A'LEVEL INORGANIC CHEMISTRTY NOTES

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

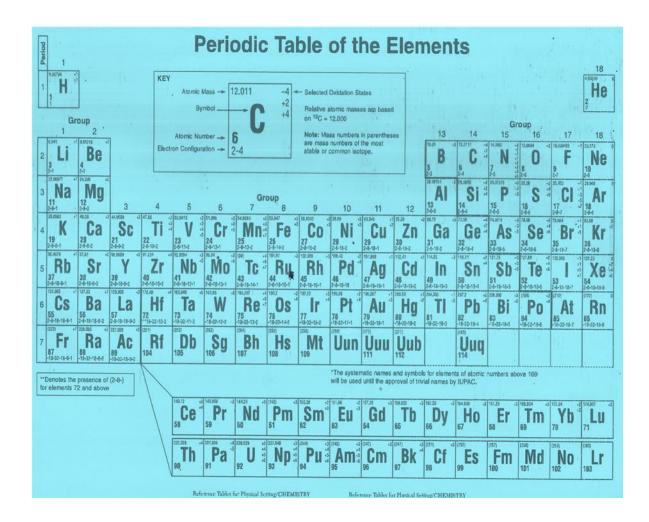
Periodic Table

The original form of the periodic table was first put forward by Mendeleev 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 law*



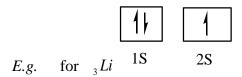
Electronic configuration

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

Rules for filling electrons

Rule 1: Aufbau Principle

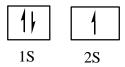
The electrons in the ground state occupy orbitals in order of the orbital energy. The lowest energy orbitals are always filled first



Rule 2: Pauli Exclusion Principle

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

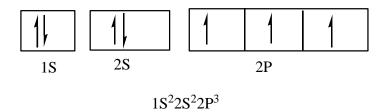
e.g. ₃Li



Rule 3: Hund's Rule

This states that the orbitals of a sub shell must be occupied singly first and with parallel spins before they can be occupied in pairs

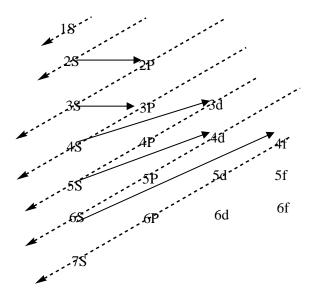
e.g. ₇ N



Rule 4:

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

The order of filling in the electrons in subshells is summarized in the diagram below.



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

This is the main energy level of an atom which determines the energy of an electron.

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 sub shells 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

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. 1S²2S²2P⁶3S²3P⁶4S¹3d⁵ and 1S²2S²2P⁶3S²3P⁶4S¹3d¹⁰ respectively

Determination of Block of an element

The block to which an element belongs is determined by the orbitals which are in the process of filling up.

E.g.
$$_{11}Na - 1S^2 2S^2 2P^6 3S^1$$
 belongs to the S- block

Selenium 34 with electronic configuration[Ar]4s² 3d¹⁰4p⁴ is a p block element

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 inter-nuclear 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 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	0.156	0.136	0.125	0.117	0.110	0.104	0.09	0.094
radius(nm)								

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

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

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 increase. However, the increase in screening effect is more than 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 nucleus.

Example of such variation is in group 1:

Element	Li	Na	K	Rb	Cs
Atomic Radius (nm)	0.123	0.156	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 ⁻	0	O^{2-}
Radius (nm)	0.09	0.18	0.066	0.140

2. Ionization 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 ions.

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 structures 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	В	C	N	0	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 2S², 2P⁶ and 2P³ 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

Ionization 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	В	С	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 uninegatively 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 indirectly from Born-Haber cycle.

Variation across the period

Across the period, E.A increases. This is due to decrease in atomic radius and increase in effective 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 of 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 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 ionic 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 polarizable

Polarization 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 neighbors 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

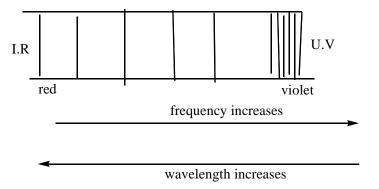
See physical chemistry notes

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. the energy levels get closer as energy decreases due to decreased nuclear attraction on the electrons in the energy levels which nearly become constant and converge into continuous spectrum.

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



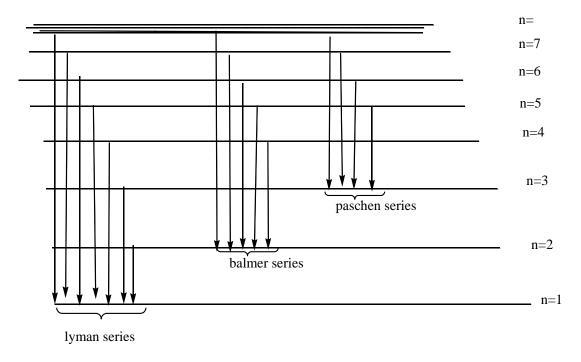
Explanation of the line Spectrum

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

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$
 Where R_H is Rybergs constant = 109678

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

 $\Delta E = hf$ Where h-Planck's constant and f-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 .ionization

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 ionization?
- (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 $(h=6.63X10^{-34}Js)$

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 spectra-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 lines?
- (b) Explain why each series converge
- (c) Explain how ionisation energy of an element can be calculated from spectralmeasurement
- (d) Explain the term convergence limit

(e)What is meant by the term principal quantum number?

(f)State the information that can be obtained from the separate lines about the electronic structure of hydrogen atom.

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 a polar covalent compound

Properties of covalent compounds

- They contain simple discrete molecules held by weak vanderwaals forces in simple molecular structure e.g Sulphur, carbondioxide and giant atomic structure e.g. Silicon (IV)oxide, Diamond
- They are soluble in non-polar solvents e.g. benzene
- They are non-electrolyte in fused state

- They have low melting and boiling point
- * They react together slowly especially organic compounds

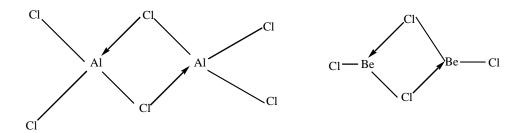
(b) Co-ordinate/ Dative bond

This is weak covalent bond formed between an electron rich atom and 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 AlCl₃ and BeCl₂ 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 his compound has a density of 2.28X10³ gm⁻³ at 1427K and 1.013X10⁵Pa

- (a) Calculate the molecular formula Q and draw its structure.
- (b) 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.

Properties of Electrovalent compounds

- * At ordinary temperatures they are invariably exist as crystalline solids. The crystal consist of infinite assembly of ions joined together in a regular pattern
- They have high melting and boiling point owing to strong electrostatic force of attraction between oppositely charged ions.
- In fused state or molten state they are good conductors of electricity due presence of free ions which are attracted and discharged at electrodes
- They dissolve readily in water
- When oppositely charged ions react together in aqueous solution they do so almost instantaneously.

(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 of the periodic table

Element Na	Mg	Al	Si	P	S	Cl
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At. no.	11	12	13	14	15	16	17
Melting							
point(°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 ₃ CH ₂ CH ₂ OH	$CH_3CH_2CH_2NH_2$	H_2O	HF	NH ₃
98	49	100	24	-33

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

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

3. Density and Volume

Hydrogen bonds increase 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 VII 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 electrons placed in the S-orbital. The outer most configurations are:

Group I (Alkali metals) -ns1

Group II (Alkaline earth metals)-ns² where n is principal quantum number.

The physical properties include:

Group I (Table 1)

Element	Li	Na	K	Rb	Cs
I 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 ⁻	-499	-390	-305	-281	-248
1)					
Electrode potential(V)	-3.05	-2.71	-2.92	-2.93	-3.02

Group II(Table 2)

Element	Be	Mg	Ca	Sr	Ba
I 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	-2385	-1897	-1561	-1414	-1274
energy(KJmol ⁻¹)					
Electrode potential(V)	-1.85	-2.37	-2.87	-2.89	-2.91

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.

$$2Na(s) + H_2(g)$$
 $\longrightarrow 2NaH(s)$

$$Mg(s) + H_2(g) \longrightarrow MgH_2(s)$$

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

2. WATER

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

$$2K\left(s\right) \quad + \quad 2H_{2}O\left(l\right) \qquad \qquad \underline{\qquad \qquad 2KOH} (aq) \qquad + \qquad H_{2}\left(g\right)$$

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

Reactivity of group (II) elements with water increases down the group as atomic radius increases due to increase of Electropositivity.

Magnesium reacts slowly with cold water but vigorously with steam

$$Mg\left(s\right) + H_2O\left(g\right) \qquad \qquad MgO\left(s\right) + H_2\left(g\right)$$

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

$$M(s) + 2 H_2O(l)$$
 $M(\Theta H)_2 (aq) + H_2 (g)$

Where M = Ca, Ba and Sr.

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.

Ba (s)
$$+ H_2SO_4$$
 (aq) _______ BaSO_4 (s) $+ H_2$ (g)

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

$$Mg(s) + 2HNO_3(aq) - Mg(NO_3)_2(aq) + H_2(g)$$

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

4. OXYGEN

Group II elements form normal oxides .i.e.

$$2M(s) + O_2(g)$$
 $-2MO(s)$

However barium and Strontium can form peroxides when the normal oxide is heated in more oxygen .e.g.

$$2BaO(s) + O_2(g)$$
 ______2 $BaO_2(s)$

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

Lithium forms only a normal oxide .i.e.

$$4 \text{ Li (s)} + O_2 \text{ (g)}$$
 _______ 2 Li₂O (s)

Sodium forms a yellow normal peroxide .i.e.

$$2\text{Na}(s) + \text{O}_2(g) - \text{Na}_2\text{O}_2(s)$$

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

$$K(s) + O_2(g)$$
 $KO_2(s)$

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

$$BeO(s) + 2 H^{+} (aq)$$
 \longrightarrow $Be^{2+} (aq) + H_2O (l)$

BeO(s) + 2 OH⁻ (aq) + H₂O (l)
$$\longrightarrow$$
 Be (OH)₄²⁻(aq)

The peroxides form hydroxides or/and hydrogen peroxides when dissolved in water

$$Na_2O_2(s) + 2 H_2O(l) \longrightarrow 4NaOH(aq) + O_2(g)$$

$$BaO_2(s) + 2 H_2O(l)$$
 — $Ba(OH)_2(aq) + H_2O_2(aq)$

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

$$2KO_2(s) + 2H_2O(1)$$
 $2KOH(aq) + O_2(g) + H_2O_2(aq)$

- **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.

$$2 \text{ Na (s)} + \text{Cl}_2 (g)$$
 — \longrightarrow ACl (s)

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.

 $\Delta H_s = \Delta H_h + U$ Where ΔH_s 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.

Some hydrated salts e.g hydrated copper (II) sulphate crystals dissolve endothermically while anhydrous salt dissolves exothermically.

This is because for hydrated salt, the ions are already partly hydrated therefore hydration energy is lost thus when the crystals are dissolved in water this hydration energy is not enough to outweigh lattice energy. For anhydrous salt, the hydration energy is readily available and able to outweigh lattice energy.

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.

$$2$$
NaOH (s) + CO₂ (g) \longrightarrow Na₂CO₃ (aq) + H₂O (l)

$$Na_2CO_3 (aq) + H_2O (1) + CO_2 (g) \longrightarrow 2NaHCO_3 (s)$$

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

$$M^{2+}$$
 (aq) + 2OH⁻ (aq) \longrightarrow M (OH)₂ (s)

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

$$CaO(s) + H2O(l)$$
 Ca $(OH)2(s)$

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

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

$$Be(OH)_2(s) + 2OH^-(aq) \longrightarrow Be(OH)_4^{2-}(aq)$$

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 increase 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 solvary process on a large scale.

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

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

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

$$Ba^{2+}$$
 (aq) + CO_3^{2-} (aq) _____ BaCO₃ (aq)

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 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 I decompose to nitrites and oxygen gas except lithium nitrate I.e.

$$2NaNO_3(s)$$
 \longrightarrow $2NaNO_2(s) + O_2(g)$
 $4LiNO_3(s)$ \longrightarrow $2Li_2O(s) + 4NO_2(g) + O_2(g)$

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 groupie ie elements decompose to metal oxide, nitrogen dioxide and oxygen gas. e.g.

$$2Mg (NO_3)_2 (s)$$
 $2MgO (s) + 4NO_2 (g) + O_2 (g)$

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 Vander Waals forces which makes it easily decompose

On:

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

The table below shows the decomposition temperatures for group II carbonates

Carbonate	BeCO ₃	MgCO ₃	CaCO ₃	SrCO ₃	BaCO ₃
Temperature (°C)	100	350	900	1290	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 M^{2+} ions have higher charge density than M^{+} ions therefore they polarize the large carbonates more than M^{+}

COMPLEX FORMATION

Complex formation is favored by:

- High charge density of the cations I.e. Small and highly charges 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:

Be
$$(H_2O)_4^{2+}$$
, Be $(H_2O)_4^{2-}$, Be F_4^{2+} , Al $(H_2O)_6^{3+}$

HYDROLYSIS OF SALTS

Hydrolysis is the reaction of salts with water molecules which results in change Ph.

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 used in acid-base titration.

Salts containing cations of high charge density undergo hydrolysis e.g. Soluble beryllium salt exists as $Be(H_2O)_4^{2+}$ in aqueous solution which hydrolyses to release a proton which causes the solution to be acidic.

$$Be(H_2O)_4^{2+}$$
 (aq) $=$ $[Be(H_2O)_3OH]^+$ (aq) $+ H^+$ (aq)

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	Oxides and hydroxides are amphoteric.	Both form acidic oxide as B_2O_3 and SiO_2

hooting to	Do(OH) (a) + 20H- ()	
heating to	Be(OH) ₂ (s) + 2OH ⁻ (aq)	
form	$Be(OH)_4^{2-}$ (aq)	
nitrides.	$Al(OH)_3$ (s) $+ OH^-$ (aq)	
	$Al(OH)_4$ (aq)	
Their	Both react with Conc.	Both form series of covalent hydrides.
hydrogen	Sodium hydroxide	
carbonates	solution to form a	
exist in	complex and hydrogen	
solution	gas.	
	$Be(s) + 2OH^{-}(aq) +$	→
	$2H_2O(1)$ Be(OH) ₄ ² -	
	$(aq) + H_2(g)$	
	2Al(s) + 2OH(aq)	
	$+6H_2O(1)$ 2Al(OH) ₄	
	$(aq) + 3H_2(g)$	
Both form	Their chlorides and	
normal	bromides are covalent	Both form chlorides which hydrolyze
oxides when	and dimerize in vapour	readily.
heated in	phase as Be ₂ Cl ₄ and	3
oxygen (air)	Al ₂ Cl ₆ .	
oxygen (an)	$2AlCl_3(s)$	
	$Al_2Cl_6(g)$	
	A12C16 (g)	
Their		Form covalent compounds.
hydroxides	Both form ionic carbides	1 orm covarent compounds.
and	which hydrolyze to form	
carbonates	methane.	
are	Be ₂ C (s) + $4H_2O(1)$	
sparingly	$CH_4(g) + 2Be(OH)_2$ (aq)	
soluble in	$Al_4C_3(s) + 12H_2O(1)$	
	1 1	
water	$3CH_4(g) + 4Al(OH)_3(aq)$	F
Carbonates	Dath and northern t	Form borides and silicides with metals.
and	Both are rendered	
hydroxides,	passive by concentrated	
decompose	nitric acid.	
on heating		
to give an		
oxide.		
Nitrates		
decompose	Both form fluoro	
on heating	complexes.e.g. BeF4 ²⁻	
to give an		
_		
oxide,		
oxide, nitrogen		
oxide,		

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.
- (d) Beryllium resembles other elements in groupie of the periodic table

QUALITATIVE ANALYSIS OF Ca²⁺, Mg²⁺ and Ba²⁺

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

Mg²⁺ - No observable change

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

Potassium Chromate solution

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

Ca²⁺ - Yellow precipitate soluble in Ethanoic acid

Ammonium Oxalate followed by Ammonia Solution

Ca²⁺- white precipitate.

 Mg^{2+} - No observable change

Ba²⁺???

Disodium Hydrogen Phosphate

Mg²⁺ - A white precipitate insoluble in excess Ammonia solution

 Ca^{2+} and Ba^{2+} - A white precipitate soluble in acid.

Qn: Name the reagent that can be used to distinguish between the following pairs of ion/salt. In each case state what would be observed if the reagent is treated with each ion/salt

- (a) MgSO₄ and CaSO₄
- (b) PbSO₄ and PbCl₂
- (c) Zn^{2+} and Ca^{2+}

GROUP VII ELEMENTS (HALOGENS)

Elements	formul	Nature	Boiling	Bond	Electron	Electro	Electrode
	a		point	energy	Affinity	negativity	potential
Fluorine	F_2	Gas (-188	37	-322.6	4.0	+2.87
		Yellow)					
Chlorine	Cl ₂	Gas(Greenish-	-34	57.2	-364	3.0	+1.39
		Yellow)					
Bromine	Br ₂	Liquid	58	45.4	-342	2.8	+1.07
		(Red-brown)					
Iodine	I_2	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 van der waals 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 van der waals 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 pair electrons 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 or enthalpy of atomization

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 and itself reduced to Hydrofluoric acid.

$$2H_2O(1) + 2F_2(g)$$
 \longrightarrow $O_2(g) + 4 HF (aq)$

Chlorine and bromine reacts with water to form a mixture of halic (I) acid and hydrohalic acid

$$Cl_2(g) + H_2O(l)$$
 \longrightarrow $HCl(aq) + HOCl(aq)$

$$Br_2(l) + H_2O(l)$$
 \longrightarrow $HBr(aq) + HOBr(aq)$

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.

$$I_2(s) + I^-(aq) \longrightarrow I_3^-(aq)$$

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

2HOCl (aq)
$$\longrightarrow$$
 2HCl (aq) + O₂ (g)

(b) Alkalis

(i) Cold dilute Alkalis:

Fluorine forms oxygen difluoride, fluoride and water

$$2F_2(g) + 2OH^-(aq)$$
 \longrightarrow $OF_2(g) + 2F^-(aq) + H_2O(l)$

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

$$Cl_2(g) + 2OH^-(aq)$$
 \longrightarrow $Cl^-(aq) + OCl^-(aq) + H_2O(l)$

$$Br_2(l) + 2OH^-(aq)$$
 \longrightarrow $Br^-(aq) + OBr^-(aq) + H_2O(l)$

$$I_2(s) + 2 OH^-(aq)$$
 \longrightarrow $I^-(aq) + OI^-(aq) + H_2O(1)$

$$2OCl^{-}(aq) \longrightarrow O_2(g) + 2Cl^{-}$$

(ii) Hot concentrated Alkali:

Fluorine reacts to form oxygen, fluoride and water.

$$2F_2(g) + 4OH^-(aq)$$
 \longrightarrow $O_2(g) + 4F^-(aq) + 2H_2O(1)$

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

$$3X_2 + 6OH^-$$
 (aq) X^- (aq)

(c) **Hydrogen**

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

$$F_2(g) + H_2(g)$$
 \longrightarrow 2HF (g)

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

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(g)$$

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

$$Br_2(1) + H_2(g) \xrightarrow{Pt/200^{\circ}C} 2HBr(g)$$

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

$$I_2(s) + H_2(g) = Pt/400^{\circ}C$$
 2HI (g)

(d) **Oxidation reactions**

Chlorine, Bromine and Iodine Oxidize:

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

$$Sn^{2+}\left(aq\right) \ + \ Cl_{2}\left(g\right) \qquad \longrightarrow \quad Sn^{4+}\left(aq\right) \ + \ 2 \ Cl^{\text{-}}\left(aq\right)$$

(ii) Hydrogen sulphide to Sulphur

$$I_{2}\left(s\right) \quad + \quad H_{2}S\left(g\right) \qquad \qquad \qquad \qquad \qquad \qquad 2HI\left(g\right) \; + \; S\left(s\right)$$

$$Br_2(l) + H_2S(g) \longrightarrow 2HBr(g) + S(s)$$

(iii) Thiosulphate ions to different products:

$$2S_{2}O_{3}^{2-}(aq) + I_{2}(aq) \longrightarrow S_{4}O_{6}^{2-}(aq) + 2I^{-}(aq)$$

$$S_{2}O_{3}^{2-}(aq) + Cl_{2}(g) + H_{2}O(l) \longrightarrow SO_{4}^{2-}(aq) + S(s) + 2Cl^{-}(aq) + 2H^{+}(aq)$$

$$S_{2}O_{3}^{2-}(aq) + 4Cl_{2}(g) + 5H_{2}O(l) \longrightarrow 2SO_{4}^{2-}(aq) + 10H^{+}(aq) + 8Cl^{-}(aq)$$
In excess Cl_{2}

Similar reactions occur for bromine.

- **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.
- (c) State what is observed when chlorine gas is bubbled through a solution of potassium iodide hence write the equation of reaction

COMPOUNDS OF HALOGENS

(a) Hydrides/ Halogen acids

	HF	HCl	HBr	HI
Bond Energy (KJmol ⁻¹)	556	431	336	229
B.p.t (°C)	+19.9	-85	-66.7	-35.4
Ka	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 releases a proton.

HF slightly ionizes in dilute solution as:

$$HF (aq) \longrightarrow H^+ (aq) + F^- (aq)$$

N.B. When concentrated, HF is a stronger acid than in dilute solution . Hydroflouric acid dissociates as follows

$$HF (aq) \longrightarrow H^+ (aq) + F^- (aq)$$

The fluoride ions formed associate with more hydrogen fluoride forming hydrogen difluoride ion

2HF (aq)
$$\longrightarrow$$
 H⁺ (aq) + HF₂⁻ (aq)

More HF molecules dissociate to restored the used fluoride ions leading to release more protons which make the solution more acid

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

2HBr (aq) + Mg (s)
$$\longrightarrow$$
 MgBr₂ (aq) + H₂ (g)

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.

2HBr (aq) +
$$H_2SO_4$$
 (aq) \longrightarrow Br_2 (l) + SO_2 (g) + $2H_2O$ (l)

However, Conc. Hydrochloric acid can be oxidized by the stronger oxidizing agents such as MnO₂, PbO₂ and KMnO₄

$$MnO_2(s) + 4HCl(aq)$$
 \longrightarrow $Cl_2(g) + 2H_2O(l) + MnCl_2(aq)$

$$PbO_2(s) + 4HCl(aq)$$
 \longrightarrow $Cl_2(g) + 2H_2O(l) + PbCl_2(aq)$

$$2MnO_4$$
 (aq) +10 Cl (aq) + 16H (aq) \longrightarrow 5Cl₂ (g) +8H₂O (l) +2Mn²⁺ (aq)

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

$$6HF (aq) + SiO_2 (s)$$
 \longrightarrow $H_2SiF_6 (aq) + 2H_2O (l)$

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.

$$Cl_2(g) + H_2O(1) \longrightarrow HOCl(aq) + HCl(aq)$$

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

$$Cl_2(g) + 2OH^-(aq) \longrightarrow OCl^-(aq) + Cl^-(aq) + H_2O(l)$$

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

$$3OCl^{-}(aq)$$
 \longrightarrow $ClO_3^{-}(aq) + 2Cl^{-}(aq)$

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

$$2OCl^{-}(aq) \longrightarrow O_2(g) + 2Cl^{-}(aq)$$

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

$$2H^{+}(aq) + I^{-}(aq) + OCl^{-}(aq) \rightarrow I_{2}(aq) + Cl^{-}(aq) + H_{2}O(l)$$

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

$$ClO^{-}(aq) + 2H^{+}(aq) + Cl^{-}(aq) \longrightarrow Cl_{2}(g) + H_{2}O(l)$$

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.

$$3Cl_2(g) + 6OH^-(aq)$$
 $ClO_3^-(aq) + 5Cl^-(aq) + 3H_2O(l)$

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

$$ClO_3^-(aq) + 6H^+(aq) + 6e$$
 $Cl^-(aq) + 3H_2O(l)$

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

$$6Fe^{2+}(aq) + 6H^{+}(aq) + ClO_{3}^{-}(aq) \longrightarrow 6Fe^{3+}(aq) + Cl^{-}(aq) + 3H_{2}O(l)$$

$$ClO_3^-(aq) + 3SO_3^{2-}(aq) \longrightarrow 3SO_4^{2-}(aq) + Cl^-(aq)$$

$$ClO_3^-(aq) + 6H^+(aq) + 6I^-(aq)$$
 \longrightarrow $3I_2(aq) + 3H_2O(l) + Cl^-(aq)$

- **Qn**:(a) A solution of halate (V) ion YO₃⁻ 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 Na₂S₂O₃.5H₂O. 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:
- (i) ClO₂
- (ii) BrO₃
- (iii) I_2O_5
- (iv) Cl₂O₇
- (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, AB₃, AB₅ and AB₇where A- is a less electronegative atom with a vacant orbital and a higher oxidation state while B- is more electronegative.

Examples include: ICl -Iodine monochloride, ClF₃- Chlorine trifluoride, *Iodine pentafluoride IF*₅

Qn: *Draw the shapes of the following interhalogen compounds:*

- (i) Iodine pentafluoride.
- (ii) Chlorine trifluoride

QUALITATIVE ANALYSIS OF Cl., Br. and I.

1. Silver nitrate solution;

Procedure

Add a few drops of silver nitrate solution to the test solution

Observation

Cl⁻ White precipitate

Br Pale yellow precipitate

I⁻ Yellow precipitate

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

Procedure

Add a few drops of lead(II) nitrate solution to the test solution

Observation

Cl- white precipitate

Br pale yellow precipitate

I yellow precipitate

The precipitate dissolves on heating and recrystallizes on 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 ns²np²where n is the principal quantum number.

Elements	Melting point	Density	Electronic cofiguration
	(°C)		
Carbon	4000	2.25(graphite),	$1s^2 2s^2 2p^2$
		3.5(Diamond)	
Silicon	1680	2.33	$1s^2 2s^2 2p^2 3s^2 3s^2 3p^2$
Germanium	1210	5.35	$1s^2 2s^2 2p^2 3s^2 3s^2 3p^2_{3d}{}^{10} 4s^2 4p^2$
Tin	505	7.28(white),	$1s^2$
		5.75(grey)	$2s^22p^23s^23s^23p^2_{3d}^{10}4s^24p^24s^24p^2$
Lead	600	11.3	$1s^2 2s^2 2p^2 3s^2 3s^2 3p^2 4s^2 4p^2$

1. Existence

Carbon exists as graphite, diamond and amorphous carbon. Silicon occurs as Silica (SiO₂). Tin exist as grey tin and white tin. Lead occurs as an ore in form of galena (PbS)

2. **Melting point.**

The melting points of groupIV 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 nS^2 electrons become more reluctant to participitate 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

$$PbCl_{4}\left(l\right) \longrightarrow \qquad \qquad PbCl_{2}\left(s\right) \quad + \quad Cl_{2}\left(g\right)$$

Carbon monoxide is readily oxidized to carbon dioxide by air

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

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

$$2PbO_2(s)$$
 \longrightarrow $2PbO(s) + O_2(g)$

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 long chains or 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.

$$H_2O\left(g\right)$$
 + $C\left(s\right)$ \longrightarrow $CO\left(g\right)$ + $H_2\left(g\right)$

Ge and Sn do not react with water.

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

$$Si(s) + 2H_2O(g)$$
 \longrightarrow $SiO_2(s) + 2H_2(g)$

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

$$2Pb(s) + 2 H_2O(l) + O_2(g)$$
 \longrightarrow $2Pb(OH)_2(s)$

2. Air

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

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

$$Si(s) + O_2(g) \longrightarrow SiO_2(s)$$

$$2Pb(s) + O_2(g)$$
 \longrightarrow $2PbO(s)$

However in limited amount of air, Carbon forms carbon monoxide

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

3. Acids

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

$$NO_3^-(aq) + 4 Sn(s) + 10 H^+(aq)$$
 \longrightarrow $4 Sn^{2+}(aq) + NH_4^+(aq) + 3 H_2O(l)$

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

$$Si(s) + 6 HF(aq)$$
 \longrightarrow $H_2SiF_6(aq) + 2 H_2(g)$

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

$$3Sn(s) + 4HNO_3(aq) \longrightarrow 3SnO_2(s) + 4NO(g) + 2H_2O(l)$$

$$C(s) + 4HNO_3(aq)$$
 \longrightarrow $CO_2(g) + 4NO_2(g) + 2H_2O(l)$

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

$$3Pb(s) + 8HNO_3(aq) \longrightarrow 3Pb(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

Hot sulphuric acid oxidizes carbon, tin lead and germanium

$$Sn(s) + 4H_2SO_4(aq)$$
 \rightarrow $Sn(SO_4)_2(aq) + 2SO_2(g) + 4H_2O(l)$

$$C(s) + 2H_2SO_4(aq) \longrightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$$

Pb (s)
$$+ 2H_2SO_4$$
 (aq) \longrightarrow PbSO₄ (s) $+ SO_2$ (g) $+ 2H_2O$ (l)

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

$$\operatorname{Sn}(s) + 2\operatorname{HCl}(aq) \longrightarrow \operatorname{SnCl}_2(aq) + \operatorname{H}_2(q)$$

Pb (s)
$$+ 2$$
 HCl (aq) \longrightarrow PbCl₂ (aq) $+$ H₂ (g)

N.B. lead (II) chloride is sparingly soluble in water but highly soluble in Conc. Acid due formation of a complex. I.e. PbCl₄²⁻

4. Alkalis

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

Si (s) + 2OH⁻ (aq) + H₂O (l)
$$\longrightarrow$$
 SiO₃²⁻ (aq) + 2H₂ (g)
Ge (s) + 2OH⁻ (aq) + H₂O (l) \longrightarrow GeO₃²⁻ (aq) + 2H₂ (g)
Sn (s) + 2OH⁻ (aq) + 2 H₂O (l) \longrightarrow Sn(OH)₄²⁻ (aq) + 2H₂ (g)
Pb(s) + 2OH⁻ (aq) + 2H₂O (l) \longrightarrow Pb(OH)₄²⁻ (aq) + 2H₂ (g)

5. Non- metals

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

$$Sn (s) + 2HCl (g)$$
 \longrightarrow $SnCl_2(s) + H_2 (g)$
 $Sn (s) + 2Cl_2 (g)$ \longrightarrow $SnCl_4 (l)$
 $Pb (s) + Cl_2 (g)$ \longrightarrow $PbCl_2 (s)$
 $Si (s) + 2Cl_2 (g)$ \longrightarrow $SiCl_4 (g)$

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:

HCOOH (aq)
$$\xrightarrow{\text{Conc.H}_2\text{SO}_4}$$
 CO (g) $+$ H₂O (l)

H₂C₂O₄(aq) $\xrightarrow{\text{Conc.H}_2\text{SO}_4}$ CO₂ (g) $+$ CO (g) $+$ H₂O (l)

GeO₂ (s) $+$ Ge (s) $\xrightarrow{\text{Cop}_2}$ 2GeO (s)

SiO₂ (s) $+$ Si (s) $\xrightarrow{\text{Cop}_3}$ 2SiO (s)

Pb(OH)₂ (s) $\xrightarrow{\text{PbO}}$ (s) $+$ H₂O (g)

SnC₂O₄ (s) $\xrightarrow{\text{SnO}}$ SnO (s) $+$ CO₂ (g) $+$ CO (g)

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

PbO (s) +2 OH⁻ (aq) + H₂O (l)
SnO (s) +2OH⁻ (aq) + H₂O (l)
Sn (OH)₄

$$CO (g) + NaOH (aq) \xrightarrow{150^{\circ}C} HCOONa (aq)$$

With Acids

SnO (s) + 2 H⁺ (aq)
$$\longrightarrow$$
 Sn²⁺ (aq) + H₂O (l)

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) Ans =90%

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

$$Pb_3O_4(s) + 4HNO_3(aq)$$
 \longrightarrow $2Pb(NO_3)_2(aq) + PbO_2(s) + 2H_2O(l)$

The rest of the oxides are prepared by heating the metals with oxygen.

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

$$2PbO_2(s)$$
 \longrightarrow $2PbO(s) + O_2(g)$

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
SnO_2	Amphoteric	Giant ionic and giant
PbO ₂	Amphoteric	Metallic

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

$$PbO_2(s) + 4HCl(aq)$$
 \longrightarrow $Cl_2(g) + PbCl_2(s) + 2H_2O(l)$

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

$$PbO_{2}(s) + 4HCl(aq) + 2Cl^{-}(aq)$$
 \longrightarrow $PbCl_{6}^{2-}(aq) + 2H_{2}O(l)$

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

Qn: Discuss the reactions of Lead(IV) oxide 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.

$$2PbO_{2}(s) + 2H_{2}SO_{4}(aq)$$
 \longrightarrow $2PbSO_{4}(s) + O_{2}(g) + 2H_{2}O(l)$

The same reaction occurs with Pb₃O₄

- **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.

• Preparation.

Are prepared by reduction of their tetrachlorides with lithium aluminum tetra hydrides at 0° C in ether.

$$SiCl_4(l) + LiAlH_4(l)$$
 \longrightarrow $SiH_4(l) + LiCls) + AlCl_3(s)$

- 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 carbondioxide 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.

$$SiCl_4(l) + 2H_2O(l)$$
 \longrightarrow $SiO_2(s) + 4HCl(g)$

$$SnCl_4(s) + 4H_2O(l)$$
 \longrightarrow $SnO_2.2H_2O(s) + 4HCl(g)$

$$PbCl_4(l) + 2H_2O(l)$$
 \longrightarrow $PbO_2(s) + 4HCl(g)$

(b) Dichlorides

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

$$Sn(s) + 2HCl(g)$$
 \longrightarrow $SnCl_2(s) + H_2(g)$

$$Pb(s) + Cl_2(g)$$
 \longrightarrow $PbCl_2(s)$

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

$$SnCl_2(s) + H_2O(l)$$
 \longrightarrow $Sn(OH)Cl(s) + HCl(aq)$

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

$$SnCl_{2}(s) + 2H_{2}O(l)$$
 \longrightarrow $Sn(OH)_{2}(s) + 2HCl(aq)$

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

$$PbCl_2(s)$$
 \longrightarrow $Pb^{2+}(aq) + 2Cl^{-}(aq)$

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)

$$PbCl_2(s) + 2Cl^-(aq)$$
 \longrightarrow $PbCl_4^{2-}(aq)$

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

$$Sn^{2+}$$
 (aq) + S^{2-} (aq) \longrightarrow SnS (s)

$$Pb^{2+}(aq)$$
 $S^{2-}(aq)$ \longrightarrow $PbS(s)$

- **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.
- (a) Identify the substances A-E inclusive
- (b) 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 +121KJmol⁻¹ respectively. The average bond energy of Si-Cl bond is +383KJmol⁻¹
- (a) Determine the average bond energy of Sn-Cl bond
- (b) 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+}

THIRD SHORT PERIOD OF PERIODIC TABLE

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	799	1020	1000	1260	1530
Atomic radius	1.57	1.36	1.28	1.17	1.10	1.04	0.99	
Electron Affinity	-20	+67	-30	-135	-60	-200	-364	
Oxidation states	+1	+2	+3	+4	+3, +5	2,+4,+	+1,+3,-	
						6,	1,+5, +7	
Structure	Close packed	Close packe d	Close packed	Giant molecu lar	→ 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 van der waals forces of attraction
- From phosphorous-Sulphur, these are discrete molecules which are as P_4 and S_8 held by weak Van der 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 therefore the magnitude of the van der waals 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. With Chlorine

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

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

Aluminium forms a covalent chloride which dimerises in the vapour phase

$$2Al(s) + 3Cl_2(g)$$
 \longrightarrow $2AlCl_3(s)$

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.

$$Si(s) + 2Cl_2(g)$$
 \longrightarrow $SiCl_4(l)$

$$2P(s) + 5Cl_2(g)$$
 \longrightarrow $2PCl_5(s)$

$$2P(s) + 3Cl_2(g)$$
 \longrightarrow $2PCl_3(g)$

$$2S (l) + Cl2 (g) \longrightarrow S2Cl2 (l)$$

2. Oxygen

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

$$2Na(s) + O_2(g)$$
 \longrightarrow $Na_2O_2(s)$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

$$Si(s) + O_2(g)$$
 \longrightarrow $SiO_2(s)$

$$P_4(s) + 3O_2(g) \longrightarrow P_4O_6(s)$$

$$P_{4}\left(s\right) \qquad + \ 5O_{2}\left(g\right) \qquad \longrightarrow \quad P_{4}O_{10}\left(s\right)$$

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

3. Hydrogen

Sodium and Magnesium burn vigorously in hydrogen gas to form ionic hydrides.

$$2Na(s) + H_2(g)$$
 \longrightarrow $2NaH(s)$

$$Mg(s) + H_2(g) \longrightarrow MgH_2(s)$$

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.

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(g)$$

$$S(l) + H_2(g) \longrightarrow H_2S(g)$$

4. WITH 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

$$Na(s) + 2HNO_3(aq) \longrightarrow NaNO_3(aq) + NO_2(g) + H_2O(l)$$

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.

$$S(s) + 4HNO_3(aq) \longrightarrow SO_2(g) + 4NO_2(g) + 2H_2O(l)$$

$$P_4(s) + 10HNO_3(aq) + H_2O(l) \longrightarrow 4H_3PO_4(aq) + 5NO_2(g) + 5NO(g)$$

COMPOUNDS OF PERIOD 3 ELEMENTS

1. Chlorides

Chlorides	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃ ,	S ₂ Cl ₂ ,	Cl ₂
					PCl ₅		
b.p.t	1465	1418	423	57	74, 164	138	-35
mpt	808	714	192	-68	160	-76	-101
Bond	ionic	Ionic	•	— Coval	ent —		
structure	Giant	Giant	4	— Simpl	e molecula	r structure	
	ionic	ionic					

Reaction of the chlorides with water

Sodium chloride dissociates in water to form neutral aqueous solution.

Aluminium chloride undergoes hydrolysis due to high charge density and aluminium ions become heavily hydrated in solution as Al $(H_2O)_6^{3+}$

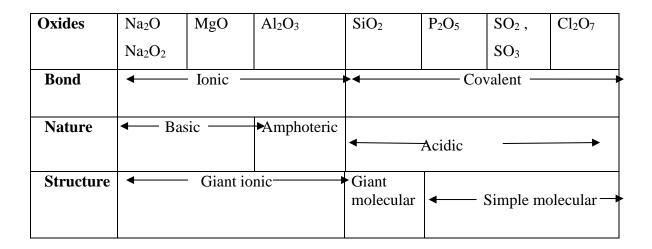
The hydrated ions undergo hydrolysis to release a proton in solution which causes the solution to be acidic

$$Al(H_2O)_6^{3+}$$
 (aq) = $[Al(H_2O)_5OH]^{2+}$ (aq) + H^+ (aq)

The other chlorides react with water to form hydrogen chloride

SiCl₄ (l) + 2H₂O (l)
$$\longrightarrow$$
 SiO₂ (s) + 4HCl (g)
PCl₅ (l) + 4H₂O (l) \longrightarrow H₃PO₄ (aq) + 5HCl (g)
2S₂Cl₂ (s) + 2H₂O (l) \longrightarrow 3S (s) + SO₂ (g) + 4HCl (aq)
Cl₂ (g) + H₂O (l) \longrightarrow HCl (aq) + HOCl (aq)

2. Oxides



Reaction with water

Sodium oxide is highly soluble in water

$$Na_2O(s) + H_2O(l)$$
 2NaOH (aq)

Magnesium Oxide is slightly soluble in water

$$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(aq)$$

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

Oxides of Phosphorous, chlorine and Sulphur are acidic oxide.

$$P_4O_{10}(s) + 6H_2O(l)$$
 \longrightarrow $4H_3PO_4(aq)$ $SO_2(g) + H_2O(l)$ \longrightarrow $H_2SO_3(aq)$ $SO_3(g) + H_2O(l)$ \longrightarrow $H_2SO_4(aq)$ $Cl_2O_7(l) + H_2O(l)$ \longrightarrow $2HClO_4(aq)$

Reaction with sodium hydroxide solution

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

$$Al_2O_3 (s) + 2OH^- (aq) + 3H_2O (l)$$
 $-2[Al (OH)_4]^- (aq)$
 $SiO_2 (s) + 2OH^- (aq)$ $-SO_3^{2-} (aq) + H_2O (l)$
 $SO_2 (g) + 2OH^- (aq)$ $-SO_3^{2-} (aq) + H_2O (l)$

$$Cl_2O_7(1) + 2OH^-(aq) - \frac{2Cl\Theta_4}{(aq)} + H_2O(1)$$

3. Hydrides

Hydrides	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H_2S	HCl
Bond	← Ion	ic —	•	•	C ovalent		
Structure	← Gia	nnt ionic —		>	Simple mol	ecular	

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.

$$SiH_4(g) + 2OH^-(aq) + H_2O(l)$$
 $-SiO_3^{2-}(aq) + 4H_2(g)$

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

EXTRACTION OF ALUMINIUM

Ore: Bauxite Al₂O₃. 2H₂O

Bauxite is roasted to convert Iron (II) Oxide (impurity) to Iron (III) Oxide and drive off the water of crystallization.

The roasted ore is Crushed to powder and heated with concentrated sodium hydroxide solution to remove aluminum oxide from the impurities.

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

$$Al_2O_3 (s) + 2OH^- (aq) + 3H_2O (l)$$
 $\longrightarrow 2Al(OH)_4^- (aq)$
 $SiO_2 (s) + 2OH^- (aq)$ $\longrightarrow SiO_3^2 (aq) + H_2O (l)$

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

$$2Al(OH)_4^-(aq) + CO_2(g) - \frac{2Al(\Theta H)_3(s) + CO_3^{2-}(aq) + H_2O(l)}{2Al(OH)_4^-(aq) + CO_3^{2-}(aq)}$$

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

Al
$$(OH)_4^ (aq)$$
 \longrightarrow Al $(OH)_3$ $(s) + OH^ (aq)$

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:

$$2O^{2-}(1)$$
 $O_2(g) + 4e$

N.B. The disadvantage of using low voltage is that a lot of energy is used and anode is replaced several time since it burns off in oxygen produced.

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

- (a) (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.
- (c) Explain briefly Aluminium utensils should not be washed using Soap.
- (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		Configuration
		number	
Scandium	Sc	21	$1S^22S^22P^63S^23P^64S^23d^1$
Titanium	Ti	22	$[Ar]4S^23d^2$

Vanadium	V	23	$[Ar]4S^23d^3$
Chromium	Cr	24	$[Ar]4S^13d^5$
Manganese	Mn	25	$[Ar]4S^23d^5$
Iron	Fe	26	$[Ar]4S^23d^6$
Cobalt	Co	27	$[Ar]4S^23d^7$
Nickel	Ni	28	$[Ar]4S^23d^8$
Copper	Cu	29	[Ar]4S ¹ 3d ¹⁰
Zinc	Zn	30	$[Ar]4S^23d^{10}$

(a) Explain why Fe²⁺ is easily oxidized to Fe³⁺ On:

- (b) Write the electronic configuration of the following ions
- (i) Fe^{2+} (ii) Fe^{3+} (iii) Cr^{3+}

Soln: (a) Because Fe³⁺ is has 3d⁵ subshell electrons which is thermodynamically stable compared to Fe²⁺ with 3d⁶ which is unstable.

- (b) (i) $1S^22S^22P^63S^23P^63d^6$ (ii) $1S^22S^22P^63S^23P^63d^5$ (iii) $1S^22S^22P^63S^23P^63d^3$

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 3Selectron 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 most electron increases resulting into decrease 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. Ionization 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	\mathbf{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 red 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					
				+7					

Some of the compounds with the oxidation state include:

Ti	V	Cr	Mn	Fe	Со	Ni	Cu
TiO,TiCl ₂	VCl ₂ ,	CrCl ₂ ,	MnO,MnCl ₂ ,	FeCl ₂	CoO,CoCl ₂ ,	NiO	CuO
Ti_2O_3 ,	V_2O_3 ,	Cr ₂ O ₃ ,CrCl ₃	MnCl ₃ ,	FeCl ₃	$Co(NH_3)_6^{3+}$	Ni ₂ O ₃ .xH ₂ O	Cu ₂ O
TiCl ₃	VO_2	CrCl ₄ ,	MnO_2 ,				CuCl
TiO ₂ ,	V_2O_5	CrO_3 ,	MnO_4^{2-}				CuCl ₂
TiCl ₄		$\text{Cr}_2\text{O}_7^{2\text{-}}$	MnO_4				

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

Since Zinc has one oxidation state, 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 metalin the following complex

(i) K₂Cr₂O₇

(iii) [Co (NH₃)₅SO₄]Br

(ii) MnO₄²-

(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 arises due to spinning of unpaired electrons about their axes which generates electric current

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. The remaining visible light which is not absorbed is reflected as that colour shown by a transition metal/ion.

Examples of hydrated ions include

$$V(H_2O)_6{}^{2+} \text{ - Violet} \hspace{1cm} Mn(H_2O)_6{}^{2+} \text{ - pale pink} \hspace{1cm} Fe(H_2O)_6{}^{2+} \text{ - Pale green}$$

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

Nature of Ligand and Oxidation state of the metal

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

4. Catalytic activity

Transition elements and their compounds act as catalysts in 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.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \xrightarrow{Fe^{2+}(aq)} 2SO_4^{2-}(aq) + I_2(aq)$$

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 van der waals forces.

Examples include; V₂O₅- 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 an ion or molecule with lone pairs of electrons linked to the central metal ion by a dative bond

Co-ordination number is the number of ligands molecules that form dative bonds with central metal ion 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 central metal i.e.

(a) Monodentate ligands / Unidentate ligands

These are ligands with one donor atom per ligand molecule.e.g.NH₃, H₂O, CH₃NH₂, Cl⁻

(b) Polydentate/ Chelating ligands

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

H₂NCH₂CH₂NH₂ (Ethane-1,2-diamine) -with two donor atoms therefore it is called bidentate

Also ligands can be classified based on charges;

•	Neutral ligand	Anionic ligands	Cationic ligand
	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-di	iamine 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 it oxidation state.

Examples include:

[CuCl₄]²⁻ tetrachlorocuprate (II)ion

SiF₆²-Hexafluorosilicate(IV)ion

 $[Cr(OH)_5NH_3]^{3-}$ pentahydroxoamminechromate(II)ion

 $[CoCl_4(H_2O)_2]^{\bar{}} tetrachlorodia quacobal tate (III) ion$

LiAlH₄Lithiumtetrahydridoaluminate(III)

(c) Neutral complexes

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

- Ni(CO)₄ Tetracarbonylnickel.
- V(CO)₆ hexacarbonylvanadium.

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

 $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

Bromopentaamminecobalt(III)sulphate Sulphatopentaamminecobalt(III)bromide

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

[Co(NH₃)₅Br]SO₄ – white precipitate is formed

[Co(NH₃)₅SO₄]Br - No observable change

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

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

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

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

Soln:

(a) [Cr(H₂O)₆]Cl₃ Hexaaquachromium(III)chloride -violet

[Cr(H₂O)₅Cl]Cl₂.H₂O Chloropentaaquachromium(III)chloride -light green

[Cr(H₂O)₄Cl₂]Cl.2H₂O Dichlorotetraaquachromium(III)chloride -dark green

(b) 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;

$$M^{n+}(aq) + 6L(aq) = [ML_6]^{n+}(aq)$$

The equilibrium expression is written as:

$$K_{eq} = \frac{[[ML_6]^{n+}]}{[[L]^6][M^{n+}]}$$
 where K_{eq} 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 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.

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

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

$$CuCl_4^{2-}$$
 (aq) + 4NH₃ (aq) \longrightarrow [Cu(NH₃)₄]²⁺ (aq) + 4Cl⁻ (aq)

COPPER

Extraction:

Ores:

- Copper Pyrites (CuFeS₂)- principal ore
- Copper glance(Cu₂S)
- Cuprite(CuO)
- Malachite (CuCO₃.Cu(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

$$2\text{CuFeS}_2(s) + 4\text{O}_2(g)$$
 \rightarrow $\text{Cu}_2\text{S}(s) + 2\text{FeO}(s) + 3\text{SO}_2(g)$

(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

$$FeO(s) + SiO_2(s)$$
 FeSiO₃(l)

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 sulphur dioxide gas.

$$2Cu_2S(s) + 3O_2(g)$$
 $\longrightarrow 2Cu_2O(l) + 2SO_2(g)$

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

$$2Cu_2O(l) + Cu_2S(s)$$
 \longrightarrow $6Cu(l) + SO_2(g)$

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

At anode: Cu (s)
$$\longrightarrow$$
 Cu²⁺ (aq) + 2e

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

$$Cu(s) + 2H_2SO_4(aq) \longrightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$$

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

$$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

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

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

$$2Cu (s) + O2 (g) \xrightarrow{300^{\circ}C} 2CuO (s)$$

$$4Cu (s) + O2 (g) \xrightarrow{1000^{\circ}C} 2Cu2O (s)$$

$$Cu (s) + Cl2 (g) \xrightarrow{} CuCl2 (s)$$

(d) Hot copper foil glows red in sulphur vapour forming copper(I) sulphide

$$2Cu(s) + S(g) \longrightarrow Cu_2S(s)$$

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.

$$Cu^{+}(aq) + e$$
 \longrightarrow $Cu(s)$ $\Delta H = -602 K J mol^{-1}$ $Cu^{2+}(aq) + 2e$ \longrightarrow $Cu(s)$ $\Delta H = -795 K J mol^{-1}$

 \therefore The enthalpy of conversion of Cu^+ to Cu^{2+} is -409KJmol⁻¹and 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 Aldehydes in the presence of an alkali

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

$$Cu_2O(s) + 2H^+ (aq)$$
 $Cu_2O(s) + C(s)$ $Cu_2O(s) + C(s)$ $Cu_2O(s) + C(s)$ $Cu_2O(s) + C(s)$ $Cu_2O(s) + C(s)$

(b) Copper (I) chloride

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

$$CuCl_2$$
 (aq) + Cu (s) $-2e$ uCl (s)

It dissolves in excess hydrochloric acid to form a colourless solution

$$CuCl(s) + Cl-(aq)$$
 \longrightarrow $[CuCl_2]^-(aq)$

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

CuCl (s)
$$+ 2NH_3$$
 (aq) $- [Cu(NH_3)_2]^+$ (aq) $+ Cl^-$ (aq)

- **Qn:** 8.0g of a copper ore was leached with dilute sulphuric acid and the resultant solution diluted to 250cm³. Excess 10% potassium iodide was added to 30cm³ of the solution. The iodine liberated 23.5cm³ of 0.05M sodium thiosulphate solution for complete reaction.
- (a) Write all the equations of reactions involved.
- (b) Calculate the percentage of copper in ore

- (c) Describe the application of copper (I) compounds in distinguishing organic compounds and synthesis
- (d) Explain the similarity between silver (I) and copper (I) ions
- **Qn:** A double salt $Cu(NH_3)_xCl_y.zH_2O$ 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

$$CuCO_3$$
 (s) CuO (s) + CO_2 (g)

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

CuO (s)
$$+ 2 H^+$$
 (aq) $-$ Cu \rightarrow (aq) $+ H_2O$ (l)

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

$$3CuO(s) + CH_4(g)$$
 $3Card(s) + 2H_2O(l) + CO$
 $CuO(s) + C(s)$ $Cu(s) + CO(g)$

(b) Copper (II) hydroxide

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

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

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

Cu (OH)₂(s) + 4NH₃ (aq)
$$\frac{\text{[Cw}(NH_3)_4]^{2+}}{\text{[aq)}}$$
 + 2OH⁻ (aq)

(c) Copper (II) chloride

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

$$\operatorname{Cu}(s) + \operatorname{Cl}_2(g)$$
 — $\operatorname{CuOl}_2(s)$

The chloride dissolves in concentrated hydrochloric acid to form a yellow- green solution of tetrachloro cuprate(II)

$$CuCl_2(s) + 2Cl-(aq)$$
 [CuCl₄]²⁻ (aq)

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 $[Cu(H_2O)_6]^{2+}$ and this undergoes hydrolysis to release hydrogen ions in solution which causes the solution to be acidic

$$[Cu(H_2O)_6]^{2+} \left(aq\right) = \qquad \qquad [Cu(H_2O)_5OH]^+ \left(aq\right) \ + \ H^+ \left(aq\right)$$

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 electronic configuration $1S^22S^22P^63S^23P^64S^23d^6$

Extraction

Ore:

Haematite (Fe₂O₃)

Spathic (siderite) (FeCO₃)

Magnetite(Fe₃O₄)

Iron pyrites (FeS₂)

The mixture of haematite, coke and limestone are fed into the furnace from top. Air enriched with 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

$$C(s) + O_2(g)$$
 $\longrightarrow CO_2(g)$ $C(s) + CO_2(g)$ $\longrightarrow 2CO(g)$

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

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(l) + 3CO_2(g)$$

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

$$CaCO_3 (s) \longrightarrow CaO (s) + CO_2 (g)$$
 $CaO (s) + SiO_2 (s) \longrightarrow CaSiO_3 (l)$

The slag 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 slag 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
- **N.B.** If Iron (II) carbonate or Sulphide is used; it is concentrated by froth floatation and roasted in air to convert it to an oxide

$$2\text{FeCO}_3(s) + \frac{1}{2}O_2(g)$$
 Fe₂O₃(s) + 2 CO₂(g)

PROPERTIES OF IRON

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

$$3\text{Fe}\left(s\right) + 2O_{2}\left(g\right)$$
 Fe₃O₄ $\left(s\right)$

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

$$3Fe(s) + 4H_2O(g)$$
 Fe₃O₄(s) + $4H_2(g)$

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

2Fe (s) + xH₂O (l) +
$$\frac{3}{2}$$
 O₂ (g) — Fe₂O₃.xH₂O (l)

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

Fe (s) + S (s) FeS (s)

2Fe (s) +
$$3 \text{ Cl}_2$$
 (g) \longrightarrow 2FeCl₃ (s)

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

Fe (s) +
$$2H^+$$
 (aq) \longrightarrow Fe²⁺ (aq) + H_2 (g)

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

$$2Fe(s) + 6H_2SO_4(l) \longrightarrow Fe_2(SO_4)_3(aq) + 3SO_2(g) + 6H_2O(l)$$

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

$$FeC_2O_4(s)$$
 \longrightarrow $FeO(s) + CO_2(g) + CO(g)$

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

FeO (s) +
$$2H^+$$
 (aq) Fe²⁺ (aq) + H_2O (l)

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

$$\frac{1}{2}O_{2}(g) + 2FeO(s)$$
 Fe₂O₃(s)

(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

$$2\text{Fe}(OH)_2(s) + \frac{1}{2}O_2(g) + H_2O(1)$$
 \longrightarrow $2\text{Fe}(OH)_3(s)$

An aqueous solution of iron (II) salts contains $[Fe(H_2O)_6]^{2+}$ and don't undergo hydrolysis due to low charge density

(c) Iron (II) sulphate (FeSO₄.7H₂O)

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

$$3Fe^{2+}$$
 (aq) $+4H^{+}$ (aq) $+NO_{3}^{-}$ (aq) \longrightarrow $3Fe^{3+}$ (aq) $+NO$ (g) $+2H_{2}O$ (l) $2NO$ (g) $+O_{2}$ (g) \longrightarrow $2NO_{2}$ (g)

(ii) Chlorine gas

The green solution turns yellow

$$2Fe^{2+}$$
 (aq) + Cl_2 (g) \longrightarrow $2Fe^{3+}$ (aq) + $2Cl^{-}$ (aq)

(iii) Hydrogen peroxide

The green solution turns yellow

$$H_2O_2$$
 (aq) + $2H^+$ (aq) + $2Fe^{2+}$ (aq) \longrightarrow $2Fe^{3+}$ (aq) + $2H_2O$ (l)

(iv) Potassium dichromate

$$6Fe^{2+}\left(aq\right) + Cr_{2}O_{7}^{2-}\left(aq\right) \\ + 14H^{+}\left(aq\right) \\ - - - \\ \bullet \\ Fe^{3+}\left(aq\right) \\ + 2Cr^{3+}\left(aq\right) \\ + 7H_{2}O\left(l\right) \\ + Cr^{3+}\left(aq\right) \\ + Cr^{3+}\left(a$$

(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 $[Fe(H_2O)_6]^{3+}$ hence it undergoes hydrolysis to release protons which cause the solution to be acidic

$$[Fe(H_2O)_6]^{3+}$$
 (aq) $=$ $[Fe(H_2O)_5OH]^{2+}$ (aq) $+$ H^+ (aq)

Complete hydrolysis is represented as

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

(a) Iron (III) oxide

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

$$2\text{FeSO}_4(s)$$
 \rightarrow $\text{Fe}_2\text{O}_3(s) + \text{SO}_2(g) + \text{SO}_3(g)$

It is basic and dissolves in dilute mineral acids

$$Fe_2O_3$$
 (s) + 6HCl (aq) \longrightarrow 2FeCl₃ (aq) + 3H₂O (l)

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

$$2\text{Fe}_2\text{O}_3(s) + 3\text{C}(s)$$
 \longrightarrow $4\text{Fe}(s) + 3\text{CO}_2(g)$

(b) Iron (III) sulphate

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

$$2FeSO_4 (aq) + 2H_2SO_4 (aq)$$
 $\longrightarrow Fe_2(SO_4)_3 (aq) + SO_2 (g) + 2H_2O (l)$

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.

$$[Fe(H_2O)_6]^{3+}$$
 (aq) $=$ $[Fe(H_2O)_3(OH)_3]$ (s) $+ 3H^+$ (aq)

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

$$H^{+}(aq) + CO_{3}^{2-}(aq) \longrightarrow CO_{2}(g) + H_{2}O(l)$$

REDUCTION OF Fe³⁺ TO Fe²⁺

(i) Zinc and hydrochloric acid

$$Zn(s) + 2Fe^{3+}(aq) \longrightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$

(ii) Hydrogen sulphide gas

The brown solution turns pale green and yellow solid is deposited

$$S^{2-}(aq) + 2 Fe^{3+}(aq) \longrightarrow 2Fe^{2+}(aq) + S(s)$$

(iii) Sulphur dioxide

The brown solution turns pale green

$$SO_2(g) + 2Fe^{3+}(aq) + 2H_2O(1) \longrightarrow 2Fe^{2+}(aq) + SO_4^{2-}(aq) + 4H^+(aq)$$

N.B. Fe³⁺ ions are confirmed by use of potassium hexacyanoferrate (II) solution, a dark blue precipitate is observed.

ZINC

The following a 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(ZnO)

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 in air to form the oxide

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

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

$$ZnO(s) + CO(g)$$
 \longrightarrow $Zn(g) + CO_2(g)$

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 nitride

$$Zn(s) + \frac{1}{2}O_2(g)$$
 ZnO(s)

$$3Zn(s) + N_2(g)$$
 Zn₃N₂(s)

Steam reacts with heated Zinc form Zinc oxide and Hydrogen gas

$$Zn(s) + H_2O(g) \longrightarrow ZnO(s) + H_2(g)$$

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

$$Zn(s) + 2H^{+}(aq)$$
 \longrightarrow $Zn^{2+}(aq) + H_{2}(g)$

Hot concentrated sulphuric acid oxidizes zinc to zinc sulphate

$$Zn(s) + 2H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + SO_2(g) + 2H_2O(1)$$

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

$$Zn(s) + 2H_2O(l) + 2OH^{-}(aq) \longrightarrow [Zn(OH)_4]^{2-}(aq) + H_2(g)$$

Compound of Zinc

Zinc oxide and zinc hydroxide are amphoteric compounds

$$ZnO(s) + 2H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_2O(l)$$

$$ZnO(s) + 2OH^{-}(aq) + H_{2}O(l) \longrightarrow [Zn(OH)_{4}]^{2-}(aq)$$

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

$$Zn(OH)_2(s) + 4 NH_3(aq)$$
 = $[Zn (NH_3)_4]^{2+}(aq)$

N.B In aqueous solution salts of Zinc are colourless due to $[Zn(H_2O)_4]^{2+}$ and are confirm 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

$$3Mn (s) + 2O_2 (g) \longrightarrow Mn_3O_4 (s)$$
 $3Mn (s) + N_2 (g) \longrightarrow Mn_3N_2 (s)$

$$Mn(s) + Cl_2(g) \longrightarrow MnCl_2(s)$$

$$Mn(s) + S(s) \longrightarrow MnS(s)$$

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

$$Mn(s) + H_2O(g) \longrightarrow Mn(OH)_2(s) + H_2(g)$$

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, and +7 but +2 is the most stable oxidation state due to thermodynamically stable half filled 3d- orbital

Mn2+

(a) Potassium permanganate

A mixture of potassium hydroxide, potassium chlorate and manganese (IV) oxide is fused. Hot water is added and carbon dioxide gas passed through the solution until it is purple(green traces are removed)

6KOH (aq) + KClO₃ (aq) + 3MnO₂ (s)
$$\longrightarrow$$
 3K₂MnO₄ (aq) + 3H₂O (l) + KCl (aq)

Carbon dioxide turns MnO_4^{2-} to MnO_4^{-} by disproportionation $3MnO_4^{2-}$ (aq) $+ 4H^+$ (aq) $-\frac{2MnO_4^{-}}{4}$ (aq) $+ MnO_2$ (s) $+2H_2O$ (l)

In neutral or alkaline solution the manganate (VII) is reduced to manganese (IV) oxide

$$MnO_4^-(aq) + 4H^+(aq) + 3e$$
 $MnO_2(s) + 2H_2O(l)$

In presence of manganese (IV) oxide, manganate (VII) is reduced to manganate (VI)

$$2MnO_{4}^{-}(aq) \ + \ MnO_{2}(s) \ + \ 4OH^{-}(aq) = 3MnO_{4}^{2-}(aq) \ + \ 2H_{2}O(l)$$

(b) Manganese (IV) oxide

It is black solid obtained by thermo-decomposition of manganese (II) nitrate

$$Mn (NO_3)_2 (s)$$
 \longrightarrow $MnO_2 (s) + 2NO_2 (g)$

It oxidizes:

Warm concentrated hydrochloric acid to chlorine

$$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$$

Oxalic acid or oxalate ions in presence of an acid to form carbon dioxide

$$MnO_2(s) + C_2O_4^{2-}(aq) + 4H^+(aq)$$
 $Mn\Theta(s) + 2CO_2(g) + 2H_2O(l)$

 Hot concentrated sulphuric acid to form oxygen, manganese (II) sulphate and water

$$2MnO_{2}(s) + 2H_{2}SO_{4}(aq) - \Theta_{2}(g) + 2MnSO_{4}(aq) + 2H_{2}O(l)$$

(c) Manganese (II) oxide

It is prepared by thermo-decomposition of manganese (II) carbonate or Manganese (II) oxalate

$$MnCO_3(s)$$
 \longrightarrow $MnO(s) + CO_2(g)$

The oxide is basic and reacts with oxygen at high temperatures to form trimanganese tetraoxide

MnO (s) + H⁺ (aq)
$$\longrightarrow$$
 Mn²⁺ (aq) + H₂O (l)
6MnO (s) + O₂ (g) \longrightarrow 2 Mn₃O₄ (s)

The mixed oxide reacts with acid to form manganese (II) ions and Manganese (III) salts which disproportionate to form manganese (II) salts and manganese (IV) oxide

$$Mn_3O_4(s) + 8H^+(aq)$$
 $Mn^{2+}(aq) + 2Mn^{3+}(aq) + 4H_2O(l)$ $2Mn^{3+}(aq) + 2H_2O(l)$ $Mn^{2+}(aq) + MnO_2(s) + 4H^+(aq)$

(d) In an aqueous solution, the salts exist as $[Mn (H_2O)_6]^{2+}$ which is a pale pink solution. The solution forms a white precipitate on addition of sodium hydroxide which is immediately turns brown due to aerial oxidation

$$Mn^{2+}$$
 (aq) + 2OH⁻ (aq) \longrightarrow Mn(OH)₂ (s)
 $4Mn(OH)_2$ (s) + O₂ (g) \longrightarrow 2Mn₂O₃.2H₂O (s)

When hydrogen sulphide gas is bubbled through a solution of Manganese (II) ions in presence of Ammonia, a pink precipitate of manganese (II) sulphide is formed.

Manganese (II) ions are oxidized to manganate (VII) by strong oxidizing agent such as lead (IV) oxide or Sodium bismuthate (V) in presence of concentrated nitric acid

$$2Mn^{2+}$$
 (aq) + $5BiO_3^-$ (aq) + $14H^+$ (aq) $\longrightarrow 2MnO_4^-$ (aq) + $5Bi^{3+}$ (aq) + $7H_2O(l)$
 $2Mn^{2+}$ (aq) + $5PbO_2$ (s) +2 H^+ (aq) $\longrightarrow 2MnO_4^-$ (aq) +5 Pb^{2+} (aq) + $2H_2O(l)$

CHROMIUM

It exists as the chrome iron ore

The following are some of the reactions of chromium:

(a) Non-metal

Chromium reacts with non-metals when heated

$$4Cr(s) + 3O_2(g)$$
 \longrightarrow $2Cr_2O_3(s)$

(b) Acids

Dilute mineral acids react to form blue solution of chromium (II) salt which turns green in air due to oxidation

$$Cr(s) + 2H^{+}(aq)$$
 \longrightarrow $Cr^{2+}(aq) + H_{2}(g)$ \longrightarrow $2Cr^{3+}(aq) + 2H^{+}(aq) + \frac{1}{2}O_{2}(g)$ \longrightarrow $2Cr^{3+}(aq) + H_{2}O(1)$

Hot concentrated sulphuric acid oxidizes Chromium to Chromium (III) sulphate and itself reduced to sulphur dioxide gas and water

$$2Cr(s) + 12H^{+}(aq) + 3SO_{4}^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_{2}(g) + 6H_{2}O(l)$$

(c) Sodium hydroxide solution

It reacts with hot sodium hydroxide solution to form a chromite and hydrogen gas

$$2Cr(s) + 6OH^{-}(aq) \longrightarrow 2CrO_3^{3-}(aq) + 3H_2(g)$$

On:

- (a) Discuss the reaction of chromium with:
- (i) Air (ii) Sulphuric acid

- (b) Compare the chemistry of Chromium and Aluminium in terms of the following themes
 - (i) Reaction with sodium hydroxide solution
- (ii) Nature of the oxide
- (iii) Nature of the chlorides

Compounds of chromium

Oxidation states are +2, +3 and +6

Chromium (III) compounds

The compounds exist as $[Cr(H_2O)_6]^{3+}$ and due to high charge density the solution are acidic due to hydrolysis.

$$[Cr(H_2O)_6]^{3+}_{(aq)} \longrightarrow [Cr(H_2O)_5OH]^{2+}_{(aq)} + H^{+}_{(aq)}$$

Chromium (III) Oxide

It is prepared by thermo-decomposition of Chromium (III) hydroxide as a green insoluble solid

$$2Cr(OH)_3$$
 (s) \longrightarrow Cr_2O_3 (s) + $3H_2O$ (l)

The oxide is stable and resistant to reduction by hydrogen and carbon monoxide

It is an amphoteric oxide i.e.

$$Cr_2O_3(s) + 6H^+(aq)$$
 \longrightarrow $2Cr^{3+}(aq) + 3H_2O(l)$ $Cr_2O_3(s) + 6OH^-(aq)$ \longrightarrow $2CrO_3^{3-}(aq) + 3H_2O(l)$

Chromium (III) hydroxide

It is precipitated as a green solid on addition of sodium hydroxide solution to a solution containing Chromium (III) ions

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

It is an amphoteric hydroxide and thus dissolves in sodium hydroxide solution to form a green solution

$$Cr(OH)_3(s) + OH^-(aq) \longrightarrow Cr(OH)_4^-(aq)$$

It is oxidized by hydrogen peroxide in alkaline medium to form a yellow chromate (VI) solution

$$2Cr^{3+}(aq) + 3H_2O_2(aq) + 10 OH^{-}(aq)$$
 $\longrightarrow 2CrO_4^{2-}(aq) + 8H_2O(1)$

It dissolves in excess ammonia solution to form a violet solution of hexaamminechromium(III) complex

$$Cr(OH)_3(s) + NH_3(aq)$$
 \longrightarrow $[Cr(NH_3)_6]^{3+}(aq) +3 OH^-(aq)$

Chromium (VI) oxide

This is a dark red solid precipitated when concentrated sulphuric acid is added to a saturated solution of potassium dichromate and cooled

$$Cr_2O_7^{2-}(aq) + 2H^+(aq)$$
 \longrightarrow $2CrO_3(s) + H_2O(l)$

It is deliquescent and soluble in water to form chromic (VI) acid

$$CrO_3(s) + H_2O(l)$$
 \longrightarrow $H_2CrO_4(aq)$

It is an acidic oxide which dissolves in alkaline solution to form chromate

$$CrO_3 (s) + 2OH^- (aq)$$
 \longrightarrow $CrO_4^{2-} (aq) + H_2O (l)$

Chromate (VI)

These are yellow salts of Chromic (VI) acids which are isomorphic to sulphate ions

It is prepared by the action of alkaline sodium hydroxide solution on dichromate

$$Cr_2O_7^{2-}$$
 (aq) + 2OH⁻ (aq) \longrightarrow 2CrO₄²⁻ (aq) + H₂O (l)

In acidic medium, the orange dichromate is formed

$$2CrO_4^{2-}(aq) + 2H^+(aq)$$
 — $Cr_2O_7^{2-}(aq) + H_2O$

Qn: (a)A solution of potassium chromate was added to barium chloride solution followed by dilute nitric acid. State what was observed and write the equation of the reaction

- (b) The K_{sp} of silver chloride and silver chromate is 1.0×10^{-12} and 1.0×10^{-10} respectively.
- (i) State which salt is precipitated first if 0.1M KCl and 0.1MK₂CrO₄ are separately added to silver nitrate solution
- (ii) Explain the trend in the solubility of the chromates of group (II) of the periodic table.

Dichromate

It is prepared by acidifying a solution of chromate

It can be acidified by dilute sulphuric acid and hydrochloric acid unlike permanganate which is only acidified by sulphuric acid.

It oxidizes I⁻, SO₃²⁻, Sn²⁺, NO₂⁻, H₂S and Fe²⁺ in acidic medium

Dichromates in dilute acidified solution react with hydrogen peroxide solution to form a blue chromium pentaoxide

$$Cr_2O_7^{2-}(aq) + 2H^+(aq) + 4H_2O_2(aq) \longrightarrow 2CrO_5(s) + 5H_2O(l)$$

COBALT

The oxidation states are +2 and +3 but +2 is more stable than +3 due to low ionization enthalpy

Cobalt is a blue metal and less reactive than Iron

Reactions of Cobalt

1. When heated slowly reacts with air to form a mixture of oxides

$$2\text{Co }(s) + \text{O}_2(g) \longrightarrow 2\text{CoO}(s)$$

$$3\text{Co}(s) + 2\text{O}_2(g)$$
 — Co₃O₄(s)

2. Liberates hydrogen from dilute hydrochloric acid and Sulphuric acid

Co (s)
$$+ 2H^{+}(aq)$$
 \longrightarrow Co²⁺ (aq) $+$ H₂(g)

Dilute nitric acid forms cobalt forms Cobalt (II) nitrate, nitrogen dioxide and water

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

The metal is rendered passive by concentrated nitric acid due to a layer of Co₃O₄

When heated under pressure, cobalt reacts with carbon monoxide to form a neutral carbonyl

$$2\text{Co}(s) + 8\text{CO}(g) \longrightarrow \text{Co}_2(\text{CO})_8$$

It does not react with sodium hydroxide, water and halogens.

Compounds of Cobalt

Cobalt (II) Oxide

Green basic oxide obtained by thermal decomposition of nitrate, carbonate, hydroxide in absence of air

$$2\text{CoCO}_3(s)$$
 \longrightarrow $\text{CoO}(s) + \text{CO}_2(g)$

The green solid dissolves in an acid to a pink solution

CoO (s) +
$$2H^+$$
 (aq) \longrightarrow Co²⁺ (aq) + H₂O (l)

Cobalt (II) hydroxide

Blue basic hydroxide obtained by precipitation as

$$Co^{2+}$$
 (aq) + $2OH^{-}$ (aq) $\longrightarrow Co(OH)_2$ (s)

The blue turns pink then brown in air due to aerial oxidation

It dissolves in excess ammonia solution to form a pale yellow solution which turns pink due to aerial oxidation

Co (OH)₂(s) + 6NH₃ (aq)
$$\longrightarrow$$
 [Co (NH₃)₆]²⁺ (aq) + 2OH⁻ (aq)
[Co (NH₃)₆]²⁺ (aq) \longrightarrow [Co(NH₃)₆]³⁺ (aq) + e

Cobalt (II) Chloride

It is prepared by reacting dilute hydrochloric acid with Cobalt (II) oxide or hydroxide or carbonate

$$CoCO_3(s) + 2HCl(aq) \longrightarrow CoCl_2(aq) + CO_2(g) + H_2O(l)$$
 $CoO(s) + 2HCl(aq) \longrightarrow CoCl_2(aq) + H_2O(l)$

The anhydrous salt is blue but in aqueous solution exist as $[Co (H_2O)_6]^{2+}$ which is pink.

The aqua ligands in the hydrated complex can be substituted by NH₃, CN⁻ and Cl⁻ due to higher stability constant

$$[Co(H_2O)_6]^{2+} (aq) + 4Cl^{-} (aq) \longrightarrow CoCl_4^{2-} (aq) + 6H_2O (l)$$
Pink
$$[Co(H_2O)_6]^{2+} (aq) + 6NH_3 (aq) \longrightarrow [Co(NH_3)_6]^{2+} (aq) + 6H_2O (l)$$
Pale yellow
$$Co^{2+} (aq) + 2CN^{-} (aq) \longrightarrow Co(CN)_2 (s)$$
Reddish brown

A solution of cobalt (II) ions react with hydrogen peroxide in presence of an acid to form cobalt (III)

$$2\text{Co}^{2+}$$
 (aq) + H_2O_2 (aq) + 2H^+ (aq) \longrightarrow 2Co^{3+} (aq) + $2\text{H}_2\text{O}$ (l) Pink

N.B. Cobalt (III) compounds are more stable when complexed.

Qn: An aqueous solution of cobalt (III) salt is CoCl₃.6NH₃ whose concentration is 1M. The complex was reacted with 1M silver nitrate solution to precipitate 1M of silver chloride.

- (a)(i) Identify the complex
- (ii) Write the structural formulae for the possible isomers and give their I.U.P.A.C name
- (iii) State the type of isomerism indicated
- (b) Explain:
- (i) Why Cu^{2+} is colourless while $Cu(H_2O)_4^{2+}$ ion is blue and that of $Cu(NH_3)_4^{2+}$ is deeper blue.
- (ii) Aluminium hydroxide dissolves in sodium hydroxide solution while Magnesium hydroxide does not
- (iii)Copper (I) chloride and Lead (II) chloride are both insoluble in water but dissolves in concentrated hydrochloric acid
- (iV) A blue solution of Copper (II) chloride turns green on addition of chloride ions

SAMPLE INORGANIC CHEMISTRY PRACTICAL

Sample Practical 1

You are provided with substance X which contains two cations and two anions. You are required to carry out the following tests on X and to identify the anions and cations in X.

TESTS	OBSERVATION(S)	DEDUCTION(S)
a) Heat a spatula end ful of <i>X</i> in adry test tube	A colourless liquid condenses on sides of test tube and turns anhydrous Copper (II) Sulphate from white to blue.	Water of crystallization Or: Hydrated salt CO ₂ from CO ₃ ² -,C ₂ O ₄ ² -
	A colourless gas turns damp blue litmus red and lime water milky	CH ₃ COO
	White residue	Oxide of Ca^{2+} , Ba^{2+} , Mg^{2+} , Al^{3+}
b) Shake two spatula end ful of <i>X</i> with about 5cm ³ of water and	White residue	Non- transition metal cation suspected
filter. Keep both the filtrate and residue. Divide the filtrate in six parts	Colourless filtrate	Ca^{2+} , Mg^{2+} , Ba^{2+} , Al^{3+} probably present.
(i) To the first part of the filtrate, add dilute sodium hydroxide drop wise until in excess.	White precipitate insoluble in excess	Ca^{2+} , Mg^{2+} , Ba^{2+} suspected
(ii)To the second part of the filtrate, add dilute ammonia solution drop wise until in excess.	No observable change	Ca ²⁺ , Ba ²⁺ suspected
iii) To the third part of the filtrate, add 2-3 drops of dilute sulphuric acid	White precipitate	Ca ²⁺ , Ba ²⁺ suspected
iv) To the fourth part, add 2-3 drops of Potassium Chromate (VI) and then add dilute Sodium hydroxide solution drop wise until in excess and allow the mixture to stand.	Yellow precipitate	Ba ²⁺ confirmed
v) To the fifth part, add 2-3 drops of lead (II) nitrate solution.	White precipitate	SO4 ²⁻ , Cl ⁻ ,SO3 ²⁻ suspected

vi) To the sixth part, carry a test of your own to confirm the anion in the filtrate. To the portion, add silver nitrate solution Or: To the portion, add lead	White precipitate	Cl ⁻ confirmed
ethanoate		
c) Wash the residue with water, transfer the residue to the test tube and add dilute Nitric acid drop wise to dissolve the	Effervescence of a colourless that turns damp blue litmus red and lime water milky.	Carbondioxide gas from CO3 ²⁻ ∴ CO3 ²⁻ confirmed
residue. Divide the resultant solution into five parts.	Colourless solution formed.	Transition metal ion present.
i) To the first part, add dilute Sodium hydroxide drop wise until in excess.	White precipitate insoluble in excess	Mg^{2+} , Ca^{2+} , Ba^{2+} suspected
ii) To the second part, add dilute ammonia solution drop wise until in excess.	No observable change	Ca ²⁺ , Ba ²⁺ suspected
iii) To the third part, add 2-3 drops of dilute sulphuric acid.	White precipitate formed	Ba ²⁺ , Ca ²⁺ suspected
iv) To the fourth part, add 2-3 drops of Potassium chromate (VI) solution and then Ethanoic acid.	Yellow precipitate soluble in Ethanoic acid to form a yellow solution	Ca ²⁺ confirmed
v) To the fifth part, carry out a test of your own to confirm the cation in the residue.	White precipitate	Ca ²⁺ confirmed

To the solution, add ammonium ethanedioate solution	

d) Identify the;

(i) Cations in X
$$Ca^{2+}$$
 and Ca^{2+} (ii) Anions in X CO_3^{2-} and Cl^{-}

Sample Practical 2

You are provided with substance **E** which contains **three** cations and **one** anion.

Carry out the following tests and identify the ions in E.

TEST	OBSERVATION(S)	DEDUCTION(S)
a) Heat three spatula end ful of E strongly until no further change. Leave the	A colourless that turns red litmus blue	NH ₃ gas from NH ₄ ⁺ salt
residue to cool.	A colourless liquid condenses along side test tube and turns anhydrous copper (II) sulphate blue.	Water of crystallization
	A black residue	Oxide of Cu^{2+} , Fe^{2+} , Ni^{2+}
b) To the cool residue in (a), add about 10cm ³ of water, shake well and	White residue	Ba^{2+} , Ca^{2+} , Mg^{2+} , Al^{3+} , Pb^{2+}
filter. Divide the resultant solution into six parts.	Yellow solution	Fe ³⁺ suspected
(i) To the first part, add dilute sodium hydroxide drop wise until in excess.	A brown precipitate insoluble in excess	Fe ³⁺ suspected
(ii) To the second part, add ammonia solution followed by solid ammonium chloride then sodium carbonate.	A brown precipitate insoluble in excess	Fe ³⁺ suspected

(iii) To the third part, add Potassium chromate solution.	A yellow precipitate	Fe ³⁺ suspected
(iv) To the fourth part, add Ethanoic acid	A reddish brown solution	Fe^{3+} confirmed
(v) To the fifth part, add lead (II) nitrate solution and heat the mixture.	A white precipitate	SO_4^{2-}
(vi) To the sixth part, carry out a test of your own to confirm the anion in E	No observable change	Cl ⁻ absent
To the solution, add Silver nitrate solution c) Wash the residue in (b)		$\therefore SO_4^{2-}$ confirmed
and dissolve in dilute hydrochloric acid. Warm. and divide the resultant solution in to two parts	Colourless solution formed	Transition metal ion present. $Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Pb^{2+}$ suspected
(i) To the first part, add ammonia solution drop wise until in excess.	White precipitate insoluble in excess.	Mg^{2+} , Ca^{2+} , Ba^{2+} suspected
(ii) To the second part, carry out a test of your own to confirm the Cation in E	White precipitate forms - I	Ca2+ confirmed
To the solution, add ammonium ethanedioate solution	White precipitate formed	Ca ²⁺ confirmed

Ions are;

(i) Cations
$$\stackrel{\text{NH}_4^+}{\dots}$$
, $\stackrel{\text{Ca}^{2+}}{\dots}$ and $\stackrel{\text{Fe}^{3+}}{\dots}$

(ii) Anion SO_4^{2-}

Sample Practical 3

You are provided with substance \mathbf{X} which contains \mathbf{two} cations and \mathbf{two} anions. You are required to identify the anions and cations in \mathbf{X} . Record your observations and deductions in the table below.

TEST	OBSERVATION(S)	DEDUCTION(S)
a) Heat a spatula end- ful of X in a dry test tube	A colourless liquid condenses a long side a test tube and turns anhydrous copper (II) sulphate blue	Water of crystallization
	Colourless gas turns a damp blue litmus red	CO_2 from CO_3^{2-} , $C_2O_4^{2-}$ and CH_3COO^- suspected
	A residue which yellow when hot and white when cold	Oxide of Pb ²⁺
b) Shake two end ful of X with water and filter. Keep both filtrate and residue. Divide the filtrate in to six parts.	Colourless filtrate White residue	$Pb^{2+},Zn^{2+},Al^{3+},Ca^{2+},\\ Mg^{2+},Ba^{2+} \ suspected$
(i) To the first part, add dilute sodium hydroxide drop wise until in excess.	White precipitate insoluble in excess	Ba ²⁺ , Ca ²⁺ and Mg ²⁺ suspected
(ii) To the second part, add ammonia solution drop wise until in excess.	No observable change	Ba ²⁺ , Ca ²⁺ suspected
(iii) To the third part, add 2-3 drops of dilute sulphuric acid.	White precipitate	Ba ²⁺ , Ca ²⁺ suspected
(iv) To the fourth part, add 2-3 drops of Potassium chromate (VI) followed by dilute sodium hydroxide drop wise until in excess and allow the mixture to stand.	Yellow precipitate insoluble	Ba ²⁺ confirmed
(v) To the fifth part, add 2-3 drops of lead (II) nitrate solution, heat and allow to stand.	White precipitate soluble on heating and reappears on cooling	Cl ⁻ suspected

(vi) To the sixth part, carry out a test of your own choice to confirm the anion in the filtrate.To the solution, add silver nitrate solution	A white precipitate	Cl ⁻ confirmed
c) Wash the residue with water, transfer to the test tube and add dilute nitric acid drop wise to dissolve the residue. Divide the solution into five parts	Effervescence of a colourless gas which turns a damp blue litmus red A colourless solution	CO_2 gas from CO_3^{2-} Pb^{2+} , Al^{3+} , Zn^{2+} suspected
(i) To the first part, add dilute sodium hydroxide drop until excess.	A white precipitate soluble to form a colourless solution	Zn ²⁺ ,Al ³⁺ and Pb ²⁺ suspected
(ii) To the second part, add dilute ammonia solution drop wise until.	A white precipitate insoluble in excess	Pb^{2+} and Al^{3+} suspected
(iii) To the third part, add dilute 2-3 drops of dilute sulphuric acid.	A white precipitate formed	Pb^{2+} confirmed
(iv) To the fourth part, add 2-3 drops of Potassium chromate (VI) solution then sodium hydroxide until in excess.	A yellow precipitate formed	Pb^{2+}
(v) To the fifth part, carry out a test of your own choice to confirm cation in X		
To the solution, add potassium iodide solution	A yellow precipitate	Pb^{2+} confirmed
Or: To the solution, add dilute hydrochloric acid	A white precipitate	Pb^{2+} confirmed

- d) (i) The cations in \mathbf{X} are $\begin{array}{ccc} Ba^{2+} & \text{and} & Pb^{2-} \\ & & \end{array}$
- (ii) The anions in \mathbf{X} are $\frac{\text{Cl}^2}{\text{Cl}^3}$ and $\frac{\text{CO}_3}{\text{CO}_3}$

Sample Practical 4

You are provided with substances **F**, **G** and **H** each of which contains a single anion and a common cation. You are required to identify the cation and the three anions.

TEST	OBSERVATION(S)	DEDUCTION(S)
a) Heat a small amount of F until no further change	A colourless gas that turns a damp blue litmus red and lime water milky A colourless liquid condenses along side a test tube which turns white anhydrous copper (II) sulphate blue	CO ₂ from CO ₃ ²⁻ , C ₂ O ₄ ²⁻ , CH ₃ COO ⁻ suspected Water of crystallization
	A black residue formed	Oxide of Cu^{2+} , Fe^{2+} , Ni^{2+} , Co^{2+} suspected
b) To a spatula end ful of F add a little ethanol and few drops of concentrated sulphuric acid. Warm the mixture.	A sweet fruity smell	CH ₃ COO ⁻ confirmed
c) Dissolve a small amount of F in 5cm ³ of water. Warm and allow to stand. Divide the solution into three parts.	A blue solution	Cu ²⁺ suspected
(i) To the first part, add2-3 drops of iron (III) chloride solution and warm.	A reddish brown solution	CH₃COO ⁻ confirmed
(ii) To the second part, add dilute sodium hydroxide solution drop wise until in excess.	A pale blue precipitate insoluble in excess	Cu^{2+}
(iii) To the third part, add aqueous ammonia drop wise until in excess.	A pale blue precipitate soluble in excess forming a deep blue solution	Cu ²⁺ confirmed

(iv)To the fourth part, add concentrated hydrochloric acid.	A yellow solution	Cu ²⁺ confirmed
d) Dissolve a small amount of G in 5cm ³ of water. Divide the solution into two parts;	A pale blue solution	Cu^{2+}
(i) To the first part, add lead (II) nitrate solution and warm.	A white precipitate insoluble on warming	SO ₄ ²⁻ suspected or Cl ⁻ absent
(ii) To the second part, carry out a test of your own choice to the anion in G.		
To the solution, add Barium nitrate solution	White precipitate insoluble in the acid.	SO_4^{2-} confirmed
followed by dilute nitric acid. Or: To the solution, add silver nitrate solution	No observable change	SO ₄ ²⁻ confirmed
e) Dissolve a small amount of H in 5cm ³ of water and divide the resultant solution into two parts.	A green solution	Transition metal ions present. Cu ²⁺ , Ni ²⁺ , Cr ³⁺ suspected
(i) To the first part, lead (II) nitrate solution followed by dilute nitric acid and warm.	White precipitate soluble on heating and reappears on cooling	Cl ⁻ suspected
(ii) To the second part, add silver nitrate solution.	White precipitate	Cl⁻ confirmed

f) Identify (i) the cation in \mathbf{F} , \mathbf{G} and \mathbf{H} -----

g) Explain your observation in test e (ii)

The silver ions from silver nitrate solution react with the chloride ions forming Silver chloride which appears as a white solid

$$Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$$

Sample Practical 5

You are provided with substance \mathbf{H} which contains two cations and two anions. Carry out the following tests to determine the ions in \mathbf{H} .

TEST	OBSERVATION(S)	DEDUCTION(S)
a) Heat a spatula end ful of H Strongly until no further change	Substance melt A colourless liquid condenses along side a test tube which turns a white anhydrous Copper (II) sulphate blue A colourless gas which turns a damp blue litmus red and acidified potassium dichromate solution green	Water of crystallization SO_2 gas from SO_4^{2-} and SO_3^{2-}
	A black residue	Oxide of Cu^{2+} , Ni^{2+} , Fe^{2+} suspected
b) Dissolve two spatula end ful of H in 10cm ³ of water. Shake well and filter. Keep both the filtrate and the residue. Divide the filtrate into four parts	Colourless filtrate Green residue	Al^{3+} , Pb^{2+} , Zn^{2+} , Ca^{2+} , Mg^{2+} , Ba^{2+} suspected Fe^{2+} , Cu^{2+} , Ni^{2+} , Cr^{3+} suspected
(i) To the first part, add dilute sodium hydroxide drop wise until in excess.	A white precipitate soluble in excess forming a colourless solution	Al^{3+} , Pb^{2+} and Zn^{2+} suspected
(ii) To the second part, add ammonia solution drop wise until in excess	A white precipitate soluble in excess forming a colourless solution	Zn ²⁺ confirmed
(iii)To the fourth part, add lead (II) nitrate solution and warm.	A white precipitate persists on heating	SO4 ²⁻ suspected
(v)To the fifth part, add barium chloride solution	A white precipitate insoluble in excess	SO4 ²⁻ conformed

	T	T
and dilute hydrochloric		
acid.		
d) To the residue, add	Effervescence of a	CO_2 gas from CO_3^{2-}
dilute nitric acid to dissolve	colourless gas that turns a	
the residue. Divide the	damp blue litmus red and	
resultant solution into three	limewater milky	Transition metal ion
parts.		present
parts.	A green solution formed	Ni^{2+} , Fe^{2+} , Cu^{2+} , Cr^{3+}
		suspected
(i) To the first part, add dilute sodium hydroxide solution drop wise until in excess.	A green precipitate insoluble in excess	Ni ²⁺ suspected
(ii) To the second part, add ammonia solution drop wise until in excess.	A green precipitate soluble in excess forming a blue solution	Ni ²⁺ suspected
(iii) To the third part, carry		
out the test of your own		
choice to confirm the cation		
in the residue		
	A red precipitate	Ni ²⁺ confirmed
To the solution, add		
ammonia solution followed		
by dimethylglyoxime		

e) Identify the ions in ${\bf H}$

(i) Cations
$$\frac{\text{Ni}^{2+}}{\text{SO}_4^{2-}}$$
 and $\frac{\text{Zn}^{2+}}{\text{CO}_3^{2-}}$

Sample Practical 6

You are provided with substance W which contains two cations and two anions. Cary out the following tests to identify the ions in W and record your observation(s) and deduction(s) in the table below.

TEST	OBSERVATION(S)	DEDUCTION(S)
	A colourless liquid	Water of crystallization
a) Heat a spatula end ful of	condenses along side test	
W in a dry Pyrex tube until	tube and turns white	
no further change.		

b) Dissolve two spatula	anhydrous copper (II) sulphate blue A white residue A colourless gas that turns blue damp litmus red and limewater milky. Colourless filtrate	Oxide of Al ³⁺ , Mg ²⁺ , Ca ²⁺ ,Ba ²⁺ probably present CO ₂ gas from CO ₃ ²⁻ , C ₂ O ₄ ²⁻ , CH ₃ COO
end ful of W in about 3cm ³ of water. Shake and filter. Keep both the filtrate and residue. Divide the filtrate into six parts.	White residue	Mg^{2+} , Ca^{2+} , Al^{3+} , Ba^{2+} probably
(i) To the first part, add dilute sodium hydroxide solution drop wise until in excess.	A white precipitate insoluble in excess and turns brown on standing	Probably Mn^{2+} present Mn^{2+} oxidized to MnO_2
(ii) To the second part, add ammonia drop wise until in excess.	A white precipitate insoluble in excess and turns brown on standing	Probably Mn ²⁺ present Mn ²⁺ oxidized to MnO ₂
(iii) To the third part, add concentrate nitric acid followed by lead (IV) Oxide and boil.	Purple solution	Mn ²⁺ confirmed
(iv) To the fourth part, add sodium bismulthate followed by concentrated nitric acid and boil.	Purple solution	Mn ²⁺ confirmed
(v) To the fifth part, add Lead (II) nitrate solution and warm. Allow it to cool down.	White precipitate disappears on warming and reappears on cooling.	Cl ⁻ probably present
(vi) To the sixth part, carry out the test of your own choice to confirm the anion in the filtrate.To the solution, add silver nitrate solution	White precipitate	Cl ⁻ confirmed

a) Week the residue and	Efformacion of a	CO_2 from CO_3^{2-}
c) Wash the residue and	Effervescence of a	
add dilute hydrochloric	colourless gas which turns	
acid to dissolve the	blue damp litmus red	
residue. Divide the		
resultant solution into three	Colourless solution remains	Probably Al^{3+} , Ca^{2+} , Ba^{2+} ,
parts.		Mg ²⁺ present
1		
(i)To the first part, add	A white precipitate insoluble	Probably Ca^{2+} , Ba^{2+} , Mg^{2+}
dilute sodium hydroxide	in excess	present
solution drop wise until in		T
excess.		
	A	D l l. l. M . 2+
(ii) To the second part, add	A white precipitate insoluble	Probably Mg ²⁺ present
ammonia solution drop	in excess	
wise until in excess.		
(iii) To the third part, add	A white precipitate insoluble	Mg^{2+} confirmed
disodium hydrogen	in excess ammonia solution	
phosphate followed by		
ammonium chloride and		
ammonia solution drop		
wise until in excess.		

d) Identify the ions in W;

(i) Cations
$$\frac{Mn^{2+}}{\cdots}$$
 and Mg^{2+} Cl^{-} and CO_3^{2-}

Sample Practical 7

You are provided with substance \mathbf{R} which contains two cations and two anions. Carry out the following tests on \mathbf{R} and identify the cations and anions in it. Identify any gases evolved. Record your observations and deductions in the table.

TEST	OBSERVATION(S)	DEDUCTION(S)
(a) Heat a small spatula end ful of R in dry Pyrex	Substance melted	
tube.	Cracking sound produced	
	A colourless liquid condenses along side test tube and turns white	Water of crystallization

	anhydrous copper (II) sulphate blue A colourless gas burns with a pop sound A brown gas turns damp blue litmus red A green substance turns yellow/black	Oxygen is released NO ₂ gas released from NO ₃ ⁻ Oxide of Cu ²⁺ , Pb ²⁺ suspected
(b) To a spatula end ful of R in a test tube. Add 5cm ³ of 2M sodium hydroxide solution. Shake well and filter. Keep both filtrate and residue.	Colourless filtrate Pale- blue residue	Al ³⁺ , Zn ²⁺ and Pb ²⁺ suspected Probably Cu ²⁺ present
(c) Wash the residue with water and transfer it to a test tube. Add 2cm³ of dilute nitric acid and warm to dissolve. Cool the solution and divide it into two portions.	A green/ blue solution	Probably Cu ²⁺ present
(i) To the first portion, add dilute sodium hydroxide solution drop wise until in excess.	Pale blue precipitate insoluble in excess	Probably Cu ²⁺ present
(ii) To the second portion, add dilute ammonia solution drop wise until in excess.	Pale blue precipitate soluble in excess forming a deep blue solution	Cu ²⁺ confirmed
(d) To the filtrate from (b), add dilute nitric acid until the solution is acidic. Divide the solution into three parts.	Colourless solution	Probably Al ³⁺ , Zn ²⁺ and Pb ²⁺ present
(i) To the first part, add dilute sodium hydroxide solution drop wise until in excess.	A white precipitate soluble in excess forming a colourless solution	Probably Al ³⁺ , Zn ²⁺ and Pb ²⁺ present

(ii) To the second part, add ammonia solution drop wise until in excess.	A white precipitate in soluble in excess	Al^{3+} , Pb^{2+} probably present
(iii) To the third part, carry out a test of your own to confirm the cation.		
To the solution, Add Potassium iodide solution	A yellow precipitate	Pb ²⁺ confirmed
Or To the solution, add dilute sulphuric acid	A white precipitate	Pb^{2+} confirmed
(e) To a spatula end ful of R , add 2cm ³ of dilute nitric acid. Heat the mixture to dissolve the solid. Cool the solution and divide it into two parts.	A green solution	Probably Cu ²⁺ present
(i) To the first part, add barium nitrate solution.	No observable change	SO4 ²⁻ absent ∴ Cl ⁻ present
(ii) To the second part, add 3 drops of silver nitrate solution.	White precipitate formed	Cl ⁻ confirmed

- (i) The cations in **R** are Cu^{2+} and Pb^{2+}
- (ii) The anions in \mathbf{R} are $\frac{\text{Cl}^{-}}{\cdots}$ and $\frac{\text{NO}_{3}^{-}}{\cdots}$

Sample Practical 8

You are provided with substance **W** which contains three cations and one anion. You are required to carry out the following tests on **W** to identify the cations and anion in it. Identify any gases evolved. Record your observations and deductions in the table below.

TESTS	OBSERVATION(S)	DEDUCTION(S)
(a) Heat a spatula end ful ofW in dry tube until there is no further change	Substance melted A colourless gas that turns a damp red litmus blue	NH3 gas from NH4 ⁺
	Colourless liquid condenses along side test tube and turns white anhydrous	Water of crystallization
	Copper (II)suphate blue	Oxide of Cu^{2+} , Fe^{2+} , Mn^{2+} ,
	A black residue	Ni ²⁺ suspected
(b) Shake two spatula endful of W with about 3cm ³ of water. Add dilute ammonia solution drop	A green residue	Probably Fe ²⁺ present
wise until in excess. Warm and filter. Keep both the filtrate and residue.	A deep blue solution	Probably Cu ²⁺ present
(c) To the filtrate, add dilute nitric acid drop wise until the solution is just acidic. Divide the acidic solution into six parts.	A green solution	Probably Cu ²⁺ present
(i) To the first part, add dilute sodium hydroxide solution drop wise until in excess. Warm the mixture.	A pale blue precipitate insoluble in excess and turns black on heating	Probably Cu ²⁺ present
	A colourless gas that turns red damp litmus blue	NH_3 gas $:: NH_4^+$ present
(ii) To the second part, add dilute ammonia solution drop wise until in excess.	Pale blue precipitate soluble in excess forming a deep blue solution	Cu ²⁺ confirmed
(iii) To the third part, add potassium iodide solution.	A yellow solution with a white precipitate	Cu ²⁺ confirmed
(iv) To the fourth part, add 2-3 drops of litmus solution	A red solution	Acidic salt

		<u>, </u>
followed by ammonia solution drop wise until in excess.		Cu ²⁺ present
(v)To the fifth part, add 3-4 drops of lead (II) ethanoate solution	A white precipitate	Probably SO ₃ ²⁻ ,SO ₄ ²⁻ ,Cl ⁻ present
(vi) Use to the sixth part to carry out a test of your own choice to confirm the anion in W To the solution, add Barium nitrate solution followed by dilute nitric acid	White precipitate insoluble in excess acid	SO_4^{2-} confirmed
Or To the solution, add barium chloride solution followed by dilute hydrochloric acid	White precipitate insoluble in excess acid	SO4 ²⁻ confirmed
(d) Wash the residue with water and dissolve it in dilute hydrochloric acid and divide the solution into three parts	A pale- green solution	Probably Fe ²⁺ ,Ni ²⁺ suspected
(i) To the first part, add sodium hydroxide solution drop wise until in excess	A green precipitate insoluble in excess and turns brown on standing	Fe ²⁺ suspected
(ii) To the second part, add dilute ammonia solution drop wise until in excess	A green precipitate insoluble in excess and turns brown on standing	Fe ²⁺ suspected
(ii) To the third part, add 3-4 drops of potassium hexacyanoferrate (III) solution	A dark blue precipitate	Fe^{2+} confirmed

(e) (i) The anion in **W** is

SO₄²⁻

 NH_4^+ , Fe^{2+} and Cu^{2+}

(ii) The cations in W are

Sample 9

You are provided with substance X which contains one cation and two anions.

Carry out the following tests on X to identify the cation and anions in X.

Tests	Observations	Deductions
Heat a spatula end-ful of X strongly in a dry test tube	Droplets of a colourless liquid turned white anhydrous copper(II) sulphate blue. Colourless gas turned blue litmus red and acidified	Hydrated salt Sulphurdioxide gas from SO_4^{2-} or SO_3^{2-}
	potassium dichromate solution green. White residue	Non-transition metal ion present.
Dissolve three spatula end —ful of X in about 6cm³ of water. Divide the solution into five parts.	White solid dissolves to form a colourless solution.	Non-transition metal ion present.
i) To the first part of the solution, add sodium hydroxide solution dropwise until in excess	White precipitate soluble forming a colourless solution.	Zn^{2+} , Pb^{2+} or Al^{3+} suspected.
ii) To the second part of the solution, add aqueous ammonia solution dropwise until in excess	White precipitate insoluble in excess	Pb ²⁺ or Al ³⁺ suspected
iii) To the third part of the solution, add 2-3 drops of potassium iodide solution.	No observable change. Or No yellow precipitate formed	Al^{3+} confirmed Pb^{2+} absent
iv) To the fourth part of the solution, add 2-3 drops of lead(II) Nitrate solution followed by dilute Nitric acid	White precipitate insoluble in acid.	Cl ⁻ , SO ₄ ²⁻ suspected.

v) To the fifth part of the solution, add barium Nitrate solution drop-wise until in excess. Filter and divide the filtrate into two	White residue Colourless filtrate	SO ₄ ²⁻ confirmed
portions. (i) To the first portion, add equal volume of lead (II) Nitrate solution followed by 2-3 drops of dilute Nitric acid. Boil and cool using cold water	White precipitate insoluble in acid. Dissolves on boiling and reappears on cooling.	Cl ⁻ confirmed
(ii) To the second portion, add silver nitrate solution followed by dilute nitric acid.	White precipitate insoluble in acid.	Cl ⁻ confirmed

The cation in X is Al^{3+} and anions are SO_4^{2-} and Cl^{-}

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