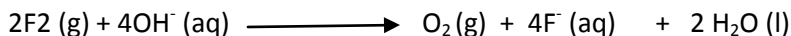


Chlorine, Bromine and Iodine form the halide, halite (I) and water.

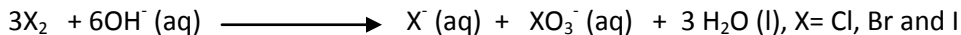


(ii) **Hot concentrated Alkali:**

Fluorine reacts to form oxygen, fluoride and water.

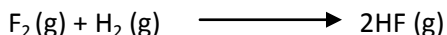


Chlorine, Bromine and Iodine forms the Halide, halate (V) and water.



(c) **Hydrogen**

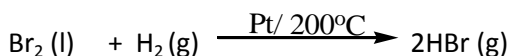
Fluorine explodes in dry hydrogen even in the dark to form hydrogen fluoride.



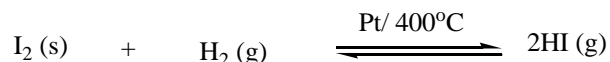
Chlorine reacts vigorously with hydrogen in presence of sunlight or ultraviolet light to form hydrogen chloride.



Bromine reacts with hydrogen gas at 200°C in presence of platinum catalyst.



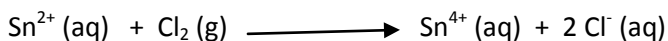
Iodine reacts with hydrogen at 400°C to hydrogen iodide and the reaction is reversible.



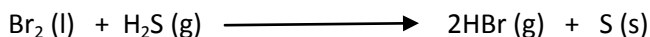
(d) **Oxidation reactions**

Chlorine, Bromine and Iodine Oxidize:

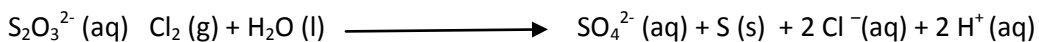
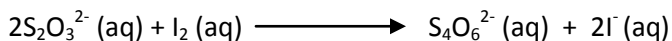
(i) Tin (II) to Tin (IV)



(ii) Hydrogen sulphide to Sulphur



(iii) Thiosulphate ions to different products:



- Qn:** (a) State what is observed when chlorine gas is bubbled through a solution of sodium thiosulphate solution. Write the equation of reaction.
- (b) State what would be observed when chlorine gas is bubbled through a solution of Iron (II) chloride solution hence write the equation of reaction.

COMPOUNDS OF HALOGENS

(a) **Hydrides/ Halogen acids**

	HF	HCl	HBr	HI
B.E (KJmol ⁻¹)	556	431	336	229
B.p.t (°C)	+19.9	-85	-66.7	-35.4
K _a	5.6×10 ⁻⁴	1.0×10 ⁷	1.0×10 ⁹	1.0×10 ¹¹

1. **Boiling point**

The boiling point increases from HCl to HI. This is because they are simple molecules held by van der -waals whose magnitude increases with molecular mass.

However, HF has extremely high boiling point because the molecules associate by hydrogen bonding due small ionic radius of the fluoride ions.

2. **Bond energy**

It decreases from HF to HI due to:

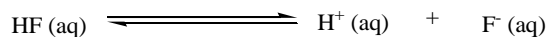
- Increased atomic radius which increases the bond length
- Decrease in electronegativity down the group thus the bonds become less polar.

3. **Acidic Strength**

The acid strength depends on the degree of dissociation of the acid thus the concentration of the hydrogen ion in aqueous solution.

Since electronegativity decreases down the group due to increase in atomic radius therefore the bond strength is in the order HF> HCl> HBr> HI thus HF is H-F bond is not easily broken hence it does not easily release a proton in aqueous solution thus it's a weakest acid. The H-I bond is the weakest bond therefore in aqueous solution it easily release a proton.

HF slightly ionizes in dilute solution as:



N.B. When concentrated, HF is a weaker acid than in dilute solution due to hydrogen bonding which reduces the concentration of hydrogen ions. I.e.



Qn: Describe how the hydrides of group (VII) elements are prepared in the Laboratory.

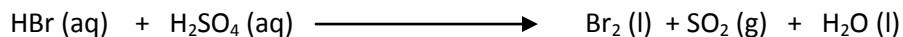
REACTIONS OF HALOGEN ACIDS

1. In aqueous solutions, they behave as strong acids except HF .e.g.

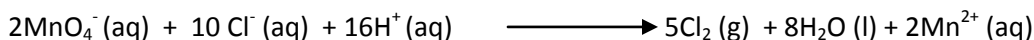
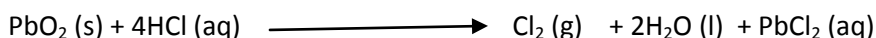


I.e. Liberates hydrogen gas when reacted with electropositive metals.

2. HF and HCl don't react with concentrated sulphuric acid. HBr and HI are strong reducing agents therefore are oxidized to bromine and iodine by conc. Sulphuric acid. I.e.

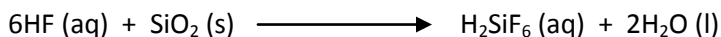


However, Conc. Hydrochloric acid can be oxidized by the stronger oxidizing agents such as MnO_2 , PbO_2 and KMnO_4



N.B. Hydroiodic acid (acidified Potassium Iodide) is the strongest reducing agent thus it is easily oxidized.

Hydrofluoric acid reacts with silicon (IV) Oxide to form Hexafluoro silicic acid



Qn: Explain the following observations:

(a) When hydroiodic acid is exposed in air, it turns brown.

(b) A colourless solution of acidified hydrogen peroxide turns brown on addition of acidified potassium iodide.

(b) **Oxo- acids / ions**

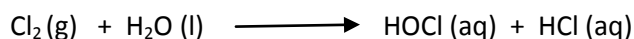
All halogens except fluorine form oxo-ions and oxo-acids e.g. HOCl, HClO₂, HClO₃ and HClO₄

Qn: Draw and name the structures of the above oxo- acids.

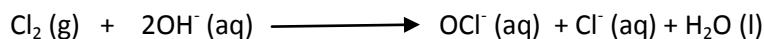
1. **Acid Strength**

The acidic strength depends on the number of oxygen atoms in the acid molecule. Since oxygen is more electronegative than chlorine, it pulls the bonding electrons towards itself and this negative inductive effect is transmitted to the O-H bond weakening it thus hydrogen ions are released in solution. The greater the number of the oxygen atom, the greater the effect and the weaker the O-H bond. Thus the strength of the acid is HClO₄ > HClO₃ > HClO₂ > HClO.

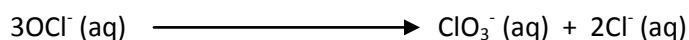
2. Chloric (I) acid is obtained by when chlorine is bubbled through water.



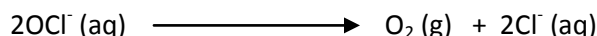
Chlorate (I) salts are obtained when chlorine gas is bubbled through dilute alkali solution.



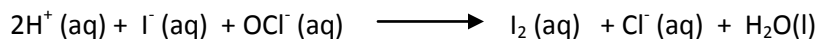
Aqueous solutions of Chlorate (I) disproportionate at about 75°C to form Chlorate (V) and Chloride



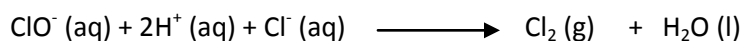
They decompose in presence of sunlight to form oxygen and a chloride



However, in presence of an acid chlorate (I) ions act as oxidizing agent e.g. it oxidizes iodide ions to iodine



With concentrated Hydrochloric acid, Chlorate (I) ions liberate chlorine gas



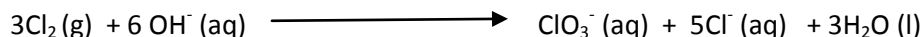
N.B. The reaction above is used to determine the percentage of chlorine in bleaching agent.

Qn: (a) 0.6cm³ of jik was dissolved in water and solution made in 250cm³ volumetric flask. 25cm³ of this solution was acidified and 10cm³ of 0.2M potassium iodide solution added. The iodine liberated required 5.0cm³ of 0.2M Sodium thiosulphate solution for complete reaction. Calculate the percentage of Chlorine in Jik

- (b) Describe an experiment to determine the concentration of Sodium Hypochlorite using Volumetric analysis.

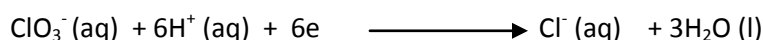
3. Chloric (V) acid

This is a powerful oxidizing agent that only occurs in aqueous solution. Its salts are more stable and can be obtained by passing chlorine gas through hot Conc. Alkali.

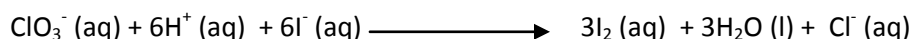
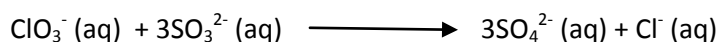


The Chlorate(V) and Chloride are separated by fractional crystallization.

In Acidic medium, Chlorate (V) ions are strong Oxidizing Agents and the reduction half cell equation



It oxidizes Iron (II) to Iron (III), Sulphite ions to Sulphate ions and Iodide ions to Iodine.



Qn : (a) A solution of halate (V) ion YO_3^- contains 2.94g/l. 25cm³ of this solution was added to an equal volume acidified potassium iodide solution. The iodine liberated required 25.2cm³ of 24.8g/l $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Calculate the relative atomic mass of Y hence identify Y.

(b) Give the I.U.P.A.C name for the following oxide and calculate the oxidation number of the halogen in :



(c) Explain the following observations:

(i) The oxidation states of halogen in Oxides are positive.

(ii) Chlorine dioxide is a mixed acid anhydride.

(c) Interhalogen compounds

These are compounds formed between halogens with the molecular formula AB , AB_3 , AB_5 and AB_7 where A- is a less electronegative atom with a vacant orbital and a higher oxidation state while B- is more electronegative.

Exams include: ICl -Iodine monochloride, ClF_3 - Chlorine trifluoride.

Qn: Explain the shapes of the following interhalogen compounds:

(i) Iodine pentafluoride.

(ii) Chlorine trifluoride.

QUALITATIVE ANALYSIS OF Cl^- , Br^- and I^-

1. Silver nitrate solution;

Cl^- White ppte

Br^- Pale yellow ppte

I^- Yellow ppte

2. Lead (II) Nitrate solution or lead Acetate.

Cl^- white ppte

Br^- pale yellow ppte

I^- yellow ppte

The pptes disappear on heating and reappear cooling.

Qn : Describe an experiment how the concentration of chloride ions can be determined by Volumetric analysis

GROUP IV ELEMENTS

The outer most electronic configuration is $n\text{S}^2 n\text{P}^2$ where n is the principal quantum numbers.

Elements	Melting point ($^{\circ}\text{C}$)	Density
Carbon	4000	2.25(graphite), 3.5(Diamond)
Silicon	1680	2.33
Germanium	1210	5.35
Tin	505	7.28(white), 5.75(grey)
Lead	600	11.3

1. Existence

Carbon exists as graphite, diamond and amorphous carbon. Silicon occurs as Silica (SiO_2). Tin exist as grey tin and white tin. Lead occurs as a ore in form of galena (PbS)

2. Melting point.

The melting points of group IV elements depend on the structure. Carbon and Silicon have giant atomic structures which require a lot of energy to break. However the melting point of silicon is lower than that of carbon since the covalent bonds in silicon atoms are longer thus weaker.

Germanium is a Metalloid with an intermediate giant atomic structure.

Tin and Lead are weak metals with a metallic structure however lead is more metallic than tin hence has a higher melting point.

3. Electropositivity

Increases down the group thus metallic character also increases.

4. Electronegativity

Decreases down the group

5. Oxidation states

The elements exhibit both +2 and +4 oxidation states. The +4 oxidation state is attained by promoting one S- electron to an empty P orbital to avail four electrons.

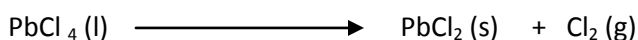
Down the group, the $n\text{S}^2$ electrons become more reluctant to participate in bonding. This is called inert pair effect. Therefore the stability of +2 oxidation state increases while that of +4 decreases.

Qn: Explain the cause of inert pair effect

Soln: AS the radius of the atoms increase down the group there is increasing tendency for the two bonding electrons in the S- Sub energy level to resist taking part in bonding.

Examples of inert pair effect include:

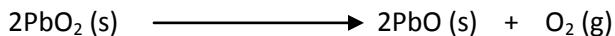
Carbon forms carbon tetrachloride while lead (IV) chloride readily decomposes to form Lead (II) chloride and Chlorine



Carbon monoxide is readily oxidized to carbondioxide by air



Lead (IV) oxide decomposes on heating to form lead (II) oxide and Oxygen



Carbon behaves differently from the rest of the group members due:

- Small Atomic radius
- High electronegativity
- Lack of vacant orbital

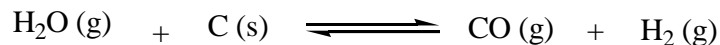
Some of the properties in which Carbon differs from the rest of the members include:

- It forms a stable multiple bonds with itself and with other non-metals.
- Carbon can form a number of hydrocarbons because it can catenate. Catenation is the ability of the element to form bonds between atoms of the same element.
- It forms gaseous oxides unlike other members
- The halides are stable to hydrolysis.

REACTIONS OF GROUP (IV) ELEMENTS

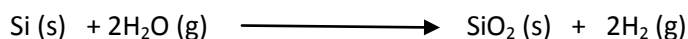
1. Water

When heated, coke reacts with steam to form water gas.

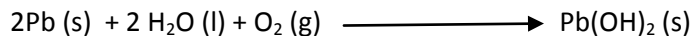


Ge and Sn do not react with water.

Hot silicon reacts with steam to form silicon dioxide and hydrogen gas i.e.

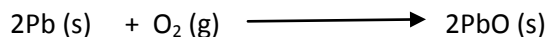


Lead reacts slowly with soft water in presence of air (oxygen) to form lead (II) hydroxide

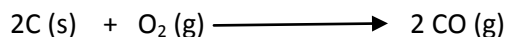


2. Air

The elements burn in air to form dioxides except lead which forms lead (II) oxide

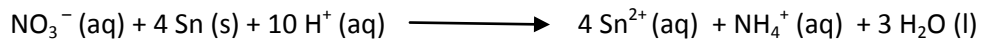


However in limited amount of air, Carbon forms carbonmonoxide



3. Acids

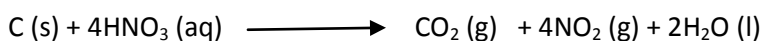
The elements do not react with dilute acids except tin which reacts with dilute nitric acid as :



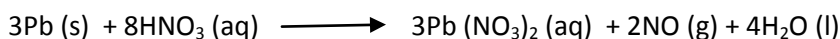
Silicon reacts with **only** with conc hydrofluoric acid to form hexafluoro silicic acid and Hydrogen gas



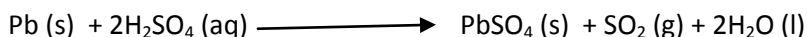
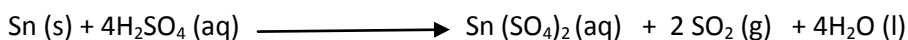
Hot conc nitric acid oxidizes tin, germanium and Carbon to dioxide and itself reduced to oxides of nitrogen



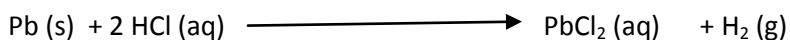
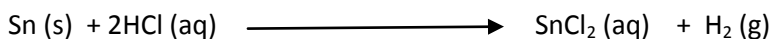
Lead forms lead (II) nitrate, nitrogen monoxide and water



Hot sulphuric acid oxidizes carbon, tin lead and germanium



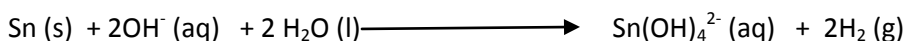
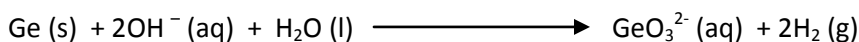
Lead and tin react with hot conc. Hydrochloric acid to form dichloride and hydrogen gas.

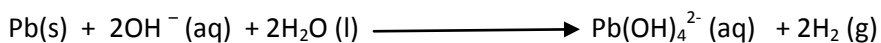


N.B. lead (II) chloride is sparingly soluble in water but highly soluble in Conc. Acid due formation of a complex. I.e. PbCl_4^{2-}

4. Alkalis

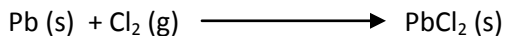
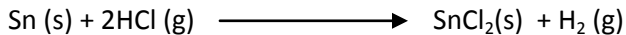
All the elements except Carbon react with Conc. Alkali to form complex salts and hydrogen gas. I.e.





5. Non- metals

When heated, the elements react with Sulphur, chlorine, fluorine and hydrogen chloride.e.g.



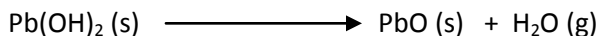
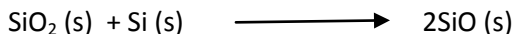
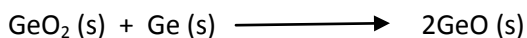
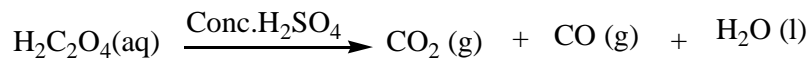
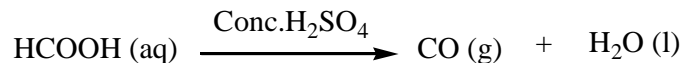
COMPOUNDS OF GROUP (IV) ELEMENTS

1. Oxides

(a) **Monoxides:** CO and SiO are covalent compounds with simple molecular structure.

GeO, SnO and PbO are amphoteric oxides with giant ionic structure

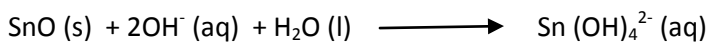
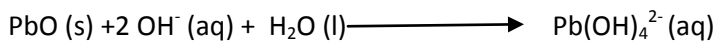
Preparation:

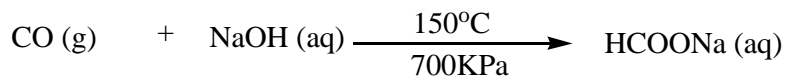


Qn : Explain why Tin (II) Oxalate is used instead of Tin (II) nitrate to prepare Tin (II) Oxide.

Some of the reactions of the monoxide according to equations include:

With alkaline solution





With Acids



Qn : (a) 1.5g of impure tin (II) Oxide was dissolved in excess dilute hydrochloric acid and the resultant solution made to 250cm³ with distilled water. 25cm³ of this solution was titrated with 0.02M potassium permanganate until the colour turned pink. The volume of Potassium permanganate solution used was 20cm³. Calculate the percentage impurity of tin (II) oxide (Sn= 119, O=16)

(b) Write an ionic equation when tin (II) ions are added to :

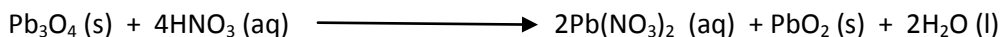
(i) Acidified potassium dichromate solution

(ii) Sodium oxalate solution

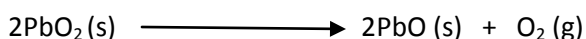
(iii) Iron (III) chloride solution

(b) **Dioxides**

Lead (IV) is prepared by reacting dilead (II) lead (IV) oxide with dilute nitric acid.



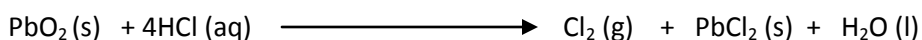
The dioxides are more stable than the monoxides except lead (IV) oxide.i.e.



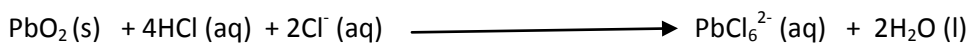
The table below shows the nature of the dioxides

Oxide	Nature	Structure
CO ₂	Acidic	Simple molecular
SiO ₂	Acidic	Giant molecular
GeO ₂	Amphoteric	Intermediate Giant ionic and giant metallic
SnO ₂	Amphoteric	
PbO ₂	Amphoteric	

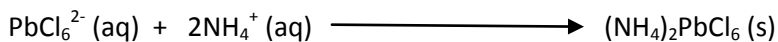
Lead (IV) oxide oxidizes strong hot concentrated hydrochloric acid to chlorine gas



When excess concentrated hydrochloric acid is reacted with lead (IV) oxide at 0°C it forms a complex ion



Addition of concentrated ammonium chloride to the complex produces a yellow precipitate. i.e.



Qn : Discuss the reactions of Lead(IV) and Pb_3O_4 with sulphuric acid.

Soln: If heated lead (IV) Oxide reacts with concentrated sulphuric acid to form lead(II)sulphate, oxygen and water.



The same reaction occurs with Pb_3O_4

Qn: (a) A compound Q contains 90.65% by mass of lead and the rest Oxygen. Deduce the molecular formula of Q if its molar mass is 685g.

(b) State what is observed when Q is reacted with the following and in each case write the equation of reaction.

(i) Dilute Nitric acid

(ii) Hot concentrated sulphuric acid.

(iii) Hot concentrated hydrochloric acid

2. Hydrides

The elements form covalent tetrahydrides whose thermo-stability decreases down the group.

Read on:

- Preparation.
- Hydrolysis of the hydrides
- Reactions of the hydrides with Alkalis

Qn : (a) Gaseous hydride of silicon diffuses through a narrow hole for 27.8s. The same volume of carbon dioxide under the same temperature and pressure through the same in 32.6s

Determine the molecular formula of the hydride.

(b) Write the equation of reaction between the hydride of silicon and sodium hydroxide solution

3. Chlorides

(a) Tetrachlorides

These are covalent liquids with simple molecular structure and become less stable down the group due to an increase in M-Cl bond length

Read on: Preparation of the tetrachlorides of group (IV) elements.

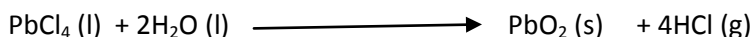
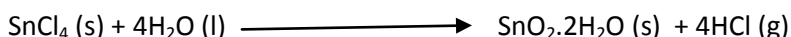
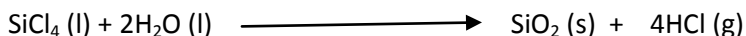
N.B. Lead (IV) chloride readily decomposes to form chlorine and lead (II) chloride

Qn: Explain why Lead (IV) iodide does not exist.

Reactions of tetrachlorides with water

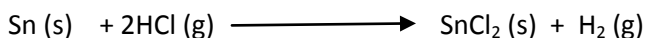
Carbon tetrachloride does not react with water because of lack of vacant d-orbital.

Other chlorides react with water rapidly to liberate hydrogen chloride. For silicon tetrachloride, the second product depends on the degree of hydration.

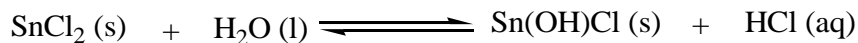


(b) Dichlorides

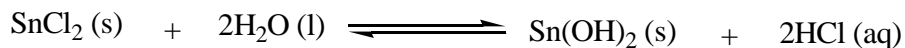
The stable chlorides in the +2 oxidation state are only formed by tin and lead



Tin (II) chloride reacts with water to form a basic chloride and hydrochloric acid. i.e. it undergoes hydrolysis



However, in excess hot water tin (II) hydroxide is formed.



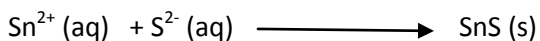
Lead (II) Chloride is sparingly soluble in water and does not undergo hydrolysis. However it dissolves on heating since solubility increases with temperature.



N.B. Lead (II) chloride is more soluble in concentrated hydrochloric acid than in water due to formation of a soluble complex of tetrachloro plumbate (II)



N.B. A solution containing tin (II) ions and lead (II) ions react with hydrogen sulphide gas to precipitate the metal sulphide (black)



Qn : When a yellow solid **A** is heated with air at 450°C, a red solid **B** is formed. **B** reacts with hot dilute nitric acid to form a dark brown solid **C** on precipitation and after filtration and crystallization of the filtrate; a white solid **D** is obtained. When **C** is heated with concentrated hydrochloric acid, a pale green gas was evolved and when hydrochloric acid is added to aqueous solution of **D** at room temperature, a white precipitate **E** was formed.

- Identify the substances **A-E** inclusive
- Account for your answers in (a) above with aid of equations of reactions.

Qn : The standard enthalpy of formation of tin tetrachloride is -508KJmol^{-1} . The standard enthalpy of atomization of tin and chlorine are $+301$ and $+121\text{KJmol}^{-1}$ respectively. The average bond energy of Si-Cl bond is $+383\text{KJmol}^{-1}$

- Determine the average bond energy of Sn-Cl bond
- Comment on the difference between the average bond energies.

(c) State a reagent that can be used to differentiate between the following ions and in each case state what would be observed when each is treated with the reagent.

(i) Pb^{2+} and Sn^{2+}

(ii) Pb^{2+} and Al^{3+}

(iii) Sn^{2+} and Zn^{2+}

PERIOD 3 ELEMENTS

The period runs from sodium to Argon. The table below shows some physical parameters of the elements involved.

Elements	Na	Mg	Al	Si	P	S	Cl	Ar
Melting point	98	651	660	1410	44	114	-101	-189
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0	
Ionization energy	502	745	587	792	1020	1000	1260	1530
Atomic radius	1.57	1.36	1.28	1.17	1.10	1.04	0.99	
Electron Affinity	2.0	-6.7	3.0	13.5	6.0	20.0	36.4	
Oxidation states	+1	+2	+3	+4	+3, +5	-2, +4, +6,	+1, +3, -1, +5, +7	
Structure	Close packed	Close packed	Close packed	Giant molecular	← Discrete molecular structure →			

1. Melting point

This is a constant temperature at which an element in its solid state changes to liquid state under constant pressure.

The abrupt change in melting point is explained as:

- From sodium- aluminium, the strong metallic bonds have to be broken down. The strength of the metallic bond increases due to increase in the number of electrons used per atom and also due to decrease to metallic radius.
- From Aluminium- Silicon, the increase is due to the strong covalent bonds that have to be broken for a giant atomic structure of Silicon where each silicon atom contributes four electrons towards covalent bonding.
- From Silicon-phosphorous, the decrease is due to change from giant atomic structure to molecular discrete structure where the molecules are held by weak vanderwaals forces of attraction
- From phosphorous-Sulphur, these are discrete molecules which are as P_4 and S_8 held by weak Vander waals force whose magnitude increases with increase in molecular mass. Since the molar mass of S_8 is greater than that of P_4 therefore an increase in melting point.
- From Sulphur-chlorine, the diatomic molecule has a lower molar mass than sulphur there fore the magnitude of the vanderwaals forces are weaker hence low melting point.

Qn: Explain the trend of the following parameters across period 3 of the periodic table

(a) Ionization energy

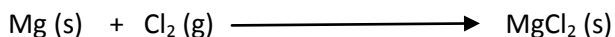
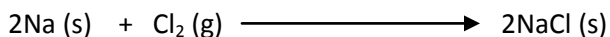
(b) Electron affinity

(c) Electronegativity

REACTIONS OF PERIOD 3 ELEMENTS

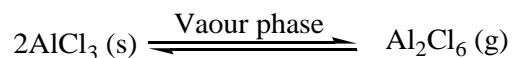
1. Chlorine

Sodium and Magnesium when heated react with chlorine to form ionic chlorides



Aluminium forms a covalent chloride which dimerises in the vapour phase

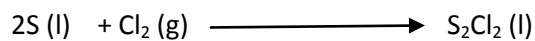
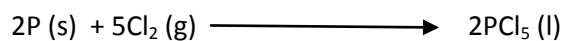
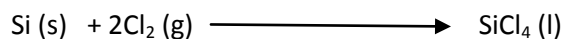




Qn: Explain why aluminium chloride is covalent.

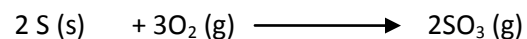
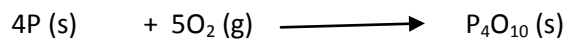
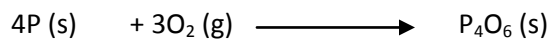
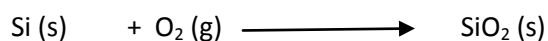
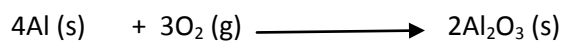
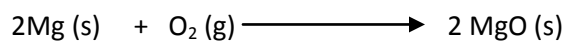
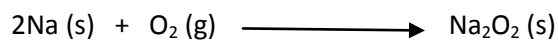
Soln: This is because the aluminium ions have a high charge density which greatly polarizes the chloride ions to form a covalent compound hence reducing the charge separation.

Silicon, phosphorous and Sulphur also react with chlorine to form covalent chlorides with simple molecular structure.



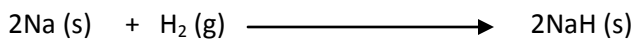
2. Oxygen

All the elements except chlorine react with oxygen to form oxides.



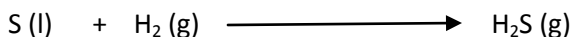
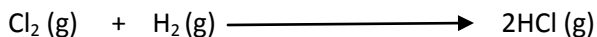
3. Hydrogen

Sodium and Magnesium react vigorously with hydrogen gas to form ionic hydrides.



Aluminium, Silicon and Phosphorous do not react with hydrogen gas.

Chlorine and Sulphur form the corresponding covalent hydrides. Chlorine reacts in presence of Sunlight or ultraviolet light.

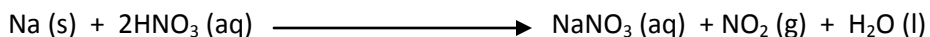


4. Acids

Sodium, Magnesium and Aluminium react with dilute acids to form salts and hydrogen gas i.e. hydrochloric acid and sulphuric acid.

Other elements do not react with dilute mineral acids.

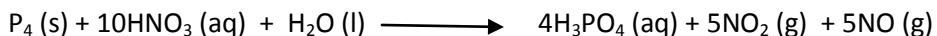
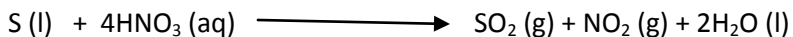
Concentrated Nitric acid reacts violently with sodium and magnesium to form the nitrate, water and nitrogen dioxide



Aluminium forms a layer of the oxide that prevents further reaction

Silicon and Chlorine do not react with concentrated nitric acid

Phosphorous and Sulphur are oxidized to their respective oxides and itself reduced to nitrogen dioxide.



COMPOUNDS OF PERIOD 3 ELEMENTS

1. Chlorides

Chlorides	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃ , PCl ₅	S ₂ Cl ₂ , SCl ₂	Cl ₂
b.p.t	1465	1418	423	57	74, 164	138	-35
Bond	ionic	ionic	←———— Covalent —————→				
structure	Giant ionic	Giant ionic	←———— Simple molecular structure —————→				

Reaction of the chlorides with water

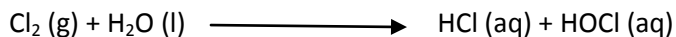
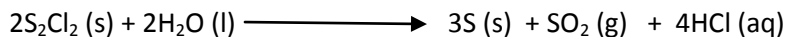
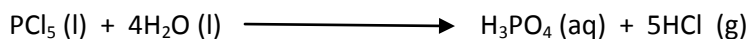
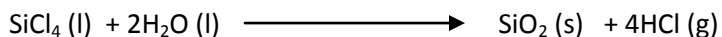
Sodium chloride and Magnesium chloride dissociate to form neutral aqueous solution

Aluminium chloride undergoes hydrolysis due to high charge density and aluminium ions become heavily hydrated in solution as Al (H₂O)₆³⁺

The hydrated ions undergo hydrolysis to release a proton in solution which causes the solution to be acidic



The other chlorides react with water to form hydrogen chloride

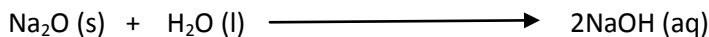


2. Oxides

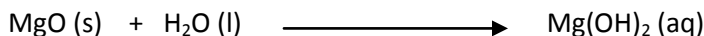
Oxides	Na ₂ O Na ₂ O ₂	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₂ , SO ₃	Cl ₂ O ₇
Bond	← Ionic →			← Covalent →			
Nature	← Basic →		Amphoteric	← Acidic →			
Structure	← Giant ionic →			Giant molecular	← Simple molecular →		

Reaction with water

Sodium oxide is highly soluble in water

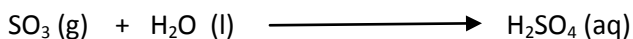
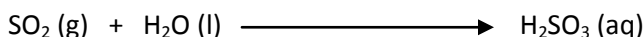


Magnesium Oxide is slightly soluble in water



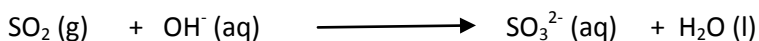
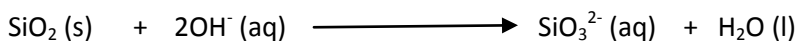
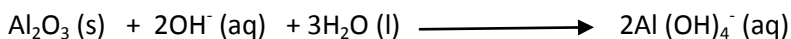
Silicon (IV) oxide and aluminium oxide do not react with water.

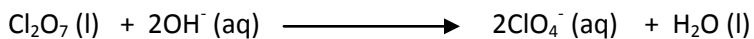
Oxides of Phosphorous, chlorine and Sulphur are acidic oxide.



Reaction with sodium hydroxide solution

Sodium and Magnesium oxide are basic oxides therefore they do not react with sodium hydroxide solution

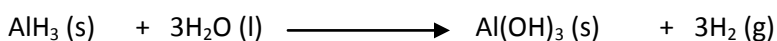
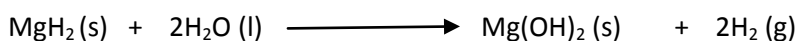
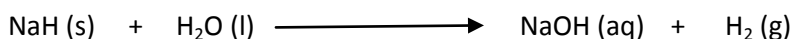




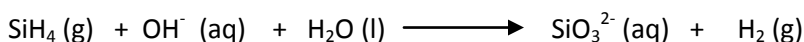
3. Hydrides

Hydrides	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl
Bond	← Ionic →			← Covalent →			
Structure	← Giant ionic →			← Simple molecular →			

The ionic hydrides react with water to form hydroxide and hydrogen gas



Phosphine does not react with water. Hydride of silicon reacts with water in presence of a strong base. i.e.



Hydrogen Sulphide and Hydrogen chloride reacts with water to form acidic solution.

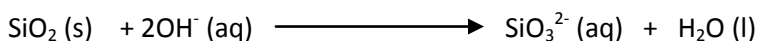
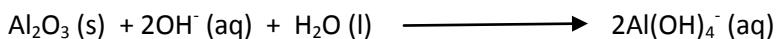
EXTRACTION OF ALUMINIUM

Ore : Bauxite $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

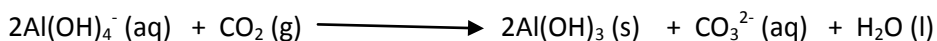
Roast bauxite to convert Iron (II) Oxide (impurity) to Iron (III) Oxide and drive off the water of crystallization.

Crush the roasted ore to powder and heat with concentrated sodium hydroxide sodium hydroxide solution.

The amphoteric ore and the acidic silicon (IV) Oxide (impurity) dissolves in the alkaline to form complex salts while the Iron (III) oxide remains undissolved.



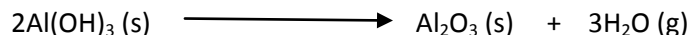
The mixture is filtered and the filtrate diluted with water. Carbondioxide gas is passed through the mixture to precipitate pure aluminium hydroxide.



Or. The solution is seeded by adding a little aluminium hydroxide to the aluminate to precipitate aluminium hydroxide.



The insoluble hydroxide is filtered off, washed and dried. Pure aluminium hydroxide is then heated to form pure aluminium oxide

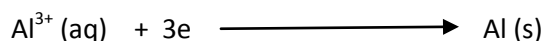


The oxide is then dissolved in molten cryolite to increase conductivity. A small amount of Calcium fluoride is added to lower the melting point of the electrolyte. Also Aluminium fluoride is added to lower the solubility of the molten aluminium.

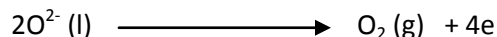
The mixture is electrolyzed between the graphite electrodes at 900°C using a low voltage to avoid the decomposition of Cryolite and high charge density.

Aluminium ions are discharged at the cathode while oxygen is liberated at the anode.

Cathode:



Anode:



Qn: (a) During the extraction of aluminium, the ore is first purified.

- (i) Write the name and formula of the ore
 - (ii) Name two main impurities in the ore.
- (b) Describe briefly how purification process is carried.
- (c) Write an equation to show how anhydrous aluminium chloride can be obtained from aluminium.
- (d) State any four uses of aluminium

TRANSITION METAL ELEMENTS

Introduction:

Some statistic about types of elements of the periodic table up to atomic number to 103

- (a) Non- metals = 19

(b) Metalloid = 3

(c) Metals = 81

Of the metals, the following are the division:

(i) Non- metals – 22

(ii) Transition metals – 59

Transition metals are divided into two:

(a) d- block transition elements located in period 4, 5 and 6

(b) f- block transition elements located in period 6 and 7

Electronic Configuration

After the second energy level, an overlap starts occurring between 3d-subshell which is nearer the nucleus than 4s- subshell but at a higher energy level. Thus after filling 3S and 3P subshells further electrons after the 4S- subshell (2electrons) later 3d- subshell.

From the electronic configuration, a transition metal is defined as that element having a partially filled 3d-subshell (between 1-9 electrons) therefore Zinc is not regarded as transition metal.

However, anomalous behavior occurs between Chromium (Z=24) and Copper (Z=29) because configuration giving half filled d-subshell are thermodynamically more stable.

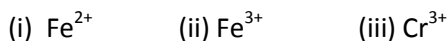
Transition metals form ions by losing electrons from 4S-subshell rather than the 3d-subshell.

The table below shows the electronic configuration of the short series of the transition metals

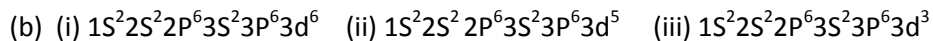
Element	symbol	Atomic number	Configuration
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
Titanium	Ti	22 $4s^2 3d^2$
Vanadium	V	23 $4s^2 3d^3$
Chromium	Cr	24 $4s^1 3d^5$
Manganese	Mn	25 $4s^2 3d^5$
Iron	Fe	26 $4s^2 3d^6$
Cobalt	Co	27 $4s^2 3d^7$
Nickel	Ni	28 $4s^2 3d^8$
Copper	Cu	29 $4s^1 3d^{10}$
Zinc	Zn	30 $4s^2 3d^{10}$

Qn: (a) Explain why Fe^{2+} is easily oxidized to Fe^{3+}

(b) Write the electronic configuration of the following ions



Soln: (a) Because Fe^{3+} has $3d^5$ subshell electrons which is thermodynamically stable compared to Fe^{2+} with $3d^6$ which is unstable.



PHYSICAL PROPERTIES OF TRANSITION METALS

The physical properties of transition metals do not vary greatly and many of them show a regular trend. Some of the properties include:

1. Metallic character.

The transition metals are true metals and many of them are widely used industrially. They are hard, strong and lustrous and have high melting and boiling point and high enthalpies of atomization. These properties suggest presence of strong metallic bonding.

The strong metallic bonding is due to availability of d-electrons. e.g Sodium with only 3s-electron available for bonding therefore it has a low melting point compared to iron with two 4s-electrons and a maximum of six 3d-electrons.

2. Metallic radius, density and atomic volume

The metallic radius decreases from scandium to nickel and it slightly increases from nickel to Zinc.

As atomic number increases, the nuclear charge increases. However, the electrons are being added to inner 3d-subshell therefore these electrons are poorly shielded from the nuclear charge hence the nuclear attraction for the outer for the most electron increases resulting into increase in atomic radius/ metallic radius.

The slightly increase from nickel to Copper is because the 3d-subenergy level in copper is fully filled with electrons and this increases the shielding of the outer electrons from the nuclear charge hence atomic radius increases.

The decrease in radius coupled with increasing atomic mass causes an increase in the density and decrease in atomic volume in passing from Scandium to Nickel.

3. Ionisation energy

There is a fairly general increase in ionization energy in passing from Scandium to nickel due to increasing nuclear charge holding the electrons more strongly resulting into decrease in atomic radius.

Qn. The table below shows the electronegativity values for elements in d-block of the periodic table

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Cu	Zn
At. No.	21	22	23	24	25	26	27	29	30
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.9	1.6

(a) Plot a graph of electronegativity against atomic number

(b) Explain the trend of your graph in (a)

GENERAL CHARACTERISTICS OF TRANSITION METALS

1. Variable oxidation states

The elements exist in variable oxidation states in variety of the compounds due to availability of the 3d-electrons which can participate in bond formation by either ionic or covalent

The commonest stable oxidation states are in bold as shown in the table

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4					
		+5	+5	+5					
			+6	+6	+6				
				+7					

Some of the compounds with the oxidation state include:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Sc ₂ O ₃ ScF ₃	TiO, TiCl ₂ Ti ₂ O ₃ , TiCl ₃ TiO ₂ , TiCl ₄	VCl ₂ , V ₂ O ₃ , VO ₂ V ₂ O ₅	CrCl ₂ , Cr ₂ O ₃ , CrCl ₃ CrCl ₄ , CrF ₅ , CrO ₃ , Cr ₂ O ₇ ²⁻	MnO, MnCl ₂ , MnCl ₃ , MnO ₂ , , MnO ₄ ²⁻ , MnO ₄ ⁻	FeCl ₂ FeCl ₃	CoO, CoCl ₂ , Co(NH ₃) ₆ ³⁺	NiO Ni ₂ O ₃ .xH ₂ O	CuO Cu ₂ O CuCl CuCl ₂	ZnO

The relative stability of these oxidation states is also indicated by the standard reduction electrode potential.

Since Zinc has one oxidation state for this reason it is regarded non-transition metal.

Qn: (a) Define the following terms;

(i) Oxidation state

(ii) Oxidising agent

(b) Determine the oxidation state of the transition metal in the following complex

(i) $K_2Cr_2O_7$

(iii) $[Co(NH_3)_5SO_4]Br$

(ii) MnO_4^{2-}

(iv) $[CuCl_2(CH_3NH_2)_2]$

2. Paramagnetism

A substance that can be drawn into a strong magnetic field is known as paramagnetic substance.

Transition metals are paramagnetic due to the presence of unpaired 3d-electrons. Every spinning electron acts as a tiny magnet. However, in an orbital with 2 paired electrons, the magnetic moment of one electron cancels out.

Paramagnetism increases with increase in the number of unpaired 3d-electrons.

3. Formation of Coloured Compounds

The 3d-electrons in isolated metal atom are degenerate, i.e. Energetically alike. However, in presence of ligands, the orbitals overlap differently and split into two levels of different energy. This excites electrons from a lower to higher level of energy. The frequency of light absorbed from this energy transition is from the visible region of the spectrum hence this appears as colour.

Examples of hydrated ions include

$V(H_2O)_6^{2+}$ - Violet

$Mn(H_2O)_6^{2+}$ - pale pink

$Fe(H_2O)_6^{2+}$ - Pale green

$Zn(H_2O)_6^{2+}$ - Colourless

$Sc(H_2O)_6^{2+}$ - Colourless

$Cr(H_2O)_6^{3+}$ - Blue-green

N.B. Scandium and Zinc form colourless compounds therefore they are regarded as non-transition metals.

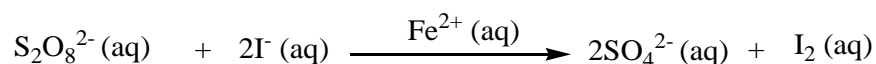
Qn: (a) State two factors that affect the colour of transition metal compounds

(b) Explain why compounds of S-block elements don't form coloured compounds

4. Catalytic activity

Transition elements and their compounds act as catalysts with several chemical processes

Homogeneous catalysis (where the catalyst are in the same phase with the reactants), due to variable oxidation state transition metals/ ions form with the activated complex thus providing an alternative reaction path way of lower reaction energy e.g.



Heterogeneous catalysis (where the catalyst and reactants are in different phases), finely divided solid transition metals/ compound provide an active interface for adsorption of the reactant where they are bound to the surface by vanderwaals forces.

Examples include; V_2O_5 - contact process, Iron- Haber process etc

5. Complex formation

Transition metals form complexes due to:

- Small and highly charged ions
- Presence of vacant 3d-orbitals to accommodate lone pairs of electrons from the ligands

A ligand is anion or molecule with lone pairs of electrons linked to the central metal ion by a dative bond

Co-ordination number is the number of atoms of ligands molecules that form dative bonds in the complex ion.

A metal complex or co-ordination compound is a chemical system composed of electron donor and electron acceptor.

Ligands are classified on basing on the number of atoms directly bonded to the metal centre (Denticity). i.e.

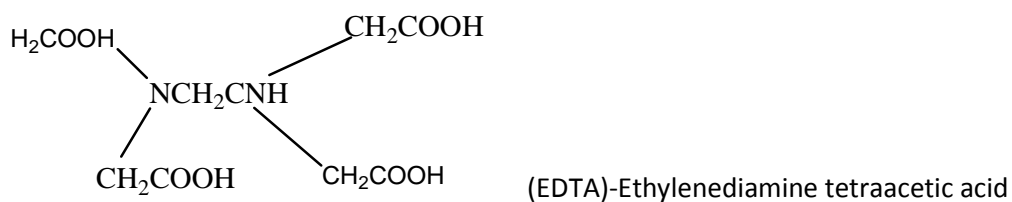
- (a) **Monodentate ligands / Unidentate ligands**

These are ligands with one donor atom per ligand molecule.e.g. NH_3 , H_2O , CH_3NH_2 Cl^-

- (b) **Multidentate/ Chelating ligands**

These are ligands with two or more donor atoms per ligand molecule e.g.

$H_2NCH_2CH_2NH_2$ (Ethane-1,2-diamine) -with two donor atoms there fore it is called bidentate



Also ligands can be classified based on charges;

• Neutral ligard	Anionic ligards	Cationic ligard
H ₂ O- aqua	Cl ⁻ -chloro	
NH ₃ -ammine	Br ⁻ -bromo	
CO-carbonyl	SO ₄ ²⁻ - Sulphato	
NO-nitrosyl	OH ⁻ -hydroxo	
H ₂ NCH ₂ CH ₂ NH ₂ (en)-ethane-1,2-diamine	CN ⁻ - cyano	
	NO ₂ ⁻ Nitro	
	H ⁻ -hydrido	

Nomenclature of Complexes

(a) **Cationic complexes**

- (i) Name and number of ligands
- (ii) Name central atom with its oxidation state
- (iii) If different ligands exist, list them in order of anion, neutral and cation. If the ligands are of the same nature, use the alphabetical order

Examples include:

- [Cu(NH₃)₄]²⁺ Tetraamminecopper(II)ion
- [Cr(H₂O)₄(NH₃)₂]³⁺ diamminetetraaquachromium(III)ion
- [Pt(NH₃)₂NO₂Cl]²⁺ chloronitrodiammineplatinum(IV) ion
- [Co(NH₃)₅SO₄]Br Sulphatopentaammine cobalt(III)bromide

(b) **Anionic complexes**

Name of the central atom ends in -ate or -ic for an acid followed by its oxidation state.

Example include:

[CuCl₄]²⁻ tetrachlorocuprate(II)ion

SiF₆²⁻ Hexafluorosilicate(IV)ion

[Cr(OH)₅NH₃]³⁻ pentahydroxoamminechromate(II)ion

[CoCl₄(H₂O)₂]⁻ tetrachlorodiaquacobaltate(III)ion

LiAlH₄ Lithiumtetrahydridoaluminate(III)

(c) **Neutral complexes**

These are formed between the central metal atom and a neutral ligand e.g.

- $\text{Ni}(\text{CO})_4$ Tetracarbonylnickel(0)
- $\text{V}(\text{CO})_6$ hexacarbonylvandium(0)

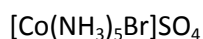
ISOMERISM

The following are the kinds of isomerism in complexes;

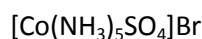
(a) **Ionisation isomerism**

This occurs when an ion can occupy positions inside and outside complex ion .i.e. acts as a free ligand

Example



and



Bromopentaamminecobalt(III)sulphate

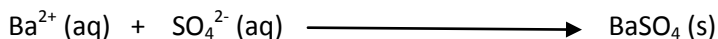
Sulphatopentaamminecobalt(III)bromide

These isomers can be differentiated by use of acidified barium nitrate solution and the observations are:

$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ – white precipitate is formed

$[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ - No observable change

The sulphate ions in bromopentaamminecobalt(III)sulphate are uncomplexed therefore they are free to react with barium nitrate solution to precipitate the sparingly soluble barium sulphate.i.e.



Qn: Hydrated Chromium(III)chloride forms three isomers which form a white precipitate with silver nitrate solution.

- Write the formula and I.U.P.A.C name of each isomer
- Describe how the isomer can be distinguished.

Soln:

(a) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ Hexaaquachromium(III)chloride

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ Chloropentaaquachromium(III)chloride

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ Dichlorotetraaquachromium(III)chloride

- Add excess 1M Silver nitrate solution to equimolar solution of each isomer. The number of moles of silver chloride precipitated by isomer is in the ratio of 3:2:1.

Or: Conductivity measurements

Conductivity depends on the number of conducting ions present in solution. The isomer with more ions gives the highest conductivity.

(b) **Geometrical isomerism**

The isomers differ in the spatial arrangement of two ligand molecules in square planar or octahedral complex giving rise to *cis and trans isomers*

Read on the structure of complexes:

- ❖ **Linear structure formed by complexes with coordination number 2**
- ❖ **Tetrahedral/ square planar formed by complexes with co-ordination no. 4**
- ❖ **Octahedral formed by complexes with co-ordination no.6**

STABILITY CONSTANT

Consider;



The equilibrium expression is written as:

$$K_{eq} = \frac{[[ML_6]^{n+}]}{[[L]^6][M^{n+}]} \quad \text{where } K_{eq} \text{ is the stability constant}$$

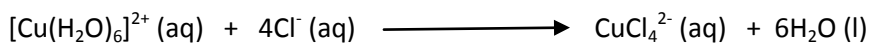
A ligand with a higher stability constant substitutes/ displaces others from the complex

Qn: To an aqueous solution of copper (II) sulphate, concentrated hydrochloric acid was added followed by aqueous ammonia solution

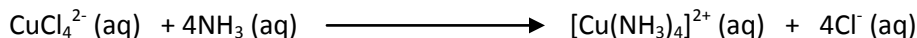
- (a) State what was observed
- (b) Explain your observation in above in (a)

Soln:

- (a) A blue solution turns green to yellow finally deep blue.
- (b) In dilute solution of copper(II) sulphate, the blue colour is due to $[Cu(H_2O)_6]^{2+}$. On addition of concentrated hydrochloric acid the aqua ligand are displaced to form a yellow tetrachlorocuprate (II) complex.



On addition of ammonia molecules with a higher stability constant displaces the chloro ligands to form tetraamminecopper(II) ions which is deep blue.



COPPER

Extraction :

Ores:

- Copper Pyrites (CuFeS_2)- principal ore
- Copper glance(Cu_2S)
- Cuprite(CuO)
- Malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$)

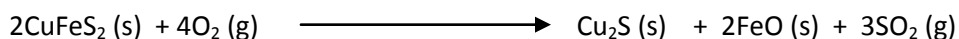
(a) Concentration of the ore (Froth floatation/ selective wetting)

The ore is crushed to powder and mixed with water containing a frothing agent such as pine oil. Air is blown through the mixture to agitate the ore.

High density impurities become wet and sink to the bottom. Particles of the ore rise to the surface and adhere to the air bubbles. They float on the surface as a froth which is skimmed off, filtered and dried.

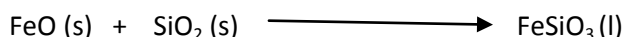
(b) Roasting

The concentrated ore is roasted in air to convert pyrites into iron (II)oxide, copper(I)sulphide and sulphur dioxide gas



(c) Smelting

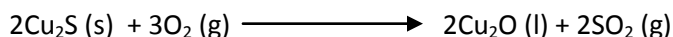
The mixture is heated in furnace with silicon (IV) oxide in absence of air. Iron (II)oxide reacts to form a slug of Iron(II)silicate



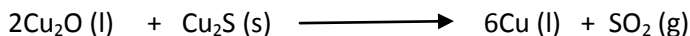
The molten slug floats on the molten Copper(I)sulphide and can be trapped off.

(d) Conversion to blister copper

Copper(I)sulphide is heated in air to form copper(I)oxide and sulphurdioxide gas.



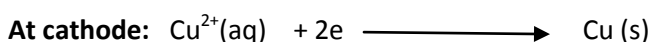
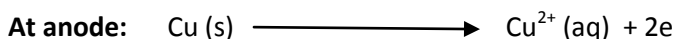
The mixture of copper(I)oxide and unchanged copper(I)sulphide is then heated strongly in absence of air to form blister copper.



The molten copper is run off into moulds.

(e) Purification/Refining of blister copper

Copper (II) sulphate solution is electrolysed using blister copper as the anode and pure copper as cathode. The pure copper dissolves from the anode into solution and it is deposited at the cathode



The anode loses mass and cathode gains an equal mass of copper.

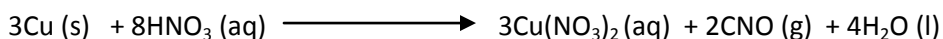
PROPERTIES OF COPPER

Copper has a low Electropositivity and thus it is an inert and not attacked by dilute mineral acids and water.

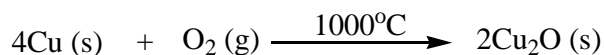
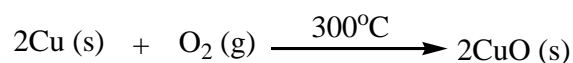
(a) It is oxidized by hot concentrated sulphuric acid to copper (II) sulphate, sulphur dioxide and water



(b) It is oxidized by cold and hot concentrated nitric acid as shown below respectively



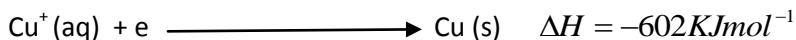
(c) When heated, copper reacts with oxygen and dry chlorine as:



COMPOUNDS OF COPPER

Common oxidation states are +1 and +2.

Copper (I) is less stable compared to copper (II) despite the stable electronic configuration of copper (I) ions. With respect to copper, both copper (I) and Copper (II) ions are unstable i.e.



∴ The enthalpy of conversion of Cu^+ to Cu^{2+} is -409KJmol^{-1} and this shows that Cu^+ ions are thermodynamically unstable with respect to both Cu and Cu^{2+}

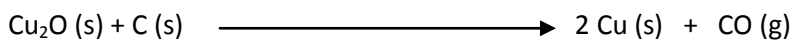
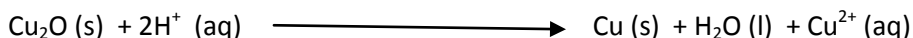
Copper (I) Compounds

They are unstable in aqueous solution and undergo disproportionation

(a) Copper (I) Oxide

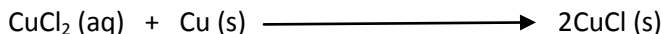
It is prepared by reduction of copper (II) sulphate with an aldehyde in the presence of an alkali

It is a basic oxide and can be reduced to copper by hydrogen and carbon

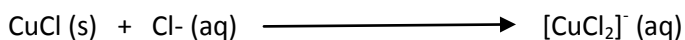


(b) Copper (I) chloride

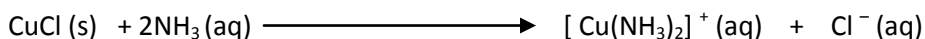
It is prepared by boiling copper (II) chloride with copper in presence of concentrated hydrochloric acid.



It dissolves in excess hydrochloric acid to form a colourless solution



It dissolves in excess aqueous ammonia (concentrated) to form complex



Qn: 8.0g of a copper ore was leached with dilute sulphuric acid and the resultant solution diluted to 250cm^3 . Excess 10% potassium iodide was added to 30cm^3 of the solution. The iodine liberated 23.5cm^3 of 0.05M sodium thiosulphate solution for complete reaction.

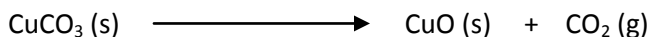
- Write all the equations of reactions involved.
- Calculate the percentage of copper in ore
- Describe the application of copper (I) compounds in distinguishing organic compounds and synthesis
- Explain the similarity between silver (I) and copper (I) ions

Qn: A double salt $\text{Cu}(\text{NH}_4)_x\text{Cl}_y \cdot z\text{H}_2\text{O}$ where x, y and z are whole numbers. The molar mass of salt is 277.5g. The chloride in 1.388g of the salt is precipitated as silver chloride. After washing and drying the mass of the precipitate was 2.870g. When 1.388g of the salt is boiled with excess sodium hydroxide solution, the ammonia liberated neutralizes 10cm^3 of 1.0M hydrochloric acid. Determine the formula of the salt.

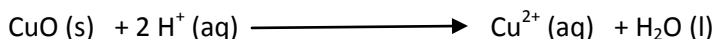
Copper (II) compounds

(a) Copper (II) oxide

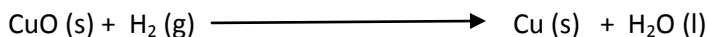
This a black basic oxide obtained by the action of heat on copper (II) nitrate, carbonate, sulphate or copper (II) hydroxide



It reacts with dilute mineral acids to form copper (II) salts and water

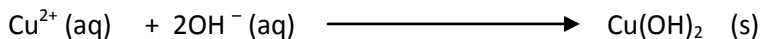


It is reduced to copper by carbon, hydrogen, methane and ammonia

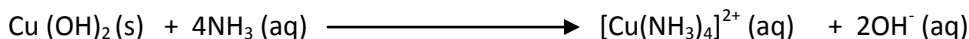


(b) Copper (II) hydroxide

This a pale blue precipitate formed when dilute sodium hydroxide solution is added to a solution of Copper (II) ions

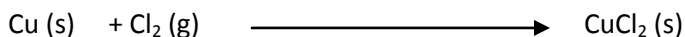


It dissolves in ammonia solution due to formation of a soluble complex. i.e.

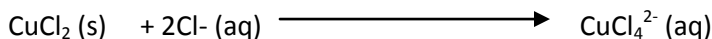


(c) Copper (II) chloride

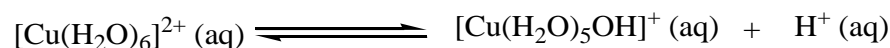
The anhydrous chloride is prepared by reacting dry chlorine gas with heated copper metal



The chloride dissolves in concentrated hydrochloric acid to form a yellow- green solution of tetrachloro cupricate



An aqueous solution of copper (II) salts are slightly acidic because the Cu^{2+} ions have a high charge density therefore they are heavily hydrated as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and this undergoes hydrolysis to release hydrogen ions in solution which causes the solution to be acidic



The copper (II) salt in solution reacts with:

- Potassium ferrocyanide solution to form brown precipitate
- Excess potassium cyanide solution to form a colourless solution
- Potassium iodide solution to form a white precipitate and brown stains

IRON

Extraction

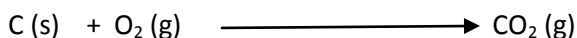
Ore: Haematite (Fe_2O_3)

Magnetite (Fe_3O_4)

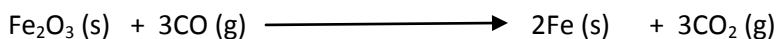
Iron pyrites (FeS_2)

The mixture of haematite, coke and limestone are fed into the furnace. Air enriched in oxygen is passed into the bottom of the furnace whose temperature varies from about 2000°C - 200°C at the top

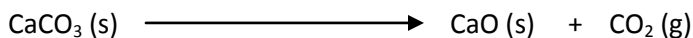
Coke is constantly used to generate carbon monoxide gas



The reaction is exothermic and thus increases the temperature of the furnace. Carbon monoxide reduces iron (III) oxide to iron



Limestone decomposes to form calcium oxide which removes the major impurity, Silicon (IV) Oxide as a slug of calcium silicate.



The slug is less dense than the molten iron hence it protects it from re-oxidation. The excess hot gases pass out of the furnace while the iron and slug are periodically tapped off from the bottom

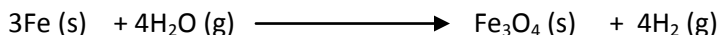
N.B. The pig iron can be converted to steel by open-hearth process where the carbon is converted to gaseous oxide by heating and other impurities form oxides which react with limestone to form slag

PROPERTIES OF IRON

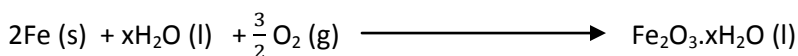
(a) When heated, iron reacts with oxygen to form black solid of triiron tetraoxide



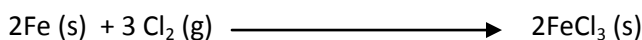
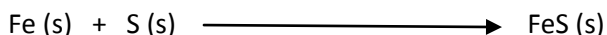
(b) Red hot iron reacts with steam as shown by the equation



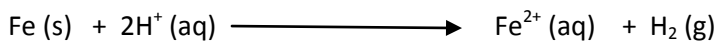
Iron slowly reacts with cold water in the presence of oxygen to form hydrated iron (III) oxide



(c) When heated iron reacts with sulphur, chlorine, hydrogen chloride, carbon and carbonmonoxide



(d) It liberate hydrogen gas when reacted with dilute mineral acids



Hot concentrated sulphuric acid oxidizes it to iron (III) sulphate and itself reduced to sulphurdioxide and water



Concentrated nitric acid renders iron passive due to the formation of layer of the oxide.

COMPOUNDS OF IRON

Oxidation states are +2 and +3

The +3 oxidation state is more stable compared to +2 (why?).

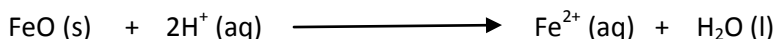
Iron (II) compounds

(a) Iron (II) oxide

This a black basic oxide prepared by thermal decomposition of iron (II) oxalate in absence of air

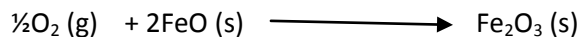


It reacts with dilute mineral acids to form iron (II) salt and water



The salts solutions are pale green and are readily oxidized by atmospheric oxygen to the corresponding iron (III) salts. However, they are stable in presence of an acid.

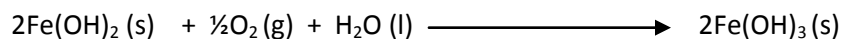
It rapidly turns brown on exposure to air



(b) Iron (II) hydroxide

This a green precipitate formed by action of dilute sodium hydroxide or ammonia solution on a solution containing Fe^{2+}

On exposure to air, it turns brown due to the formation of Iron (III) hydroxide



An aqueous solution of iron (II) salts contains $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and don't undergo hydrolysis due to low charge density

(c) Iron (II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

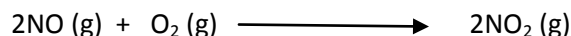
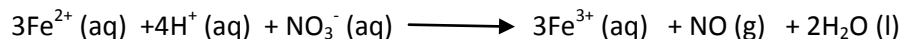
It is prepared by warming Iron with excess dilute sulphuric acid and evaporate the resultant solution to crystallize pale green crystal. The crystals are efflorescent and oxidized on exposure to air with formation of brown patches of iron (III) sulphate

Ammonium ferrous sulphate is normally preferred to standardize potassium permanganate because it is resistant to atmospheric oxidation, non-efflorescent and has higher relative molecular mass.

(d) Oxidation reactions

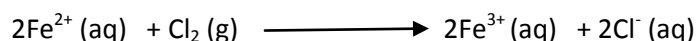
(i) Hot concentrated nitric acid

A green solution turns yellow with effervescence of a colourless gas which forms brown fumes in air



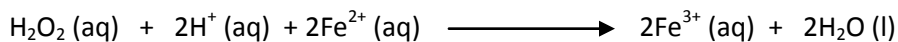
(ii) Chlorine gas

The green solution turns yellow

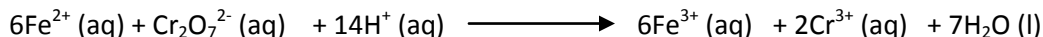


(iii) Hydrogen peroxide

The green solution turns yellow



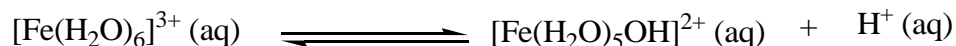
(iv) Potassium dichromate



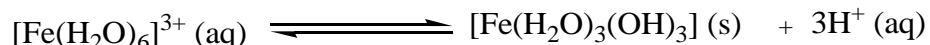
(d) Potassium hexacyanoferrate (III) solution. It forms a dark blue precipitate

Iron (III) compounds

The iron (III) ions have a high charge density and are heavily hydrated therefore in aqueous solution they exist as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ hence it undergoes hydrolysis to release protons which cause the solution to be acidic

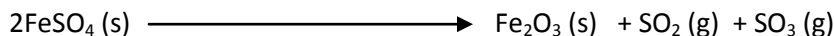


Complete hydrolysis is represented as

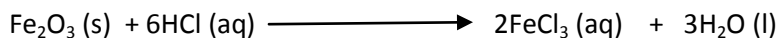


(a) Iron (III) oxide

It is prepared by thermal decomposition of iron (II) sulphate or iron (III) hydroxide



It is basic and dissolves in dilute mineral acids

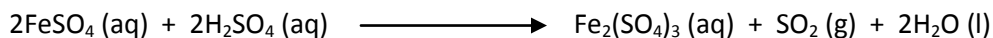


The oxide can be reduced by hydrogen, carbon and carbon monoxide to form iron



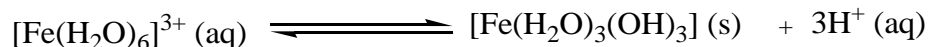
(b) Iron (III) sulphate

Obtained by oxidation of iron (II) sulphate using concentrated sulphuric acid

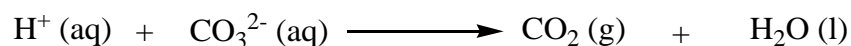


Qn: Sodium carbonate solution was added to aqueous solution of iron (III) sulphate. Bubbles of a colourless gas and a brown precipitate were observed. Explain this observation

Soln: Due to high charge density, the hydrated ion undergoes hydrolysis to form insoluble iron (III) hydroxide and hydrogen ions which cause the solution to be acidic i.e.

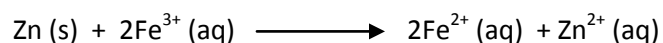


The hydrogen ions react with carbonate ions from sodium carbonate to form carbon dioxide gas which is colourless gas



REDUCTION OF Fe^{3+} TO Fe^{2+}

(i) Zinc and hydrochloric acid



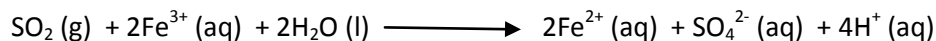
(ii) Hydrogen sulphide gas

The brown solution turns pale green and yellow solid is deposited



(iii) Sulphur dioxide

The brown solution turns pale green



N.B. Fe^{3+} ions are confirmed by use of potassium hexacyanoferrate (II) solution, a dark blue precipitate is observed.

ZINC

The following are reasons why zinc is referred to as a non-transition metal

- It forms colourless compounds in aqueous state
- It exhibits only one oxidation state
- It is not paramagnetic
- It does not act as catalyst or has limited catalytic activity

However, like other transition elements, Zinc forms complexes.

Extraction

Ore: - zinc blende (ZnS)

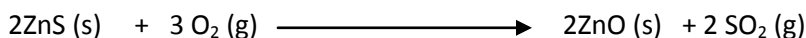
-Zincite

Concentration of ore

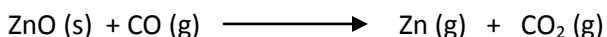
Zinc blende is crushed into powder and mixed with water containing a frothing agent. Air is bubbled through the mixture. The low density ore floats as a froth which is skimmed off.

Roasting

The concentrated ore is roasted to form the oxide



Zinc oxide is then mixed with coke and limestone in a blast furnace. The oxide is reduced to zinc metal by carbon monoxide



The metal distils off with other blast furnace gases. The mixture of gases is allowed to cool (quenched) to obtain crude zinc which is purified by redistillation.

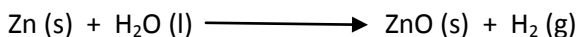
The major impurities are lead (II) sulphide, Cadmium and iron.

Reactions of Zinc

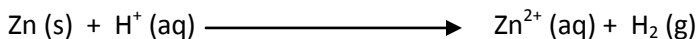
(a) It burns in oxygen to form zinc oxide and a little nitrite



(b) Steam reacts with heated Zinc form Zinc oxide and Hydrogen gas



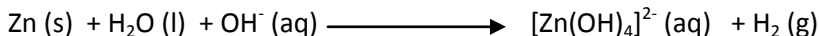
(c) Warm dilute mineral acids readily react with Zinc to liberate hydrogen gas



Hot concentrated sulphuric acid oxidizes zinc to zinc sulphate

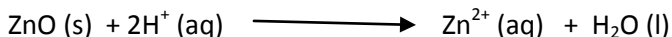


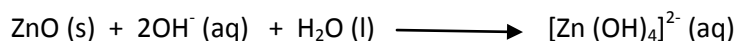
(d) It reacts with sodium hydroxide solution in presence of water to form zincate and water



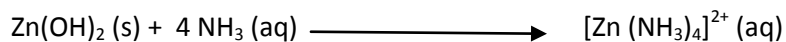
Compound of Zinc

Zinc oxide and zinc hydroxide are amphoteric compounds





The hydroxide dissolves in excess ammonia solution to form a colourless solution



N.B. In aqueous solution salts of Zinc are colourless due to $[\text{Zn(H}_2\text{O)}_4]^{2+}$ and are confirmed by use of disodium hydrogen phosphate where they form a white precipitate soluble in ammonia solution

Question:

- (a) Name one ore of zinc and give its formula
- (b) (i) Describe briefly how the ore you have named in (a) is concentrated
 - (ii) What further treatment of the ore is required immediately after concentration?
- (c) Outline the process, giving equations for the production of zinc metal from the treated ore
- (d) Zinc belongs to d-block in the periodic table yet it is not a transition metal. Explain this statement.
- (e) A piece of zinc metal was suspended in a solution of copper (II) sulphate in water. State what was observed and write the equation for the change that took place.

MANGANESE

ORES

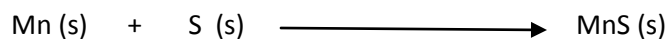
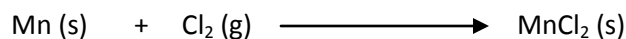
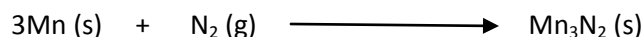
- Pyrolusite-MnO₂
- Hausmannite-Mn₃O₄

The extraction is done by reduction of the oxide using aluminium followed by vacuum distillation

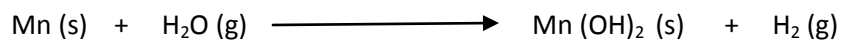
Direct reduction of manganese (IV) oxide is explosive thus the oxide is heated in oxygen to be converted to trimanganese tetraoxide

CHEMICAL PROPERTIES OF MANGANESE

1. When heated, manganese reacts with non-metals as



2. Manganese reacts with hot water to form sparingly soluble Manganese (II) hydroxide and hydrogen gas



3. Dilute hydrochloric and sulphuric acid form pink solution of manganese (II) salts and hydrogen gas.

Qn: 4.0g impure manganese was dissolved in 20cm³ of 0.2M sulphuric acid.

(a) State what was observed

(b) Calculate the percentage purity of manganese in the impure sample

Compounds of Manganese

Oxidation states are +2,+3,+4,+6,+7

I WISH YOU THE BEST OF LUCK IN THIS BRANCH OF CHEMISTRY