THE PERIODIC TABLE

TABLE OF CONTENTS

Chapter 1:

1. ATOMIC STRUCTURE

1.1. Cathode rays

When a gas is enclosed in a glass tube at very low pressure and high voltage is applied across it, there is observed a stream of rays moving from the cathode towards the anode.
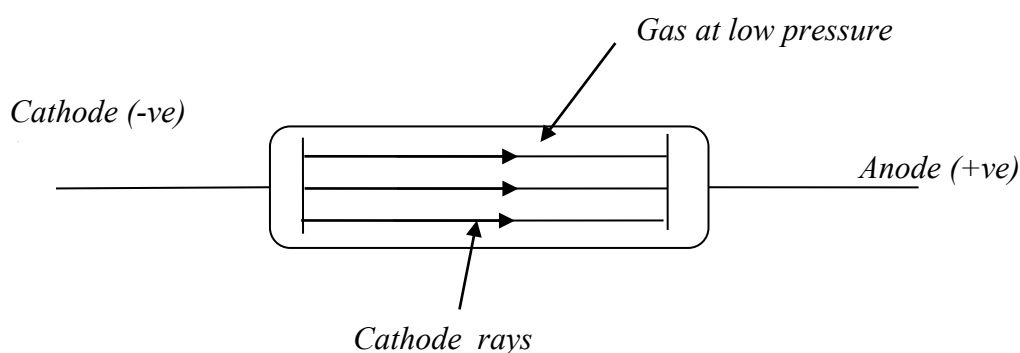
Figure 1: Cathode ray tube with anode directly opposite the cathode

The rays are not necessarily attracted by the anode because when the anode is placed at a different position, these rays just pass the anode.
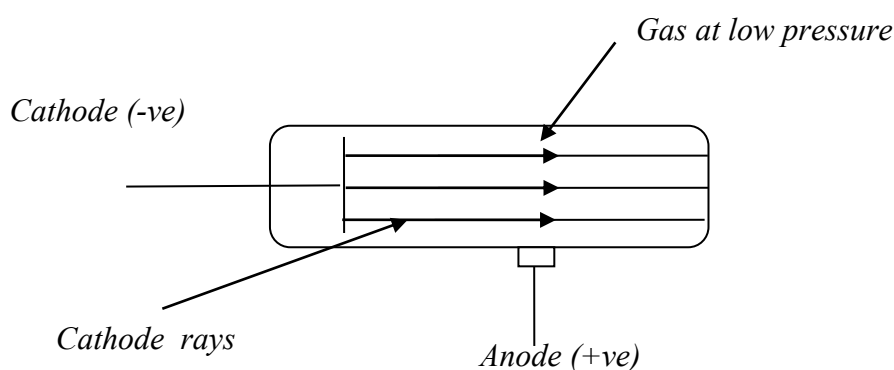
Figure 2: Cathode ray tube with the anode at the side of the tube

However when an electric field is applied across the path of these rays, they get deflected towards the positive plate.

The simplified version of inorganic chemistry by SSERWADDA Walter
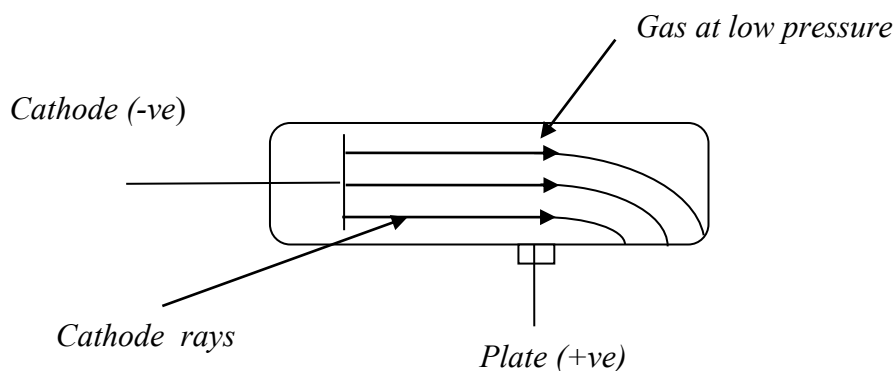
Figure 3: Cathode ray tube with an electromagnetic field

These shows that the rays consist of negatively charged particles

Properties of cathode rays

When they strike the opposite end of the cathode ray tube, the tube fluorescences with a green light.

An object placed in the path of the rays gives a sharply defined shadow at the extreme end of the tube. This shows the rays travel in straight lines.

When the blades of a paddlewheel mounted on an axle are placed in the path of the rays the wheel is made to rotate in a direction away from the cathode. This shows that the cathode rays are particles that have mass and momentum

They are deflected by a magnetic field and an electric field in a direction that shows that the particles are negatively charged. JJ Thompson later determined the charge and mass of these particles as follows; mass of one particle was found to be equal to *1/1837* of the mass of a hydrogen atom and a charge of *1.6 × 10^{-19}* coulombs hence cathode rays are a stream of electrons.

Protons

When different gases are used in a cathode ray tube and perforated cathode is used, positively charged particles are observed to move in a direction of the electrons. Using hydrogen gas resulted in production of positively charged protons which were identical in mass and charge to the positive particles in the nucleus. These positive ions are produced by collision of electrons from the cathode with the gaseous atoms of the molecules in the tube.

Rutherford's α-particles scattering experiment

Geirgerand Marden working under Rutherford bombarded thin metallic foils of gold with α-particles. Many of the particles were observed to pass through the foil undeflected and a few were deflected at different angles
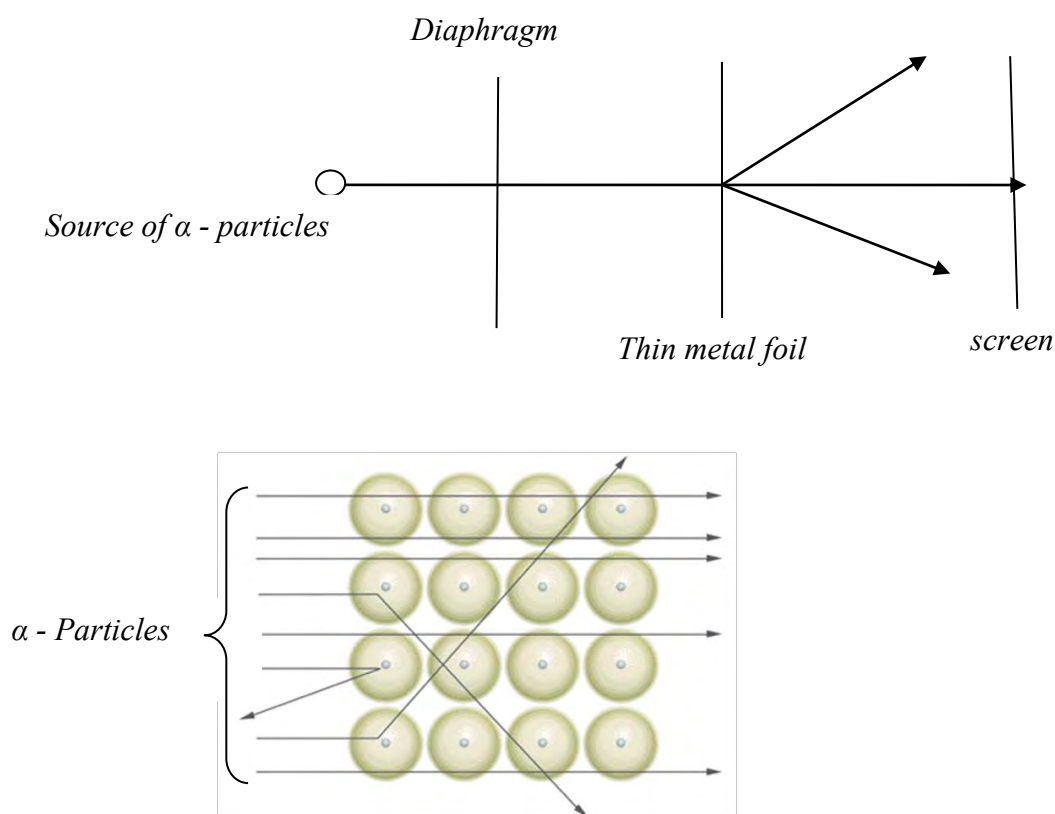
Figure 4: Rutherford's α – Particles scattering Experiment

The many undeflected α-particles were explained to have passed in a space within an atom where there are no positive particles (protons) hence most of the atom has space occupied by electrons. The small volume occupied by the

nucleus is where there is high concentration of positive charge and it's located at the centre of the atom.

1.2. Neutrons

These were later discovered when Beryllium was bombarded with α-particles

$$^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n$$
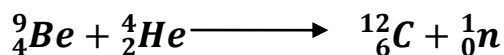
These were found to have no charge but had mass of the magnitude of the proton. These particles are also found within the nucleus.

1.3. Electronic structure of atoms

Atomic / Emission spectrum of hydrogen

When electricity passes through a discharge tube containing hydrogen gas at low pressure, many of the hydrogen molecules break up into single atoms. These atoms emit both visible and invisible radiations; some of the later being in the infrared and some in the ultraviolet part of the spectrum. If the radiations are analyzed by the spectrograph, they yield a line spectrum which can be photographed. Each line in the spectrum represents a definite wave length of the radiation. The series of lines in the visible part of the spectrum is called *Balmerseries*.

The 3 most prominent lines in these series are labeled *Hγ, Hβ* and *Hα*.

Another series of lines in the spectrum is called the Lyman series and is found in the ultraviolet part of the spectrum and a further series occurs in the infrared part.

Measurement of wave length corresponding to lines in the various series shows regularity and wave lengths are in accordance with the simple equation.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Where λ=wave length,

R_H=Rydberg'sconstant,

n_1 and $n_2$are simple whole numbersindicating the quantum shell.

Where $n_1=1$, and $n_2=2, 3, 4$ etc
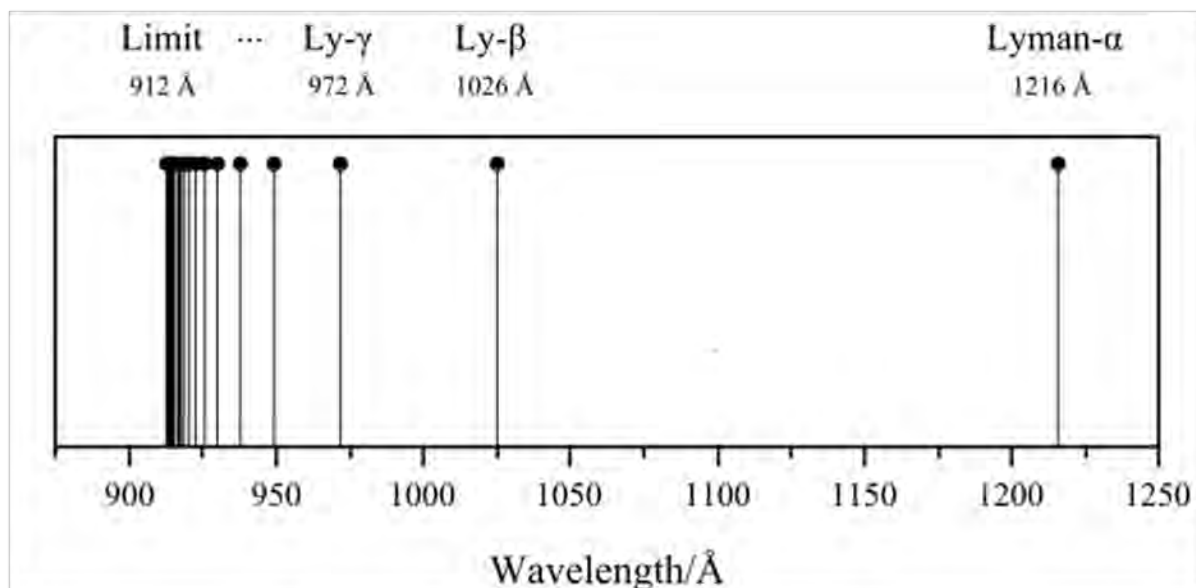
Figure 5: Hydrogen Spectral lines

Explanation

1.4. Bohr's theory of electronic energy levels

Electrons in an atom could only rotate in certain passable orbits/ energy levels. The energy levels are given principal quantum numbers *1, 2, 3, 4 etc* with *1* being the one nearest to the nucleus. Under normal conditions, electrons occupy quantum no. *1* first. This is a state of lowest energy called the ground state / stationary state.

When atoms absorb energy, they become excited i.e. electrons are promoted to energy levels with higher energy. But the excited state is an unstable state and so electrons get rid of the energy as electromagnetic radiations and fall to lower energy levels frequently in a series of discrete steps. The wave length of the radiation emitted is determined by the energy difference of the electron in the 2 levels and is given by

$$E_1 - E_2 = hv$$

Where E_1 and E_2 are energies of the electron in the higher and lower levels respectively

H is the Planck's constant, and

5

V is the frequency of light in a vacuum. $V = \frac{c}{\lambda}$

Where c is the velocity of light in a vacuum

Therefore $E_1 - E_2 = \frac{hc}{\lambda}$
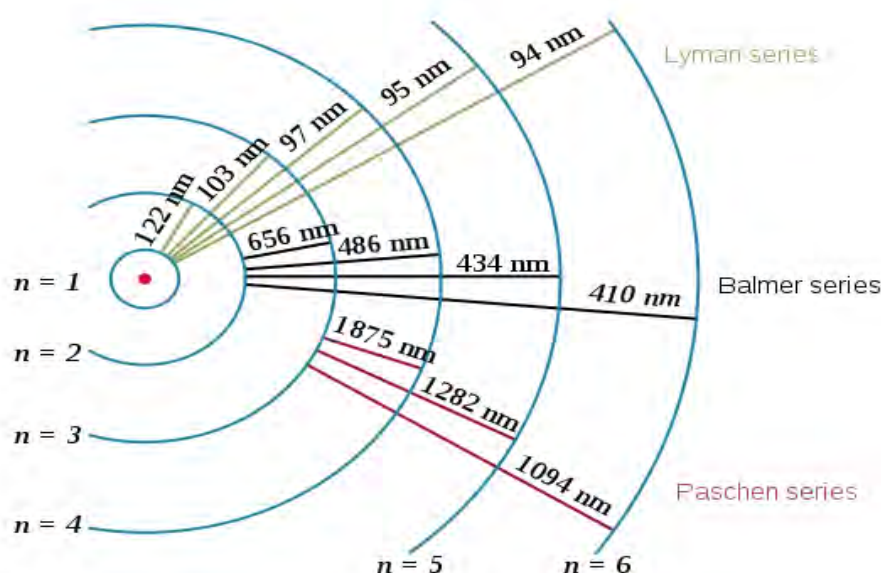
Figure 6: Hydrogen spectral series

The spectral lines get closer and closer as the wave length of the emission decreases. This is an indication that within an atom of hydrogen or any other element, the energy levels become closer and closer and their energy of separation decreases as the distance from the nucleus increases.

The very much close lines got from emission from higher levels to lower levels are studied and are an indication that within the energy levels where electrons are distributed, the energy difference between these sub energy levels is very small since they are so close.

<u>Significance of line spectrum of hydrogen</u>

The line spectrum gives the fact that within atoms, electrons exist in different energy levels (sub shells, shells, orbitals) in which electrons are distributed around the nucleus. These energy levels become closer and closer as the distribution from the nucleus increases.

Question

Hydrogen has only one electron but why does its line spectrum consists of several lines?

Answer

Hydrogen has a single electron. When the electron absorbs sufficient energy, it gets excited and moves from its ground state to higher energy levels. But the excited state is an unstable state and so the electron gets rid of the excess energy as electromagnetic radiations and fall to its lowest energy level in a series of discrete steps.

Each emission has a different wave length corresponding to the different energy levels and hence a single electron emits the absorbed energy in stages in definite amounts giving rise to the different lines in the spectrum.

1.5. Electronic configuration of atoms
This refers to the arrangement of electrons in atoms.

Within an atom, electrons are arranged in shells/energy levels around the central part of an atom called the nucleus.

The energy levels are numbered *1,2,3,4*etc or *k, l, m, n etc*, with *1* or *k* being the shell nearest to the nucleus.

With the exception of the first energy level, the other shells are divided into sub- energy levels/sub shells.

Within the shells, electrons are found in what is referred to as orbitals.

An orbital is a volume or space around the nucleus within the shells where electrons are found.

1) The 1st energy level has only one orbital called *1s* and like any other **s** orbital can take a maximum of two electrons.

$1S^2$

| ↑↓ |

Therefore when full the 1ˢᵗ shell has 2 electrons.

2) The 2ⁿᵈ energy level has 2 sub shells called the **2s** and **2p**.

The **2s** sub shell takes in a maximum of two electrons because it has one orbital.

The **2p** sub shell like any other *p* sub shell has 3 orbitals and when full has 6 electrons.

$2s^2$ $2p^6$

| ↑↓ | | ↑↓ | ↑↓ | ↑↓ |
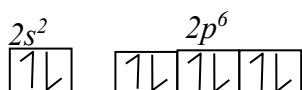
Therefore the maximum number of electrons that can be accommodated within the 2ⁿᵈ shell of any atom is 8.

3) The 3ʳᵈ energy level has 3 sub shells, namely *3s, 3p* and *3d*.

The **3s** takes in up to 2 electrons.

The **3p** takes in up to 6 electrons and the **3d** shell like any other d sub shell consists of 5 orbitals and takes up to 10 electrons when full. Therefore the maximum number of electrons that can be accommodated within the 3ʳᵈ shell of an atom is 18.

$3s^2$ $3p^6$ $3d^{10}$

| ↑↓ | | ↑↓ | ↑↓ | ↑↓ | | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |
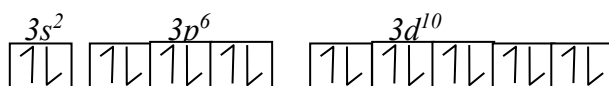
4) The 4ᵗʰ energy level has 4 sub shell given denoted by *4s, 4p, 4d* and *4f.*

The 4s sub shell has one orbital and takes in up to 2 electrons.

The *4p* sub shell has 3 orbitals and can have up to 6 electrons when full.

The *4d* sub shell has 5 orbitals and has up to 10 electrons when full.

The *4f* sub shell has 7 orbitals and when full accommodates 14 electrons.

$4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$

| ↑↓ | | ↑↓ | ↑↓ | ↑↓ | | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |
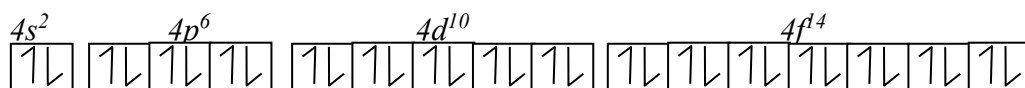
Therefore the maximum number of electrons that can be accommodated within the fourth shell of an atom is 32.

Note:

From the 4ᵗʰ shell onwards there are 4 sub shells, namely *s, p, d* and *f.*

For e.g. the 5ᵗʰ shell has *5s, 5p, 5d* and *5f* as its sub shells.

1.6. Rules/principles for writing electronic configurations of atoms

a) *Pauli Exclusion Principle*.

States that, an orbital can take in a maximum of two electrons on a condition that the electrons have parallel and opposite spins.

b) *Hund's Rule of maximum multiplicity*

States that when electrons are present in a number of degenerate orbitals (orbitals with more or less equal energy) they occupy all the orbitals singly first with parallel spins before pairing can occur in any one orbital.

c) *Aufbau pattern of filling energy level*

States that electrons fill in the sub shells in order of increasing energy beginning with the sub shell of lowest energy, followed by that of second lowest energy and so and so forth.

After filling the second energy level, the first in a series of several overlap of energy occurs between the *3d* and the *4s* sub energy levels. The *3d* sub shell though nearer to the nucleus than the *4s* sub shell happens to be at a higher energy level therefore the electrons are filled in the *4s* sub energy level before filling the *3d* sub shell. After filling the *4s* sub shell, electrons then fill the *3d* energy level.
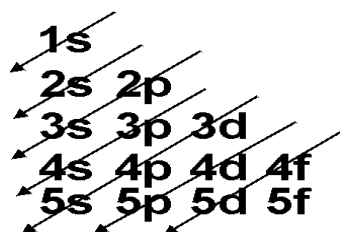
Figure   7Aufbau   pattern   of   filling   energy   levels

The simplified version of inorganic chemistry by SSERWADDA Walter

Chapter 2

2. THE MODERN PERIODIC TABLE OF ELEMENTS

Table 1 Periodic table

The Modern periodic table consists of two major divisions; namely

a) The horizontal arrangement of elements referred to as the _periods_

b) The downward arrangement of elements referred to as the _groups_.

Usually atoms within the same group in the periodic table have similar chemical properties because they contain equal number of electrons in their outer most shell.

In the periodic table the elements are arranged in accordance with their atomic numbers. Earlier attempts to arrange the elements in accordance with their atomic weights failed due to the existence of isotopy amongst some elements like hydrogen, carbon, chlorine etc.

By using atomic numbers as a basis for placing elements on the periodic table, the different isotopes of the same element do take up a common place on the periodic table.

2.1. Variation of physical properties in the periodic table (periodic properties)

2.2. Atomic radius
Definition:

This is the distance of closest approach from the nucleus of an atom to another identical atom in a bonding situation.

The bonding situation is metallic bonding if the two identical atoms are metal atoms and if the identical atoms are non metals, the bonding situation is covalent bonding.

At such a distance, the sum of the inter-electronic and the inter-nuclear repulsions just balance the nuclear–electronic attraction.

Alternative definition

Atomic radius is half the inter-nuclear distance between two identical atoms in a bonding situation.

Still the bonding situation is covalent if the two identical atoms are covalent atoms and metallic bonding for two identical metallic atoms.

Factors determining the radius of an atom of an element

1) *Nuclear charge.*

   This is determined by the number of protons present in the nucleus of an atom e.g. sodium atom with 11 protons in its nucleus has a nuclear charge of +11.

   If an atom has a high nuclear charge, then the attraction the nucleus of that atom has for the electrons present in its shells will also be high leading to a decrease in atomic radius. If the nuclear charge is low, then the attraction the nucleus of the atom has for the electrons present will be low as well leading to an increase in atomic radius.

2

2) *Screening (shielding) effect*.

This refers to the shielding (screening) of the electron(s) in the outer most shell by the electrons present in the inner shell(s). Increase in screening effect on the outer most electrons increases the atomic radius and the decrease in screening effect on the outermost electrons decreases the atomic radius.

Variation in atomic radius down a group in the periodic table

Example;

Consider Group IA elements (Alkali metals)..

Table 2 Atomic radius of group 1 elements

Element	Atomic Number	Electronic configuration	Atomic radius /^{0}A
Li	3	$1s^2 2s^1$	1.52
Na	11	$1s^2 2s^2 2p^6 3s^1$	1.54
K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	2.27
Rb	37	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$	2.48
Cs	55	--------	2.65

Trend

Atomic radius increases from one atom to the next one down any group in the periodic table.

Explanation.

Down any group in the periodic table, both the nuclear charge and screening effect increase but the increase in screening effect outweighs that due to nuclear charge because of an extra shell of electrons added from one element to the next one.

The effective nuclear charge therefore decreases i.e. the nuclear attraction for the outer most electron(s) decreases leading to an increase in atomic radius.

Variation in Atomic radiuscross period 2 and period 3 in the periodic table

Trend

Atomic radius decreases across the periods.

Explanation

Across the period from one atom to the next, there is an increase in nuclear charge but the shielding effect of the electrons in the inner shell(s) on the electron(s) in the outermost shell remains more or less constant because electrons are being added to the same shell.

As a result the effective nuclear charge increases and electron(s) in the outer most shell is increasingly attracted more strongly to the nucleus leading to a decrease in atomic radius.

Elements	*Li*	***Be***	*B*	*C*	*N*	*O*	*F*	*Ne*
At. Number	3	4	5	6	7	8	9	10
Electronic configuration	$1s^2 2s^1$	$1s^2 2s^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6$
Atomic radius $/^0A$	1.52	1.13	0.83	0.77	0.71	0.66	*0.71*	1.60

The diagrams below show how the atomic radius changes across Period 3.
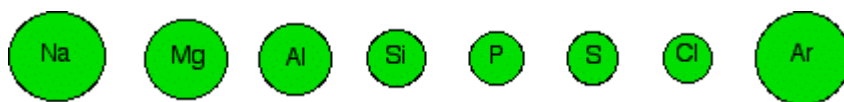
The figures used to construct this diagram are based on:

Metallic radii for *Sodium, Magnesium* and *Aluminium*;

Covalent radii for *Silicon, Phosphorus, Sulphur* and *Chlorine*;

<u>Note</u>

The atomic radius of argon is higher than expected because its atoms do no form covalent bonds because they already have stable electronic configuration.

Instead the atoms have inter atomic van der Waal's forces and the inter nuclear distance between any neighboring argon atoms is therefore larger.

<u>Variation in atomic radius among the d-block elements in periodic table</u>

Element	At. no	Elect. Conf
Scandium (Sc)	*21*	$1s^2$ $2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium(Ti)	*22*	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium (V)	*23*	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
Chromium (Cr)	*24*	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese (Mn)	*25*	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron (Fe)	*26*	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Cobalt (Co)	27	$1s^22s^22p^63s^23p^63d^74s^2$
Nickel (Ni)	28	$1s^22s^22p^63s^23p^63d^84s^2$
Copper (Cu)	29	$1s^22s^22p^63s^23p^63d^{10}4s^1$
Zinc (Zn)	30	$1s^22s^22p^63s^23p^63d^{10}4s^2$

Trend

Among the d-block elements, the atomic radius remains more or less the same.

Explanation

This is because the increase in nuclear charge from one atom to the next one is roughly balanced by the increase in screening effect on the outer 4s electrons by the electrons in the inner shells as the number of electrons on the inner 3d sub shell (penultimate shell) increases. The effective nuclear charge therefore is more or less the same throughout and the atomic radius as well.

Cations

A Cation (a positive ion) is formed by the removal of one or more electrons from an atom. The radius of a cation is smaller than the radius of the atom from which it's formed.

Explanation

After the loss of one or more electrons by an atom, the number of protons in the nucleus becomes greater than the number of remaining electrons, thus the proton-electron ratio increases.

As a result, the nuclear attraction for the remaining electrons increases leading to a decrease in cationic radius.

Anions

An anion (a negatively charged ion) is formed by the gain of one or more electrons by an atom. The radius of an anion is larger than that of the atom from which it is formed.

Explanation

After the gain of one or more electrons by an atom, the number of electrons present becomes more than the number of protons present in the nucleus thus the proton-electron ratio decreases.

The nuclear attraction for the now electrons now decreases leading to increase in anionic radius.

Isoelectronic ions

Isoelectronic ions are ions that have the same number of electrons and the same electronic structure.

For example**:**

Isoelectronic ions	Number of electrons
1. $Al^{3+}, Mg^{2+}, Na^+, F^-$	10 electrons
2. $S^{2-}, Cl^-, K^+, Ca^{2+}$	18 electrons

Isoelectronic ions

$Al^{3+}, Mg^{2+}, Na^+, F^-$ all have 10 electrons):

Al^{3+} has 13 protons; a nuclear charge of $+13$.

Mg^{2+} has 12 protons; a nuclear charge of $+12$.

Na^+ has 11 protons; a nuclear charge of $+11$.

F⁻ has 9 protons; a nuclear charge of $+9$.

Al^{3+}, with the largest nuclear charge has the highest proton-electron ratio and therefore the strongest nuclear attraction for the electrons.

Therefore Al^{3+} has the smallest ionic radius.

Therefore the radius of the ions increase in the order $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$

Ion	Al3+	Mg2+	Na+	F-
Ionic radius /nm	0.050	0.065	0.095	

Ionization Energy

Definition**:**

Ionization energy is the energy required to remove one mole of electrons from one mole of gaseous atoms of a given element to form one mole of gaseous ions.

i.e.

$M_{(g)} \rightarrow M^{+}_{(g)} + e$ ΔH= Ionization energy

First Ionisation energy

This is the enthalpy change when one of electrons is removed from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions of the element.

$M_{(g)} \rightarrow M^{+}_{(g)} + e$ $^{\Delta}H$= 1st ionization energy.
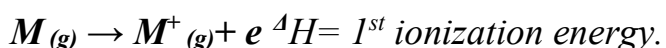
For example

For a sodium atom,

$Na_{(g)} \rightarrow Na^{+}_{(g)} + e$ $H=+494 kjmol^{-1}$

Second ionization energy

Is the minimum energy required to remove one mole of electrons from one mole of unipositively charged gaseous ions to form one mole of dipositively charged gaseous ions of the element.

$M^{+}_{(g)} \rightarrow M^{2+}_{(g)} + e$ Δ H= 2nd ionization energy.

8

Example; for a sodium atom;

$$Na^+_{(g)} \rightarrow Na^{2+}_{(g)} + e \qquad \qquad \triangle H = +4560 KJmol^{-1}$$
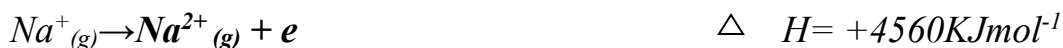
The higher the ionization energy value, the more difficult it is to remove the electron.

For example, it is more difficult to remove the 2nd electron in sodium than the 1st electron as can be seen from the 1st and 2nd ionisation energies values above.

2.2.1. Factors that determine the magnitude of 1st ionization energy
1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius
4) Electronic configuration of the atom

Explanation

Nuclear charge.

If the nuclear charge of an atom is high, then the electrons present in the outer most shell of that atom experience a high nuclear attraction.

Therefore removing an electron from the atom requires more energy leading to high 1st ionization energy.

For a low nuclear charge, the electrons present in the atom experiences a low attraction from the nucleus of such an atom leading to low 1st ionization energy.

Shielding effect of the electrons in the inner shells

If the screening effect by the electrons in the inner shells on the electrons in the outermost shell is high, then the outermost electron experiences a low nuclear attraction leading to low 1st ionization energy.

If the screening effect on the outermost electron is low, then electron experiences a high nuclear attraction leading to a high 1st ionization energy value.

Atomic radius.

If the radius of an atom is small, then the outer most electrons are closer to the nucleus and thus experience a high nuclear attraction leading to high 1st ionization energy.

If the radius of an atom is large, the outer most electrons are further away from the nucleus and hence experiences a low nuclear attraction leading to low 1st ionization energy value.

Electronic configuration of the outer most shell

When the first electron being removed is from an atom whose electronic configuration is stable (*e.g. N: $1s^2 2s^2 2p^3$ or Ne; $1s^2\ 2s^2\ 2p^6$*), a lot more of energy is needed to remove the 1st electron leading to a high 1st ionization energy.

But if the 1st electron being removed is from an atom whose electronic configuration is thermodynamically less stable (*e.g. O; $1s^2 2s^2 2p^4$*) then less energy is required to remove the 1st electron from such an atom i.e. the 1st ionization energy value is low.

Variation in first ionization energy down a group in the periodic table

For example consider group IA elements.

Table 3Variation in first ionization energy down groupI in the periodic table

Element	Atomic number	Electronic configuration	First ionisation energy/ KJmol^{-1}
Li	3	$1s^2 2s^1$	513
Na	11	$1s^2 2s^2 3s^2 2p^6 3s^1$	496
K	19	$1s^2 2s^2 2p^6 s^2 3p^6 4s^1$	418
Rb	37		403
Cs	55		376

Trend

Ionisation energy generally decreases down any group in the periodic table

Explanation

Down a group in the periodic table from one atom to the next one, both the nuclear charge and screening effect increase but the increase in screening effect on the electrons in the outer most shell by the electrons in the inner shells outweighs the increase in nuclear charge.

This leads to a decrease in the effective nuclear charge and hence the nuclear attraction for the outer most electrons decreases making the removal of the outer most electron require less energy. i.e. 1st ionisation energy generally decreases.

2.2.2. Variation in 1st ionisation energy across period 2 and period 3 in the periodic table

Consider across period 2 elements

Element	Li	Be	B	C	N	O	F	Ne
1st Ionisation energy /kjmol^{-1}	513	899	800	1086	11402	1313	1681	2080

The simplified version of inorganic chemistry by SSERWADDA Walter
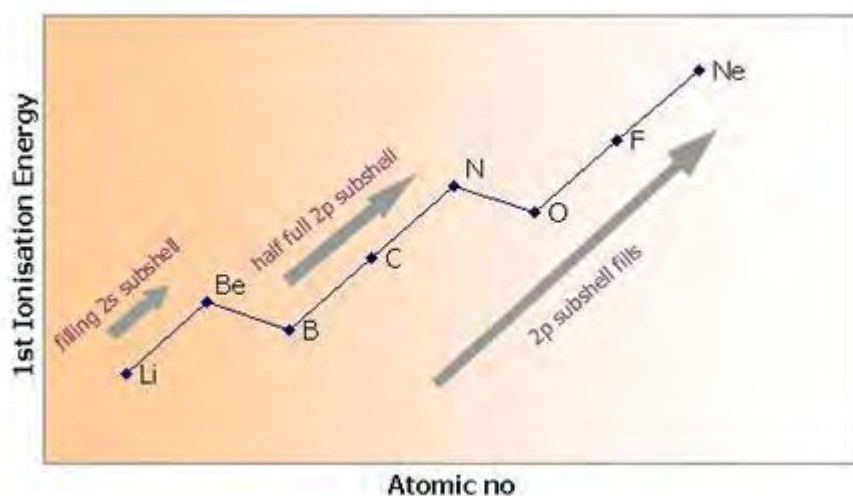
Trend

Ionization energy generally increases across period 2 in the periodic table except that the one for Beryllium is unexpectedly lower than for Boron and also that for Nitrogen unexpectedly lower than for Oxygen.

Explanation

Across period 2 in the periodic table from one atom to the next one, an electron is being added to shell number 2 and also the next atom has one more proton in its nucleus compared with the previous atom. The nuclear charge therefore increases while the screening effect of the electrons in the inner shell on the outer most electrons remains approximately constant.

These leads to an increase in the effective nuclear charge leading to an increase in the nuclear attraction for the outer most electron and hence increase in 1stionisation energy.

Beryllium, $1s^2 2s^2$ has a higher 1st ionization energy than Boron because the outer most 2s sub shell is full of electrons and energetically stable.

Boron, $1s^2 2s^2 2p^1$loses the outer most p-electron more easily than Beryllium despite an increase in the nuclear charge because the shielding effect of the interposing complete inner s-shells increases thus reducing the effective nuclear charge considerably i.e. Boron has an unstable electronic configuration.

There after the nuclear charge increases from boron through carbon $1s^2 2s^2 2p^2$ to nitrogen $1s^2 2s^2 2p^3$, in line with an increase in nuclear charge while electrons are being added to the same shell.

At nitrogen, the *2p*-subshell is half full, the three electrons being unpaired experience minimum repulsion thus thermodynamically stable.

In the case of oxygen $1s^2 2s^2 2p^4$, electron is being paired in one of the *2p*-orbitals as such there is mutual repulsion between the two paired electrons thus a decrease in 1st ionization energy is observed.

Further increase in ionization energy is observed on traversing the period from oxygen to neon. This is in line with increase in nuclear charge as the *2p* sub-shell is building up and reaches a maximum at neon, $1s^2 2s^2 2p^6$, which has a complete stable configuration.

A similar trend is observed on traversing the 3rd short period from sodium to argon.

<u>Note</u>:

In every period, noble gases have the highest 1st ionization energy. This is because noble gases have full outer most p sub shell and thus thermodynamically stable.

Helium: $1s^2$ has the highest 1st ionization energy of all atoms.

This is because Helium atom has the smallest atomic radius therefore electrons in its outer most shell is closer to the nucleus and is attracted more strongly. Also its outermost electronic configuration is thermodynamically stable.

2.2.3. Determination of ionization energies of an atom of an element

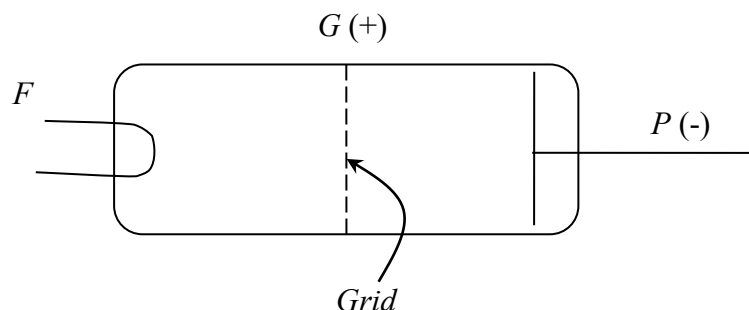*Figure 8 Determination of ionization energies of an atom of an element*

Procedure

The valve is evacuated by means of a vacuum pump and the gaseous atoms of the element whose ionistaion energies are required is introduced into the valve and the inlet closed. The filament F is heated by passing an electric current through it and it gives off electrons; a process referred to as thermo ionic emission.

The grid G is charged to varying positive potentials and the plate P is negatively charged. When the potential on G is set at zero, the electrons emitted by F do not move, but if the potential on G is gradually increased, the electrons accelerate towards G. If the potential on G is high enough, as the electrons accelerate towards G, they collide with the gaseous atoms in the valve and the atoms ionize according to the equation below

$$A_{(g)} \longrightarrow A^+_{(g)} + e$$
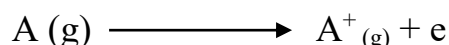
The emitted electron by A is attracted to the grid G while positive Ion A^+ move to plate P. The circuit is then complete and current thus flows and the minimum grid potential for the current to just flow is noted and it's called the 1st ionization potential, measured in electron volts (eV). $1eV = 1.6 \times 10^{-19}$ J

The grid potential is then again increased further so that the 2nd, 3rd, 4th etc electrons are ejected. Each time an increase in the amount of current flowing indicates that more electrons are being lost by A^+. The 2nd, 3rd, 4th etc ionization potentials of A are then measured.

Trend

Ionization energies of an atom of an element increases as more electrons is lost by the atom or its ions i.e. the 2nd I.E is greater than the 1st , the 3rd I.E greater than the 2nd I.E, the 4th I.E greater than the 3rd etc.

Example

Consider the ionization energies of Beryllium in $KJmol^{-1}$

1st	2nd	3rd	4th
900	1768	14905	
21060			

Explanation

The 2nd I.E is greater than the 1st I.E because after a gaseous atom of an element has lost an electron the number of protons in the nucleus of the ion formed is one more than the number of electrons remaining in the shells. Therefore the nuclear attraction for the remaining fewer electrons increases making the lost of a 2nd electron require more energy.

Note:
Still for Beryllium

		Difference
2nd I.E	1st I.E	
1,768	900	868
3rd I.E	2nd I.E	
14,905	1,768	13,137
4th I.E	3rd I.E	
21,060	14,905	6,155

The largest difference between successive ionization energies is $13,137 KJmol^{-1}$ and occurs between the 3rd and 2nd I.Es. This means the shells from which the two electrons bringing about the largest difference in I.Es come from are different i.e. the shell from which the 3rd electron is removed is different from the shell from which the 2nd electron was removed. The first two electrons in Beryllium therefore were removed from the same outer most shell before removing a 3rd electron from another shell. Beryllium therefore belongs to group II in the periodic table.

2.2.4. Importance of ionization energies in understanding the chemistry of atoms of elements:

Ionization energy provides a basis for understanding the chemistry of elements. The following information is provided:

1) _Atomic number of the element_.
   This is given by the number of successive ionization energies an atom has got e.g. sodium with _11_ successive ionization energies has atomic number _11_.

2) _The arrangement of electrons in the shells and distribution of energy level_.
   A plot of successive ionization energies of potassium shows distinct breaks. The arrangement starts with two electrons with fairly similar ionization energies which are both near the nucleus and difficult to

15

remove. These are followed by 8 electrons with fairly similar variation in ionization energies. These have less ionization energies than the first two electrons. The next are eight electrons also with similar energies but are easily removed than the previous.
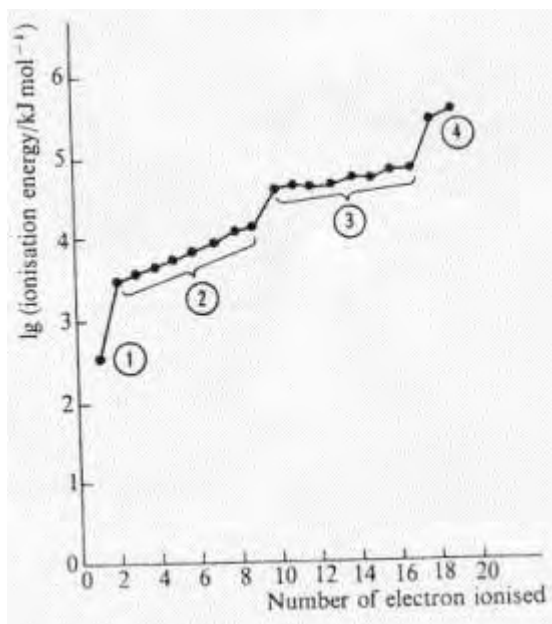
Figure 9: ionization energy of potassium against no of electron removed

In potassium atom there are 4 energy levels and the electrons are arranged as:

Shell number:	1	2	3	4
No. of electrons:	2	8	8	1

Since potassium atom has *4* energy levels and therefore belongs to period *4* in the periodic table.

Since it has one electron in the outer most shell, it belongs to group I in the periodic table.

Note

For a sodium atom with *11* electrons, a similar graph appears as shown in the figure below.
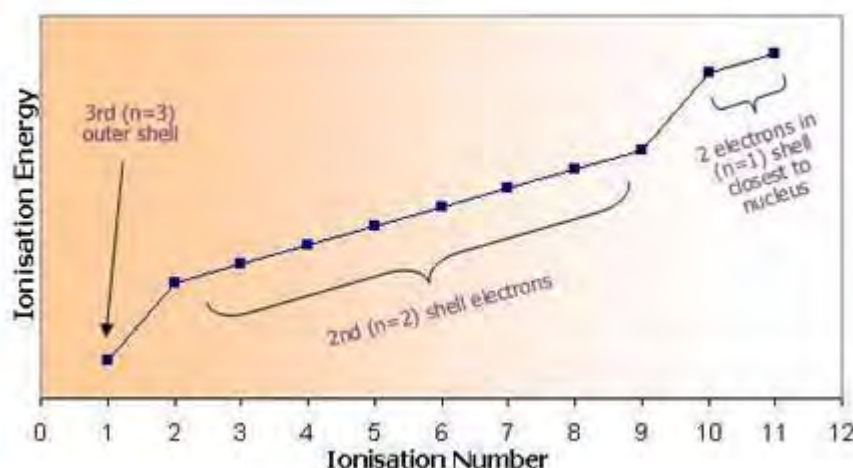
Figure 10 ionization energy of sodium against no of electron removed

Note

Ionization energies also provide information about the presence of sub energy levels.

A careful plot of successive ionization energies in the *2nd* energy level of potassium shows that there are *2* electrons with fairly similar ionization energies which are nearer to the nucleus and they are followed by *6* electrons with less energy but similar. This shows that the electrons in the *2nd* energy level are arranged as:

17

Sub energy:	S	P
No. of electrons:	2	6

3) <u>*Determination of metallic or non metallic character of an atom of an element*</u>.

The magnitude of ionization energy is used as a measure of the metallic character of an element.

The first ionization energies of metals is all nearly below *800kj per mole* while those of non metals are all nearly above *800kj per mole*

<u>Example</u>:

The first three ionization energies for elements A, B, C and D are given in the table below.

Elements	Ionization energies in kJ/mol		
	First	*Second*	*Third*
A	780	1500	7730
B	500	4560	6900
C	580	1815	4620
D	1310	3460	5300

From the first ionization energies of the elements it can be deduced that elements B and C have typical metallic properties since their 1st ionization energies are well below *800kj/mol*

Element A with first ionization energy near *800kj/mol* also would show some metallic properties.

Moving from second to third ionization energy for A there is an increase of about 5 times. This means the third electron of A comes from a different shell hence A has 2 electron on its outer most shell. A is therefore a group *2* element with a valence of *2*,

For element B, there is an increase of about *9* times from first to second ionization energies and an increase of about *1 ½ times* from second to third. Therefore element B has one electron on its outer most shell and thus is a group 1 element and has a valence of, therefore would react by giving away one electron on its outermost shell.

In element C, from *1st* to *2nd* Ionization energy, there is an increase of about 3 times and from second to third by about Therefore there is similar rise in ionization energy. This implies that the three electrons in C *2 ½ times*are from the outer most shell and C therefore has 3 electrons in its outermost shell and hence belongs to group III.

Element D with first ionization energy well over *$800kjmol^{-1}$* is a non metal.

Exercise 1

The first 8 ionization energies in KJ per mole of an element Y are shown below

1st	2nd	3rd	4th	5th	6th	7th	8th
786	1580	3230	4360	16000	20000	23600	29100

   a) Plot a graph of ionization energies against ionization number
   b) Explain the shape of the graph

c) State with reasons the group and the period in which the element belongs in the periodic table

Exercise 2

Element	A	B	C	D	E	F
1st I.E	1013	1000	1255	1519	418	590
2nd I.E	1904	2255	2297	2665	3067	1146
3rd I.E	2916	3389	3853	3933	4393	4916

The table below shows the successive ionization energies of elements A-F.

a) Which element is a noble gas? Give reason for your answer.

b) Which element belongs to;

i) Group I

ii) Group II.

Give a reason for your answer in each case.

Penetrating power of electrons

In an atom with many electrons, up to the 4th shell and beyond may contain electrons. Within the 4th shell, the sub shells are *4s, 4p, 4d* and *4f* with the 4s electrons being nearest to the nucleus followed by the 4p, 4d and finally 4f electrons being furthest to the nucleus of the atom.

The 4s electrons therefore experience the greatest nuclear attraction and hence tend to move towards the nucleus. We say the 4s electrons have the greatest penetrating power and the 4f electrons being furthest from the nucleus experience the least nuclear attraction and have the least penetrating power of all the electrons within the 4th shell of the atom.

Electron affinity

Electron affinity is defined as the enthalpy change when one mole of gaseous atoms gains one mole of electrons to form one mole of univalently charged gaseous anions.

$M_{(g)} + e \rightarrow M^-_{(g)}$ $\triangle$ $H = 1^{st}$ *Electron Affinity.*

Non-metallic electronegative elements are more likely to accept one or more electrons to form anions with a noble gas like structure as such the concept of electron affinity is more useful or important than ionization energy among non metals.

The electron affinity is a measure of the attraction for the incoming electron by the nucleus of the atom gaining the electron.

The greater the attraction, the higher the electron affinity value.
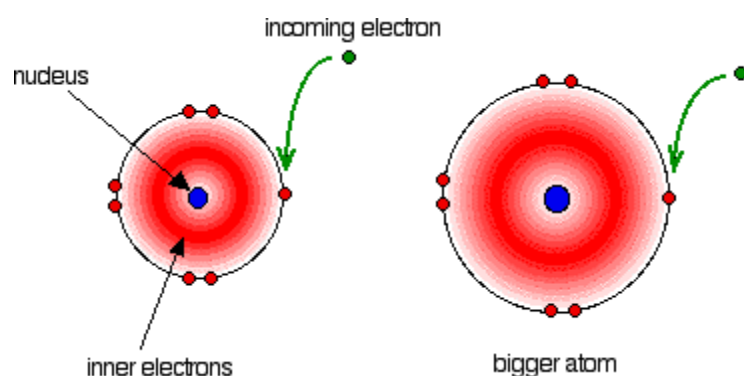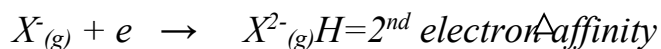

First electron affinity:

First electron affinity is defined as the enthalpy change when one mole of gaseous atoms gains one mole of electrons to form one mole of univalently charged gaseous anions.

$X_{(g)} + e \rightarrow X^-_{(g)}$ $\triangle$ $H = 1^{st}$ *electron affinity*

After the gain of an electron by a gaseous atom, the negatively charged gaseous ion formed repels any further electron to be gained.

Second electron affinity

Is defined as the enthalpy change when one mole of univalently charged gaseous anions gains one mole of electrons to form one mole of divalently charged gaseous anions.

$X^-_{(g)} + e \rightarrow X^{2-}_{(g)}$ $\Delta H = 2^{nd}$ *electron affinity*

Note

1) First electron affinity is an exothermic process for most gaseous atoms.

   Explanation:
   This is because the incoming electron experiences a greater attraction from the nucleus than repulsion from the electrons already present in the atom.

2) Second electron affinity is always an endothermic process.

   Explanation:
   This is attributed to the greater repulsive force which the electron being gained experiences from the electrons already present in the univalently charged anion; therefore work must be done to overcome the effect of this repulsion. This work involves input of heat energy.
   Because of the same reason, the *3rd, 4th, 5th etc* electron affinity will have a positive ΔH signs.

Factors determining the value of 1st electron affinity of an atom of an element

1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius
4) Electronic configuration of the atom.

Explanation

Nuclear charge

22

If the nuclear charge is high, the nuclear attraction for the incoming electron will be high. As the atom gains the electron, a lot of energy is released.

If the nuclear charge is low, the attraction for the incoming electron will be low leading to a low electron affinity.

Atomic radius

If the radius of an atom is small, the incoming electron experiences a high attraction from the nucleus of the atom. As a result a lot of energy is given out as the atom gains the electron giving rise to a high electron affinity.

If the radius of an atom is large, the incoming electron experiences a weak attraction from the nucleus of the atom. As such a lot of energy is given out as the atom gains the electron giving rise to a high electron affinity.

Shielding effect of the electrons in the inner shells

If the screening effect of the electrons in the inner shells is high, then electron being gained experiences a low attraction from the nucleus leading to a low value of electron affinity.

However, if the screening effect is low, the incoming electron experiences a high attraction from the nucleus leading to a high electron affinity value.

Electronic configuration of the outer shell.

If an electron is being added to an atom with a stable outer electronic configuration, the addition will not occur easily leading to a low electron affinity value.

Variation of electron affinity

   i)   **Across period 3 in the periodic table.**

Elements	Na	Mg	Al	Si	P	S	Cl
electron affinity in kj /mol	-20	67	-30	-135	-60	-200	-364

<u>Trend</u>

First electron affinity generally increases from one atom to the next one across period 2 and period 3 in the periodic table.

<u>Explanation:</u>

Across the period from one element to the next one, an electron is being added to the same energy level as the nuclear charge increases by 1 unit. The nuclear charge increases while the screening effect of the electrons in the inner shells on the electron to be gained is roughly constant.

The nuclear attraction for incoming electron increases leading to an increase in the 1st electron affinity.

ii)   Down a group in the periodic table

On descending any group in the periodic table, the electron affinity decreases.

<u>Explanation.</u>

Down a group from one element to the next one, both the nuclear charge and shielding effect increase but the increase in shielding effect outweighs that due to nuclear charge as a result of the more inner shell of electrons added.

The nuclear attraction for the electron being gained decreases leading to a decrease in 1st electron affinity.

<u>Example.</u>

Consider the first electron affinity in Kjmol^{-1} for group VII elements.

Element	1st electron affinity
Fluorine	-328
Chlorine	-349
Bromine	-325
Iodine	-295

Trend

The 1st electron affinity generally decreases from Chlorine to Iodine but the one for fluorine is unexpectedly lower than expected.

Explanation

Down the group, the nuclear attraction for the incoming electron decreases.

As a result the electron being gained experiences a weaker attraction from the nucleus leading to a decrease in 1st electron affinity.

Fluorine, however, has a low value for its electron affinity, numerically less than that for chlorine.

This is due to very its small atomic radius. The 7 electrons in the outermost shell are much closer to each other that they repel each other more strongly than in the other halogens and hence the electron being added experiences a great repulsive force from the electrons already present leading to a lower than expected 1st electron affinity.

2.3. Electronegativity:

This is the tendency by an atom in a covalent bond to attract the bonding electrons more towards itself.

If two atoms with same electronegativity value are covalently bonded to each other, the resultant bond is 100% covalent and the resultant molecule is non polar. This happens when the bonded atoms are atoms of the same element.

Example

Cl-Cl, Br-Br, H-H, O═O etc

If two atoms with different electronegativity values are covalently bonded, the bond electrons are not shared equally. The more electronegative atom attracts the bond electrons more towards itself and in the process acquires a partial negative charge and the less electronegative atom acquires a partial positive charge. The resultant bond molecule is said to be polar and the bond has some ionic character.

Example

$H^{\delta+} - Cl^{\delta-}$, $H^{\delta+} - F^{\delta-}$, $O^{\delta-} = C^{\delta+} = O^{\delta-}$, H_2O, NH_3 etc.

Factors determining electronegativity values

1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius

Explanation

Nuclear charge

If the nuclear charge of an atom covalently bonded to another atom is high, the nuclear attraction for the bonding electrons will be high leading to a high electronegativity value.

For a low nuclear charge, the attraction by the nucleus for the bonding electrons will be low leading to a low electronegativity value.

Atomic radius

If the radius of an atom is small, the bonding electrons are nearer to the nucleus and as such experience a high nuclear attraction leading to a high electronegativity value.

If the radius of an atom is large, the bonding electrons are far away from the nucleus and hence experience a low nuclear attraction leading to a low electronegativity value.

Shielding effect of the electrons in the inner shells

If the screening effect of the electrons in the inner shells is high, the electrons in the covalent bond experience a low attraction from the nucleus leading to a low electronegativity value.

However, if the screening effect is low, the electrons in the covalent bond experience a high attraction from the nucleus leading to a high electronegativity value.

2.3.1. Variation in electronegativity across the period 2 and period 3

Consider across period 3 elements.

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3

Trend

Across the period, electronegativity increases from one element to the next one.

Explanation:

From one element to the next one, an additional electron is added to shell number 3.

As a result, the nuclear charge increases progressively while the screening effect of the inner shells of electrons remains almost unchanged.

As a result, the effective nuclear charge increases leading to increase in the nuclear attraction for the covalent bond electrons and hence an increase in the electronegativity value.

2.3.2. b) Variation in electronegativity down a group.

For group VII elements

Element	Electronegativity
F	4.0
Cl	3.0
Br	2.8
I	2.5

On descending any group in the periodic table from one element to the next, the screening effect of the inner shells of electrons outweighs the increase in the nuclear charge due to an extra inner shell of electrons added.

The effective nuclear charge therefore decreases leading to a decrease in the nuclear attraction for the covalent bond electrons and hence a decrease in electronegativity.

Table 4: Variation of electronegativity in the periodic table

2.4. Electropositivity

This is the tendency of an atom to lose one or more electrons from its outer most shell to form a positively charged ion.

Electropositive elements are those which easily lose one or more electrons to become positively charged ions e.g. Na, Mg, Ca, K, Rb, Ba etc.

2.5. Factors affecting electropositivity value of an atom of an element

1) Nuclear charge of the atom
2) Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell
3) Atomic radius
4) Electronic configuration of the atom.

Explanation:

Atomic radius

If the radius of an atom is small, the outer most electrons are nearer to the nucleus and experience a high nuclear attraction. It's then not easy for the atom to lose one or more electrons leading to a decrease in electropositivity.

If the radius of an atom is large, the outer most electrons are far from the nucleus and hence experience a low nuclear attraction leading to a low electropositivity value.

Nuclear charge

If the nuclear charge is high, the electrons in the outer most shell are attracted more strongly to the nucleus as a result removing an electron from such an atom is difficult leading to a decrease in electro positivity.

For a low nuclear charge, the electrons in the outer most shell are attracted less strongly to the nucleus as a result removing an electron is relatively easy leading to an increase in electropositivity.

Shielding effect of inner shells

If the shielding effect of the electrons in the inner shells on the outer most electrons is high, the nuclear attraction for the outer most electrons is low leading to an increase in electropositivity.

For a low screening effect, the nuclear attraction for the outer most electrons increases leading to a decrease in electropositivity.

Electronic configuration of the atom

If an atom has thermodynamically stable electronic configuration, the lost of an electron will not occur easily leading to a decrease in electropositivity.

On the other hand if an atom has a less stable electronic configuration, then it easily loses an electron leading to a high electropositivity.

Variation of electropositivity down a group in the periodic table

Trend

Electropositivity increases in moving down a group in the periodic table.

Explanation:

Down any group in the periodic table, the increase in the screening effect outweighs that due to nuclear charge due to an extra shell of electrons added from one element to the next one.

This decreases the effective nuclear charge and as a result the nuclear attraction for the outer most electrons reduces leading to an increase in electropositivity.

2.6. Variation in electropositivity across the short periods in the periodic table
Trend

Electropositivity decreases in moving across period 2 and 3 in the periodic table.

Explanation

Across the period from one element to the next one, the nuclear charge increases while the screening effect of the electrons in the inner shells remains

more or less unchanged because the additional electron is added to a shell with similar energy.

The effective nuclear charge therefore increases and as a result the electrons in the outer most shell are attracted more strongly by the nucleus leading to an increase in electro positivity.

2.7. Melting point

Melting point is the constant temperature at which the pure solid and liquid phases of a substance co- exist in equilibrium at a given pressure.

2.7.1. Factors determining melting point

1) **Among metals**

   The melting points of metals depend on the following factors:

   a) *The number of electrons available for metallic bonding (number of delocalized electrons per metal atom)*.
   The higher the number of electrons each metal atom contributes for metallic bonding, the stronger the metallic bond formed and the higher is the melting point.

   b) *The atomic radius*.
   If the radius of a metallic atom is small, the bonding electrons are attracted more strongly by the nucleus making the inter-atomic bond length to be shorter and stronger and thus a higher melting point.
   When the radius of a metallic atom is large, the metallic bonding electrons are weakly attracted by the nucleus as a result the inter-atomic bond becomes longer and weaker leading to a low melting point.

   c) *The crystal structure of the element*.

2) *Among non-metals (Molecular substances)*

   Melting points of non-metals depend on:

   a) Molecular mass

   b) Shape of molecules

   c) Type of intermolecular forces of attraction.

2.7.2. Trends in melting point across period 2 elements

<u>Trend</u>

The Melting point of elements in period 2 increases from lithium to carbon and then decreases abruptly for the non metals nitrogen to neon.

<u>Explanation</u>

The increase in melting point or boiling point from Lithium to Carbon is attributed to:

Increase in number of electrons available for metallic bonding.

(*1* for Lithium, *2* for Beryllium,)

The greater the electrons available, the stronger the bond and the higher the melting point.

Decrease in atomic radius from Lithium to Beryllium.

The smaller the atomic radius, the closer are the bonding electrons to the nucleus and thus the shorter and stronger are the metallic bonds.

Change in the crystal structure of the elements across the period.

Lithium has a body centred cubic (b.c.c) structure which has its atoms less efficiently packed than Beryllium with hexagonal closed packed (h.c.p).

Boron and carbon have giant (macro-) molecular structure composed of large number of covalently bonded atoms with carbon atoms more strongly bonded than boron.

However, the non metallic elements form simple molecular structures held by weak van der Waals forces of attractions as such have very low melting points.

2.7.3. Trends in melting points across period 3

The chart shows how the melting and boiling points of the elements change as you go across the period. The figures are plotted in Kelvin rather than °C to avoid having negative values.
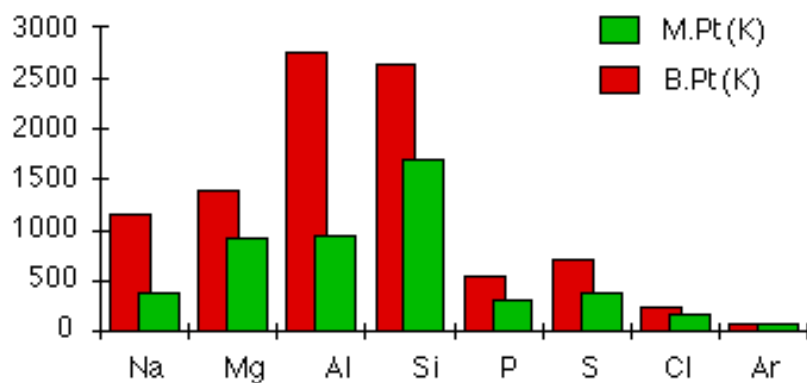
The melting points increase from Na to Si and drops abruptly for the non metallic elements phosphorus to argon.

Melting and boiling points rise across the three metals because of the increasing strength of the metallic bonds.

The number of electrons which each atom can contribute to the metallic bonding increases.

The atoms also get smaller (atomic radius decreases) as you go from sodium through magnesium to aluminium.

The nuclei of the atoms are getting more positively charged and the bonding electrons are getting progressively nearer to the nuclei and so more strongly attracted.

Silicon has the highest melting and boiling points because it has a giant covalent structure. Here strong covalent bonds have to be broken before it melts or boils.

.
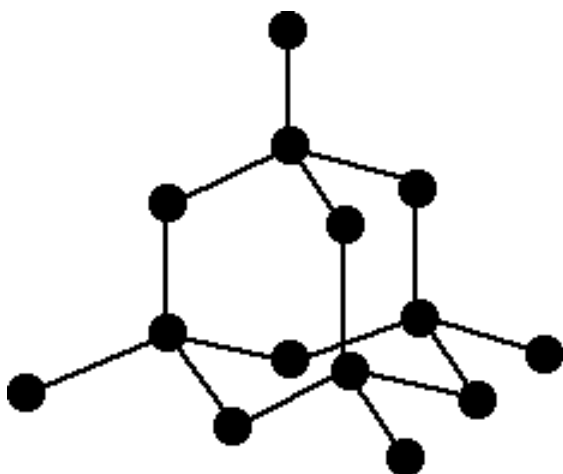
Phosphorus, sulphur, chlorine and argon have simple molecular structures held by weak van der Waals forces of attractions. Thus their melting points are much lower.

The melting and boiling points of non metals are governed entirely by the sizes of   the   molecules.
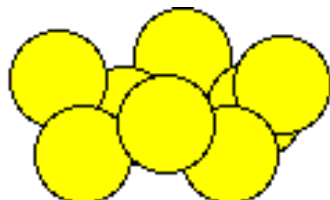
a P_4 molecule   an S_8 molecule   a Cl_2 molecule   an Ar molecule

(not drawn to scale)

Phosphorus

Phosphorus contains smaller P4 molecules. To melt phosphorus you don't have to break any covalent bonds - just the much weaker van der Waals forces between the molecules.

Sulphur

Sulphur consists of larger S8 rings of atoms. The molecules are bigger than phosphorus molecules, and so the van der Waals forces of attractions will be stronger, leading to a higher melting and boiling point.

Chlorine

Chlorine, Cl_2, is a much smaller molecule with comparatively weak van der Waals forces of attractions, and so chlorine will have a lower melting and boiling point than sulphur or phosphorus.

2.7.4. Trend in melting points of Group IIA elements

The melting and boiling points of its group IIA metals are higher than those of corresponding group I elements.

Graph of physical data
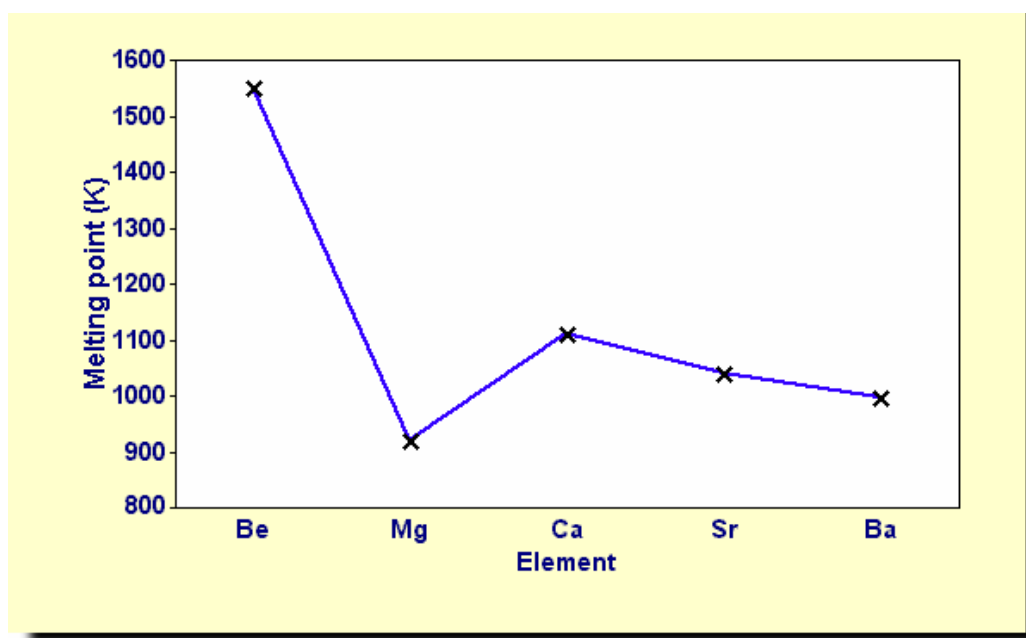
Figure 11: Variation of melting melting point down group II

Explanation

Melting points generally decrease going down Group II in the periodic table.

The Group 2 elements are all metals with metallic bonding. In metallic bonding, metal cations in a metal lattice are attracted to delocalized electrons.

Therefore going down Group II:

The number of delocalized electrons remains the same.

The charge on each metal cation stays the same at +2, but.

The atoms become larger so that the positive nucleus gets further away from the delocalized electrons.

So the force of attraction between the delocalized electrons and the metal cations decreases.

Although in general the melting point decreases going down the group, the melting point for magnesium is anomalously low.

This is because magnesium has a different metallic structure from the other elements in the group apart from beryllium.

Beryllium and magnesium have a hexagonal close-packed structure (h.c.p)

Calcium and strontium have a face-centred cubic structure (f.c.c) and

Barium has a body-centred cubic   structure (b.c.c).

Variation in melting points among the group VII elements (halogens)

Element	Molecular mass	Melting point $/^0c$	Boiling point $/^0c$
Fluorine	38	-220	-188.
Chlorine	71	-101	-34.
Bromine	160	-7	58.
Iodine	254	114	183.

Trend

Both the melting and boiling points of the halogens increase from one element to the next on e down the group.

Explanation

The halogens exist as diatomic molecules i.e. F_2, Cl_2, Br_2 and I_2

Down the group the molecular mass increases. The increase in molecular mass leads to an increase in the magnitude of the intermolecular van der Waal's forces and hence increases in both melting and boiling points.

<u>Example</u>

Consider the boiling points of the hydrides of group IV elements.

Hydride	*boiling point / ^0c*
CH_4	*.161*
SiH_4	*-112*
GeH_4	*-90*
SnH_4	*-52*
PbH_4	*-12*

<u>Trend</u>

The boiling points of the hydrides increase down the group.

<u>Explanation</u>

Down the group the magnitude of the intermolecular van der waal's forces increase with increase in molecular mass.

Chapter 3

3. BONDING AND STRUCTURES.

Atoms take part in chemical bonding to attain stable electronic configuration of noble gases. They do so either through transfer of one or more electrons from one atom to another; a process referred to as ionic or electrovalent bonding or through sharing of electrons; a process referred to as covalent bonding.

In all bonding situations, the electrons involved are those in the outer most shell of the atoms concerned.

The following types of bonding exist;

Ionic or electrovalent bonding

Covalent bonding

Dative or co-ordinate bonding

Metallic bonding

Hydrogen bonding

Van der waal's forces of attraction.

3.1. Electrovalent or ionic bonding

Electrovalent or ionic bonding arises when there is transfer of one or more electrons from a metallic atom to one or more non metallic atom.

Example

Consider the formation of sodium chloride.

Before bonding

Na

Cl

After bonding:

Na$^+$

Cl$^-$

Sodium atom looses the single electron in its outermost shell to form Na^+(isoelectronic to Neon).

A chlorine atom on the other hand gains the electron lost by the sodium atom to form a chloride ion (Cl^-)(has the same electronic configuration as argon).

The sodium and chloride ions are then attracted to each other by strong electrostatic force of attraction leading to the formation of crystalline compound with a high melting point.

Examples of other compounds formed through ionic bonding include;

Calcium chloride; $CaCl_2$

Potassium chloride; *KCl*

Potassium iodide; *KI*

Magnesium oxide; *MgO*

Calcium carbonate; *CaCO₃*etc

3.1.1. Properties of ionic compounds

a) They are usually crystalline solids of high melting and boiling points.

b) They conduct electricity in both aqueous and molten state.

c) They are usually soluble in water.

3.1.2. Polarization of ionic compounds

Consider an ionic compound *AB* with A^+ and B^- as its constituent ions. The positive ion *A+* attracts the electron clouds of the negatively charged ion B^- while at the same time repelling the positively charged nucleus of B^-. This causes distortion of the electron distribution in the B^- ions. This distortion is called polarization and leads to the covalent characteristics in the ionic compound *AB*.

The factors leading to polarization and hence covalent character in ionic compounds are summarized by the Fajan's rule. The rule states that an ionic compound will have appreciable covalent character if;

a) Either the cation or the anion is highly charged. A highly charged anion is highly polarizable and a highly charged cation is highly polarizing.

b) The cation has a small radius making it have a high charge density and hence a high polarizing power.

Example

Consider the melting points of sodium chloride, magnesium chloride and aluminium chloride

Chloride	*Melting point / ⁰C*

NaCl	800
$MgCl_2$	714
$AlCl_3$	180

Trend

Sodium chloride has the highest melting point followed by magnesium chloride and lastly by aluminium chloride.

Explanation

The polarizing power of the cations within the chlorides increase in the order Na^+, Mg^{2+} and Al^{3+} with increase in cationic charge and decrease in cationic radius. Therefore Al^{3+} is the most polarizing and Na^+ the least polarizing. The electron clouds of the chloride ion in sodium chloride are insignificantly polarized while the electron clouds of the chloride ions in $AlCl_3$ are greatly polarized. This makes aluminium chloride predominantly covalent with a low melting point.

The sodium chloride being the most ionic has the highest melting point followed by magnesium chloride.

Note

Polarization is important in explaining the diagonal relationship of elements in the periodic table.

3.1.3. Diagonal relationship

Group	I	II	III	IV	V
Period 2	Li	Be	B	C	N
Period 3	Na	Mg	Al	Si	P

This is relationship within the periodic table where by certain elements in the second period have a close chemical similarity to their diagonal neighbours in the next group of the third period.

This is particularly noticeable with the following pairs.

    a. *Lithium and Magnesium:*

    b. *Beryllium and Aluminium:*

    c. *Boron and Silicon*

Causes of diagonal relationship:

The reasons why the chemistry of the above 3 pairs of elements resemble can be summarized as follows:

    a) The cations in each pair have similar charge densities & similar polarizing powers.

    b) Similar electropositivities of the elements.

    c) Similar hydration energies of the cations,

    d) Similar electrode potentials,

Resemblance between Lithium & Magnesium

The chemistry of lithium and magnesium resemble in the following ways:

Both react directly with nitrogen on heating to form nitrides.

$$6Li_{(s)} + N_{2(g)} \longrightarrow 2Li_3N_{(s)}$$

$$3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(s)}$$
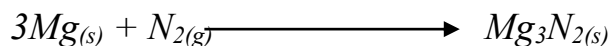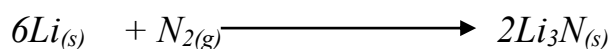
Both react with oxygen gas when heated to form normal oxides.

$$4Li_{(s)} + O_{2(g)} \longrightarrow 2Li_2O(s)$$

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO(s)$$
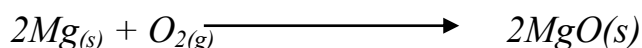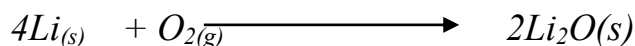
Both their nitrates decompose on heating to form normal oxide, nitrogen dioxide and oxygen gas.

6

$$4LiNO_{3\,(g)} \longrightarrow 2Li_2O_{(s)} + 4NO_{2\,(g)} + O_{2(g)}$$

$$2Mg\,(NO_3)_{2(g)} \longrightarrow 2MgO_{(s)} + 4NO_{2\,(g)} + O_{2(g)}$$
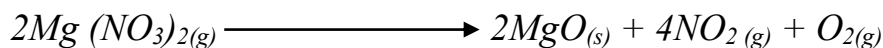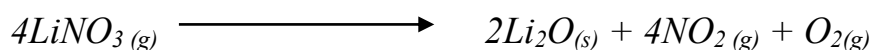
Both form carbonates that decompose on heating.

$$Li_2CO_{3(s)} \longrightarrow Li_2O_{(s)} + CO_{2\,(g)}$$

$$MgCO_{3(s)} \longrightarrow MgO_{(s)} + CO_{2(g)}$$
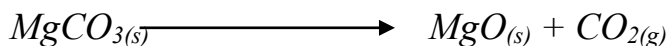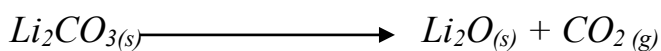
Both react with carbon when heated to form ionic carbide.

$$4Li_{(s)} + C_{(s)} \longrightarrow Li_4C_{(s)}$$

$$2Mg_{(s)} + C_{(s)} \longrightarrow Mg_2C_{(s)}$$
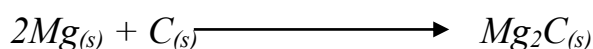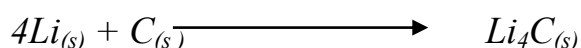
Both form chlorides and bromides that hydrolyze slowly and are soluble in ethanol;

$$MgCl_{2(s)} + 2H_2O_{(l)} \rightleftharpoons Mg(OH)Cl_{(l)} + H_3O^+{}_{(aq)} + Cl^-{}_{(aq)}$$
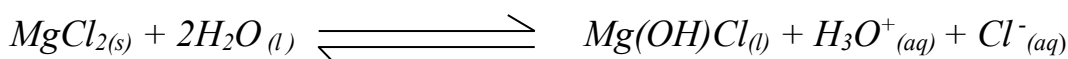
The oxonium ions produced make the resultant solution acidic.

Resemblance between Beryllium and Aluminium:

The chemistry of beryllium and aluminium resemble in the following ways;

1) Both elements are passive to concentrated nitric acid.
2) Both elements react with concentrated alkalis to form complexes. They too react with acids to form salts i.e. they are amphoteric.

$$Be_{(s)} + 2OH^-{}_{(aq)} + 2H_2O_{(l)} \longrightarrow Be(OH)_4{}^{2-}{}_{(aq)} + H_{2(g)}$$
$$2Al_{(s)} + 2OH^-{}_{(aq)} + 6H_2O_{(l)} \longrightarrow 2\,Al(OH)_4{}^-{}_{(aq)} + 3H_{2(g)}$$

$$Be_{(s)} + 2H^+{}_{(aq)} \longrightarrow Be^{2+}{}_{(aq)} + H_{2(g)}$$
$$2Al_{(s)} + 6H^+{}_{(aq)} \longrightarrow 2Al^{3+}{}_{(aq)} + 3H_{2(g)}$$
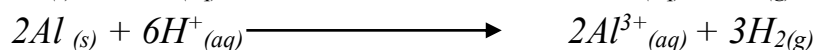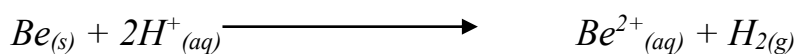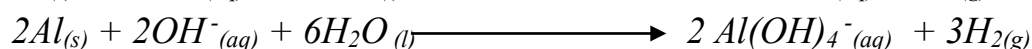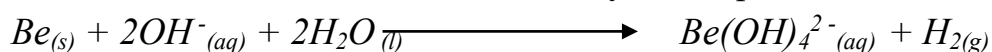
3) Both elements form chlorides which are partly covalent and exist as dimers in vapour phase.

Cl   ClClCl

ClBe —BeCl ⟍Al—— Al

Cl   ClClCl
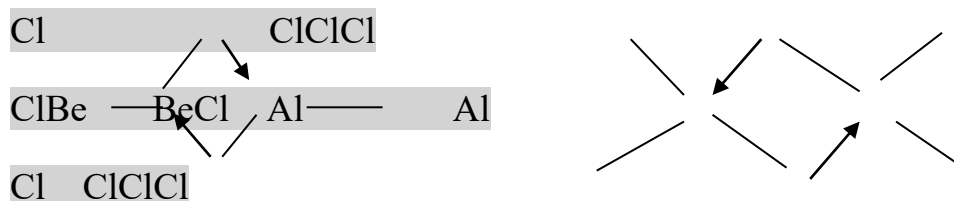
4) Their oxides are amphoteric as are their hydroxides.
   Oxides

$$BeO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Be(OH)_4^{2-}_{(aq)}$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Al(OH)_4^-_{(aq)}$$

$$BeO_{(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + H_{2(g)}$$

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

Hydroxides

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

$$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow Al(OH)^-_{4(aq)}$$

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

$$Al(OH)_{3(s)} + 3H^+_{(aq)} \longrightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)}$$
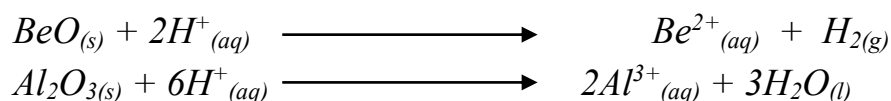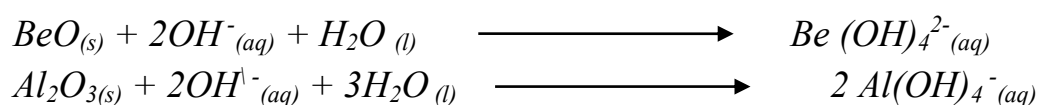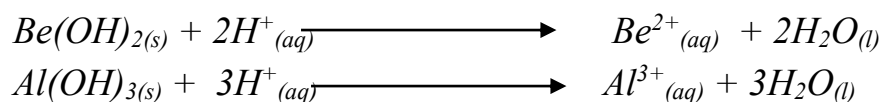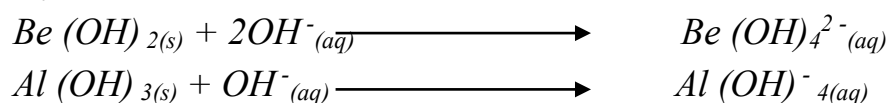
5) Both their carbides hydrolyze in water to form methane gas.

$$Be_2C_{(s)} + 4H_2O_{(l)} \longrightarrow 2Be(OH)_{2(s)} + CH_{4(g)}$$

$$Al_4C_{3(s)} + 12H_2O_{(l)} \longrightarrow 4Al(OH)_{3(s)} + 3CH_{4(g)}$$
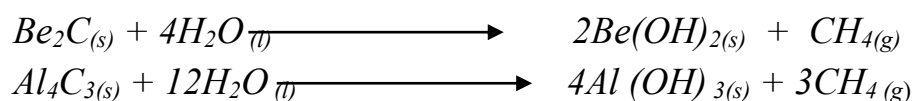
3.2. Covalent bonding

The two Fluorine atoms pair up in order to achieve the same electronic configuration as neon.

$$F \circ + \times F \longrightarrow F \overset{\times}{\underset{\circ}{\rule{2em}{0.4pt}}} F$$
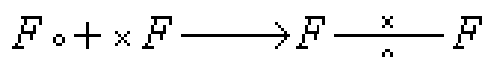
Each atom in the molecules has its outer shell electrons. The atoms in the molecules are held together by the attractive force of the two nuclei.

N.B;

It's not only atoms of the same element which may form covalent bonds. Even atoms of different elements form covalent bonds e.g.

Consider the formation of hydrogen chloride.

Some atoms achieve the noble gas electronic structure by forming double or triple bonds. e.g;

Consider the formation of oxygen and nitrogen molecules.

OXYGEN
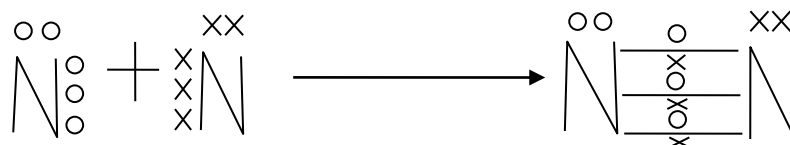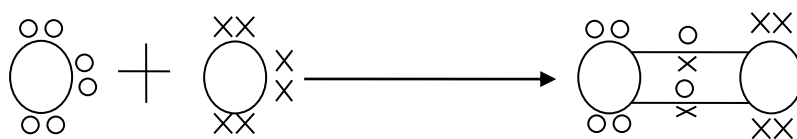
Note

Although atoms share electrons in an attempt to attain noble gas electronic configuration, they are not always successful e.g.

Consider the formation of Boron trifluoride.

$$B \; + \; 3F \longrightarrow F-B-F$$
$$\begin{array}{c} | \\ F \end{array}$$
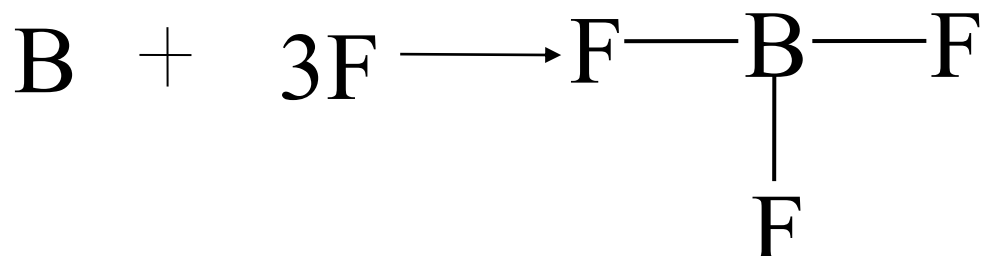
Note

In BF_3 each of the fluorine atoms has attained a stable configuration of Neon but Boron has only six electrons in its outer most shell

Properties of covalent compounds
- They consists of molecules
- They have low melting and boiling points.
- They are usually insoluble in water but soluble in non polar solvents like tetra chloromethane (*CCl₄), carbon disulphide(CS₂), and benzene (C₆H₆)* etc
- They are poor conductors of electricity in molten state.

3.2.1. Polarization of covalent bonds

Polarization of ions in some ionic compounds leads to a degree of covalent character being developed and so it would also seem feasible that polarization of covalent bonds should give them some ionic character.

Polarization of covalent bonds occurs due to atoms having different electronegativities. If two atoms of the same element are covalently bonded, the electrons in the bond will be equally shared between them and the resultant bond is 100% covalent.

However, if the two bonded atoms are different, the bond electrons will be displaced towards the atom with the higher electronegativity and the bond is said to be polarized and will have some ionic character. It is apparent that bonds

10

between atoms with a large difference in electronegativity will be highly polarized i.e. have a considerable ionic character.

Note

There are few molecules that form pure covalent bonds. Even formation of pure ionic compounds is extreme cases. Most compounds have intermediate type of bond i.e. partially ionic and partially covalent but with one character dominating.

3.3. Coordinate (dative) bonding

This is a special type of covalent bonding in which the two electrons being shared in the bond come from only one of the participating atoms (ions). The 2nd atom (ion) only provides space to accommodate the 2 electrons. Although the mode of formation is different, once formed, a coordinate bond is the same as any covalent bond.

Note

Coordinate bond is sometimes indicated by an arrow to show that they have been formed differently from covalent bonds. The arrow points away from the donor towards the recipient.

Example

I. **Consider the formation of ammonium ion from ammonia and hydrogen ion**

$$H^+ + \begin{array}{c} H \\ | \\ :N-H \\ | \\ H \end{array} \longrightarrow \left[\begin{array}{c} H \\ | \\ H-N-H \\ | \\ H \end{array} \right]^+$$
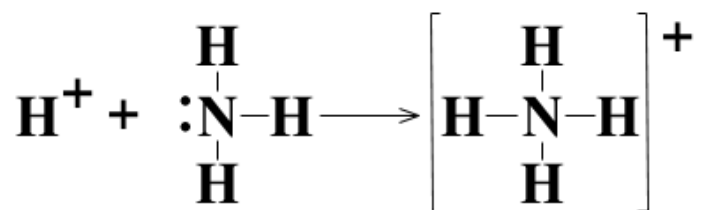
II. Consider the formation of hydroxonium ion from water and hydrogen ion.

$$H^+ + :\ddot{O}:H \longrightarrow H:\ddot{O}:H^+$$
$$\ddot{H} \qquad\qquad \ddot{H}$$
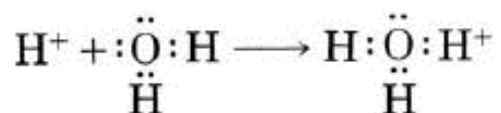
III.   Consider the reaction between BF₃ and NH₃

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}: \;+\; \underset{\underset{F}{|}}{\overset{\overset{F}{|}}{B}}-F \longrightarrow H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}{\rightarrow}\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{B}}-F$$
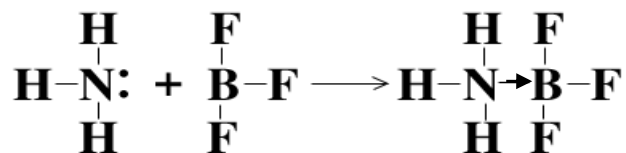
Question

The carbon-chlorine bonds in tetrachloromethane molecule are polar and yet tetrachloromethane molecule as a whole is non polar. Explain.

Answer

Because chlorine is more electronegative than carbon, the electrons in the carbon-chlorine bonds in CCl₄ areattracted more towards the chlorine atoms. The chlorine atoms develop partial negative charges and the carbon atom partial positive charge i.e. the carbon-chlorine bonds are polar. But because the 4 bonds are in opposite directions and are all equal, the polar effect cancel each other and overall CCl₄ is non polar.

3.4.   Metallic bonding

Practically metals are silverish white in colour and are bright and shiny because they reflect all frequencies of light falling on them.

Note

Light absorption and reflection are related to energy levels and so the deduction is that metals utilize similar energy levels.

Other common features metals have in common include low ionization energies and vacant orbitals in their outer most shells. The presence of vacant orbitals in their outer most shell is essential for metallic bonding. Metals may be regarded as consisting of ions occupying fixed positions with the valency electrons

moving in orbitals around the fixed ions. The valency electrons are said to be delocalized and the conduction of electricity and heat by metals is due to these delocalized electrons. The strength of the metallic bond and hence the melting point of metals increases as the number of valency electrons increases.

3.5.   Van der Waal's forces of attraction

Van der Waal's forces arise from induced fluctuating dipoles in atoms and molecules. When one atom or molecule approaches another, the electrons of one or both are temporarily displaced owing to their mutual repulsion and polarization is said to occur. The slightly positive end of one molecule attracts the slightly negative end of the neighbouring molecule. It is this attraction which is the origin of van der Waal's forces of attraction.

As the atoms/ molecules move on, their electron clouds return to normal until their next encounter.

The magnitude of the intermolecular Van der Waal's forces increase with increase in the number of electrons in the molecules which depends on molecular mass.

Note

Both the melting and boiling points of molecules depend on the magnitude of the intermolecular Van der Waal's forces.

Example 1

Variation in melting points among the group VII elements (halogens)

Element	Molecular mass	Melting point /^0c	Boiling point /^0c
Fluorine	38	-220	-188.
Chlorine	71	-101	-34.
Bromine	160	-7	58.
Iodine	254	114	183.

Trend

Both the melting and boiling points of the halogens increase from one element to the next one down the group.

Explanation

The halogens exist as diatomic molecules i.e. F_2, Cl_2, Br_2 and I_2.

Down the group the molecular mass increases. The increase in molecular mass leads to an increase in the magnitude of the intermolecular van der waal's forces and hence increases in both melting and boiling points.

Example 2

Consider the boiling points of the hydrides of group IV elements.

Hydride	boiling point / ^0c
CH_4	.161
SiH_4	-112
GeH_4	-90
SnH_4	-52

PbH₄	*-12*

Trend

The boiling points of the hydrides increase down the group.

Explanation

Down the group the magnitude of the intermolecular Van der Waal's forces increase with increase in molecular mass.

Hydrogen Bonding

This is a dipole –dipole attraction between a hydrogen atom bonded to an electronegative atom and a second electronegative atom having a lone pair of electrons. The atoms of the following elements are electronegative;

- Fluorine is the most electronegative element.
- Oxygen is the 2nd most electronegative after fluorine.
- Chlorine
- Bromine
- Iodine
- Nitrogen

For intermolecular hydrogen bonding to exist, at least one hydrogen atom within the molecule being considered must be directly bonded to an electronegative atom. The following molecules therefore exhibit intermolecular hydrogen bonding.

H_2O, NH_3, CH_3CH_2OH, HCl, HBr, HI, CH_3NH_2, CH_3COOH etc

Note

Hydrogen bonds are infact similar to Van der Waal's forces except that they are much stronger than Van der Waal's forces in molecules of comparable molecular masses.

3.5.1. Evidence for the existence of hydrogen bonding

<u>Example 1</u>

<u>Consider the hydrides of group VI elements</u>

Hydride	Molecular mass/g	boiling point/ ^0c
H_2O	18	100
H_2S	34	-60
H_2Se	81	-41
H_2Te	130	-2
H2Po	211	

<u>Trend</u>

Except for water, the boiling point increases down the group with increase in molecular mass of the hydride.

<u>Explanation</u>

Save for water, the boiling point of the hydrides increase down the group with increase in the magnitude of the intermolecular Van der Waal's forces with increasing molecular mass.

Note

Water with the lowest molecular mass has the highest boiling point due to the very strong intermolecular hydrogen bonds between its molecules.

Example 2

Consider the hydrides of group VII

Hydride	Boiling point /^0c
HF	20
HCl	-85
HBr	-67
HI	-35

Trend

Except for HF, the boiling point increases down the group with increase in molecular mass of the hydrides.

Explanation

From hydrogen chloride through hydrogen bromide to hydrogen iodide, the boiling point increases down the group due to the increase in magnitude of the intermolecular van der waal's forces with increasing molecular mass of the hydrides.

Note

In hydrogen fluoride, the intermolecular hydrogen bonds are quite strong because fluorine is highly electronegative. This explains the very high boiling point of hydrogen fluoride in comparison to the other hydrides in the group.
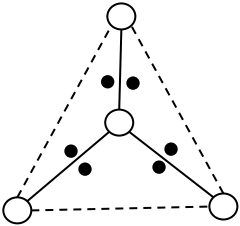
3.6. Shapes of Molecules and Ions;
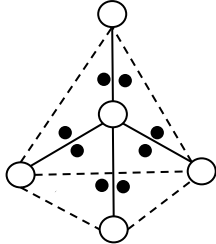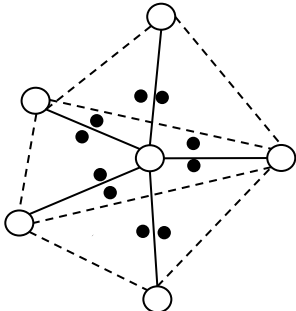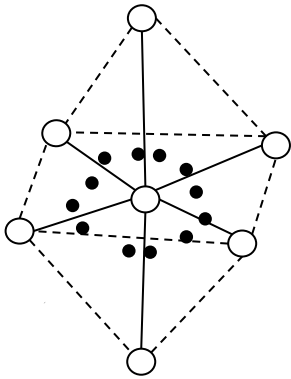
The shape of a given molecule or ion is determined by number of electron pairs present in the outermost shell of the central atom within the molecule or ion.

These electron pairs repel one another one and so they try to get as apart as possible.

- In the outer shell of the central atom there could be;
    - Only bond pairs of electrons e.g. in methane; CCl_4
    - Bond and lone pairs of electrons e.g. in NH_3, H_2O, H_2Setc
- A lone pair of electrons is closer to the nucleus of the central atom than the bond pairs and therefore the repulsion of the lone pairs of electrons have for the bond pairs is so strong i.e. the bond pairs are pushed closer to each other by a lone pair.
- Multiple (double or triple) bonds occupy only one position in space and so from the point of view of molecular shapes act as a single bond

Table 5: Structure of simple molecules

Number of bond pairs on the outer most shell of the central atom	Structure	Shape	Bond angles	Example
2 (All bond Pairs)		Linear	180^0	CO_2, HCN
3 (All bond pairs)		Trigonal Planar	120^0	BF_3, BCl_3

4 (All bond pairs)		Tetrahedral	109.5^0	CCl_4, CH_4
5 (All bond pairs)		Trigonalbipyramidal	120^0, 90^0	PCl_5
6 (all bond pairs)		Octahedral	90^0	$[Al(H_2O)_6]^{3+}$ $[Fe(H_2O)_6]^{3+}$

The above structures look like the figures shown below in three dimensions.

Pyramidal   Tetrahedral   Trigonal bipyramidal

Octahedral   Square planar   T-shaped

Example 1

<u>CH₄</u> CH_4
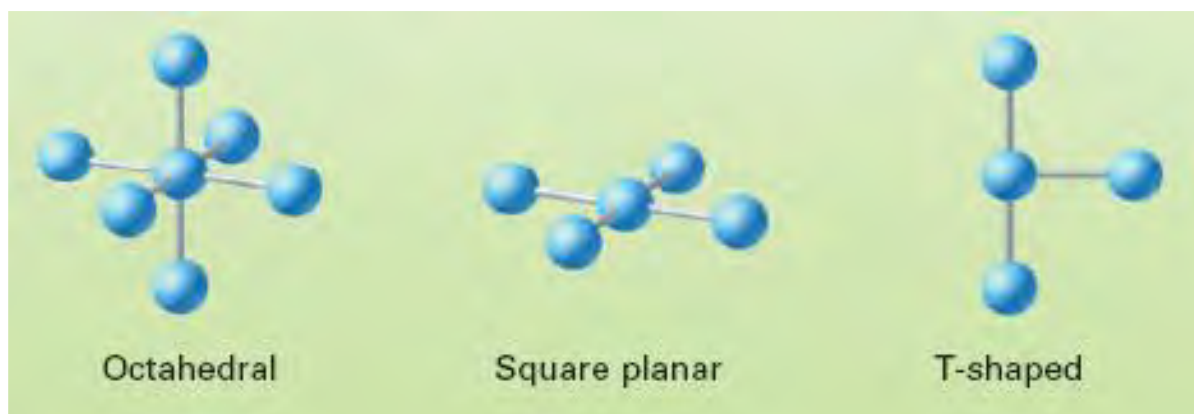
Central atom is C. Its atomic number is 6 (2:4)

The central carbon atom contributes a total of 4 electrons. (4×1)

The 4 hydrogen atoms contribute a total of 4 electrons.

Total number of electrons is 8 electrons (4 pairs, all bond pairs.)
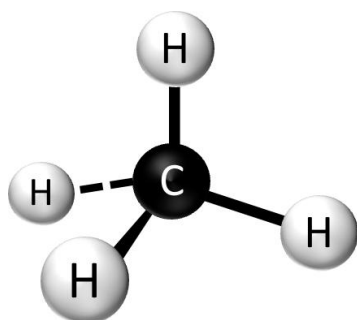
The H-C-H bond angle is 109.5^0

<u>Note</u>.

Other molecules that adopt tetrahedral shape include $CCl_4, SiCl_4$ e.t.c

<u>Example 2</u>

PCl_5

central atom is P

Its atomic number is 15 (2:8:5)

P contributes 5 electrons.

The 5 chlorine atoms contribute a total of 5×1 =5 electrons.

The total of electrons is 10 electrons = (5 pairs, all bond pairs)

Structure: shape:

Trigonalbipyramidal
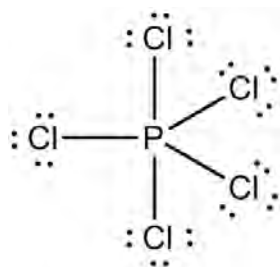
Molecules having both lone and bond pairs of electrons.

Example 1

NH_3

The central atom is nitrogen

Its atomic number is 7 (2:5)

Nitrogen atom contributes 5 electrons.

The 3 hydrogen atoms contribute (3×1) 3 electrons.

Total = 8 electrons (4 pairs; 3 bond pairs and1 lone pair).

Exercise

Draw the structure and name the shape of the above molecule

Note.

In NH_3there are 4 electron pairs in the outer shell of the central nitrogen atom. Given 4 electron pairs, the angle between any two bonds in a molecule is expected to be 109.5^0 but in ammonia, the H-N-H bond angle is only $107^0.$

Explanation.

21

Of the 4 electron pairs present in the outermost shell of the central nitrogen atom in ammonia, 1 pair is alone pair and the other 3 are bond pairs.

The lone pair being closer to the nitrogen nucleus repels the 3 bond pairs more strongly than the bond pairs repel themselves and hence the H-N-H angle reduces to *107⁰*.

Example 2

H₂O

Central atom is oxygen.

Its atomic number is 8 (2:6 or $1S^22S^22P^4$)

Oxygen contributes 6 electrons

The 2 Hydrogen atoms contribute a total of 2 electrons.

Total number of electrons = 8 electrons (4 pairs; 2 lone and 2 bond pairs).

Structure.Shape

 V- Shaped or angular or bent
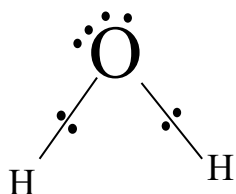
Note

The H-N-H bond angle is 104.5^0 instead of the expected 109.5^0

Explanation.

The 2 lone pairs push the 2 bond pairs more strongly than the bond pairs push themselves.

The repulsion between the bond pairs of electrons will therefore be minimal when the H-N-H bond angle is 104.5^0

Example 3

NH_4^+ $(NH_3 + H^+ \longrightarrow NH_4^+)$
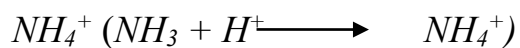
Central atom is N 7 (2:5)

N atom contributes 5 electrons

3 hydrogen atoms contributes 3 ×1= 3 electrons

H^+ contributes   0 electrons

Total number of electrons = 8 electrons (4 pairs; all bond pairs).

Structure: *shape:*

Tetrahedral

Example 5

PCl_3
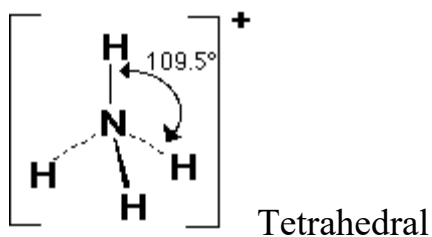
Central atom is phosphorous. 15 (2:8:5)

Phosphorus contributes 5 electrons

3 Chlorine atoms contribute a total of 3 ×1 =3 electrons

Total number of electrons =8 electrons (4pairs; 3bond and1lone pair)

23

Structureshape _____ Trigonal pyramidal

Example 6

CO₂
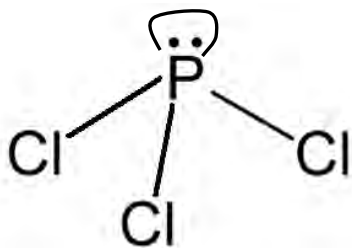
Central atom is C, 6 (2:4) ($1S^2 2S^2 2P^2$)

Carbon contributes 4 electrons.

The two 0_2 atoms contribute (2×2) = 4 electrons.

Total number of electrons =8 electrons (4 pairs.)

Structure   *shape: Linear*

$$O = C = O$$
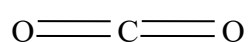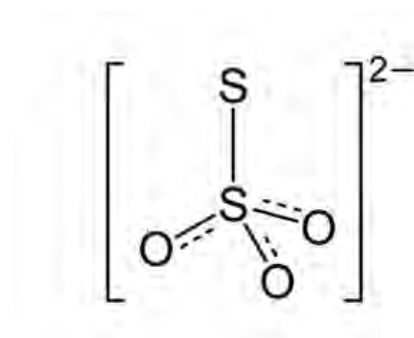
Shapes of some common ions.

a) CO_3^{2-} *(Trigonal Planar)*

Structure:

c) *$S_2O_4^{2-}$ (Tetrahedral)*

.

d) *NO_3^- (Trigonal Planar)*

Structure:

The simplified version of inorganic chemistry by SSERWADDA Walter

f) CrO_4^{2-}

Structure

g) MnO_4^-
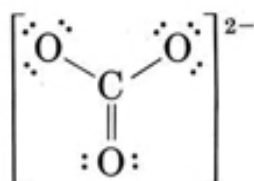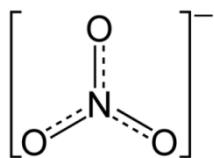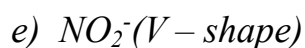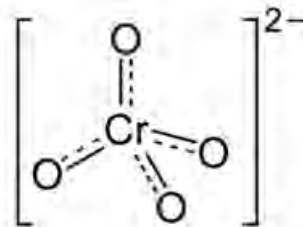
Structure,

e) NO_2^- (V – shape)
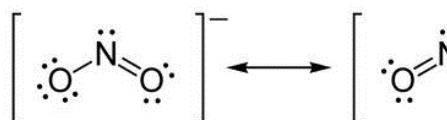
Structure:
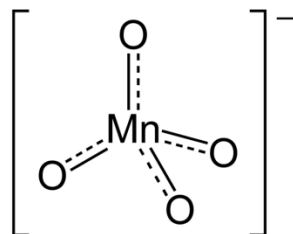
Question

Both H_2O and H_2S molecules adopt v- shaped but the bond angle in H_2O is greater than that in H_2S.

Answer

Oxygen atom being more electronegative than sulphur pulls the bond electrons more towards its self and in the process drawing the bond pairs of electrons nearer. This increases the repulsion between the bond pairs and to reduce the repulsion to a minimum, the bond angle increases.In H_2O therefore the two bond electrons repel each other more strongly than those in H_2S. The greater the repulsion between the bonds pairs the greater the bond angles.

Chapter 4

4. **GROUP IA ELEMENTS (ALKALI METALS) and GROUP IIAELEMENTS(ALKALINE EARTH METALS)**

4.1. Physical properties of group IA elements

Table 6: Physical properties of group 1 elements

Element	Atomic no	Outer elect conf	$1^{st}I.E$ /kjmol^{-1}	Atomic radius / ^{0}A	Melting pt /^{0}c
Lithium	3	$-2s^1$	520	0.15	181
Sodium	11	$-3s^1$	500	0.19	98
Potassium	19	$-4s^1$	420	0.23	63
Rubidium	37	$-5s^1$	400	0.24	39
Caesium	55	$-6s^1$	380	0.60	29

The alkali metals are solids with body centred cubic (b.c.c) arrangement.

They have one valence electron with outer most shell electronic configuration of ns^1 (where *n= 2, 3, 4, 5,6).*

They have low melting and boiling point (only one electron per atom is available for metallic bond formation).

They have the largest atomic radii and lowest ionization energies than any element within the period.

They are highly electropositive and the most reactive metals.

GROUP IIA ELEMENTS (ALKALINE EARTH METALS)

4.2. Physical properties of Group II elements.

Element	Atomic no	Outer elect conf	Ionic radius/^{0}A	1st ionization energy/kjmol^{-1}
Beryllium	4	$-2s^2$	0.31	899
Magnesium	12	$-3s^2$	0.65	738
Calcium	20	$-4s^2$	0.97	589

| Strontium | 38 | -5s² | 1.13 | 549 |
| Barium | 56 | -6s² | 1.35 | 502 |

The alkaline earth metals are electropositive metals with 2 valence electrons (i.e. two electrons in their outer most shell).

The general electronic configuration of their outer shell is ns^2 (n= *2, 3, 4, 5, 6*)

They have smaller atomic radii than corresponding group I metals.

They have higher melting and boiling points than corresponding group I metals.

They have higher 1st ionization energies than corresponding elements in group I.

They are less electropositive, less reactive and form less ionic compounds than group I.

4.3.   Chemical properties of group II and II elements
1. Reaction with Hydrogen.

The more electropositive metals of group I & II react with hydrogen when heated to form ionic hydride except Beryllium and Magnesium which form covalent hydride.

$2Na_{(s)}$ + $H_{2(g}$ ⟶ $2NaH_{(s)}$

$Ca_{(s)}$ + $H_{2(g)}$ ⟶ $CaH_{2(s)}$
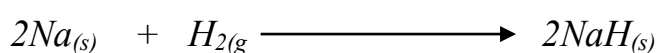
The ionic hydrides are hydrolyzed by water to form hydroxide and hydrogen gas.

$NaH_{(s)} + H_2O_{(l)}$ ⟶ $NaOH_{(aq)} + H_{2(g)}$
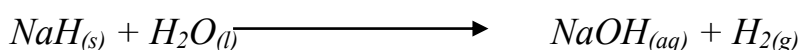
2. Reaction with Water.

All group I metals react with water more vigorously than their group II counterparts to form corresponding hydroxide and hydrogen gas. The vigor of reaction increases down the group.

Explanation

A group I element loses one electron while a group II element loses two electrons. Therefore less energy is required to remove one electron than two from the outer most shell and as such group I metals react faster with water than their neighbouring metals of group II.

As the atomic radius increases down the group, ionization energy decreases therefore increasing reactivity in each group. The lower the ionization energy, the lower the activation energy for reaction and the faster the reaction.

$2X_{(s)} + H_2O_{(l)} \longrightarrow 2XOH_{(aq)} + H_{2(g)}.$ $\qquad X = Li, Na, K, Rb, Cs.$
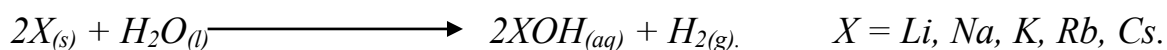
Beryllium does not react with water.

Magnesium reacts with steam to form Magnesium oxide (white solid) and hydrogen gas.

$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}.$
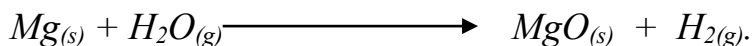
Calcium, Strontium, and Barium react with increasing vigour with cold water forming corresponding hydroxide and hydrogen gas.

$X_{(s)} + 2H_2O_{(l)} \longrightarrow X(OH)_{2(aq)} + H_{2(g)}$
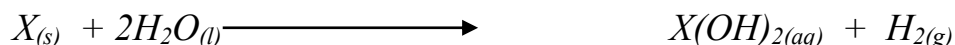
$X = Ca, Sr, \& Ba.$

Note

Solubility of group II hydroxides in water

.

Hydroxide	Solubility per 100g of water at 25^0c

Be(OH)₂	0.00
Mg(OH)₂	0.01
Ca(OH)₂	0.15
Sr(OH)₂	0.89
Ba(OH)₂	3.32

Trend

The solubility of group II hydroxides increases down the group.

Explanation

Down the group, the radius of the cations increases while the charge on them remains the same. This leads to a decrease in both the lattice and hydration energies.

But the decrease in lattice energy of the hydroxides is more rapid than the decrease in hydration energy.

As such the lattice energy is easily superseded by the hydration energy thus facilitating solubility of the hydroxides.

3. Reaction with acids.

a) Dilute and concentrated hydrochloric acid

Group II metals react with hydrochloric acid forming corresponding salt and hydrogen gas.

$$M_{(s)} + 2H^+_{(aq)} \longrightarrow M^{2+}_{(aq)} + H_{2(g)} \quad (M = Be, Mg, Ca, Sr, Ba)$$
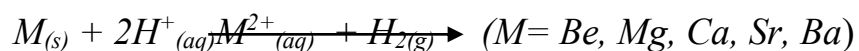
b) Dilute sulphuric acid.

Beryllium reacts with hot dilute sulphuric acid to form salt and hydrogen gas.

$Be_{(s)}$ + $2H^+{}_{(aq)}$ ~~$Be^{2+}{}_{(aq)}$ + $H_{2(g)}$~~
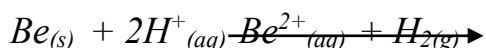
Magnesium reacts with cold dilute to form salt and hydrogen gas.

$Mg_{(s)}$ + $2H^+{}_{(aq)}$ $\longrightarrow$ $Mg^{2+}(aq)$ + $H_{2(g)}$
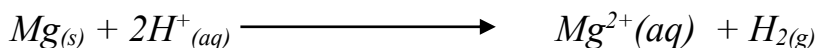
Calcium, Strontium & Barium react to form a sparingly soluble sulphate which renders the reaction passive.

c) <u>Reaction with conc. sulphuric acid</u>

Be reacts in the same way as with dilute sulphuric acid.

However other members of the group react with conc. sulphuric acid to form salt, sulphur dioxide and water.

$M_{(s)}$ + $2H_2SO_{4(l)}$ $\longrightarrow$ $MSO_{4(aq)}$ + $SO_{2(g)}$ + $2H_2O_{(l)}$ (M = Mg, Ca, Sr, Ba.)
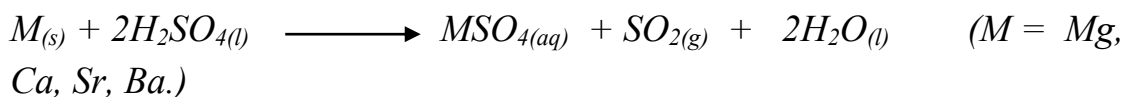
d) <u>Reaction with nitric acid.</u>

Beryllium does not react with nitric acid at all conditions.

Magnesium reacts with dilute nitric acid to form salt and hydrogen gas.

$Mg_{(s)}$ + $2HNO_{3(aq)}$ $\longrightarrow$ $Mg(NO_3)_{2(aq)}$ + $H_{2(g)}$
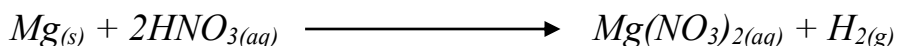
Magnesium reacts with conc. nitric acid to form salt, nitrogen dioxide and water.

$Mg_{(s)}$ + $4HNO_{3(aq)}$ $\longrightarrow$ $Mg(NO_3)_{2(aq)}$ + $2NO_{2(g)}$ + $2H_2O_{(l)}$
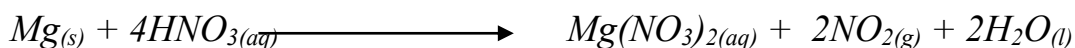
Calcium, Strontium & Barium react with nitric acid to form salt, nitrogen dioxide and water.

$Ba_{(s)}$ + $4HNO_{3(aq)}$ $\longrightarrow$ $Ba(NO_3)_{2(aq)}$ + $2NO_{2(g)}$ + $2H_2O_{(l)}$
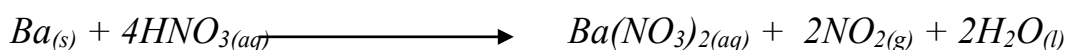
4. <u>Reaction with Oxygen.</u>

The s-block elements react with oxygen to form 3 types of oxides namely

a) *Normal oxide (O^{2-})*

b) *Peroxide (O_2^{2-})*

c) *Superoxide (O_2^-)*

All group I metals form normal oxide with oxygen.

$4M_{(s)} + O_{2(g)} \longrightarrow 2M_2O_{(s)}$ *(M= Li, Na, K, Rb, Cs.)*
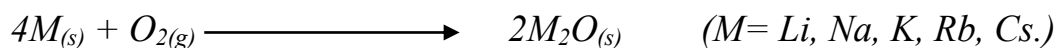
Elements sodium to caesium in addition form peroxides.

$2M_{(s)} + O_{2(g)} \longrightarrow M_2O_{2(s)}$ *(M= Na, K, Rb, Cs.)*

Elements K to Cs in addition form superoxide.

$M_{(s)} + O_{2(g)} \longrightarrow MO_{2(s)}$ *(M= K, Rb ,Cs)*
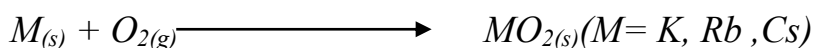
Note

Lithium is not capable of forming higher oxides due to the fact that Li^+ is very small, with high charge density & high polarizing power. Thus the larger oxides cannot be accommodated around it otherwise the compound would be highly covalent & unstable.

All group II metals when heated in air form normal oxides.

$2M_{(s)} + O_{2(g)} \longrightarrow 2MO_{(s)}$ *(M= Be, Mg, Ca, Sr, Ba)*

The more electropositive metals form peroxides e.g Strontium & Barium.

$M_{(s)} + O_{2(g)} \longrightarrow MO_{2(s)}$ *(M = Sr, Ba)*
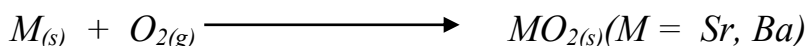
Note:

The tendency to form peroxide increases down the group. This is because the radii of the cations increase down the group, as such their charge densities and polarizing powers decrease. Therefore the larger peroxide can easily be accommodated around the cation with least polarization forming stable lattice.

Beryllium oxide is amphoteric, shows both basic and acidic properties.

$$BeO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Be(OH)_4^{2-}_{(aq)}$$

$$BeO_{(s)} + 2H^+_{(aq)} \longrightarrow Be^{2+}_{(aq)} + H_{2(g)}$$
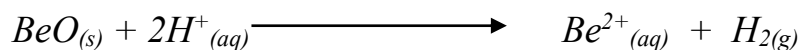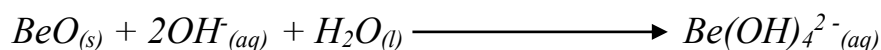
The other oxides are ionic and basic in nature.

5. <u>Reaction with halogens.</u>

All the metals of group I & II combine directly under heat to form chlorides.

$$2Li_{(s)} + Cl_{2(g)} \longrightarrow 2LiCl_{(s)}$$

$$Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$$
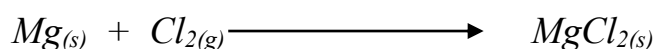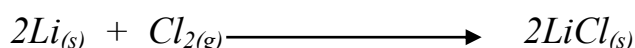
4.4. Compounds of group I and II elements

<u>Compounds of group II elements are less ionic than their corresponding group I compounds.</u>

<u>Explanation</u>

The cations of group II have smaller ionic radius than corresponding group I.

Also group II cations are doubly charged while those of group I are singly charged.

Therefore cations of group II have higher charge density and more polarizing power than corresponding group I cations. As such compounds of group II are less ionic than corresponding group I compound. e.g. Magnesium chlorideisless ionic than Sodium chloride.

<u>Solubility of ionic salts in water</u>

Solubility of an ionic salt in water is determined by two energy terms:

a) Lattice energy of the salt.

b) Hydration (solvation) energies of the constituent ions of the salt.

<u>Lattice energy</u>

This is the energy required to decompose 1 mole of an ionic salt into its constituent gaseous ions.

$$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)} \quad \Delta H = \text{Lattice energy}$$

<u>Or</u>

It is the amount of energy given out when 1 mole of an ionic salt is formed from its constituent gaseous ions.

$Na^+_{(g)} + Cl^-_{g)} \rightarrow NaCl_{(s)}$H = Lattice energy.

<u>Hydration energy</u>

This is the amount of energy released when 1 mole of gaseous ions is fully dissolved in water at a given temperature.

$Na^+_{(g)} + aq \rightarrow Na^+_{(aq)}$H = Hydration energy.
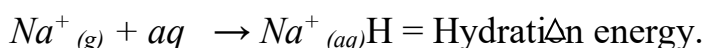
Hydration energy has a negative ΔH sign because it involves release of heat energy.

<u>Example</u>

1) Each ion has its own hydration energy.

$Mg^{2+}_{(g)} + aq \rightarrow Mg^{2+}_{(aq)}H^\theta_{Hyd(298k)} = -696kj/mol.$

$Na^+_{(g)} + aq \rightarrow Na^+_{(aq)}H^\theta_{Hyd(298k)} = -406kj/mol.$

$Cl^-_{(g)} + aq \rightarrow Cl^-_{(aq)}H^\theta_{Hyd(298k)} = -377kj/mol.$
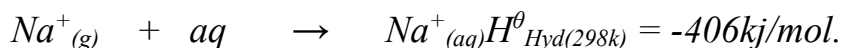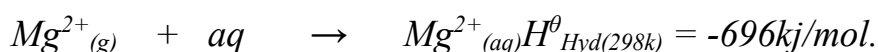
Therefore the $H^\theta_{Hyd(298k)}$ of NaCl = (-406 + -377) = -783kj/mol and that of $MgCl_2$ = (-696 + 2x-377)= -1450.

2) The smaller the ionic radius the higher the charge density and so the greater (more negative) the hydration energy.

3) Water is a suitable solvent for dissolving ionic salts because:

a) it is a polar solvent,

b) has a high dielectric constant.

c) has a large dipole moment, so that ion-dipole interaction is high.

If the hydration energy of a substance is greater than its lattice energy, the substance will dissolve exothermically in the solvent.

If the hydration energy is less than the lattice energy then the substance dissolves endothermically.

However, if lattice energy is much larger than hydration energy then the salt does not dissolve in water.

Enthalpy of solution

This is defined as the heat change when 1 mole of an ionic salt is completely hydrated in water.

$NaCl_{(s)} + aq \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ ΔH = enthalpy of solution of sodium chloride.

$Na^+_{(g)} + Cl^-_{(g)}$

$H_{lattice}$ Δ $H_{hydration}$ Δ

$NaCl_{(s)}$

$H_{solution}$ Δ

$Na^+_{(aq)} + Cl^-_{(aq)}$
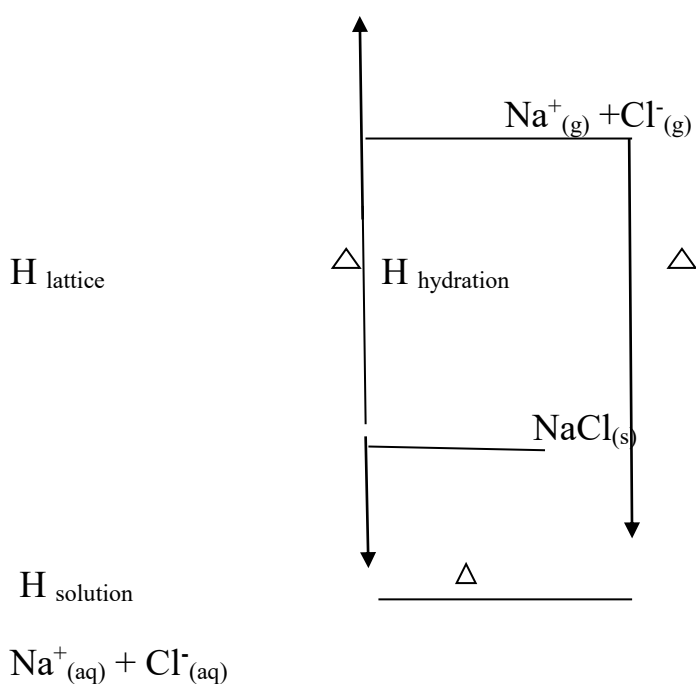
Figure shows Born-Haber cycle for solubility of sodium chloride in water.

$\triangle$H solution = $\triangle$ H lattice $+\triangle$ H hydration

Note:

Whenever this formula is being applied in calculation, the valu$\triangle$ of H lattice must be positive. This is because the formula is only valid when the salt is being decomposed as shown in the cycle above.

Exercise 1

The lattice and hydration energies of *MgCl₂* are -2644 kJmol⁻¹ and -2653 kJmol⁻¹ respectively.

a) Draw an energy diagram (Born-Haber cycle*)* for the solubility of *MgCl₂*inwater and indicate the energy changes that occur.

b) Calculate the enthalpy of solution of the salt.

Exercise 2

a) Using potassium iodide, draw energy diagram (Born Haber Cycle) to show the energy changes during the solubility of the ionic salt in water.

b) The enthalpy of solution and lattice energy of potassium iodide are +21kJmol⁻¹ and -642kJmol⁻¹ respectively. Calculate the hydration energy for potassium iodide.

Factors determining the lattice energy of a given ionic salt

a) Ionic charge (charge on the ion)

b) Ionic radius

Explanation

Ionic charge

Lattice energy is directly proportional to the ionic charge.

If ionic charge is high, then the electrostatic forces of attraction between the oppositely charged ions are stronger leading to high lattice energy.

If ionic charge is small, the electrostatic forces of attraction between the oppositely charged ions are weaker leading to low lattice energy.

Ionic radius

Lattice energy is inversely proportional to ionic radius.

If ionic radius is large, the electrostatic forces of attraction between the oppositely charged ions are weaker leading to low lattice energy.

On the other hand if the ionic radius is small, the electrostatic force of attraction between the oppositely charged ions is greater leading to high lattice energy.

Salts of group 2 elements are less soluble in water than the corresponding group 1 salts.

Explanation

The cations of group II have smaller ionic radius than corresponding group I.

Group II cations are doubly charged while those of group I are singly charged.

Therefore the lattice energy of group II salts are much higher than those of corresponding group I salts.

The higher lattice energy of group II salts makes them less soluble than their corresponding group I salts.

Sulphates of group I& II elements

Sulphates of group I are white solids which are stable to heat and are readily soluble in water.

Sulphates of group II are white solids and sparingly soluble in water.

Solubility of group II sulphates in water

.

Sulphate	Solubility per 100g of water at 25^0c
$BeSO_4$	43
$MgSO_4$	36
$CaSO_4$	0.20
$SrSO_4$	0.011
$BaSO_4$	0.0024

Trend

The solubility of the sulphates decrease down the group

Explanation

Down the group, the radius of the cations increases while the charge on them remains the same. This leads to a decrease in both the lattice and hydration energies.

Therefore the decrease in solubility of the sulphates down the group is attributed to the fact that the hydration energy of the suphates decreases more rapidly than the lattice energy down the group.

Note

Solubility of the nitrates carbonates and chromates follow a trend similar to those of the sulphates.

Carbonates of group I & II elements

The carbonates of group I metals are white solids; readily dissolve in water and are unaffected by heat except lithium carbonate which decomposes on heating.

$Li_2CO_{3(s)} \xrightarrow{} Li_2O_{(s)} + CO_{2(g)}$
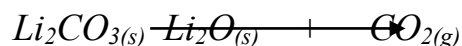
Explanation

Li⁺ ion has a very small radius giving it a high charge density and a high polarizing power. As such the Li⁺ ion is capable of forming a stable compound with an oxide ion.

However, as the group is descended the radii of the cations increase and their charged densities decrease. Thus they cannot easily be accommodated around the smaller oxide ion due to its high polarizing effect.

Carbonates of group 2 decompose on heating to form the metal oxide and carbon dioxide gas.

$MCO_{3(s)} \longrightarrow MO_{(s)} + CO_{2(g)}$ (M= Be, Mg, Ca, Sr, Ba)
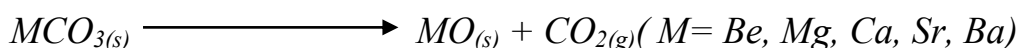
The thermal stability of the carbonates increases as the group is descended.

Carbonate	Decomposition temp. ^0C
$BeCO_3$	100
$MgCO_3$	350
$CaCO_3$	900
$SrCO_3$	1290
$BaCO_3$	1350

Explanation

On descending the group, the charge densities of the metal cations progressively decrease due to increase in cationic radius.

Since an oxide is smaller than a carbonate ion, the decomposition of metal carbonates becomes less energetically favourable down the group.

Nitrates of group I & II elements.

Group I nitrates (except lithium nitrate) decompose on heating forming nitrites and oxygen.

$$2MNO_{3(s)} \longrightarrow 2MNO_{2(s)} + O_{2(g)}(M= Na, K, Rb, Cs)$$

However lithium nitrate decomposes to form metal oxide, nitrogen dioxide and oxygen.

$$4LiNO_{3(s)} \longrightarrow 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

Explanation

The oxide (O^{2-}) ion is much smaller than the NO_3^- ion. Li^+ ion has a very small radius giving it a high charge density and a high polarizing power.

As such the smaller oxide ion (O^{2-}) approaches the Li^+ ion more closely and thus forming a stable oxide.

However, as the group is descended the radii of the cations increase and their charge densities decrease. Their nitrates decompose to relatively smaller nitrites. The decrease from nitrate to nitrite stabilizes the compound.

4.5. Complex formation by group II cations
Complex ion formation is favoured by:

a) Presence of suitable empty orbitals on the cations to accommodate the lone pairs of electrons donated by ligands.

a) Small cationic radius.

b) High cationic charge.

The tendency to form complex ions decreases rapidly down the group with increasing cationic radius & decrease in the charge density of cations. This is because the attraction for the lone pairs of electrons on the ligands decreases with decrease in cationic charge density.

Beryllium cation forms complex easily due to its very small ionic radius & high charge density e.g. *Be(OH)$_4^{2-}$, Be(H$_2$O)$_4^{2+}$*

Reactions in which Beryllium resembles other group II elements include:

   a) Burns in air to form normal oxide.

   b) Reacts with chlorine gas when heated to form chloride.

   c) Reacts with dilute hydrochloric acid liberating hydrogen gas.

Reactions in which Beryllium differs from other group II metals include:

   a) Beryllium reacts with conc. alkalis but other group II elements do not.

   b) Beryllium oxide is amphoteric i.e. shows both basic and acidic properties but other oxides of the group II elements are basic in nature.

   c) Beryllium carbide reacts with water to form methane.

   d) Beryllium chloride is partly covalent and exists as dimer in vapour state. Other members form ionic chlorides.

4.6. Analysis of Magnesium, Calcium and Barium ions in solutions

   1) Use of sodium hydroxide solution.

   Procedure

   To the solution containing the unknown cation is added sodium hydroxide solution dropwise until in excess.

   Observation

   a) With Mg^{2+}, a white precipitate of magnesium hydroxide, insoluble in excess sodium hydroxide is observed.

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Mg(OH)_{2(s)}$$
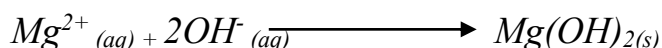
With Ca^{2+}, a white precipitate of calcium hydroxide, insoluble in excess sodium hydroxide is formed

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Ca(OH)_{2(S)}$$
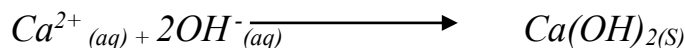
b) With Ba^{2+} a white precipitate of barium hydroxide, insoluble in excess sodium hydroxide is formed

$$Ba^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Ba(OH)_{2(S)}$$
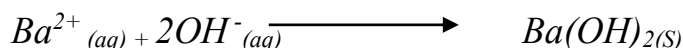
2) Aqueous ammonia solution

Procedure

To the solution containing the unknown cation is added aqueous ammonia solution dropwise until in excess.

Observation

a) With Mg^{2+}, precipitate of magnesium hydroxide, insoluble in excess ammonia is observed.

b) With Ca^{2+} or Ba^{2+} ions there is no observable change.

Explanation

Aqueous ammonia being a weak base does not have hydroxide ions in sufficient concentration to exceed the solubility products of $Ca(OH)_2$ and $Ba(OH)_2$ which are quite high.

3) Use of dilute suphuric acid or any solution containing sulphate ions.

Procedure

To a few cm^3 of the solution containing the unknown cation is added dilute sulphuric acid (sodium sulphate solution or potassium sulphate can also be used).

Observation

a) There is no observable change with Mg^{2+}

b) With either Ca^{2+} or Ba^{2+} a white precipitate of either calcium sulphate or barium sulphate is formed.
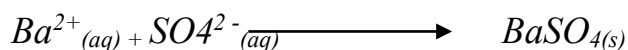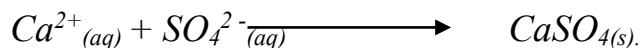
Equation

$$Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow CaSO_{4(s).}$$

$$Ba^{2+}{}_{(aq)} + SO4^{2-}{}_{(aq)} \longrightarrow BaSO_{4(s)}$$

4) Use of potassium chromate solution

Procedure

To the solution containing the unknown cation is added potassium chromate solution followed by ethanoic acid.

Observation

a) With Mg^{2+} there is no observable change.

b) With Ca^{2+} a yellow precipitate of calcium chromate soluble in ethanoic acid is formed.

$$Ca^{2+}{}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow CaCrO_{4(s)}$$
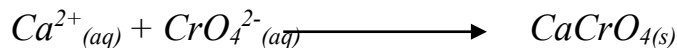
c) With Ba2+ a yellow precipitate of barium chromate insoluble in ethanoic acid is formed.

$$Ba^{2+}{}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow BaCrO_{4(s)}$$
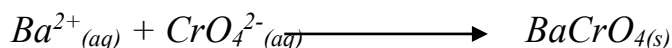
5) Use of ammonium oxalate solution

Procedure

To the solution containing the unknown cation is added ammonium oxalate solution followed by ethanoic acid.

Observation

a) With Mg^{2+} there is no observable change.

b) With Ca^{2+} a white precipitate of calcium oxalate insoluble in ethanoic acid is formed.

$$Ca^{2+}_{(aq)} + C_2O_4^{2-}_{(aq)} \longrightarrow CaC_2O_{4(s)}$$
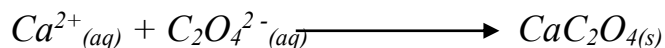
c) With Ba^{2+} a white precipitate of barium oxalate soluble in ethanoic acid is formed.

$$Ba^{2+}_{(aq)} + C_2O_4^{2-}_{(aq)} \longrightarrow BaC_2O_{4(s)}$$

6) Use of disodium hydrogen phosphate solution

Procedure

To the solution containing the unknown cation is added little aqueous ammonia followed by ammonium chloride and then a few drops of disodium hydrogen phosphate.

Observation

a) With Mg^{2+} a white precipitate is formed

b) There is no observable change with Ca^{2+} and Ba^{2+} ions.

Exercise I

A chloride of beryllium Z contains 11.25% beryllium and 88.75% of chlorine.

a) Calculate the empirical formula of Z.

b) Determine the molecular formula of Z (vapor density of Z=80).

c) Write the structural formula of Z.

Exercise II

A chloride of aluminium X, contains 20% aluminium and 80% chlorine.

a) Calculate the empirical formula of X.

b) Determine the molecular formula of X (vapor density of X= 133.5).

c) Write the structural formula of X.

Exercise III.

When 0.13g of a chloride of iron was vaporized at 600k and 1 atmosphere pressure, 20cm³ of vapor was formed.

a) Calculate the relative mass of iron chloride.

b) Determine the molecular formula of the iron chloride.

c) Write the structural formula of the iron chloride.

Exercise IV.

a) Compare the reaction of beryllium and barium with sulphuric acid under various conditions.

b) Explain how the solubility and basicity of the hydroxides of the elements of group II in the Periodic Table vary down the group.

Exercise V.

Describe the reactions, if any, between each of the following elements, Be, Mg and Ca with:

a) Warm dilute sulphuric acid.

b) Warm   conc.   sodium   hydroxide.

c)

CHAPTER 5

5. GROUP (IV) ELEMENTS

Table 7: physical properties of group IV elements

Element	Atomic no	Outer elect conf	Atomic radius /^0A	Electronegativity
Carbon	6	$-2s^2 2p^2$	0.077	2.50
Silicon	14	$-3s^2 3p^2$	0.177	1.75
Germanium	32	$-4s^2 4p^2$	0.122	2.00
Tin	50	$-5s^2 5p^2$	0.140	1.70
Lead	82	$-6s^2 6p^2$	0.154	1.55

5.1. Physical properties of group (IV) elements

All group (IV) elements have four electrons in their outermost shell with a general outer configuration of $ns^2 np^2$ (where *n= 2, 3, 4, 5, 6*).

Metallic character increases down the group as the radius of the atoms become larger. Carbon and Silicon are non metals, Germanium is a metalloid i.e. it exhibits properties characteristic of metals and non metals while Tin & Lead are weak metals.eg they form amphoteric oxides

All elements show oxidation states of +2 and +4. The +2 oxidation state arise due to the inability of the outer most paired 's' electrons to take part in bond formation. This is called the *inert pair effect*.

The stability of the +2 oxidation state increases down the group from carbon to lead. This is due to increasing metallic character and increasing inert pair effect as the group is descended.eg Carbon and Silicon form extremely unstable compounds in +2 oxidation state.

Germanium and tin compounds in +2 oxidation state are predominantly covalent and are readily oxidized ie they are powerful reducing agent.

Lead invariably forms more stable compounds in +2 oxidation state than +4 oxidation state. Also compounds of lead in +2 oxidation state are ionic in

nature. Therefore lead (IV) compounds are unstable, and readily decompose to (II) compouds.eg

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

$$PbCl_{4\ (l)} \longrightarrow PbCl_{2(s)} + Cl_{2\ (g)}$$
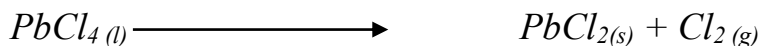
The stability of +4 oxidation state decreases down the group. Carbon, silicon and germanium form more stable compounds in +4 oxidation state than in +2. This could explain why their compounds in +2 oxidation states are good reducing agents.

Carbon is the only member of the group whose covalency is restricted to a maximum of 4.This is due to absence of the vacant 'd' orbitals. Other elements have a maximum of 6 due to the availability of vacant d-orbitals which allows them to expand their octet.

Hoverer, all the elements exhibit a covalency of 4 but compounds of the type M^{4+} or M^{4-} are rare. This is because the sum of the first four ionization energies or first four electron affinities would be highly endothermic. An ion of the type M^{4+} would be very small with high charged density as such would exert high polarizing effect on the surrounding anion thus making the compound formed highly covalent & unstable.

Note:

Carbon, however, being the most electronegative group (IV) element with the smallest atomic radius and least number of electrons is most likely to form compounds of the type M^{4+} or M^{4-}

Carbon exhibits a unique property called _catenation_. This is the ability of an element to form covalent bonds with its own atoms so as to produce long chains and rings.

Carbon therefore forms limitless hydrides i.e. alkanes, alkenes, alkynes etc due to its catenation ability. This unique property of carbon is attributed to the small atomic radius of carbon. The electrons involved in bond formation between two carbon atoms are closer to the nuclei and are strongly held by it thus making

bonds very strong and stable. However in descending the group, atomic radius increases. Therefore electrons between the atoms become more distant from the nuclei making the bond weaker and unstable.

The melting points of group (IV) elements decrease as the group is descended. Carbon, however, has a much higher melting point than others. This is because carbon has a giant molecular (macro-molecular) structure composed of many atoms due to its ability to catenate. It has abnormally high melting point because large number of short and strong carbon –carbon bonds have to be broken before it melts.

Melting point then decreases gradually from silicon to lead in line with increase in atomic radius down the group. The inter-atomic bond length (element-element bonds) becomes longer and weaker thus melting point decreases.

Chemical properties of group (IV) elements.

1) <u>Reaction with water</u>.

   Carbon reacts with steam when heated to form carbon monoxide and hydrogen gas.

   $$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)}$$
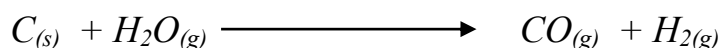
   Silicon reacts with steam when heated to form silicon dioxide and hydrogen gas.

   $$Si_{(s)} + 2H_2O_{(g)} \longrightarrow SiO_{2(s)} + 2H_{2(g)}$$
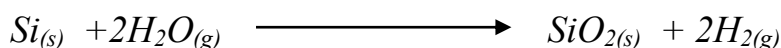
   Germanium and Tin do not react with water at any condition.

   Lead reacts slowly with soft water forming lead (ii) hydroxide.

   $$2Pb_{(s)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow 2Pb(OH)_{2(s)}$$
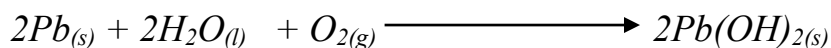
   <u>Note</u>

   The above reaction leads to lead poisoning and explains why lead pipes are not used for transporting water for drinking.

2) <u>Reaction with Oxygen (air)</u>.

a) Carbon.

When carbon is heated in limited air, carbon monoxide is formed and in excess air, carbondioxide is formed.

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

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
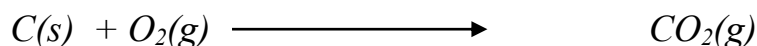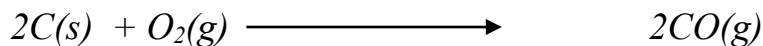
When the rest of the elements are heated inoxygen , they form dioxides except lead which forms lead(ii) oxide.

$$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$$

$$Ge_{(s)} + O_{2(g)} \longrightarrow GeO_{2(s)}$$

$$Sn_{(s)} + O_{2(g)} \longrightarrow SnO_{2(s)}$$

$$2Pb_{(s)} + O_{2(g)} \longrightarrow 2PbO_{(s)}$$
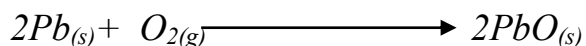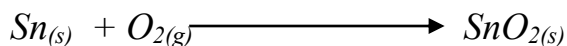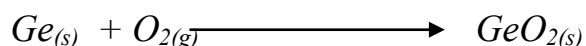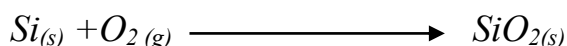
3) Reaction with acids

a) Carbon is attacked by all oxidizing acids e.g hot concentrated sulphuric acid and hot concentratednitric acids.

$$C_{(s)} + 4HNO_{3\ (aq)} \longrightarrow CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$$

$$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(l)}$$
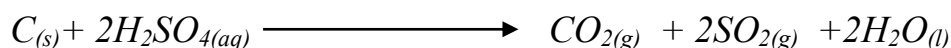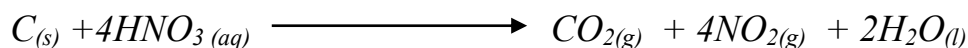
Silicon is resistant to all acids except hydrofluoric acid (HF)

$$Si_{(s)} + 6HF_{(aq)} \longrightarrow H_2SiF_{6(aq)} + 2H_{2(g)}$$
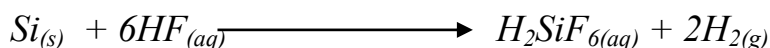
Germanium, Tin and Lead are oxidized by hot conc. nitric acid

$$3Ge_{(s)} + 4HNO_{3(aq)} \longrightarrow 3GeO_{2(s)} + 2H_2O_{(l)} + 4NO_{(g)}$$

$$3Sn_{(s)} + 4HNO_{3(aq)} \longrightarrow 3SnO_{2(s)} + 2H_2O_{(l)} + 4NO_{(g)}$$

$$Pb_{(s)} + 4HNO_{3(aq)} \longrightarrow Pb(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)}$$
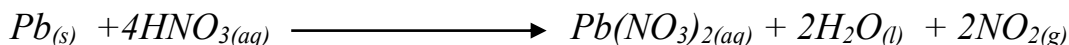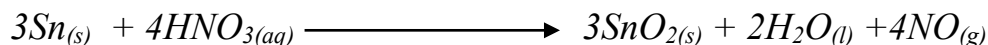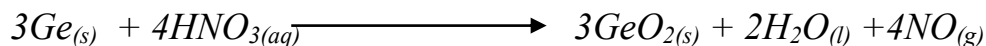
Lead is rendered passive in both cold dilute hydrochloric and sulphuric acids due to formation of insoluble salt of lead (II) chloride & lead (II) sulphate respectively.

However, lead reacts with hot dilute hydrochloric acid to form lead (ii) chloride and hydrogen gas.

$$Pb_{(s)} + 2HCl_{(aq)} \longrightarrow PbCl_{2(aq)} + H_{2(g)}$$
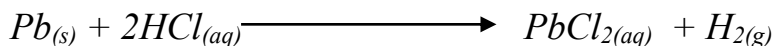
Tin reacts with hot conc. Sulphuric acid to form tin(iv) sulphate.

$$Sn_{(s)} + 4H_2SO_{4\,(aq)} \longrightarrow Sn(SO_4)_{2(aq)} + 2SO_{2(g)} + 4H_2O_{(l)}$$
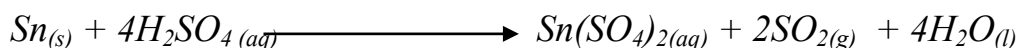
Lead reacts with hot conc. Sulphuric acid to form lead (II) sulphate, sulphur dioxide and water.

$$Pb_{(s)} + 2H_2SO_{4\,(aq)} \longrightarrow PbSO_{4(s)} + SO_{2(g)} + 2H_2O_{(l)}$$
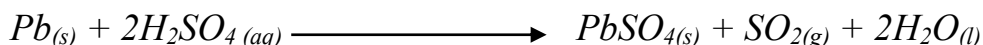
4) <u>Reaction with Alkalis</u>

Carbon is resistant to alkalis but silicon dissolves in conc. Solution to form silicate.

$$Si_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \longrightarrow Na_2SiO_{3(aq)} + 2H_{2(g)}$$
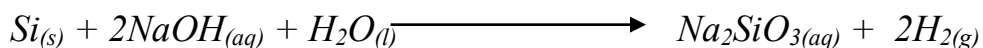
Germanium dissolves in conc. Alkalis to form hexahydroxogermanate (iv)

$$Ge_{(s)} + 2KOH_{(aq)} + 4H_2O_{(l)} \longrightarrow K_2Ge(OH)_{6(aq)} + 2H_{2(g)}$$

<u>Ionically</u>

$$Ge_{(s)} + 2\,OH^-_{\,(aq)} + 4H_2O_{(l)} \longrightarrow Ge(OH)_6^{2-}{}_{(aq)} + 2H_{2(g)}$$
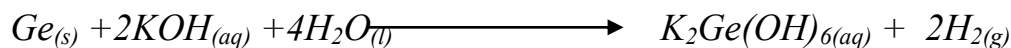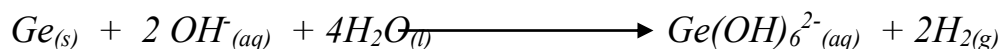
5) Tin and Lead dissolve slowly in hot conc. Solution of alkalis to form hexahydroxystannate(II) and plumbate(II) respectively.

6) $$Sn_{(s)} + 4KOH_{(aq)} + 2H_2O_{(l)} \longrightarrow K_4Sn(OH)_{6(aq)} + H_{2(g)}$$

7) $$Pb_{(s)} + 4KOH_{(aq)} + 2H_2O_{(l)} \longrightarrow K_4Pb(OH)_{6(aq)} + H_{2(g)}$$
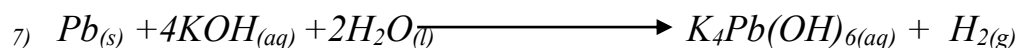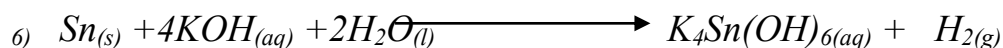
5.2. Compounds of group (IV) elements

Group (IV) elements form compounds in +2 and +4 oxidation states. The +2 oxidation state becomes more stable while the stability of +4 decreases as the group is descended.

The oxides of group (IV)

These elements form oxides of the type XO, wherein the element shows an oxidation state of +2 and also of the type XO_2, wherein the element shows an oxidation state of +4.

The oxides of the elements at the top of Group 4 are acidic, but acidity of the oxides falls as you go down the Group. Towards the bottom of the Group, the oxides become more basic - although without ever losing their acidic character completely.

The trend is therefore from acidic oxides at the top of the Group towards amphoteric ones at the bottom.

An oxide which shows both acidic and basic properties is said to be amphoteric.

Monoxides

The monoxide of carbon and silicon are usually treated as neutral oxides, but in fact carbon monoxide is very, very slightly acidic. It doesn't react with water, but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate.

$$NaOH_{(aq)} + CO_{(g)} \longrightarrow HCOONa_{(aq)}$$
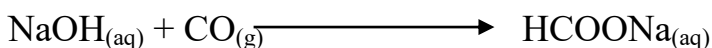
The fact that the carbon monoxide reacts with the basic hydroxide ion shows that it must be acidic

Those of germanium, tin and lead are amphoteric. The amphoteric monoxides (GeO, SnO and PbO) react with acids to give corresponding salts and alkalis to give germinate(II), stannate(II) and plumbate(II) complex ions.

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

$$SnO_{(s)} + 2OH^-_{(aq)} + H_2O_{(l)} \longrightarrow Sn(OH)_4^{2-}_{(aq)}$$
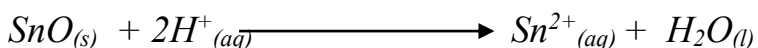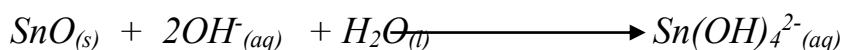
Similar reactions are undergone by Germanium monoxide & lead (ii) oxide

Alternatively:

$$XO_{(s)} + 2OH^-_{(aq)} \longrightarrow XO_2^{2-}_{(aq)} + H_2O_{(l)}$$

$$GeO_{(s)} + 2OH^-_{(aq)} \longrightarrow GeO_2^{2-}_{(aq)} + H_2O_{(l)}$$

$$SnO_{(s)} + 2OH^-_{(aq)} \longrightarrow SnO_2^{2-}_{(aq)} + H_2O_{(l)}$$

$$PbO_{(s)} + 2OH^-_{(aq)} \longrightarrow PbO_2^{2-}_{(aq)} + H_2O_{(l)}$$
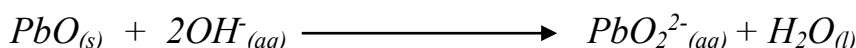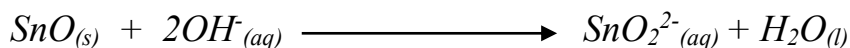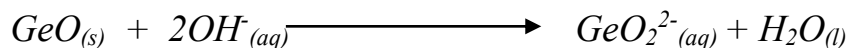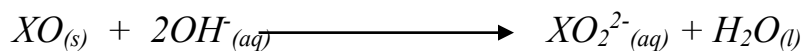
They all react with concentrated hydrochloric acid.

$$MO_{(s)} + HCl_{(aq)} \longrightarrow MCl_{2(aq)} + H_2O_{(l)}$$
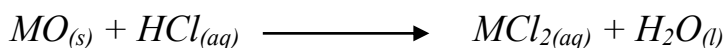
where M can be Ge or Sn.

Lead(II) chloride is fairly insoluble salt in water and, , it would form an insoluble layer over the lead(II) oxide if dilute hydrochloric acid is used - stopping the reaction from going on

$$PbO_{(s)} + 2HCl_{(aq)} \longrightarrow PbCl_2(s) + H_2O_{(l)}.$$
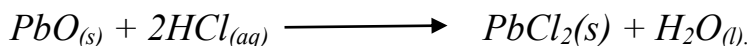
However, using concentrated hydrochloric acid the large excessof chloride ions in the concentrated acid react with the lead(II) chloride to produce a yellow soluble complex $PbCl_4^{2-}$.

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

Dioxides

The first four dioxide are prepared by heating the elements in oxygen but a similar process with lead gives lead(ii) oxide.

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

$$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$$

$$Ge_{(s)} + O_{2(g)} \longrightarrow GeO_{2(s)}$$

$$Sn_{(s)} + O_{2(g)} \longrightarrow SnO_{2(s)}$$

$$2\,Pb_{(s)} + O_{2(g)} \longrightarrow 2PbO_{(s)}$$
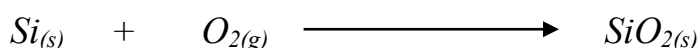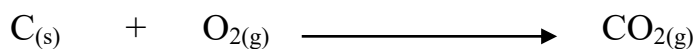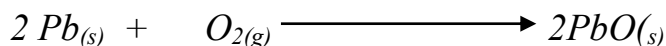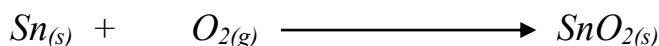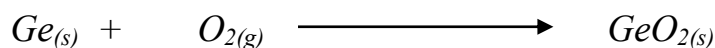
Note

Lead (IV) oxide is made by action of hot dilute nitric acid on red lead, Pb_3O_4.

$$Pb_3O_{4(s)} + 4HNO_{3(aq)} \longrightarrow PbO_{2(s)} + 2Pb(NO_3)_{2(aq)} + 2H_2O_{(l)}$$
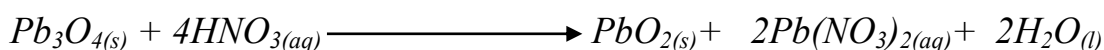
Brown solid

With warm conc. hydrochloric acid, red lead (trilead tetra oxide) reacts according to the equation:

$$Pb_3O_{4(s)} + 14HCl_{(aq)} \longrightarrow 3H_2PbCl_{4(aq)} + Cl_{2(g)} + 4H_2O_{(l)}$$
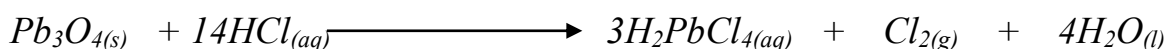
Yellow solution

Red lead is used in paints to prevent the corrosion of iron

The structure of carbon dioxide

There is an enormous difference between the physical properties of carbon dioxide and silicon dioxide (also known as silicon (IV) oxide or silica).

Carbon dioxide is a gas whereas silicon dioxide is a hard high-melting solid.

The other dioxides in Group 4 are also solids. The fact that carbon dioxide is a gas means that it must consist of simple or discrete molecules held by weak Van der Waals forces of attraction. These forces are not strong enough to bind the carbon dioxide molecules into solid.

Carbon dioxide has a linear structure because the double bonds repel each other strongly to give a structure with bond angle 180 degrees as there are no lone pairs available

The structure of silicon dioxide
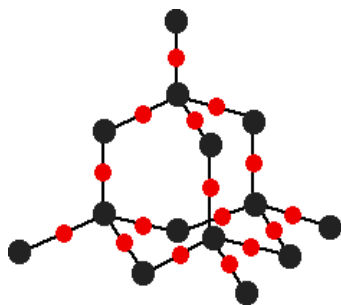
This is based on a diamond structure with each of the silicon atoms being bridged to its other four neighbors via an oxygen atom. This means that silicon dioxide exists as a giant covalent structure in which large number of strong silicon-oxygen bonds have to be broken hence it is a solid . The strong bonds in three dimensions make it a hard, high melting point solid

CO_2 & SiO_2 are weaklyacidic and covalent in nature

Reaction With water

Silicon dioxide doesn't react with water, because of the difficulty of breaking up the giant covalent structure.

Carbon dioxide does react with water to a slight extent to produce hydrogen ions.

$$H_2O_{(l)} + CO_{2(g)} \rightleftharpoons H^+_{(aq)} + HCO_3^{2-}_{(aq)}$$
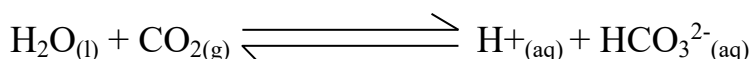
The solution of carbon dioxide in water is sometimes known as carbonic acid.

Reaction With bases

Carbon dioxide reacts with sodium hydroxide solution in the cold to give either sodium carbonate or sodium hydrogen carbonate solution - depending on the reacting proportions.

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$

$$Na_2CO_{3(aq)} + H_2O_{(l)} + CO_{2(g)} \longrightarrow 2NaHCO_{3(s)}$$
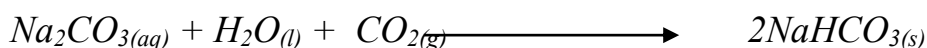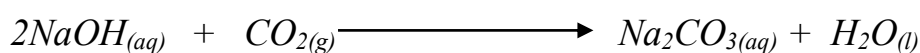
White solid

Silicon dioxide is acidic and reacts with sodium hydroxide solution, but only if it is hot and concentrated. Sodium silicate solution is formed.

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_3 \ (aq) + H_2O_{(l)}$$
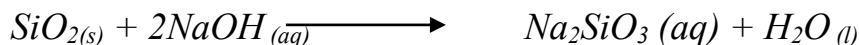
. GeO_2, SnO_2, and PbO_2 are amphoteric in nature.

<u>The basic nature of the dioxides</u>

The dioxides react with concentrated hydrochloric acid first to give compounds of the type XCl_4 e.g

$$PbO_{2(s)} + 4HCl_{(aq)} \longrightarrow PbCl_{4(aq)} + 2 \ H_2O_{(l)}$$
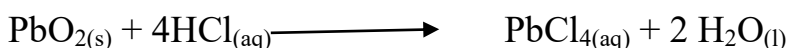
These will react with excess chloride ions in the hydrochloric acid to give complexes such as XCl_6^{2-}.

$$PbCl_{4(aq)} + 2Cl^-_{(aq)} \longrightarrow PbCl_6^{2-}_{(aq)}$$
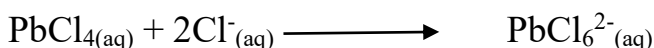
If the reaction is carried out at elevated temperature, lead (IV) oxide oxidizes hot conc. hydrochloric acid to chlorine gas.

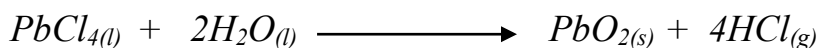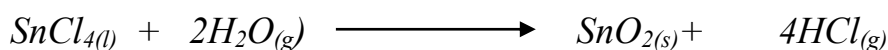$$PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{2(aq)} + 2 \ H_2O_{(l)} + Cl_{2(g)}$$
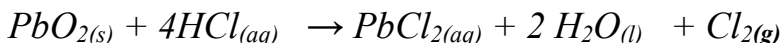
<u>The acidic nature of the dioxides</u>

The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complexes of the form $[X(OH)_6]^{2-}$.

$$GeO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Ge(OH)_6^{2-}_{(aq)}$$

$$SnO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Sn(OH)_6^{2-}_{(aq)}$$

$$PbO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Pb(OH)_6^{2-}_{(aq)}$$

<u>OR</u>

$$GeO_{2(s)} + 2OH^-_{(aq)} \rightarrow GeO_3^{2-}_{(aq)} + H_2O_{(l)}$$

$$SnO_{2(s)} + 2OH^-_{(aq)} \rightarrow SnO_3^{2-}_{(aq)} + H_2O_{(l)}$$

$$PbO_{2(s)} + 2OH^-_{(aq)} \rightarrow PbO_3^{2-}_{(aq)} + H_2O_{(l)}$$
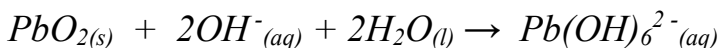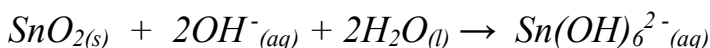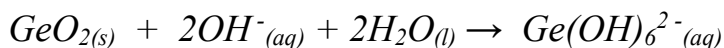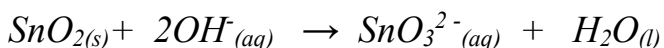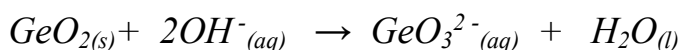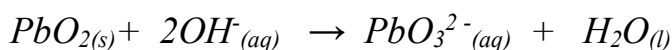
The halides of group (IV) elements

+2 halides

Carbon and Silicon do not form +2 halides. Those of Germanium, Tin and lead can be prepared by heating the tetrachlorides with the free metal.

$$GeCl_{4(l)} + Ge_{(s)} \longrightarrow 2GeCl_{2(s)}$$

$$SnCl_{4(l)} + Sn_{(s)} \longrightarrow 2SnCl_{2(s)}$$

$$PbCl_{4(l)} + Pb_{(s)} \longrightarrow 2PbCl_{2(s)}$$
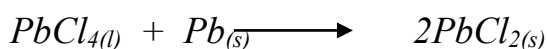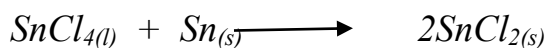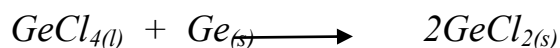
Tin (II) chloride may be prepared in anhydrous form by passing dry hydrogen chloride gas over heated tin.

$$Sn_{(s)} + 2HCl_{(g)} \longrightarrow SnCl_{2(s)} + H_{2(g)}$$
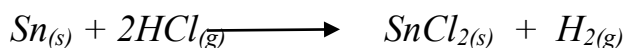
Lead (ii) chloride can also be prepared either by action of hot concentrated hydrochloric acid over lead(iv) oxide or by passing dry hydrogen chloride gas or chlorine over heated metal.

$$PbO_{2(s)} + 4HCl_{(aq)} \longrightarrow PbCl_{2(s)} + 2H_2O_{(l)} + Cl_{2(g)}$$

Note:

Lead (ii) chloride is more soluble in concentrated hydrochloric acid than in water. Explain this observation.

Explanation

Lead (II) chloride has a high lattice energy which is not over-come on addition of cold water. However on heating, the high lattice energy is overcome and therefore lead (II) chloride dissolves in hot water.

Lead (II) chloride dissolves in conc. Hydrochloric acid due to formation of soluble complex, tetrachloroplumbate (II) ions.

$$PbCl_{2(s)} + 2Cl^-_{(aq)} \rightarrow PbCl_4^{2-}_{(aq)}$$
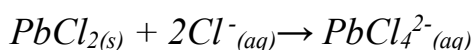
Yellow solution.

+4 halides

All the elements form tetra chlorides of the type XCl_4, which are covalently bonded and are volatile liquids.

All the tetra chlorides have a tetrahedral shape in which the element is surrounded by 4 chlorine atoms.

Preparation of the tetra chlorides

CCl_4

By reacting chlorine with carbon disulphide .

$$CS_{2(l)} + 3Cl_{2(g)} \xrightarrow{\quad AlCl_3/heat \quad} CCl_{4(l)} + S_2Cl_{2(l)}$$
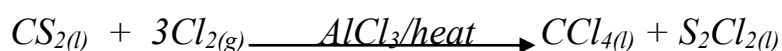
The two liquids are separated by fractional distillation.

$SiCl_4$, $GeCl_4$ & $SnCl_4$

Are prepared by passing a stream of dry chlorine over the heated metal.

$$Si_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(l)}$$

$$Ge_{(s)} + 2Cl_{2(g)} \longrightarrow GeCl_{4(l)}$$

$$Sn_{(s)} + 2Cl_{2(g)} \longrightarrow SnCl_{4(l)}$$
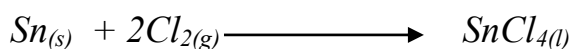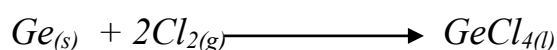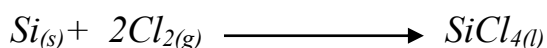
If a stream of chlorine is passed over heated lead, only lead(ii) chloride is formed.

$$Pb_{(s)} + Cl_{2(g)} \longrightarrow PbCl_{2(s)}$$
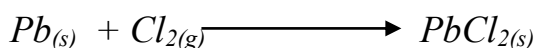
To prepare lead(iv) chloride, use ice cold concentrated hydrochloric acid on lead(iv) oxide.

$$PbO_{2(s)} + 4HCl_{(aq)} \longrightarrow PbCl_{4(l)} + 2 H_2O_{(l)}$$
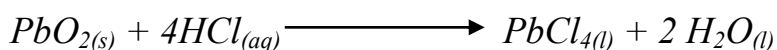
Note

If the reaction is carried out at elevated temperature, lead (IV) oxide oxidizes hot concentrated

hydrochloric acid to chlorine gas.

$$PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{2(aq)} + 2\ H_2O_{(l)} + Cl_{2(g}$$
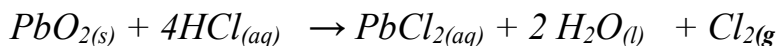
Hydrolysis of the tetrachlorides

Carbon tetrachloride (CCl_4) does not undergo hydrolysis in water. This is due to the absence of a d sub shell in carbon and as such it cannot expand its octet.

However, other tetrachlorides undergo hydrolysis in water. This is attributed to availability of the empty d-orbitals which allow the elements to expand their octet and show a covalency of more than +4. These empty d-orbitals accept the lone pairs of electrons from the oxygen atom of water molecule thus facilitating the hydrolysis of the tetra chlorides.

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$

White solid.

$$GeCl_{4(l)} + 2H_2O_{(l)} \rightarrow GeO_{2(s)} +$$

$$SnCl_{4(l)} + 2H_2O_{(g)} \longrightarrow SnO_{2(s)} + 4HCl_{(g)}$$

$$PbCl_{4(l)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4HCl_{(g)}$$
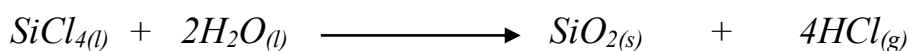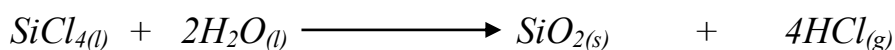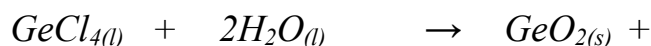
Brown solid

NB: In each case white fumes of hydrogen chloride gas is formed.

Stability of the tetrachloride

The tetrachlorides of carbon, silicon, and germanium are stable to heat, but those of tin and lead decompose on heating to form dichlorides.

$$SnCl_{4(l)} \longrightarrow SnCl_{2(s)} + Cl_{2(g)}$$

$$PbCl_{4(l)} \longrightarrow PbCl_{2(s)} + Cl_{2(g)}$$
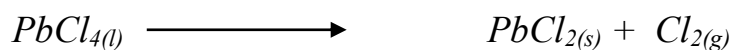
Hydrides of group IV

CH_4	Methane
SiH_4	Silane
GeH_4	Germane
SnH_4	Stannane
PbH_4	Plumbane

The boiling points of the hydrides increase from methane down to stannane.

This is due to increase in relative molecular mass and thus the Van der Waals forces of attraction holding the molecules together become progressively stronger as the molecular mass increases.

Methane, germane and stannane do not react with sodium hydroxide, but silane reacts with dilute sodium hydroxide to form sodium silicate and hydrogen gas.

$$SiH_{4(l)} + 2NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na_2SiO_{3(aq)} + 4H_{2(g)}$$

Ionically

$$SiH_{4(l)} + 2OH^-_{(aq)} + H_2O_{(l)} \rightarrow SiO_3^{2-}_{(aq)} + 4H_{2(g)}$$
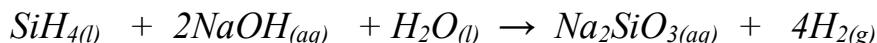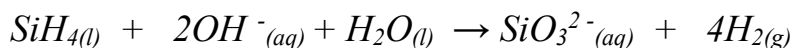
Hydrolytic behavior of hydrides of group IIV elements

Methane does not undergo hydrolysis due to absence of vacant d-orbitals.

Other hydrides are able to hydrolyze in water due to the availability of vacant d-orbitals which can accept electrons from the water molecules.

$$SiH_{4(l)} + 4 H_2O_{(l)} \rightarrow Si(OH)_{4(s)} + 4H_{2(g)}$$

$$GeH_{4(l)} + 4 H_2O_{(l)} \rightarrow Ge(OH)_{4(s)} + 4H_2(g)$$

$$SnH_{4(l)} + 4 H_2O_{(l)} \rightarrow Sn(OH)_{4(s)} + 4H_{2(g)}$$
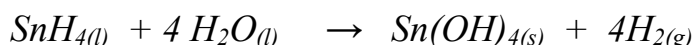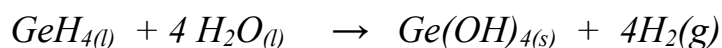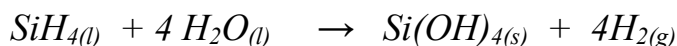
Carbon differs from other group IV elements in the following ways:

a) Its covalence is limited to 4 but others can have a maximum of 6. This is due to absence of vacant d-orbitals in carbon but others have.
b) Its unique ability to catenate.
Due to its small atomic radius, the bonding electrons between two carbon atoms are closer to the nuclei and are attracted more strongly.
Its unique ability to form multiple bonds such as: $-C=C-$, $-C\equiv C-$, $-C\equiv N$, etc.
c) Its tetrachloride does not hydrolyze in water but tetra chlorides of other elements hydrolyzedue to absence of vacant d-orbitals.
d) Carbon is the only element in group IV which forms only gaseous oxides.

Why carbon differs from other elements in group IV

a) It has the smallest radius in the group
b) Its electronegativity is the highest in the group

c) Carbon lacks a d-sub shell unlike other group members
d) Carbon is unable to show the inert pair effect and always exhibit a valency of 4 in almost all its compounds

5.3. Test for Lead (II) ions in solution

1) Use of sodium hydroxide solution

   Procedure

   To the solution containing the unknown cation is added sodium hydroxide solution dropwise until in excess.

   Observation

   A white precipitate of Lead (II) hydroxide is formed. The precipitate dissolves in excess sodium hydroxide solution to form a cololourless due to the formation of plumbate (II) ions.

   Equation

   $$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Pb(OH)_{2(S).}$$

   $$Pb(OH)_{2(S)} + 2OH^-_{(aq)} \longrightarrow Pb(OH)_4^{2-}{}_{(aq)}$$
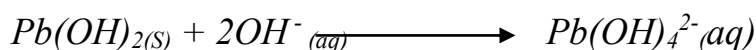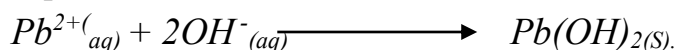
2) Use of aqueous ammonia solution.

   Procedure

   To the solution containing the unknown cation is added aqueous ammonia dropwise until in excess.

   Observation

   In the presence of Lead (II) ions, a white precipitate of Lead (II) hydroxide is formed. The precipitate is insoluble in excess aqueous ammonia.

   Equation

   $$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Pb(OH)_{2(S).}$$
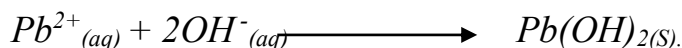
3) Use of dilute hydrochloric acid.

   Procedure

   To the solution containing the unknown cation is added a few drops of dilute hydrochloric acid.

   Observation

A white needle like precipitate of lead (II) chloride is formed. The precipitate dissolves on heating but reappears on cooling.
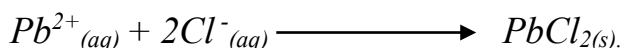
$$Pb^{2+}_{(aq)} + 2Cl^-_{(aq)} \longrightarrow PbCl_{2(s).}$$

4) Use of potassium chromate solution

Procedure

To the solution containing the unknown cation is added potassium chromate solution.

Observation

A yellow precipitate of lead (II) chromate is formed in the presence of Lead (II) ions.

Equation

$$Pb^{2+}(aq) + CrO_4^{2-}_{(aq)} \longrightarrow PbCrO_{4(s).}$$
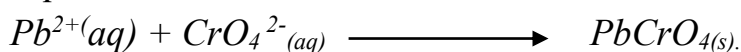
5) Use of Potassium Iodide solution.

Procedure

To the solution containing the unknown cation is added a few drops of potassium iodide solution.

Observation

A yellow precipitate of lead (II) iodide is formed in the presence of lead (II) ions.

Equation

$$Pb^{2+}_{(aq)} + 2I^-_{(aq)} \longrightarrow PbI_{2(s).}$$
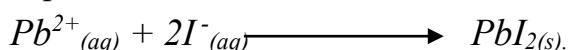
6) Use of dilute sulphuric acid.

Procedure

To the solution suspected to contain lead (II) ions is added dilute sulphuric acid.

Observation

A white precipitate of lead (II) sulphate is formed.

Equation

$$Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow PbSO_{4(s)}$$
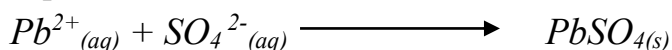
7) Use of sodium carbonate solution

In the presence of Pb^{2+} ions a white precipitate of lead (II) carbonate is formed on addition of sodium carbonate solution.

$Pb^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \longrightarrow PbCO_{3(s)}$
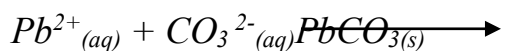
Question

When dilute hydrochloric acid is added to a solution of lead (ii) nitrate, a white precipitate is formed, but if the concentrated acid is used, there is no precipitate. Explain this observation and write an ionic equation for the reaction in each case.

CHAPTER 6

6. GROUP (VII) ELEMENTS (HALOGENS)

Table 8: Physical properties of group VII elements

Element	Atomic no	Outer elect conf	Melting pt/^{0}c	Boiling pt/0c	Bond energy /kcalmol-1
Fluorine	9	$-2s^2 2p^5$	-220	-188	37
Chlorine	17	$-3s^2 3p^5$	-101	-34	57.2
Bromine	25	$-4s^2 4p^5$	-7	58	45.4
Iodine	33	$-5s^2 5p^5$	114	183	35.6

6.1. Physical properties of the halogens.

The halogens exist as diatomic molecules i.e. F_2, Cl_2, Br_2 and I_2.

Fluorine is a pale green gas, chlorine is a yellowish green gas, bromine is a reddish brown gas while iodine is a black (dark purple) solid at room temperature which sublimes to give a purple gas.

Halogens are highly reactive non-metals. They exist as diatomic molecules X_2 containing a covalent bond.

Due to their reactivity the elements do not occur in the free state but are always combined either among themselves or with other elements.

All the elements have 7 electrons in their outer most shells with general outer most electronic configuration of ns^2np^5 (*n= 2, 3, 4, 5)*

They can complete their octet by either gaining an electron to form an ionic bond or sharing electrons with other elements or themselves in a covalent bond.

The melting and boiling points of the halogens are low but increase down the group.

Explanation

The diatomic molecules of halogens are held by weak intermolecular van der Waals forces of attraction. These forces become stronger with increasing molecular weight/ masses down the group.

In bromine and iodine, the forces are strong enough to bind their molecules to exist as liquid and solid respectively at room temperature. However, in fluorine and chlorine, the forces are not strong enough and as a result they exist as gases at room temperature.

Table 9: Melting and boiling points of group VII elemts
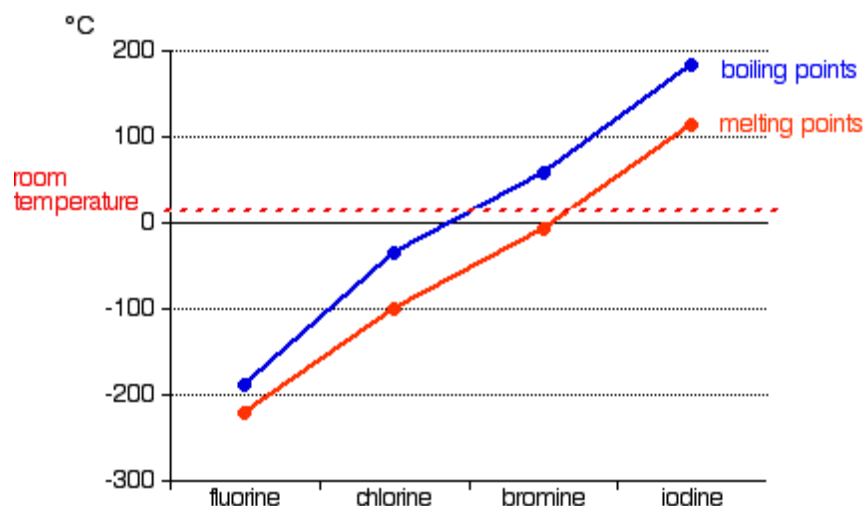
Bond dissociation energy

Bond energy is the energy required to break one mole of a covalent bond into its constituent gaseous atoms.

Or it's the energy released when one mole of a covalent bond is formed from its constituent gaseous atoms.

Bond dissociation energy of the diatomic molecules decreases down the group from chlorine to iodine. However, Fluorine has abnormally low bond dissociation energy.

Bond enthalpies
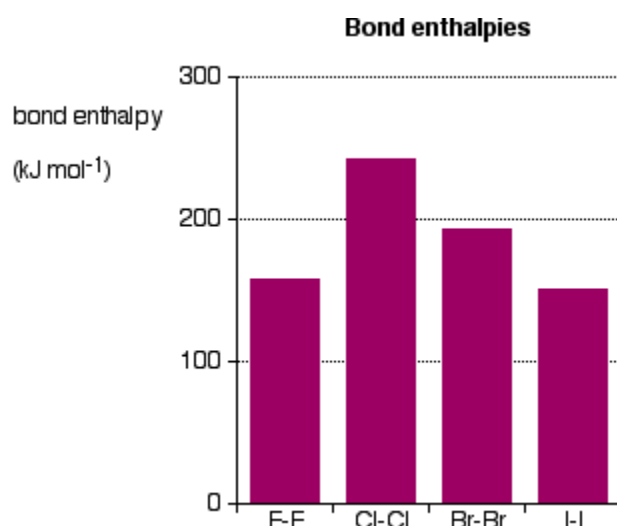
This is due to small atomic radius of fluorine atom; the non bonding p- electrons present in Fluorine molecule are closer to one another as such repel each other strongly thus weakening the F-F bond.

The decrease in bond dissociation energy from Chlorine to Iodine is attributed to increase in atomic radius as the group is descended; the bonding electrons in the halogen-halogen bond are far from the nuclei of the halogens& are attracted less strongly due to the screening effect of the inner shells of electrons thus weakening the bond progressively

68

The bonding pair is further from the nuclei, and so the bond is weaker.
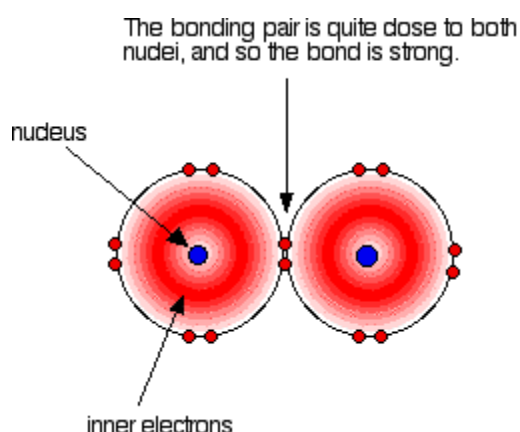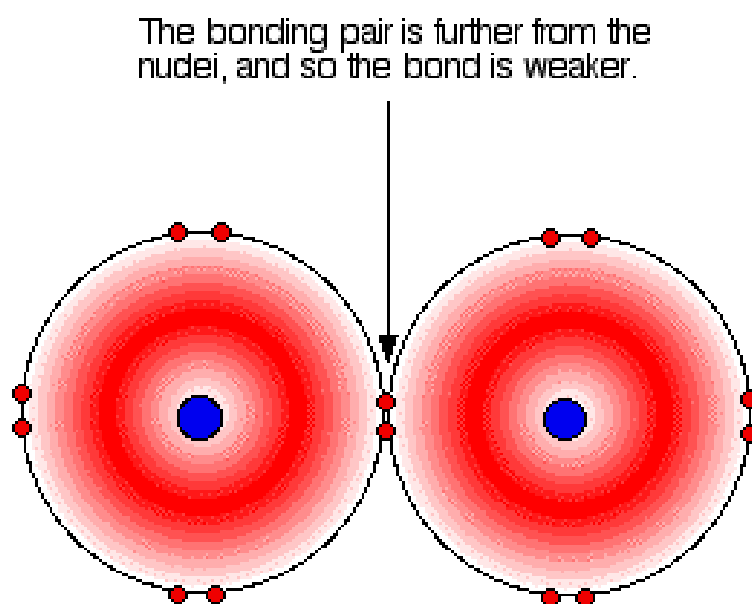
NB: The high reactivity of fluorine may be attributed to its low bond dissociation energy.

Electron affinity of halogens

E.A is the energy change when one mole of electrons is added to one mole of gaseous atoms to form one mole of negatively charged gaseous ions.

$$X_{(g)} + e \longrightarrow X_{(g)}^-$$
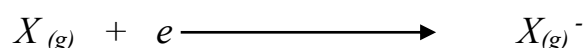
The electron affinity is a more useful concept for the halogens than first ionisation energy because the halogens need only one electron to complete their octet to attain a noble gas like structure.

Electron affinity of the Group 7 elements

electron affinity
(kJ mol^{-1})

69
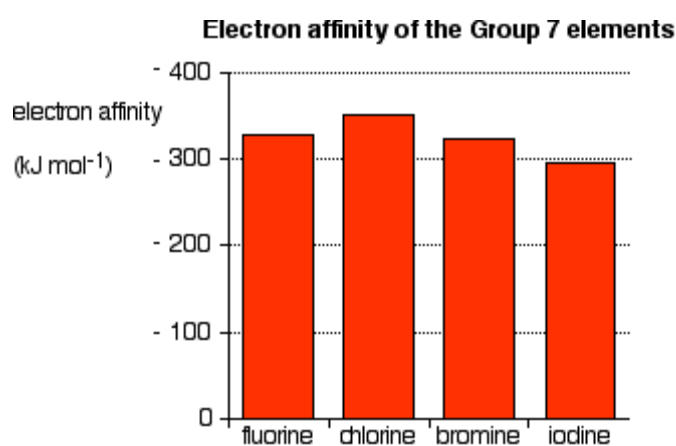
The electron affinity decreases numerically from Chlorine to Iodine. As the atomic radius increases down the group, the electron being added experiences a low attraction from the nucleus leading to a decrease in electron affinity.

Fluorine, however, has a low value for its electron affinity, numerically less than that for chlorine.

Explanation

This is due to small atomic radius of fluorine atom; the 7 electrons in the outer most shell are too close to one another therefore the electron being added experiences greater repulsive forces from the electrons already present.

The electron affinity is a measure of the attraction between the incoming electron and the nucleus. The higher the attraction, the higher the electron affinity.
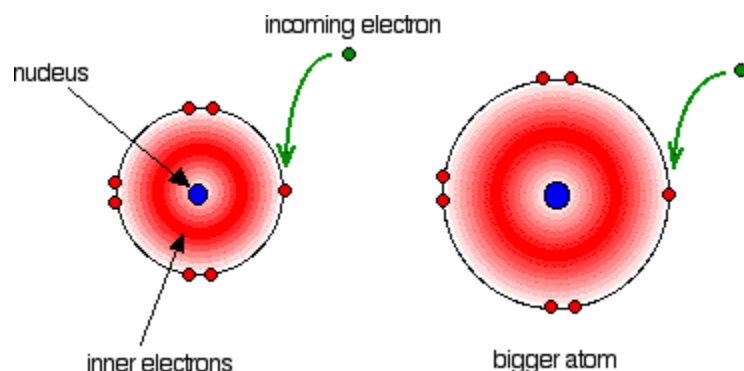
Oxidizing properties of the halogens

Halogens are very good oxidizing agents with fluorine being the most oxidizing.

This is because fluorine is the most electronegative and has the highest positive value for its standard electrode potential.

 It oxidises water to oxygen.

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4HF_{(aq)}$$
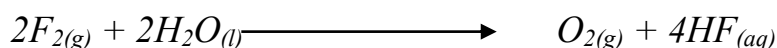
The standard electrode potential (E^θ) becomes less positive as the group is descended and so oxidising power decreases down the group.

Fluorine> Chlorine> Bromine> Iodine.

Oxidation states of the halogens

They all exhibit oxidation state of **-1** by gaining an extra electron to complete their octet Fluorine is always o univalent due to absence of d-orbitals.

Other elements can show higher oxidation states due to availability of **vacant d-orbitals** which allow them to expand their octet.

Differences in the chemistry of Fluorine from other members of its group are:

- Fluorine is has a fixed oxidation state of -1 while the other halogens have more than one oxidation states. This is because fluorine lacks a d sub shell while the other halogens have.
- Hydrogen fluoride is a liquid while other hydrogen halides are gases at room temperature. This is due to the strong hydrogen bonds between hydrogen fluoride molecules as a result of high electronegativity of fluorine atom.
- Fluorine forms the least acidic hydride whereas the hydrides of other members are fairly more acidic in aqueous solution.

This is due to the high strength of the H-F bond.

- Fluorine is the most reactive halogen due to its low bond dissociation energy and high electronegativity.
- Fluorine forms compounds with more ionic character due to its high electronegativity.
- Fluorine forms hydride with the highest boiling point due to extensive hydrogen bonds.

Why does Fluorine show a difference?

- ➢ Fluorine is the most electronegative halogen.
- ➢ The bond dissociation energy of fluorine molecule is lower than expected.
- ➢ Fluorine has a high positive value of standard electrode potential.

➢ Fluoride ion having the smallest radius compared to other halides has the highest charge density and enthalpy of hydration.
➢ Fluorine lacks a d sub shell.

6.2. General methods for preparing the halogens (excluding fluorine) in the laboratory

a) By the reaction between manganese (IV) oxide and concentrated halogen acid e.g.

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

$$4HBr_{(aq)} + MnO_{2(s)} \longrightarrow MnBr_{2(aq)} + 2H_2O_{(l)} + Br_{2(g)}$$

$$4HI_{(aq)} + MnO_{2(s)} \longrightarrow MnI_{2(aq)} + 2H_2O_{(l)} + I_{2(g)}$$
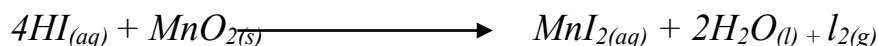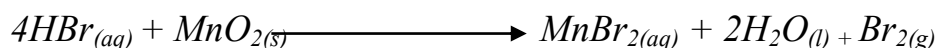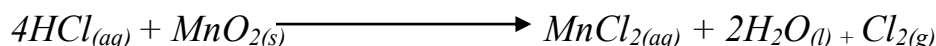
b) By the reaction between potassium manganate (VII) solution and hot concentrated halogen acid.

e.g.

$$2KMnO_{4(s)} + 16HCl_{(aq)} \longrightarrow 2KCl_{(aq)} + 2MnCl_{2(aq)} + 8H_2O_{(l)} + 5Cl_{2(g)}.$$

$$2KMnO_{4(s)} + 16HBr_{(aq)} \longrightarrow 2KBr_{(aq)} + 2MnBr_{2(aq)} + 8H_2O_{(l)} + 5Br_{2(g)}.$$
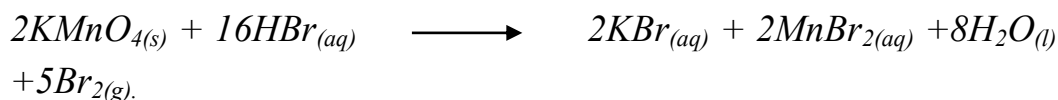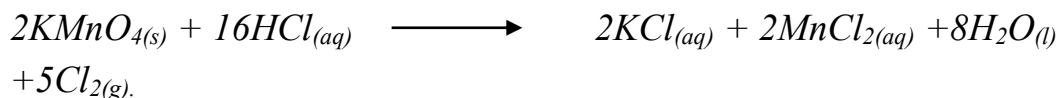
6.3. Reactions of halogens

In all their reactions the halogens act as oxidising agents. Hence, their reactivity decreases down the group.

1) ***Reaction with water***

a. Fluorine oxidises H_2O to O_2 gas in a very exothermic reaction.

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow O_{2(g)} + 4HF_{(aq)}$$
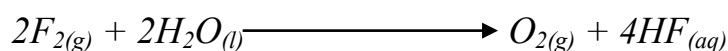
b. Chlorine dissolves in H_2O to form 'chlorine water' which is a mixture of two acids. No oxygen gas is evolved.

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl_{(aq)} + HOCl_{(aq)}$$
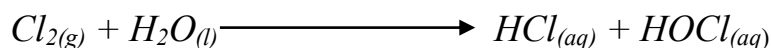
c. Bromine is only slightly soluble in water.

$$Br_{2(l)} + H_2O_{(l)} \longrightarrow HBr_{(aq)} + HOBr_{(aq)}$$
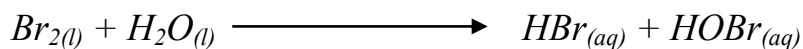
d. Iodine is virtually insoluble in water. It is however soluble in potassium iodide solution due to the formation of a soluble complex the tri-iodide anion.

$$I_{2(s)} + I^-_{(aq)} \longrightarrow I_3^-_{(aq)}$$
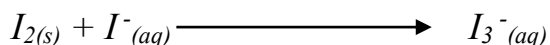
Iodine is sparingly soluble in water because the energy involved in disrupting the weak van der walls forces in molecular iodine crystal lattice and the hydrogen bonds in water exceeds the energy changes involving the weak attraction between iodine and water molecules.

Note: **All halogens are more soluble in non-polar solvents such as CCl$_4$. Cl$_2$ gives a colourlesssolution. Br$_2$ a red solution and I$_2$ a violet one**

2) *Reaction with alkalis (sodium hydroxideor potassium hydroxide solution)*

This reaction depends on the **conditions:**

a) With cold and dilute alkalis the reactions are as below:

$$2KOH_{(aq)} + F_{2(g)} \longrightarrow 2KF_{(aq)} + F_2O_{(g)} + H_2O_{(l)}$$

$$2NaOH_{(aq)} + Cl_{2(g)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$$

$$2NaOH_{(aq)} + Br_{2(l)} \longrightarrow NaBr_{(aq)} + NaOBr_{(aq)} + H_2O_{(l)}$$

$$2KOH_{(aq)} + I_{2(s)} \longrightarrow KI_{(aq)} + KOIO_{(aq)} + H_2O_{(l)}$$
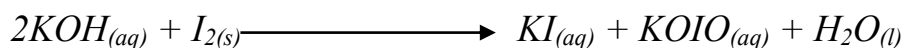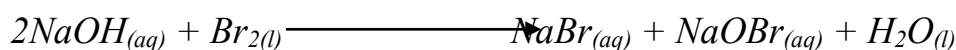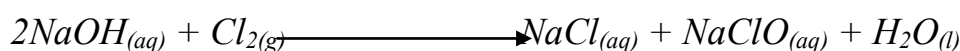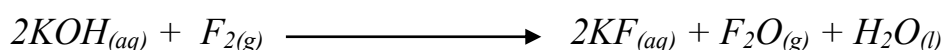
In hot solution the ClO$^-$ ions undergo disproportionation reaction.

Disproportionation reaction being a reaction in which is a species under go self oxidation& reduction reactions.

e.g.

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

$$6OH^-_{(aq)} + 3I_{2(s)} \longrightarrow 5I^-_{(aq)} + IO_3^- + 3H_2O_{(l)}$$
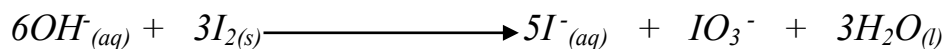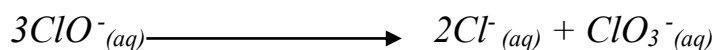
Iodine is reduced to iodide ions as its oxidation state decreases from zero to -1 and at the same time its oxidised to iodate ions as its oxidation state increases from 0 to +5.

b) *With hot and concentrated alkali, reactivity decreases down the group.*

$$4NaOH_{(aq)} + 2F_{2(g)} \longrightarrow 4NaF_{(aq)} + O_{2(g)} + 2H_2O_{(l)}$$

$$6KOH_{(aq)} + 3Cl_{2(g)} \longrightarrow 5KCl_{(aq)} + KClO_{3(aq)} + 3H_2O_{(l)}$$
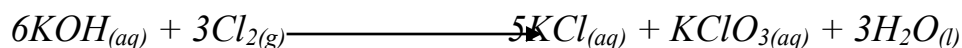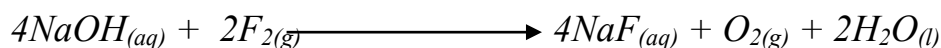
Note
Other halogens react in a similar manner.

6.4. Compounds of the halogens

Hydrides of group VII elements

a) Boiling points of hydrides increase from Hydrogen chloride through Hydrogen bromide to Hydrogen bromide but that of Hydrogen fluoride is abnormally high.

Hydrogen halide	Boiling point/ ^0C
HF	19
HCl	-85
HBr	-66
HI	-36

The increase in boiling point from Hydrogen chloride to Hydrogen iodide is attributed to _increasing molecular mass_ of the halogens.

This in turn increases the strength of van der Waals forces of attraction between their molecules hence increasing the boiling point of Hydrogen chloride to Hydrogen iodide.

Hydrogen fluoride however, has abnormally high boiling point because Fluorine atom has a very small atomic radius and high electronegativity, as a result it forms a more polar Hydrogen fluoride bond and its molecules associate through strong intermolecular hydrogen bonds which require greater amount of energy to break.
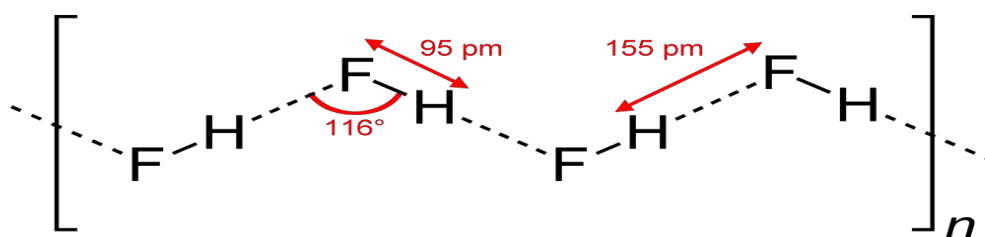
The acidity of the hydrides

The acidity of the hydrides is in the order _H-F <H-Cl< H-Br< H-I._

H-F is the weakest acid because the H-F bond is very strong as a result of small atomic radius and high electronegativity of Fluorine atom.

It is weakly dissociated in solution releasing fewer H^+ ions.

In addition, the presence of hydrogen bonding between HF molecules and water molecules inhibits the ionization of HF in aqueous solution.

However, as the group is descended, electronegativity decreases whereas atomic radius increases. As such the H- halide bonds become progressively longer and weaker. They dissociate in solution releasing more hydrogen ions.

Bond energy/enthalpy of the hydrides generally decreases in moving from Hydrogen fluoride to Hydrogen iodide i.e.

H-F > H-Cl > H-Br > H-I

Bond enthalpies
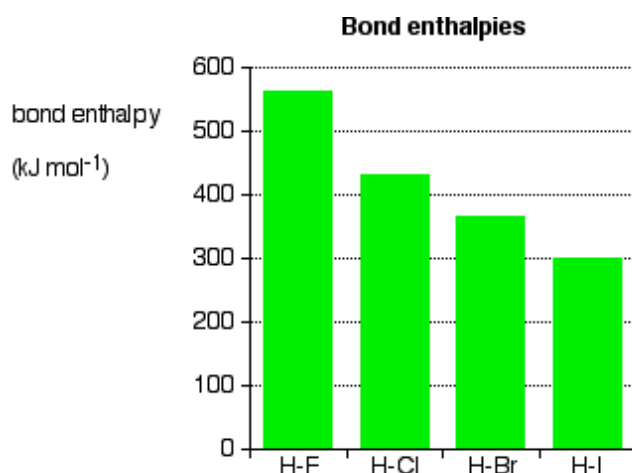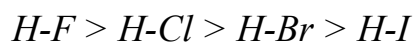
As the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less, and the bond gets weaker.

Fluorine is the most electronegative atom with the smallest atomic radius thus the H-F bond is the most polar. Iodine is the least electronegative with the largest atomic radius as a result the H-I bond is the least polar. The greater the extent of polarity, the greater the ionic character in the bond and therefore the stronger the bond.

 Reactions of the halogen acids

All the halogens acids undergo reactions typical of all acids

e.g.

They react with carbonates and hydrogen carbonates giving off carbon dioxide gas

They react with metals producing corresponding salts and hydrogen gas

They neutralise bases forming salts and water

Note

For hydrofluoric acid, as well as undergoing reactions typical of all acids, it reacts with silicon dioxide and silicon forming fluorosilic acid

$6HF_{(aq)} + SiO_{2(s)} \longrightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)}$

$6HF_{(aq)} + Si_{(s)} \longrightarrow H_2SiF_{6(aq)} + 2H_{2(g)}$
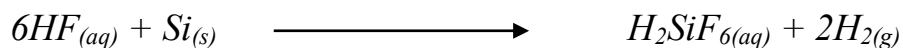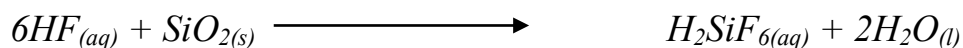
<u>Reaction of halogen acids with concentrated sulphuric acid</u>

Hydrofluoric acid and hydrochloric acid not react with concentrated sulphuric acid

Hydrobromic acid and hydroiodic acid react with hot concentrated sulphuric acid

$HBr(aq) + H_2SO_4(aq) \longrightarrow Br_2(g) + SO_2(g) + 2H_2O_{(l)}$

$Hl(aq) + H_2SO_4(aq) \longrightarrow l_2(g) + SO_2(g) + 2H_2O_{(l)}$
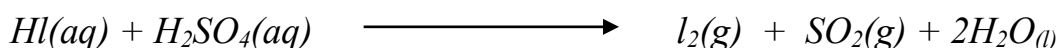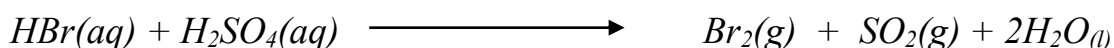
<u>Oxy acids of chlorine</u>

Table 10: Oxy acids of chlorine

Formula	structure	Name
$HOCl$	H-O-Cl	*Hypochlorous acid (chlorous (I) acid)*
$HClO_2$	$HOCl=O$	*Chlorous acid (chlorous (III) acid)*
$HClO_3$	$HOClO_2$	*Chloric acid (chlorous (V) acid)*
$HClO_4$	$HOClO_3$	*Perchloricacid (chlorous (VII) acid*

<u>Note</u>

Salts of hypochlorous acid *(HOCl)* are called hypochlorites e.g.

    a) Sodium hypochlorite *(NaOCl)* present in liquid bleaches
       e.g. JIK

b) Calcium hypochlorite $(Ca(OCl)_2)$ present in bleaching powder

The percentage of available chlorine in either JIK or bleaching powder can be determined in the laboratory.

Procedure

The JIK or bleaching powder is added to ethanoic acid or hydrochloric acid. Chlorine gas is liberated and its passed through a solution of potassium iodide solution and iodine is liberated.

The liberated iodine is then titrated against a standard solution of sodium thiosulphate using starch as indicator.

The volume of the thiosulphate solution used is noted.

Equation of reactions taking place

JIK (NaOCl and NaCl)

$$NaOCl_{(aq)} \longrightarrow Na^+_{(aq)} + ClO^-_{(aq)}$$

$$NaCl_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$
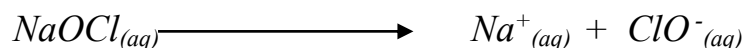
On addition of an acid to JIK the reaction below takes place,

$$OCl^-_{(aq)} + Cl^-_{(aq)} + H^+_{(aq)} \longrightarrow H_2O_{(l)} + Cl_{2(g)}$$

Available chlorine

Then,

$$Cl_{2(g)} + 2I^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + I_{2(aq)}$$

$$Cl_{2(g)} + 2I^-_{(aq)} \longrightarrow 2Cl^-_{(aq)} + I_{2(aq)}$$

$$S_2O_3^{2-}_{(aq)} + I_{2(aq)} \longrightarrow S_4O_6^{2-}_{(aq)} + 2I^-_{(aq)}$$
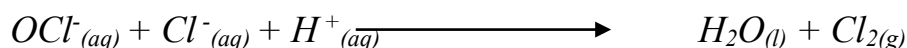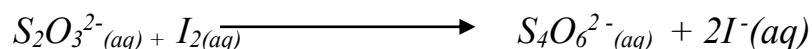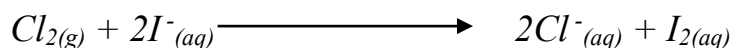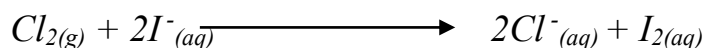
Acid strength of the oxyacids

Trend

The acidity of the oxyacids in aqueous solution increase with increase in the number of oxygen atoms present i.e. hypochlorous acid (HOCl) is the least acidic oxyacid and chloric (vii) acid (HClO$_4$)themost acidic in aqueous solution.

Explanation

Order of acidity is *HOCl<HOClO< HOClO$_2$< HOClO$_3$*

As the number of the oxygen atoms increase, the H-O bond becomes weaker and in aqueous solution the bond easily ionise producing more H+ ions in solution.

6.5. Test for Chlorides, Bromides and Iodides ions
1) Use of silver nitrate solution
Procedure
To the solution containing the unknown anion is added silver nitrate solution.

Observation

a) In the of chloride ions a white silver chloride is formed. The precipitate dissolves in excess aqueous ammonia due to the formation of a soluble complex called diammine silver (I) ions.

Equation

$$Ag^+{}_{(aq)} + Cl^-{}_{(aq)} \longrightarrow AgCl_{(s)} \quad white\ precipitate.$$

$$AgCl_{(s)} + 2NH_{3(aq)} \longrightarrow Ag(NH_3)_2{}^+{}_{(aq)} + Cl^-{}_{(aq)}$$
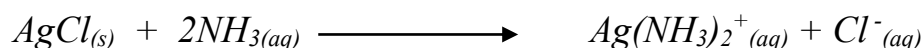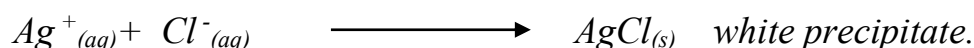
Soluble complex.

b) In the presence of bromide ions a pale yellow precipitate of silver bromide is formed. The precipitate dissolves in excess aqueous ammonia due to the formation of a soluble complex.

Equation

$$Ag^+{}_{(aq)} + Br^-{}_{(aq)} \longrightarrow AgBr_{(s)}pale\ yellow\ precipitate.$$

$$AgBr_{(s)} + 2NH_{3(aq)} \longrightarrow Ag(NH_3)_2^+{}_{(aq)} + Br^-{}_{(aq)}$$
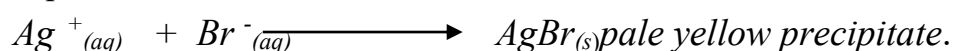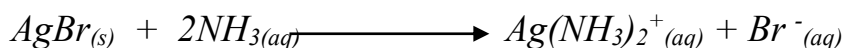
Soluble complex.

c) In the presence of iodide ions, a yellow precipitate of silver iodide is formed. The precipitate is insoluble in excess aqueous ammonia.
   Equation

$$Ag^+{}_{(aq)} + I^-{}_{(aq)} \longrightarrow AgI_{(s)} \quad yellow \ precipitate.$$
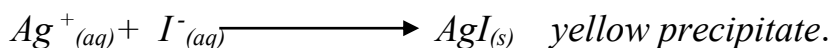
2) Use of lead (II) nitrate or lead (II)ethanoate solution.
   Procedure
   To the solution containing the unknown anion is added lead (II) nitrate or lead (II) ethanoate solution.
   Observation
   a) In the presence of chloride ions a white precipitate of lead (II) is formed. The precipitate dissolves on cooling but reappears on cooling.

$$Pb^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \longrightarrow PbCl_{2(s)}$$
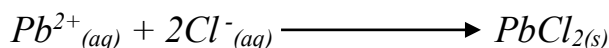
   b) In the presence of bromide ions a white precipitate of lead (II) is formed. The precipitate dissolves on warming but reappears on cooling

$$Pb^{2+}{}_{(aq)} + 2Br^-{}_{(aq)} \longrightarrow PbBr_{2(s)}$$
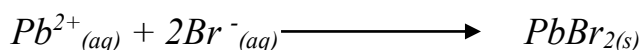
   c) In the presence of iodide ions a pale yellow precipitate of lead (II) iodide is formed. The precipitate dissolves on warming but reappears on cooling

$$Pb^{2+}{}_{(aq)} + 2I^-{}_{(aq)} \longrightarrow PbI_{2(s)}$$
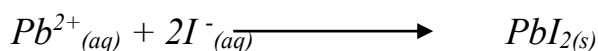
3) Use of chlorine water and tetrachloromethane
   Procedure
   To the solution containing the unknown anion is added Chlorine water followed by 2-3 drops of tetrachloromethane
   Observation
   a) In the presence of chloride ions, there is no observable change.

b) In the presence of bromide ions, a brown colour appears in the organic liquid.

c) In the presence of iodide ions, a purple/violet colour appears in the organic liquid.

4) <u>Use of concentrated sulphuric acid</u>

<u>Procedure</u>

To the a few grams of the solid containing the unknown anion is added concentrated sulphuric acid

<u>Observation</u>

a) In the presence of chloride ions, hydrogen chloride gas is evolved (white fumes).
b) In the presence of bromide ions, bromine gas (brown) and hydrogen bromide gas is evolved.
c) In the presence of iodide ions, iodine vapour (purple) and hydrogen iodide gas is evolved.

5) <u>Use of copper (II) sulphate solution</u>

<u>Procedure</u>

When the reagent is added to a solution containing iodide ions, a white precipitate of copper (I) iodide and a brown solution of iodine is formed.

<u>Equation</u>

$$Cu^{2+}_{(aq)} \longrightarrow 2I^-_{(aq)} Cu_2I_{2(s)} + I_{2(aq)}$$
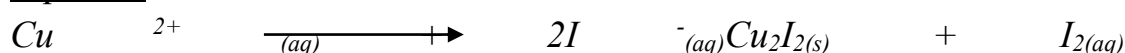
CHAPTER 7

7. PERIOD 3 ELEMENTS IN THE PERIODIC TABLE

Table 11: Physical properties of group III elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic no	11	12	13	14	15	16	17	18
Outer electronic conf	$-3s^1$	$-3s^2$	$-3s^2$ $3p^1$	- $3s^23p^2$	- $3s^23p^3$	- $3s^23p^4$	- $3s^23p^5$	$-3s^2$ $3p^6$
Melting point/^0C	97.8	650	660	1410	44	119	-101	-189
Atomic radius/^0A	1.57	1.36	1.26	1.17	1.10	1.04	0.99	
1st I.E/kjmol-1	496	737	577	786	1012	999	1255	1521
1st E.A/kjmol-1	-20	67	-30	-135	-60	-200	-364	

Revision question

State and explain the trend in the variation of the following across the 3rd period in the periodic table

- a) Atomic radius
- b) 1st ionization energy
- c) 1st electron affinity
- d) Electronegativity
- e) Electropositivity
- f) Melting point

7.1. Compounds of period 3 elements

1) Chlorides

Element	Na	Mg	Al	Si	P	S	Cl
Formula of chloride	NaCl	MgCl₂	AlCl₃	SiCl₄	PCl₃,PCl₅	S₂Cl₂	Cl₂
Type of bonding in the chloride	Ionic	Ionic	Covalent	Covalent	Covalent	Covalent	Covalent

Sodium chloride and magnesium chloride are ionic chlorides with giant structures. They have high melting points.

The melting point of sodium chloride is higher than for magnesium chloride which in turn is higher than for aluminium chloride.

Explanation

Ionic compounds tend to have higher melting points than covalent compounds.

From *NaCl,* through *MgCl₂* to *AlCl₃*, the cationic radius decreases from Na^+, through Mg^{2+} to Al^{3+} as the charge increases from +1 to +3.

This leads to an increase in cationic charge density from Na^+ to Al^{3+}.

Aluminiumion with the highest charge density greatly polarizes the electron clouds of the chloride ions to which it is bonded making aluminium chloride predominantly covalent.

Magnesium ion also polarizes the electron clouds of the chloride ions to which it is bonded but the extent of polarization is less than in aluminium chloride. Magnesium chloride is therefore predominantly ionic.

Sodium ion with the least polarizing power makes sodium chloride the most ionic chloride in the period and with the highest melting point, followed by magnesium chloride and then aluminium chloride.

Note

The other chlorides in the period; namely $SiCl_4$, PCl_3, PCl_5, S_2Cl_2 and Cl_2 are covalent molecules with weak intermolecular van der waals forces of attraction in them. The magnitude of these forces increasing with increase in molecular mass. They all therefore have low melting and boiling points.
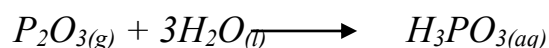
Reactions of the chlorides with water

a) Sodium chloride dissociates in water to give a neutral solution i.e the P^H of the resultant solution is 7.

$$NaCl_{(aq)} + aq \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$
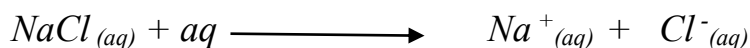
b) Magnesium chloride hydrolyses in water to form an acidic solution

$$MgCl_{2(s)} + H_2O_{(l)} \rightleftharpoons Mg(OH)Cl_{(s)} + HCl_{(aq)}$$
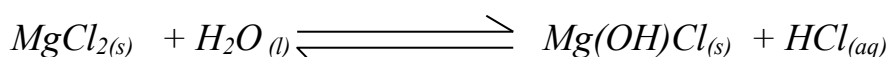
c) Aluminium chloride in water hydrolyses to form a solution whose P^H is less than 7

$$AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow Al(H_2O)_6^{3+}_{(aq)} + 3Cl^-_{(aq)}$$

$$[Al(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_5OH]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_4 2OH]^+_{(aq)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_4 2OH]^+_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_3 3OH]_{(s)} + H_3O^+_{(aq)}$$

Over all equation:

$$[Al(H_2O)_6]^{3+}_{(aq)} + 3H_2O_{(l)} \rightleftharpoons [Al(H_2O)_3 3OH]_{(s)} + 3H_3O^+_{(aq)}$$
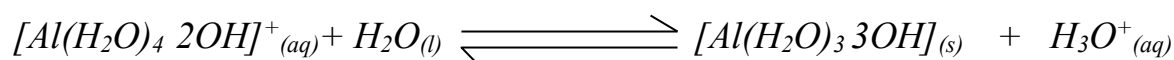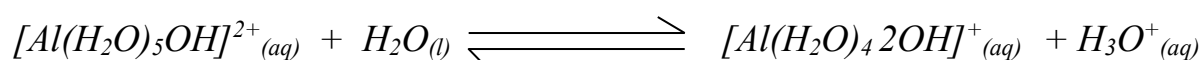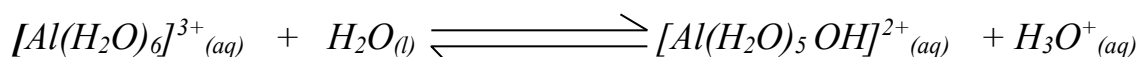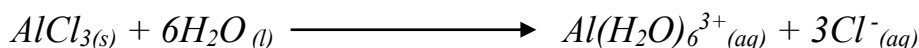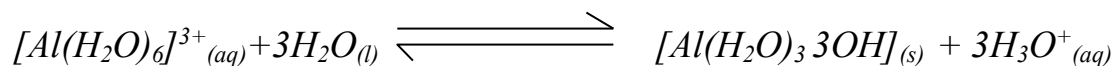
White ppt

Silicon (IV) chloride reacts with water producing silicondioxide and hydrochloric acid. The P^H of the resultant solution is therefore less than 7.

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$

White solid
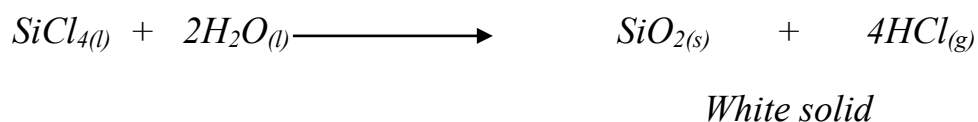
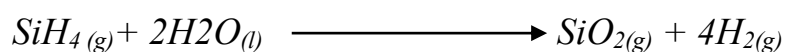a) The rest of the chlorides react with water to form acidic solutions.

$$PCl_{3(l)} + H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

$$PCl_{5(l)} + 4H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(aq)}$$

$$S_2Cl_{2(l)} + 2H_2O_{(l)} \longrightarrow 3S_{(s)} + 4HCl_{(aq)} + SO2_{(g)}$$

$$Cl_{2(g)} + H_2O_{(l)} \longrightarrow HCl_{(aq)} + HOCl_{(aq)}$$
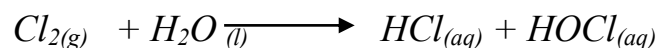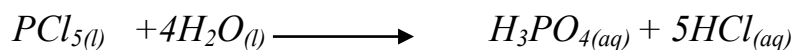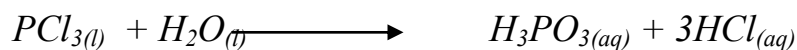
2) <u>The oxides of period 3 elements</u>.

Eement	Na	Mg	Al	Si	P	S	Cl
Oxide	Na_2O, Na_2O_2	MgO	Al_2O_3	SiO_2	P_2O_3, P_2O_5	SO_2, SO_3	Cl_2O Cl_2O_7
Type of bonding	Ionic	ionic	Ionic	covalent	covalent	Covalent	covalent

The oxide of sodium, magnesium and aluminium are ionic compounds and conduct electricity in molten state due the presence of free ions. They have giant ionic structures with high melting points.

Silicon dioxide has a giant molecular structure and therefore has a very high melting point.

The rest of the oxides have simple molecular structures with weak intermolecular van der waals forces and hence have low melting and boiling points.

Reactions of the oxides with water

a) The oxides of sodium and magnesium react with water forming alkaline solutions. Aluminium oxide is however insoluble in water.

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$

$$Na_2O_{2(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_2O_{2(aq)}$$

$$MgO_{(s)} + H_2O_{(l)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$$
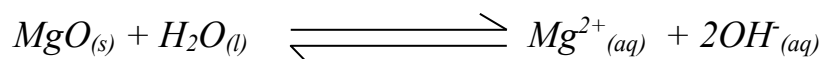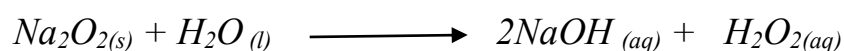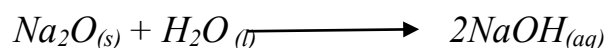
b) Silicon dioxide does not react with water. Being acidic, it however reacts with alkalis forming silicates

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_3 (aq) + H_2O_{(l)}$$
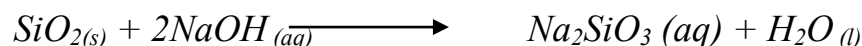
c) The rest of the oxides react with water to form acidic solutions

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$$

$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$

$$P_2O_{3(g)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)}$$

$$P_2O_{5(g)} + 3H_2O_{(l)} \longrightarrow H_3PO_{4(aq)}$$

$$Cl_2O_{(g)} + H_2O_{(l)} \longrightarrow 2HOCl_{(aq)}$$

$$Cl_2O_{7(g)} + H_2O_{(l)} \longrightarrow 2HClO4_{(aq)}$$
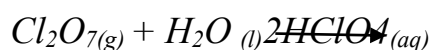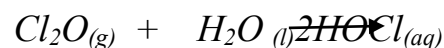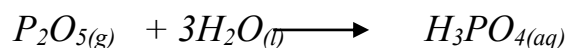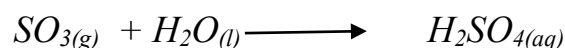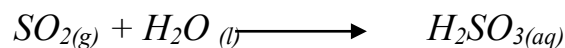
The Hydrides of period 3

Table 12: The Hydrides of period 3 elements

Hydride	Formula
Sodium hydride	NaH
Magnesium hydride	MgH_2
Aluminium hydride	AlH_3
Silane	SiH_4
Phosphine	PH_3
Hydrogen sulphide	H_2S
Hydrogen chloride	HCl

Hydrolysis of the hydrides in water

$NaH_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$

$MgH_{2(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)} + H_{2(g)}$

$AlH_{3(s)} + 3 H_2O_{(l)} \longrightarrow Al(OH)_{3(s)} + 3H_{2(g)}$

$SiH_{4(g)} + 2H2O_{(l)} \longrightarrow SiO_{2(g)} + 4H_{2(g)}$

$H_2S_{(g)} + 2H_2O_{(l)} \longrightarrow S^{2-}_{(aq)} + 2 H_3O^+_{(aq)}$

$HCl_{(g)} + H_2O_{(l)} \longrightarrow Cl^-_{aq)} + H3O^+_{(aq)}$
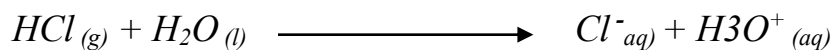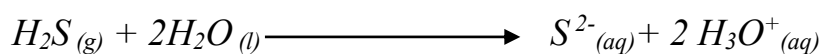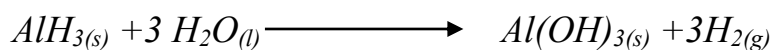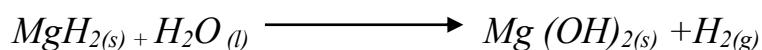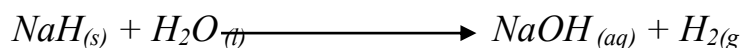
Note

PH_3 is not affected by water because it is non polar. This is because phosphorous and hydrogen have similar electronegativity values.

7.1.1. ALUMINIUM

The ore of aluminium

a) Bauxite; $Al_2O_3.2H_2O$

b) Cryolite; Na_3AlF_6

Extraction of aluminium

Aluminium is commonly extracted from its ore called bauxite.

Impurities found in bauxite are:

- *Silica, SiO_2*

- *iron(iii) oxide, Fe_2O_3*

The extraction process is divided into two stages.

1) **Purification of the impure bauxite**

   This involves purifying the impure bauxite to form pure aluminium oxide.

   The ore is first roasted at a low temperature to convert the iron (ii) oxide to iron (iii) oxide. The roasted product is then crushed to powder form and dissolved in concentrated sodium hydroxide solution.

   The dissolution in concentrated sodium hydroxide is to separate iron (iii) oxide from the ore.

   Being an amphoteric oxide, Al_2O_3 and the acidic oxide SiO_2 dissolve in the sodiumhydroxide solution as shown by the equations below

$$Al_2O_{3(s)} + 2OH^-(aq) + 3H_2O(l) \longrightarrow 2\,Al(OH)_4^-(aq)$$

$$SiO_{2(s)} + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$
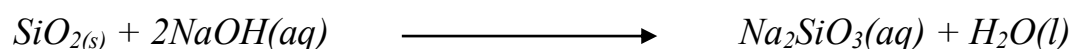
The iron (iii) oxide being basic does not dissolve and is eliminated by filtering off.

Aluminium hydroxide is then obtained from the sodium aluminate solution by either:

i.   Adding a little prepared aluminium hydroxide to aluminate solution to precipitate more aluminium oxide; a process referred to as seeding.

$$Al(OH)_4^-{}_{(aq)} \longrightarrow Al(OH)_{3(s)} + OH^-{}_{(aq)}$$
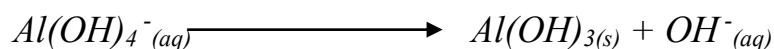
ii.   bubbling CO_2 gas through the filtrate (aluminate solution)

$$2Al(OH)_4^-{}_{(aq)} + CO_{2(g)} \longrightarrow 2Al(OH)_{3(s)} + CO_3^{2-}{}_{aq)}$$
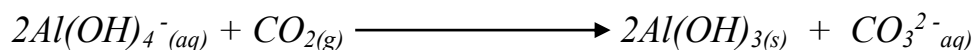
The aluminium hydroxide from either method is filtered off, washed and dried. The dry aluminium hydroxide is then heated to form aluminium (III) oxide.

$$2Al(OH)_3 \longrightarrow Al_2O_3(s) + 3H_2O(g)$$

2) <u>Electrolysis of the pure aluminium oxide</u>

The pure oxide is 1st dissolved in molten cryolite (sodium hexafluoride aluminate - Na_3AlF_6) to lower its melting point.

The molten aluminium oxide is then electrolyzed at a temperature between 800-900 ^{0}c at a high current density between graphite electrodes.

Molten aluminium sinks to the bottom at the cathode where it is tapped off while oxygen is liberated at the carbon anode.

Cathode: $Al^{3+}{}_{(l)} + 3e \longrightarrow Al_{(l)}$

Anode: $2O^{2-}{}_{(l)} \longrightarrow O_{2(g)} + 4e$

The electrolysis cell

carbon anodes

carbon lining
as cathode

solution of aluminium
oxide in molten cryolite

steel tank lined with
refractory bricks

molten aluminium
collects at the bottom
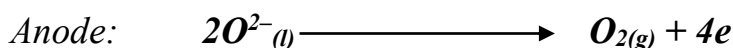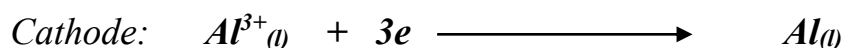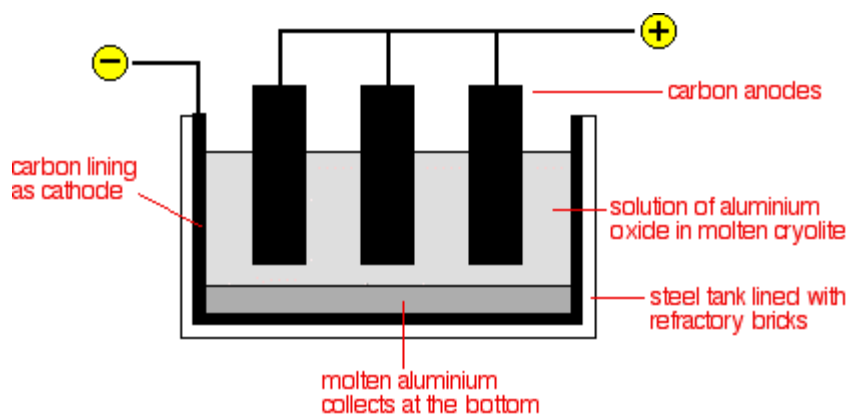
Note

The oxygen gas produced at the anode oxidizes the graphite (carbon) anode and therefore it is replaced (renewed) from time to time.

Reactions of aluminium

a) Reaction with water.

Aluminium reacts slowly with steam to form the oxide and hydrogen gas.

$$2Al_{(s)} + 3H_2O_{(g)} \longrightarrow Al_2O_{3(s)} + 3H_{2(g)}$$
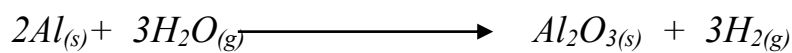
b) Reaction with chlorine.

Aluminium when heated reacts with dry chlorine to form a chloride which sublimes. The chloride is predominantly covalent.

$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(s)}$$
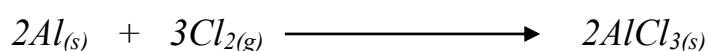
Explanation

Aluminium forms a smaller cation with high charge density & high polarizing power. It distorts the electron cloud of surrounding anions. The larger the anion, the greater the extent of polarization. Therefore the large chloride ion is polarized greatly and as such a covalent character is induced.

The chloride dimerises, Al_2Cl_6, at high temperature with a chloride bridge structure. Aluminium bromide & iodide have similar structures.

c) Reaction with alkalis.

Aluminium is an amphoteric metal. It reacts with concentrated alkalis to form aluminates complex and hydrogen gas.

$$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \longrightarrow 2\,Al(OH)_4^-_{(aq)} + 3H_{2(g)}$$
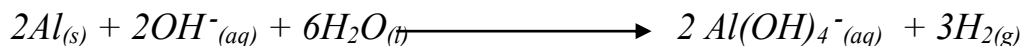
d) Reaction with acids.

With dilute mineral acids except nitric acid, aluminium forms salt and hydrogen gas.

$$2Al_{(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_{2(g)}$$
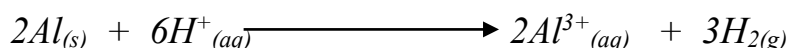
With hot conc. H_2SO_4, aluminium forms salt, sulphur dioxide gas and water.

$$2Al_{(s)} + 6H_2SO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3SO_{2(g)} + 6H_2O_{(l)}.$$
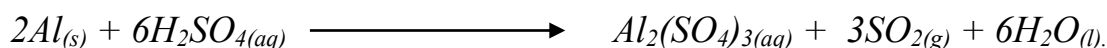
Aluminium does not react with dilute nitric acid. The metal is rendered passive due to the formation of an impervious layer of oxide.

The acidity of the hexaaqua ions

In aqueous solution, soluble salts of aluminium i.e. $AlCl_3, Al_2(SO_4)_3$ etc exist as $[Al(H_2O)_6]^{3+}$.

The resultant solution is acidic due to hydrolysis reactions:
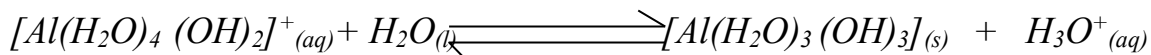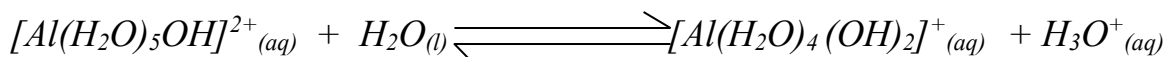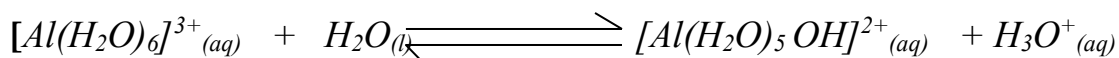
$$[Al(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5\,OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_5OH]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_4\,(OH)_2]^+_{(aq)} + H_3O^+_{(aq)}$$

$$[Al(H_2O)_4\,(OH)_2]^+_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_3\,(OH)_3]_{(s)} + H_3O^+_{(aq)}$$

Over all equation:

$$[Al(H_2O)_6]^{3+}_{(aq)} + 3H_2O_{(l)} \rightleftharpoons [Al(H_2O)_3\,(OH)_3]_{(s)} + 3H_3O^+_{(aq)}$$
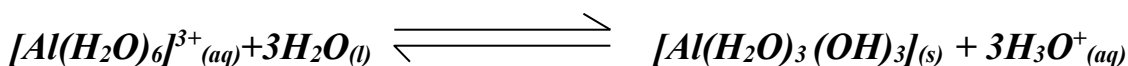
The hydroxonium ions produced make the resultant solution acidic with P^H less than 7 and a white solid is formed.

If sodium carbonate solution is bubbled through aqueous solution of aluminium salts, bubbles of a colorless gas that turns lime water milky is formed.

The oxide and hydroxide of aluminium are amphoteric. They react with both conc. alkalis and dilute acids.

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2\,Al(OH)_4^-_{(aq)}$$

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

$$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow Al(OH)_4^-_{(aq)}$$

$$Al(OH)_{3(s)} + 3H^+_{(aq)} \longrightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)}$$
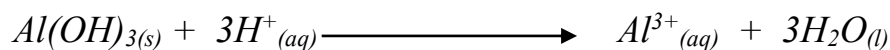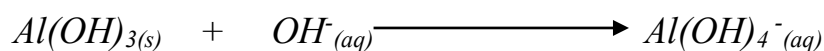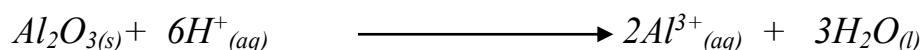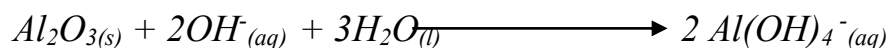
Some uses of aluminium include:

Aluminium is used for:	Useful properties
1. Aircraft	light, strong, resists corrosion
2. other transport such as ships' superstructures, container vehicle bodies, tube trains	light, strong, resists corrosion
3. Overhead power cables .	light, resists corrosion, good conductor of electricity
4. Saucepans	light, resists corrosion, good appearance, good conductor of heat

CHAPTER 8

8. TRANSITION   ELEMENTS

(Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc)

d-block elements:

A d-block element is one in which the inner 3d sub-shell is in the process of filling up with electrons after the outermost 4s sub-shell(which has a lower energy) has already been filled.

In the periodic table, they are found between the very reactive s-block elements and the less reactive p-block elements.

Transition Elements.

A transition element is one that forms at least one ion with a partially filled 3d sub shell. All transition elements are d-block elements.

The sub shells are filled up in order of increasing energy and so the 4s- orbitals are filled 1st before the 3d-orbitals.

NB:

For chromium, the electronic configuration of $[Ar]3d^54s^1$ is a more stable arrangement than $[Ar] 3d^44s^2$

This is because the former configuration has 3d sub shell half filled with electronsand therefore energetically more stable than the latter configuration where the 3d has only 4 electrons.

Unpaired electrons experience minimum repulsion between them.

For copper, the configuration $3d^{10}4s^1$ is a more stable arrangement than $3d^94s^2$. The explanation is because the 3d-subshell is full therefore energetically stable

Configuration of selected ions

Sc^{3+}	$1s^22s^22p^63s^23p^6$
Cr^{3+}	$1s^22s^22p^63s^23p^63d^3$
Mn^{2+}	$1s^22s^22p^63s^23p^63d^5$
Mn^{3+}	$1s^22s^22p^63s^23p^63d^4$
Fe^{2+}	$1s^22s^22p^63s^23p^63d^6$
Fe^{3+}	$1s^22s^22p^63s^23p^63d^5$
Cu^+	$1s^22s^22p^63s^23p^63d^{10}$
Cu^{2+}	$1s^22s^22p^63s^23p^63d^9$
Zn^{2+}	$1s^22s^22p^63s^23p^63d^{10}$

When a transition metal atom loses electrons to form ions, the 4s-electrons are lost first before 3d-electrons.

This is because the 3d sub -shell is situated closer to the nucleus than the 4s sub shell.

Thus when the 3d sub shell is occupied, the electrons in it repel the 4s-electrons further from the nucleus and in the process the energy of the 4s electrons increase more than for the 3d electrons. Therefore the 4s electrons are lost before the 3d electrons.

8.1.   General characteristics of transition elements
1) <u>High melting and boiling points</u>.

Melting points of metals depend on the number of electrons available for metallic bond formation.

Transition elements use both the 4s and 3d-electrons in metallic bond formation. The greater the number of electrons contributed to the metallic bond, the higher the melting point. Transition elements therefore have high melting and boiling points.

Melting Points of 4th Period Transition Elements
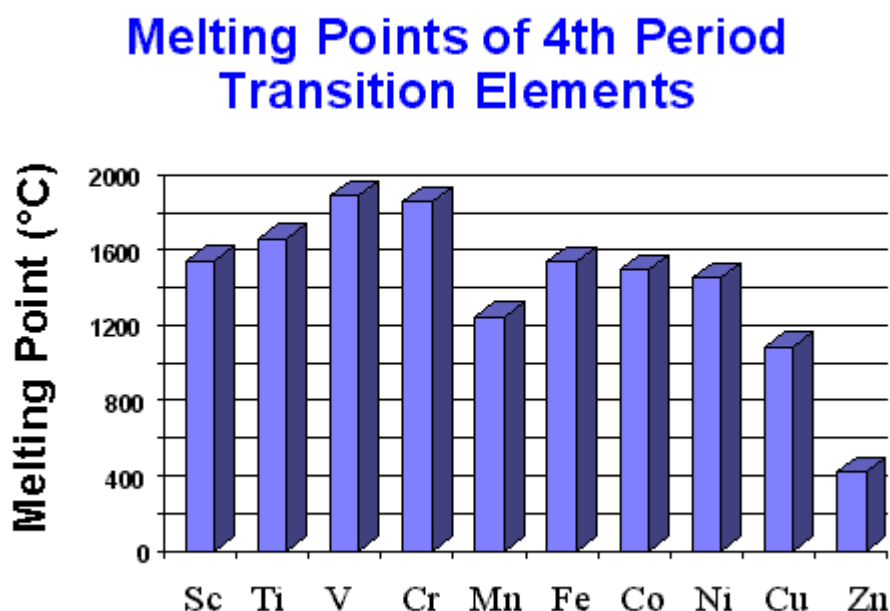
A dip in the melting point is observed at manganese $[Ar]4S^23d^5$. This is attributed to the stability of half-filled 3d-orbitals, electrons therefore being less available for metallic bond formation.

Zinc $[Ar]4S^23d^{10}$ with a full 3d-orbitals uses only the outer most 4s-electrons in metallic bond formation as such has the lowest melting point.

The melting points of these metals rise to a maximum value and then decrease with increase in atomic number

Exercise

The atomic numbers and melting points of some d-block elements are as follows:

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic.No	21	22	23	24	25	26	27	28	29
M.Point(^{0}C)	1540	1680	1900	1890	1240	1540	1500	1450	1080

i) Plot a graph of the melting points against atomic numbers. (3mks)

ii) Explain the shape of your graph.(4marks)

2) Variable oxidation states.

The variable oxidation states exhibited by transition elements are attributed to the fact that both the 4s and 3d-electrons are energetically similar and they can both be used in bond formation.

All elements with exception of scandium and zinc show variable oxidation states. For an oxidation state of +2, only the outer most *4s*-electrons are used in bond formation. For an oxidation state greater than +2, both the *4s* and *3d*-electrons are involved in bond formation.

The maximum oxidation state is achieved when all the *4s* and *3d* electrons are involved in bonding.

Oxidation States of 4th Period Transition Elements

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

a

EXERCISE

Workout the oxidation state of the transition metal in each of the following compounds or ions:

i) MnO_4^-

ii) MnO_4^{2-}

iii) MnO_2

iv) $Cr_2O_7^{2-}$

v) K_2CrO_4

vi) $Fe(CN)_6^{3-}$
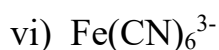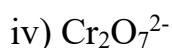
3. Catalytic activity.

Transition metals and their compounds behave as catalysts due to the presence of partially filled d-orbitals   .

In reactions involving gases, the reacting gases are adsorbed onto the surface of the catalyst where they form weak bonds by either

donating or accepting electrons.

This weakens the internal bonding of the reactant molecules and in the process reducing the activation energy for the reaction.

Also there is a higher concentration of the reactants at the surface of the catalyst as a result the rate of reaction increases.

Some common examples include:

I. Haber process in the manufacture of ammonia where finely divided iron is used.

II. Contact process in the manufacture of sulphuric acid, vanadium pent oxide is used.

III. Decomposition of hydrogen peroxide, manganese (IV) oxide is used.

IV. Hydrogenation of alkenes and alkynes, nickel metal is used.

4. Complex ion formation.

A complex ion basically consists of a central metal atom or ion surrounded by electron donating groups called ligands capable of forming

dative covalent bonds with the metal atom or ion.

Complex ion formation in transition metals is affected by the following factors:

- Presence of vacant d-orbitals.

- The high charge on the metal cation.)

- The small radius of the cation.

Example of a complex ion is $[Ni(H_2O)_6]^{2+}$, and is said to have a coordination number of 6.

Coordination number   is the number of ligands directly bonded to the central metal ion. A complex species can be cationic, anionic or neutral.

Cationic complexes are those that carry an overall positive charge

Formula	Colour	Name of complex ion	Coordination number	Ox. St. of metal ion
$Cu(H_2O)_4{}^{2+}$	Blue	Tetra-aqua copper(ii)ion	4	+2
$[Cu(NH_3)_4]^{2+}$		Tetra-ammine copper(ii)ion	4	+2
$[Co(H_2O)_6]^{2+}$	Pink	Hex-aqua cobalt(ii) ion	6	+2
$[Ni(H_2O)_6]^{2+}$	Green	Hex-aqua nickel(ii) ion	6	+2
$[Cr(H_2O)_6]^{3+}$	Violet	Hex-aqua chromium(iii)ion	6	+3
$[Cr(NH_3)_6]^{3+}$	Yellow	Hex-ammine chromium(iii)ion	6	+3
$[Cr(NH_3)_4Cl_2]^{+}$		Tetra-ammine dichlorochromium(iii)ion	6	+3

Anionic complexes are those that carry a negative charge.

Nomenclature: IUPAC Rules

- If complex is an anion, its name ends with -ate
  - appended to either the English or Latin name of the metal

Example:
scandium, Sc = scandate
titanium, Ti = titanate
vanadium, V = vanadate
chromium, Cr = chromate
manganese, Mn = manganate
iron, Fe = ferrate
cobalt, Co = cobaltate
nickel, Ni = nickelate
copper, Cu = cuprate
zinc, Zn = zincate

Formula	Color	Name of complex	Coordination number	Oxidation state of cation
$[CuCl_4]^{2-}$	Yellow	Tetra chlorocuprate(ii)ion	4	+2
$[CoCl_4]^{2-}$	Blue	Tetra chlorocobaltate(ii)ion	4	+2
$[Zn(OH)_4]^{2-}$	Colorless	Tetra hydroxozincate(ii)ion	4	+2
$[Fe(CN)_6]^{3-}$		Hexacyanoferrate(iii) ion	6	+3
$[Fe(CN)_6]^{4-}$		Hexacyanoferrate(ii) ion	6	+2
$[Ni(CN)_4]^{2-}$		Tetracyanonickelate(ii)ion	4	+2

Neutral complexes are those that carry no charge.

$Ni(CO)_4$, Tetracarbonylnickel(O)

$Fe(CO)_5$, Pentacarbonyliron(O)

Exercise

Give the name, coordination number, and the oxidation state of the metal ions in the following complexes:

i) $Cr(H_2O)_6Br_3$ \hspace{1cm} ii) $[\,Cr(H_2O)_6]Cl_3$ \hspace{1cm} iii) $[Cr(H_2O)_5Cl]^{2+}$

iv) $[Co(NH_3)_5Br]^{2+}SO_4^{2-}$ \hspace{0.5cm} v) $[Cr(H_2O)_4Cl_2]^+$.

5) Form colored compounds.

Transition metal ions are colored because they have partially filled 3d'sub shell.

A transition metal ion exhibits color when it absorbs light from the visible region.

Light in the visible region has sufficient energy to promote d-electrons from a lower energy level to a higher energy level.

6) Magnetic Properties

Molecules with one or more unpaired electrons are attracted into a magnetic field. The more unpaired electrons in the molecule the stronger the attraction.

This type of behavior is called paramagnetism.

Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called diamagnetism.

Many transition metal complexes exhibit simple paramagnetism. In such compounds the individual metal ions possess some number of unpaired electrons.

8.2. CHROMIUM

QUESTION

a) Write the electronic configuration of the following species (atomic number Cr is 24):

    i) Cr

    ii) Cr^{2+}

    iii) Cr^{3+}

    iv) Cr^{6+}

b) State the common oxidation states of chromium.

c) Aqueous sodium hydroxide was added drop wise to a solution containing Chromium (iii) ions, state what was observed and write equation for the reaction that took place.

d) Discuss using equation where applicable   the reactions of chromium with:

    i) Air

    ii) Water

    iii) Nitric acid, hydrochloric acid and sulphuric acid.

ANSWERS

a)

    i) $Cr: 1S^2 2S^2 2P^6 3S^2 3P^6 3d^5 4S^1$

    ii) $Cr^{2+}: 1S^2 2S^2 2P^6 3S^2 3P^6 3d^4$

    iii) $Cr^{3+}: 1S^2 2S^2 2P^6 3S^2 3P^6 3d^3$

    iv) $Cr^{6+}: 1S^2 2S^2 2P^6 3S^2 3P^6$

Note

Chromium adopts the above electronic configuration rather than the expected $1s^22s^22p^63s^23p^63d^44s^2$ because the 3d is half filled unlike in the expected configuration therefore it's more energetically stable.

b) +2, +3, +6

c) Observation

Grey green precipitate, soluble in excess forming a green solution.

Equations

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

$Cr\ (OH)_{3\ (s)} + 3\ OH^-{}_{(aq)} \longrightarrow Cr(OH)_6{}^{3-}{}_{(aq)}$
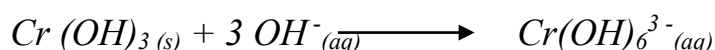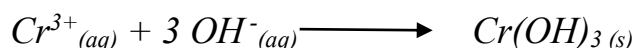
d)

With Air (oxygen)

Chromium does not react with oxygen at room temperature, when heated it forms green chromium (iii) oxide.

$4Cr_{(s)} + 3O_{2(g)} \longrightarrow 2Cr_2O_{3(s)}$ green solid.
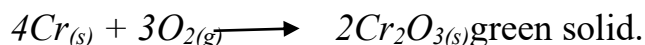
With water.

Chromium reacts with steam to form green chromium (iii) oxide and hydrogen gas.

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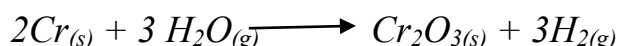
With acids.

Chromium reacts with dilute hydrochloric acid forminggreen chromium(iii) chloride solution andliberating hydrogen gas.

$2Cr_{(s)} + 6HCl_{(aq)} \longrightarrow 2CrCl_{3(aq)} + 3H_{2(g)}$
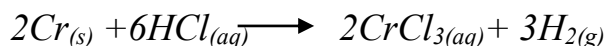
Chromium reacts with dilute sulphuric acid forming blue solution of chromium (ii) sulphate and liberating hydrogen gas.

The blue solution turns to green when exposed to air. This is due to aerial oxidation of Cr^{2+} to Cr^{3+} ions.

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

$$4CrSO_{4(aq)} + O_{2(g)} + 2H_2SO_{4(aq)} \longrightarrow 2Cr_2(SO_4)_{3(aq)} + H_2O_{(l)}$$

Ionically:

$$Cr_{(s)} + 2H^+_{(aq)} \longrightarrow Cr^{2+}_{(aq)} + H_{2(g)}$$

$$4Cr^{2+}_{(aq)} + 4H^+_{(aq)} + O_{2(g)} \longrightarrow 4Cr^{3+}_{(aq)} + 2H_2O_{(l)}$$
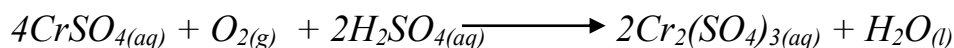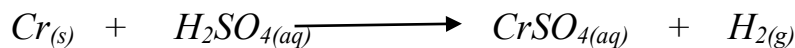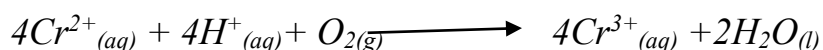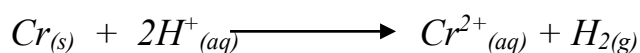
Chromium reacts with dilute sulphuric acid on heating to form chromium (iii) sulphate and hydrogen gas

$$2Cr_{(s)} + 3H_2SO_{4 (aq)} \longrightarrow Cr_2(SO_4)_{3(aq)} + 3H_{2(g)}$$
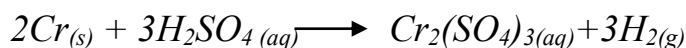
Chromium reacts with hot conc. sulphuric acid to form chromium (iii) sulphate, sulphur dioxide and water.

$$2Cr_{(s)} + 6H_2SO_{4 (aq)} \longrightarrow Cr_2(SO_4)_{3(aq)} + 6H_2O_{(aq)} + 3SO_{2(g)}$$
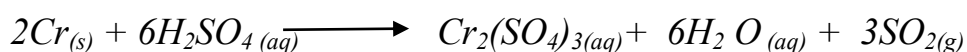
Note:

Chromium does not react with nitric acid due to the formation of a thin layer of chromium (vi) oxide which renders it passive towards nitric acid.

With chlorine

If chlorine gas is passed over heated chromium, green solid of chromium (iii) chloride is formed.

$$2Cr_{(s)} + 3Cl_{2(g)} \longrightarrow 2CrCl_{3(s)}$$
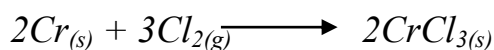
NB: If hydrogen chloride is used instead, chromium (ii) chloride is formed.

$$Cr_{(s)} + 2HCl_{(g)} \longrightarrow CrCl_{2(s)} + H_{2(g)}$$
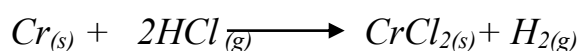
With sodium hydroxide solution

Chromium dissolves in sodium hydroxide solution giving:

- Effervescence of a colorless gas that burns with a pop sound.

- a green solution.

$$2Cr_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \longrightarrow 2Cr(OH)_4^-_{(aq)} + 3H_2_{(g)}$$
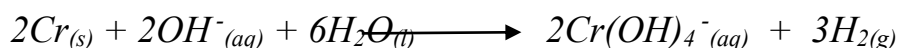
Compounds of Chromium

Chromium shows principal oxidation states of +2, +3, & +6.

The most stable oxidation state of chromium is +3.

The acidity of the hexaqua ions

In aqueous solution, soluble salts of chromium in +3 oxidation state e.g. $CrCl_3$, $Cr(SO_4)_3$ etc exist as $[Cr(H_2O)_6]^{3+}$.

The resultant solution is acidic due to hydrolysis reaction

.i.e.

$$[Cr(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Cr(H_2O)_5OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$$

$$[Cr(H_2O)_5OH]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Cr(H_2O)_4(OH)_2]^+_{(aq)} + H_3O^+_{(aq)}$$

$$[Cr(H_2O)_4 2OH]^+_{(aq)} + H_2O_{(l)} \rightleftharpoons [Cr(H_2O)_3(OH)_3]_{(s)} + H_3O^+_{(aq)}$$

Over all equation:

$$[Cr(H_2O)_6]^{3+}_{(aq)} + 3H_2O_{(l)} \rightleftharpoons [Cr(H_2O)_3(OH)_3]_{(s)} + 3H_3O^+_{(aq)}$$
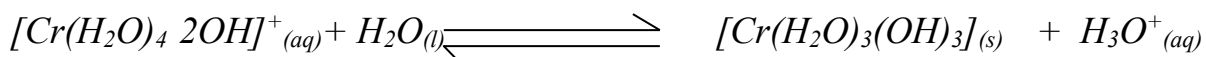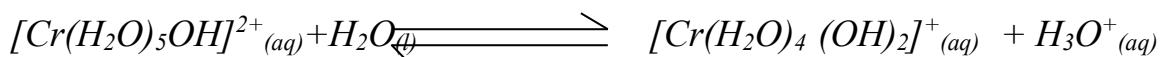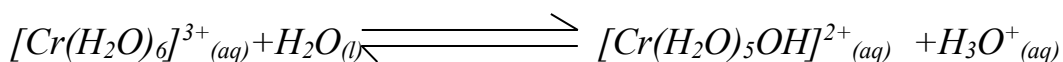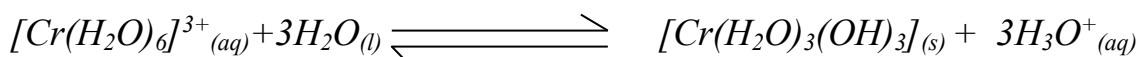
Green ppt.

The hydroxonium ions produced make the resultant solution acidic with P^H less than 7 and a green solid is observed due to the formation of hydrated chromium (iii) hydroxide.

If sodium carbonate solution is added to an aqueous solution of chromium (iii) salts, bubbles of a colorless gas that turns lime water milky is observed due to the carbon dioxide gas produced by the reaction between the hydroxonium ions and the carbonate ions.

$$CO_3^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \longrightarrow CO_{2 (g)} + H_2O_{(l)}$$
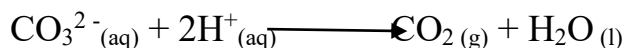
If magnesium ribbon is added to an aqueous chromium (iii) salt, a colorless gas that burns with a pop sound is liberated due to the reaction between the acidic solution and magnesium metal.

$$Mg_{(s)} + 2H_3O^+{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + H_{2(g)} + 2H_2O_{(l)}$$

or

$$Mg_{(s)} + 2H^+{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + H_{2(g)}$$
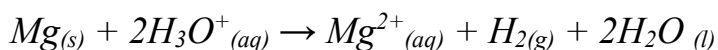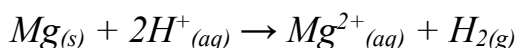
Note

Like chromium (iii) salts in aqueous solution, aqueous solution of aluminium and iron (iii) salts also undergo hydrolysis reactions to produce acidic solutions.

Chromium (iii) oxide, Cr_2O_3

It's a green solid which can be obtained by heating chromium (iii) hydroxide.

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

It is an amphoteric oxide.

It reacts with dilute mineral acids to form corresponding Cr^{3+} salt and with sodium hydroxide to forming the soluble complex $Cr\ (OH)_6^{3-}{}_{(aq)}$

$$Cr_2O_{3(s)} + 6H^+{}_{(aq)} \longrightarrow 2Cr^{3+}{}_{(aq)} + 3H_2O_{(l)}$$

$$Cr_2O_{3(s)} + 6OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Cr(OH)_6^{3-}_{(aq)}$$
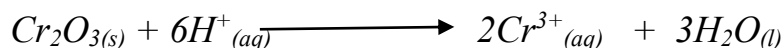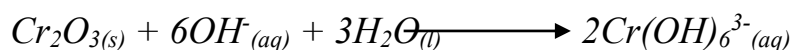
Green solution

Chromium (iii) hydroxide

It's a green solid formed when little sodium hydroxide is added to a solution containing Cr^{3+}ions. It's an amphoteric hydroxide; reacting with dilute acidsforming corresponding Cr^{3+} salts and with aqueous alkalis forming the complex $Cr(OH)_6^{3-}_{(aq)}$.

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

$$Cr(OH)_{3(s)} + 3OH^-_{(aq)} \longrightarrow Cr(OH)_6^{3-}_{(aq)} \text{chromite ion}$$
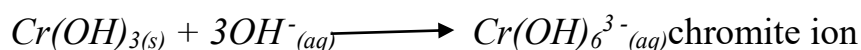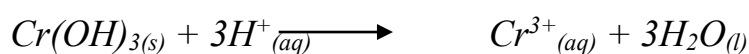
Hydrated Chromium (iii) Chloride.$CrCl_3.6H_2O$

This salt of chromium exhibits hydration isomerism i.e. existence of compounds with the same molecular formula but different structural formulae due to the difference in the number of water molecules directly bonded to the central chromium (iii) ion.

The following are the isomers of hydrated chromium (iii) chloride:

   i. $[Cr(H_2O)_6]^{3+}\ 3Cl^-$

(Hexaquachromium (iii) chloride)

   ii. $[Cr(H_2O)_5Cl]^{2+}.2Cl^-.H_2O$
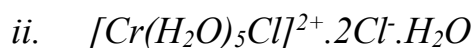
(Chloropentaqua chromium (iii) chloride monohydrate)

   iii. $[Cr(H_2O)_4Cl_2]^+.Cl^-.2H_2O$
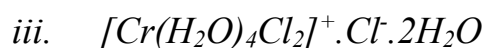
(Dichlorotetraaqua chromium (iii) chloride dihydrate)

Identification/test for the isomers

1) Using silver nitrate solution:

- The first isomer precipitates 3moles of silver chloride because all the $3Cl^-$ ions can be precipitated because they are not directly bonded to the central metal cation,

- The 2nd isomer precipitates 2moles of silver chloride per mole of the isomer.

- The 3rd isomer precipitates 1mole of silver chloride per mole of the isomer.

2) Using conductivity measurement:

- This test provides the number of moles of conducting ions in solution for every mole of isomer.

- The 1st isomer contains 4moles of conducting ions i.e. $[Cr(H_2O)_6]^{3+}$ and $3Cl^-$

- The 2nd isomer contains 3moles of conducting ions i.e. $[Cr(H_2O)_5Cl]^{2+}$ and $2Cl^-$

- The 3rd isomer contains 2moles of conducting ions i.e. $[Cr(H_2O)_4Cl_2]^+$ and Cl^-

Compounds of chromium in +6 oxidation states

Because of the high charge density of Cr^{6+} ion, it can only exists as oxo- ions.eg , CrO_3

, CrO_4^{2-} , $Cr_2O_7^{2-}$

Chromates, CrO_4^{2-}

Chromates are salts of chromic acid; they have a characteristic yellow color. e.g.

K_2CrO_4 and Na_2CrO_4.

A Chromate ion has a tetrahedral structure

Chromates are obtained when an alkaline solution is added to a solution containing dichromate ions.

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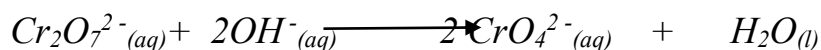
Orange   yellow

Chromates are stable in alkaline medium; however Chromates react with acids to form dichromate.

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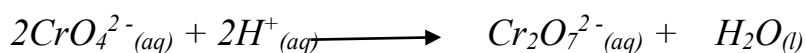
ALUMS

Alums are double sulphate salts with general formula $M_2SO_4.M_2(SO_4)_3.24H_2O$

The 1st M is a group (I) metal e.g. Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+ etc

The 2nd M is a group (III) metal or a metal bearing a +3 charge e.g. Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Co^{3+} etc

Examples of common alums are:

Chrome alum; $K_2SO_4.Cr_2(SO_4)_3.24H_2O$

Its solution in water is acidic because the chromium (iii) ions undergo hydrolysis making the solution acidic.

The complex ion is acting as an acid by donating a hydrogen ion to water molecules in the solution.

The water is, of course, acting as a base by accepting the hydrogen ion.

$$[Cr(H_2O)_6]^{3+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Cr(H_2O)_5OH]^{2+}{}_{(aq)} + H_3O^+{}_{(aq)}$$

$$[Cr(H_2O)_5OH]^{2+}{}_{(aq)} + H_2O_{(l)} \longrightarrow [Cr(H_2O)_4 2OH]^+{}_{(aq)} + H_3O^+{}_{(aq)}$$

$[Cr(H_2O)_4\ 2OH]^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Cr(H_2O)_3\ 3OH]_{(s)} + H_3O^+{}_{(aq)}$

Over all equation:

$[Cr(H_2O)_6]^{3+}{}_{(aq)} + 3H_2O_{(l)} \longrightarrow [Cr(H_2O)_3\ 3OH]_{(s)} + 3H_3O^+{}_{(aq)}$
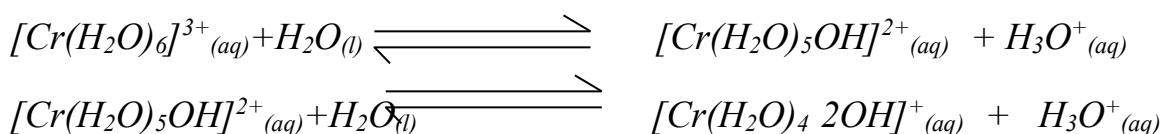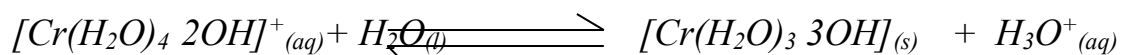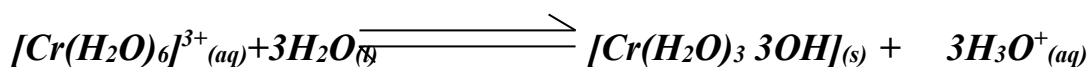
The accumulation of hydroxonium ions renders the resultant solution acidic.

If aqueous sodium carbonate is added, an efferverscence of a colorless gas which turns lime water milky is formed and a greeen solid.

$2\,[Cr(H_2O)_6]^{3+} + 3CO_3{}^{2-} \longrightarrow 2\,[Cr(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$

2) Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$

3) Ammonium alum $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

Preparation of Chrome Alum

By bubbling sulphur dioxide gas through an acidified potassium dichromate solution, chrome alum is formed.

$SO_{2(g)} + H2O_{(l)} \longrightarrow H_2SO_{3\ (aq)}$

$H_2SO_{3\ (aq)} \rightleftharpoons 2H^+{}_{(aq)} + SO_3{}^{2-}{}_{(aq)}$

$SO_3{}^{2-}{}_{(aq)} + H_2O_{(l)} \longrightarrow SO_4{}^{2-}{}_{(aq)} + 2H^+{}_{(aq)}\ 2e$

$Cr_2O_7{}^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e \longrightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}$
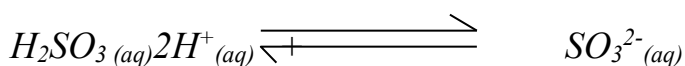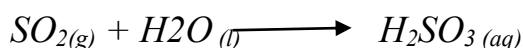
The ions present after the above reactions are in the correct proportion for the formation of chrome alum on crystallizing.

Similarities between the chemistry of chromium and lead

Cr^{3+} and Pb^{2+} form complex with sodium hydroxide solution.

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

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

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

$$Pb(OH)_{2(s)} + 2\ OH^-_{(aq)} \longrightarrow [\,Pb(OH)_4]^{2-}_{(aq)}$$
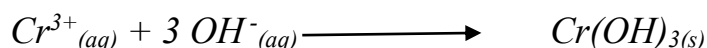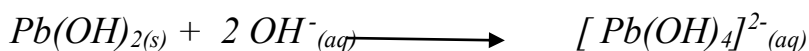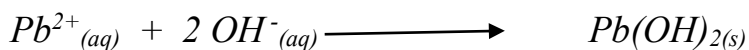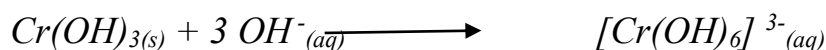
Both their oxides in higher oxidation states are acidic.

$$CrO_{3(s)} + 2NaOH_{(aq)} \longrightarrow Na_2CrO_{4(aq)} + H_2O_{(l)}$$

$$PbO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2PbO_{3(aq)} + H_2O_{(l)}$$
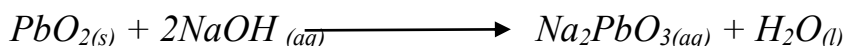
Their oxides in higher oxidation states are strong oxidizing agents.

$$CrO_{3(s)} + Al_{(s)} \longrightarrow Cr_{(s)} + Al_2O_{3(s)}$$

$$PbO_{2(s)} + 4HCl_{(aq)} \longrightarrow PbCl_{2(s)} + 2H_2O_{(l)} + Cl_{2(g)}$$
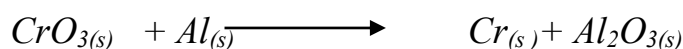
They both form compounds with variable oxidation statesie

Lead: $+2$ & $+4$ and Chromium: $+2, +3$ & $+6$

Chromium and Lead in higher oxidation states Cr^{6+} and Pb^{4+} form covalent compounds e.g. $PbCl_4$ and $CrCl_6$

8.2.1. Similarities between the chemistry of Chromium& Aluminium

1. Cr^{3+} and Al^{3+} form complexes with Alkalis.

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

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

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

$$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow [\,Al(OH)_4]^-_{(aq)}$$
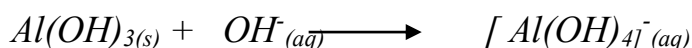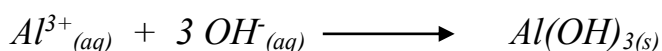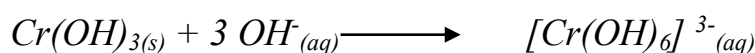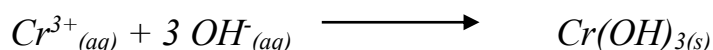
2. Oxides and hydroxides of Chromium and Aluminium are amphoterici.e react with both acids and bases.

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2\ Al(OH)_4^-{}_{(aq)}$$

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

$$Al(OH)_{3(s)} + OH^-_{(aq)} \longrightarrow [\,Al(OH)_4]^-_{(aq)}$$

$$Al_2O_{3(s)} + 6H^+_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$$

$$Al(OH)_{3(s)} + 3H^+_{(aq)} \longrightarrow Al^{3+}_{(aq)} + 3H_2O_{(l)}$$
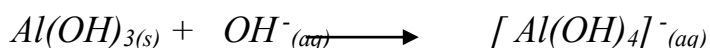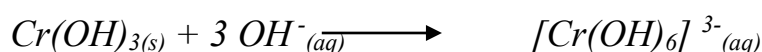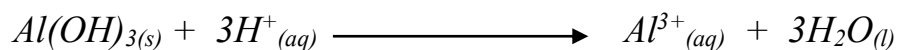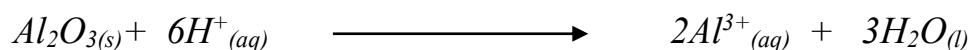
8.2.2. Test for Cr³⁺ ions in solution

Use of sodium hydroxide solution:

Observation

Grey green precipitate, soluble in excess forming deep green solution.

Equations

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

$$Cr(OH)3_{(s)} + 3\ OH^-_{(aq)} \rightarrow Cr(OH)_6^{3-}_{(aq)}$$
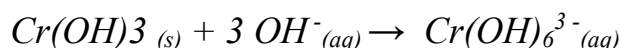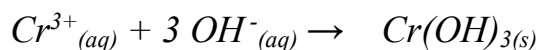
Note:

Chromium (iii) hydroxide is oxidized by hydrogen peroxide solution in an alkaline medium to chromate ions (CrO_4^{2-}) which has a characteristic yellow colour.

Procedure

Sodium hydroxide solutionis added drop-wise till excess to a solution containing Cr^{3+} ions followed by a little H_2O_2 and the resultant solution warmed.

Observation:

A grey green precipitate soluble in excess alkali forming a green solution. The solution turns yellow on addition of hydrogen peroxide.

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

$$Cr(OH)_{3(s)} + 3OH^-(aq) \longrightarrow Cr(OH)_6^{3-}_{(aq)}$$

$$2\ Cr(OH)6^{3-}_{(aq)} + 3H_2O_{2\ (aq)} \longrightarrow 2CrO_4^{2-}_{(aq)} + 2\ OH^-_{(aq)} + 8H_2O_{(l)}$$
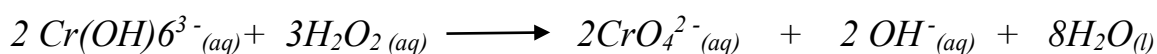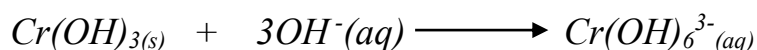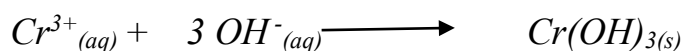
The presence of the chromate ions produced can be confirmed by:

a) Addition of Lead(ii) ethanoate or Lead(ii) nitrate solution.

   <u>Observation</u>

   A yellow precipitate of lead (ii) chromate is formed.

   <u>Equation</u>

$$Pb^{2+}_{(aq)} + CrO_4^{2-}_{(aq)} \longrightarrow PbCrO_{4(s)}$$
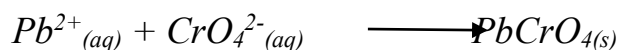
b) Addition of Barium nitrate or Barium chloride solution.

   <u>Observation</u>

   A yellow precipitate of barium chromate is formed

   <u>Equation</u>

$$Ba^{2+}_{(aq)} + CrO_4^{2-}_{(aq)} \longrightarrow BaCrO_{4(s)}$$
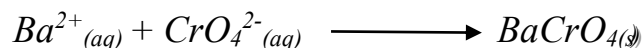
c) Addition of silver nitrate solution.

d) <u>Observation</u>

   A brick red precipitate of silver (i) chromate is formed.

   <u>Equation</u>

$$2Ag^{+}_{(aq)} + CrO_4^{2-}_{(aq)} \longrightarrow Ag_2CrO_{4(s)}$$

e) Addition of a little amyl alcohol (eg Butan-1-ol) followed by dilute sulphuric acid.

   <u>Observation</u>

   A blue color is observed in the organic layer.

<u>Use of aqueous ammonia solution:</u>

Observation

Green precipitate slowly dissolves in excess concentrated ammonia solution to form a purple solution.

Equations

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

$Cr(OH)_{3(s)} + 6NH_{3(aq)} \rightarrow [Cr(NH_3)_6]^{3+}_{(aq)} + 3\ OH^-_{(aq)}$
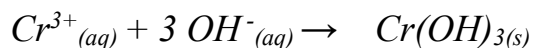
Use of sodium carbonate / potassium nitrate mixture

Procudure

Fuse the solid suspected to contain Chromium (III) ions with (Na_2CO_3/KNO3) mixture

Observation

A yellow mass of Chromate (CrO_4^{2-}) is formed

8.3. MANGANESE
Atomic number is 25

Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

8.3.1. Reactions of manganese
a) Reactions with acids

Manganese being a metal reacts with both dilute hydrochloric and sulphuric acid producing corresponding manganese (ii) salts and hydrogen gas.

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

$Mn_{(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_4(aq) + H_2(g)$
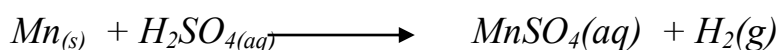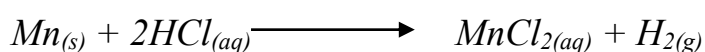
Note

The products when manganese react with dilute nitric acid are not well defined.

b) Reaction with steam

Like magnesium, manganese reacts with hot water to produce manganese (ii) hydroxide and hydrogen gas.

$Mn_{(s)} + H_2O_{(l)} \longrightarrow Mn(OH)_{2(s)} + H_{2(g)}$
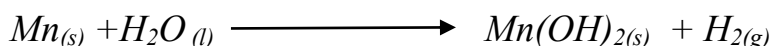
c) Reaction with oxygen

Manganese burns in air when heated forming trimanganese tetra oxide

$Mn_{(s)} + O_{2(g)} \longrightarrow Mn_3O_{4(s)}$
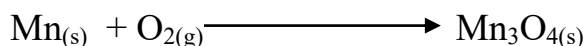
8.3.2. Compounds of manganese

Manganese exhibits the following oxidation states; *+2, +3, +4, +5, +6* and *+7*. The *+2* oxidation state being the most stable state because the 3d sub shell is half filled with electrons and therefore energetically stable.

Compound of manganese in the +2 oxidation state

i) Manganese (ii) oxide

On heating either manganese (ii) carbonate or manganese (ii) oxalate, manganese (ii) oxide is produced as a green solid.

$MnCO_{3(s)} \longrightarrow MnO_{(s)} + CO_{2(g)}$

$MnC_2O_{4(s)} \longrightarrow MnO_{(s)} + CO_{(g)} + CO_{2(g)}$
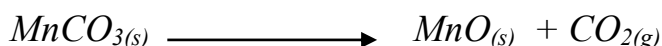
ii) Manganese (ii) hydroxide

On addition of dilute sodium hydroxide solution or aqueous ammonia solution to a solution containing manganese (ii) ion, manganese (ii) hydroxide is formed as a white precipitate. The precipitate rapidly turns brown due to the aerial oxidation of manganese (ii) oxide formed to manganese hydrated manganese (iv) oxide

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

$$2Mn(OH)_{2(s)} + O_{2(g)} \longrightarrow 2MnO_2.H_2O_{(s)} \text{ brown ppt}$$
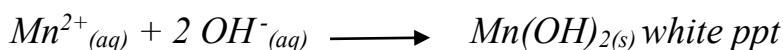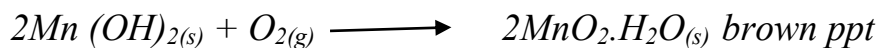
Note

Manganese (ii) compounds are pink in solid state but in aqueous solution, the pink colour is sometimes too faint to be noticed and so manganese (ii) compounds in aqueous solution may appear colourless.

Compounds of manganese in +4 oxidation state

The most important compound of manganese in this oxidation state is manganese (iv) oxide (manganese dioxide).

It is a dark solid produced on heating manganese (ii) nitrate.

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

It is insoluble in water and not attacked by dilute acids.

It reacts with cold concentrated hydrochloric acid to form the complex hexachloro manganate (iv) ion.

$$MnO_{2(s)} + 4H^+{}_{(aq)} + 6Cl^-{}_{(aq)} \longrightarrow MnCl_6{}^{2-}{}_{(aq)} + 2H_2O_{(l)}$$
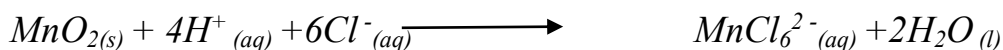
With hot concentrated hydrochloric acid, manganese (iv) oxide reacts forming chlorine gas as one of the products.

$$MnO_{2(s)} + 4HCl_{(aq)} \longrightarrow MnCl_{2(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$$
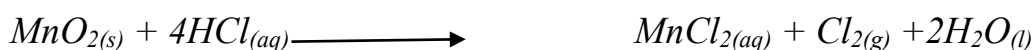
Warm concentrated sulphuric acid reduces manganese (iv) oxide to manganese (ii) sulphate.

$$MnO_{2(s)} + H_2SO_{4(aq)} \longrightarrow MnSO_{4(aq)} + O_{2(g)} + H_2O_{(l)}$$

Note

Manganese (iv) oxide is a powerful oxidizing agent. Some of the oxidizing reactions of manganese (iv) include the following

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

ii) $MnO_{2(s)} + C_2O_4^{2-}{}_{(aq)} + H^+{}_{(aq)} \longrightarrow Mn^{2+}{}_{(aq)} + 2H_2O_{(l)} + 2CO_{2(g)}$
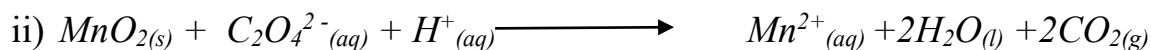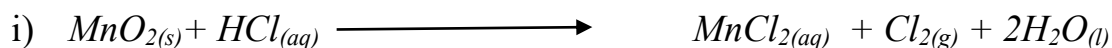
Compounds of manganese in the +6 oxidation state

Potassium manganate (vi); K_2MnO_4 isthe only stable compound of manganese in the +6 oxidation state.

It is a dark green solid prepared on fusing together manganese (iv) oxide with potassium hydroxide in the presence of excess oxygen

$MnO_2(s) + KOH(s) + O_2 (g) \longrightarrow K_2MnO_4(s) + H_2O(s)$
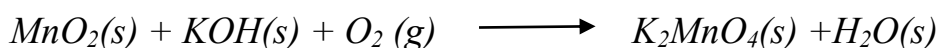
It can also be prepared by heating manganese (iv) oxide, potassium hydroxide and potassium chlorate.

$MnO_{2(s)} + 6KOH_{(aq)} + KClO_{3(aq)} \longrightarrow K_2MnO_{4(s)} + KCl_{(aq)} + 3H_2O_{(l)}$
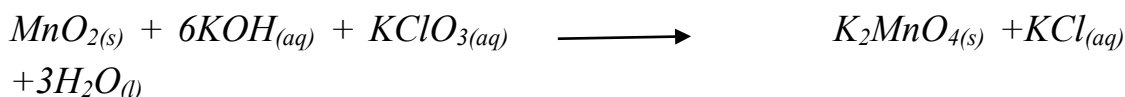
Potassium manganate (vi) is also a powerful oxidizing agent.

Behavior of potassium manganate (VI) in

a) Acidic medium

$MnO_4^{2-}{}_{(aq)} + H^+{}_{(aq)} \longrightarrow 2MnO_4^-{}_{(aq)} + MnO_{2(s)} + 2H_2O_{(l)}$

b) Neutral medium

$3K_2MnO_{4(s)} + 2H_2O_{(l)} \longrightarrow KMnO_{4(s)} + MnO_{2(s)} + 4KOH_{(aq)}$
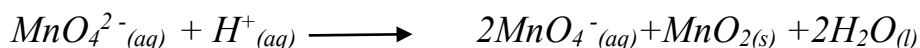
Compounds of manganese in the +7 oxidation state

Potassium manganate (vii) (potassium permanganate) is the most important compound of manganese in the +7 oxidation state.

Potassium permanganate is a powerful oxidizing agent and although not a primary standard, it's commonly used in volumetric analysis because of the following;

1) End points involving manganate (vii) titrations do not need indicators. The persistence of the intense purple colour of the permanganate solution when added from a burette indicates the end point of the titration has been reached.

2) Permanganate titrations have sharp end points

3) Potassium permanganate is fairly soluble in water.

4) Potassium manganate (vii) has a fairly high formula mass and this reduces errors due to weighing inefficiencies.

Note

1) Potassium manganate is not a primary standard because it aqueous solution on standing is reduces to manganese (iv) oxide which appears as brown solid.

2) In acidic medium in the presence of an oxidizing agent, manganate (vii) ions react as shown by the equation below

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$
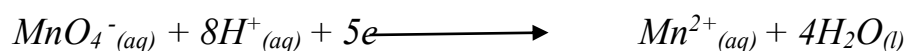
3) The purple colour of the manganate (vii) solution turns colourless due to the formation of manganese (ii) ions.

4) Only dilute sulphuric acid is used to acidify the solution.

5) Dilute hydrochloric acid is not used because it is oxidizes by the manganate (vii) solution forming chlorine gas which is an interference to the desired reaction

$$2KMnO_4{}_{(aq)} + 16HCl{}_{(aq)} \longrightarrow 2MnCl_2{}_{(aq)} + 2KCl_{(aq)} + 5Cl_{2(g)} + 8H_2O_{(l)}$$

6) Dilute nitric acid is not used because itself like potassium manganate (vii) is an oxidizing agent and therefore would interfere with the desired reaction.

7) Some of the oxidizing properties of manganate (vii) ions (MnO_4^-) in acidic medium include:

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

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

c) $2MnO_4^-{}_{(aq)} + 5H_2O_{2(aq)} + 6H^+{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 5O_{2(g)}$

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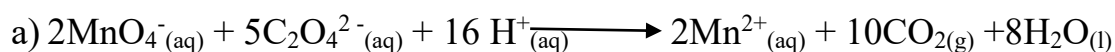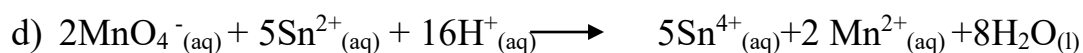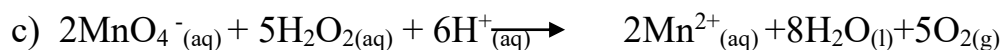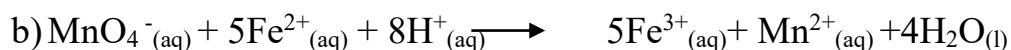
Revision questions

a) Write the electronic configuration of the following species (atomic number= 25):

   i.   *Mn*

   ii.   *Mn^{2+}*

   iii.   *Mn^{3+}*

   iv.   *Mn^{7+}*

b) State the most stable oxidation state of Manganese. Give a reason for your answer.

c) State the possible oxidation states of manganese.

d) Explain why manganese shows variable oxidation states.

e) Aqueous sodium hydroxide was added drop wise to a solution containing Mn^{2+},

State what was observed and write equation for the reaction that took place.

f) Give a formula of a compound or ion containing Manganese in an oxidation state of +7 oxidation state?

g) Write equation to show the reduction of MnO_4^- in :

   i.   Alkaline medium.

   ii.   Acidic medium.

h) Discuss the chemistry of manganese and magnesium showing similarities.

Answer

a)

i) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

iii) $1s^2 2s^2 2p^6 3s^2 3p^6$
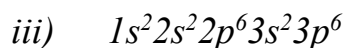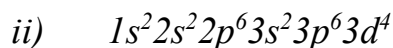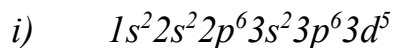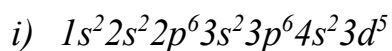
b) The most stable oxidation state is +2. This is because after using the 4s-electrons, a half filled 3d -orbital that is stable is left.

c) +2, +3, +4, +5, +6, +7.

   Acidity of the oxide of manganese increases with the increasing oxidation state.

d) The variable oxidation state of manganese is due to the fact that both the 4s and the 3d- electrons take part in bond formation.

   This is because electrons are being removed from energetically similar 4s and 3d- orbitals.

   For +2 oxidation states, only the 4s-electrons are utilized for bond formation, forming stable Mn^{2+}. For higher oxidation states, both the 4s and 3d- electrons are utilized.

e) Observation:

   White precipitate insoluble in excessturns brown on standing due to aerial oxidation to Manganese iv oxide.

   Equation:

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

   $2Mn(OH)_{2(s)} + O_{2(g)} \longrightarrow 2MnO_2.H_2O_{(s)} brown\ ppt$
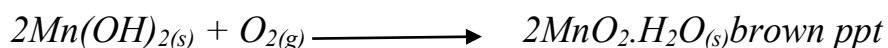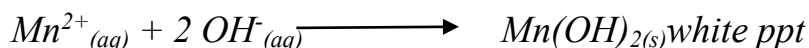
Note

A similar observation & reactions occur on addition of aqueous ammonia solution to a solution containing Manganese (ii) ions.

f) MnO_4^-

Manganese $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$ shows an oxidation state of +7 by using all the 4s and 3d- electrons in the bond formationbecause they are energetically similar.

g) In alkaline condition, the change in oxidation state is from $^+7$ to $^+4$ since potassium manganate (vii) is a mild oxidizing agent in alkaline medium

$$MnO_4^-{}_{(aq)} + 2H_2O_{(l)} + 3e \longrightarrow MnO_{2(s)} + 4OH^-{}_{(aq)}$$

Or

$$MnO_4^-{}_{(aq)} + 4H^+{}_{(aq)} + 3e \longrightarrow MnO_{2(s)} + 2H_2O_{(l)}$$
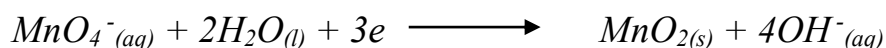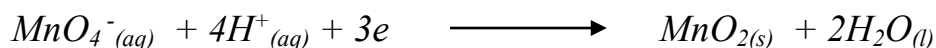
In acidic medium, the reaction is as shown below.

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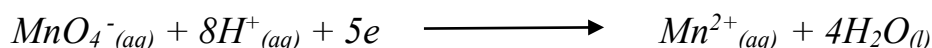
Note

$KMnO_4$ has wide applications in the laboratory including the following:

- Being used as indicator in volumetric analysis titrations involving its solution.

- To test for reducing agents e.g. sulphur dioxide.

- Estimating iron (ii) salts and oxalates.

- Preparation of gases e.g. chlorine gas is liberated when Conc. hydrochloric acid is reacted with it.

Hydrochloric acid is not used to acidify $KMnO_4$ during titration because potassium permanganate solution is a very strong oxidizing

agent, oxidizes chloride ions fromhydrochloric acid to chlorine which interferes with the desired reaction.

$2KMnO_{4(} + 16HCl_{(aq)} \longrightarrow 5Cl_{2(g)} + 2KCl_{(aq)} + 2MnCl_{2(aq)} + 8H_2O_{(l)}$
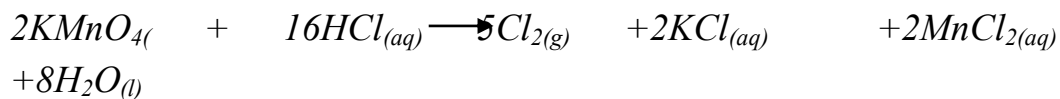
h) They both react with chlorine to form chloride when heated.

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

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$
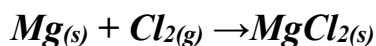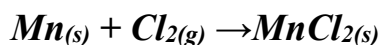
They both react directly with nitrogen to form similar nitrides

$$3Mn_{(s)} + N_{2(g)} \rightarrow Mn_3N_{2(s).}$$

$$3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)}$$
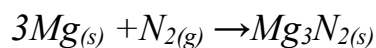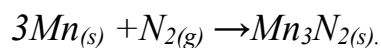
They both react with dilute hydrochloric acid to liberate hydrogen gas.

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

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$
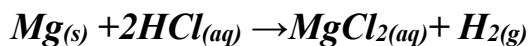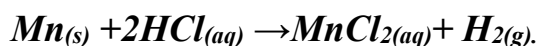
Manganese reacts with hot water to form oxide. Magnesium reacts with steam in a similar way.

$$Mn_{(s)} + H_2O_{(l)} \rightarrow MnO_{(s)} + H_{2(g)}$$

$$Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2(g)}$$
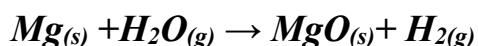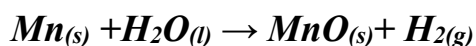
Note:

Confirmatory test of Manganese, Mn^{2+} ions in solution

Procedure

To solid manganese (II) salt is added concentrated nitric acid and little solid lead (IV) oxide or sodium bismuthate solution and the mixture

boiled.

Observation

A purple solution forms due to the formation of manganate (vii) ions

Equations

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

$2Mn^{2+}_{(aq)} + 5PbO_{2(s)} + 4H^+{}_{(aq)} \rightarrow 2MnO_4^-{}_{(aq)} + 5Pb^{2+}{}_{(aq)} + 2H_2O_{(l)}$
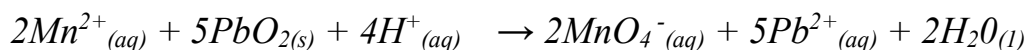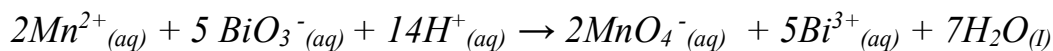
8.4. IRON

Ores of iron:

- *Haematite , Fe_2O_3*

- *Magnetite , Fe_3O_4*

- *Iron Pyrite , FeS_2*

- *Siderite   , $FeCO_3$*

The 1st two ores are fed directly into a blast furnace but the last two must first be roasted in air to convert them to stable iron (iii) oxide before feeding them into the blast furnace. i.e.

$4FeS_{2(s)} + 11\ O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$

$4FeCO_{3(s)} + O2_{(g)} \rightarrow 2Fe_2O_{3(s)} + 4CO_{2(g)}$
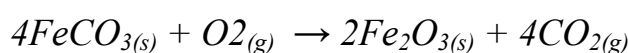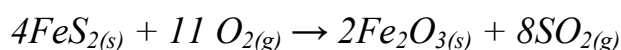
Extraction of iron

Iron is commonly extracted from its ore called haematite (Fe_2O_3)using a blast furnace

The raw materials used in the extraction are:

1) *The ore, Haematite*

2) *Coke*

3) *Limestone(calcium carbonate)*

4) *Hot air*

The hot blast of air enters the blast furnace through narrow pipes called <u>tuyeres</u> located at the lower part of the furnace.

The other materials are fed into the furnace from the top.

<u>Reactions taking place in the blast furnace</u>

In the presence of hot air coke burns to produce carbon dioxide gas

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
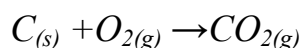
As the carbon dioxide ascends, it reacts with unburnt coke to form carbon monoxide

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

The carbon monoxide produced reduces the ore to iron.

$Fe_2O_{3(s)} + 3CO_{(g)} \rightleftharpoons 2Fe_{(l)} + 3CO_{2(g)}$
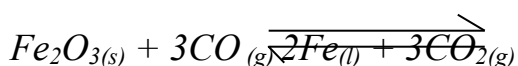
The role of the limestone is to remove impurities like silica (SiO_2)

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

The quick lime then combines with silica and alumina present as impurities to form slag.

$CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(l)}$

$CaO_{(s)} + Al_2O_{3(s)} \rightarrow CaAl_2O_{4(l)}$
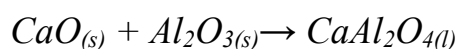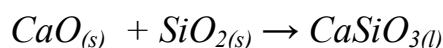
Molten iron and slag both sink to the bottom of the furnace and they can be tapped off separately. The molten iron at the bottom is coveredby the slag to prevent oxidation.

The molten iron solidifies on cooling to form PIG iron.

<u>Properties of pig iron</u>:

- Low melting point.

- Impure i.e. contain impurities such as carbon, silicon, sulphur, etc.

Pig iron can be used in making gas stove, drainage pipes, bunsen burner bases, boiler plates etc

Purification of pig iron

The Bessemer process:

This involves pouring the molten iron into a large tab called the converter and air is blown into it to oxidize the impurities such as carbon, sulphur and phosphorus to their gaseous oxides.

Reactions of iron

a) With air

Iron combines with oxygen when heated to form black solid of tri-iron tetra oxide.

$$3Fe_{(s)} + 2\ O_{2\ (g)} \rightarrow Fe_3O_{4(s)}$$
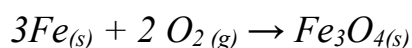
Ax

Iron reacts with moist cold air to form brown hydrated iron (iii) oxide or rust.

$$2Fe_{(s)} + 6H_2O_{\ (l)} + 3\ O_{2\ (g)} \rightarrow 2Fe_2O_3.3H_2O_{(s)}$$
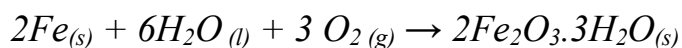
How rusting occurs:

Rusting is an electrochemical process which takes place when different parts of iron act as anode and cathode.

At the cathodic region:

$$Fe_{(s)} \rightarrow Fe^{2+}_{\ (aq)} + 2e$$
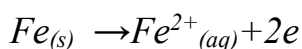
At the anodic region:

$$2\ H_2O_{\ (l)} + O_{2\ (g)} + 4e \rightleftharpoons 4OH^-_{\ (aq)}$$
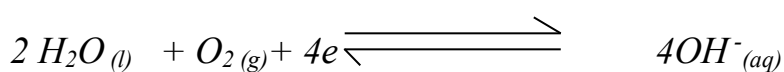
If the cathodic and anodic areas are close enough, iron (ii) hydroxide is formed.

$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$
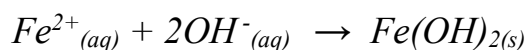
Moist air then oxidizes the iron (ii) hydroxide to rust.

$4Fe(OH)_{2(s)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 2Fe_2O_3.3H_2O_{(s)}$
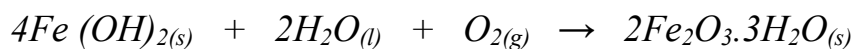
Prevention of rusting

> a. Painting
>
> b. Greasing
>
> c. Galvanizing (coating with zinc)

b) With water

Heated iron reacts with steam to form black tri-iron tetra oxide.

$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$
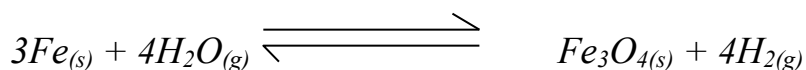
c) With acid.

Iron reacts with dilute acids (HCl & H_2SO_4) to form hydrogen gas and iron (ii) salts.

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

$Fe_{(s)} + H_2SO_{4(aq)} \rightarrow FeSO_{4(aq)} + H_{2(g)}$
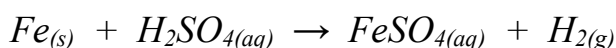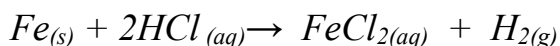
Hot conc. sulphuric acid oxidizes iron to iron (iii) sulphate, sulphur dioxide and water.

$2Fe_{(s)} + 6H_2SO_{4(aq)} \rightarrow Fe_2(SO_4)_{3(aq)} + 3SO_{2(g)} + 6H_2O_{(aq)}$
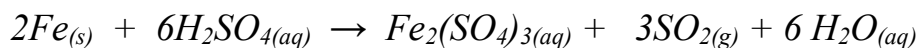
d) With halogens.

Heated iron reacts with dry chlorine gas to form iron (iii) chloride.

$2Fe_{(s)} + 3Cl_{2(g)} \rightarrow FeCl_{3(s)}$
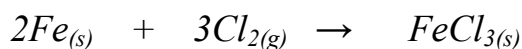
Compounds of iron

+2 oxidation state

In aqueous solution exists as $[Fe(H_2O)_6]^{2+}$ which is a green solution. It undergoes hydrolysis making the resultant solution acidic.

Iron (ii) hydroxide

It's a green ppt formed when sodium hydroxide solution is added drop wise to a solution of Fe^{2+} solution. The ppt is insoluble in excess and turns brown due to aerial oxidation on exposure to air.

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

$$4Fe(OH)_{2(s)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow 2Fe_2O_3.3H_2O_{(s)}$$
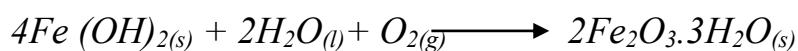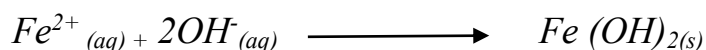
NB:

Similar reaction occurs on addition of ammonia solution to aqueous Fe^{2+} solution

Hydrated iron (ii) sulphate. $FeSO_4.7H_2O$

It's prepared by heating iron fillings with dilute sulphuric acid and crystallizing the salt from solution.

During the crystallization process, hydrated iron (ii) sulphate forms as green crystals.

$$Fe_{(s)} + H_2SO_{4(aq)} \longrightarrow FeSO_{4(aq)} + H_{2(g)}$$
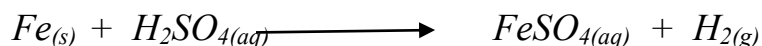
Action of heat on hydrated iron (ii) sulphate

On gentle heating

$$FeSO_4.7H_2O_{(s)} \longrightarrow FeSO_{4(s)} + 7H_2O_{(g)}$$

On further heating.
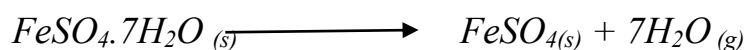
$$2FeSO_{4(s)} \longrightarrow Fe_2O_{3(s)} + SO_{3(g)} + SO_{2(g)}$$
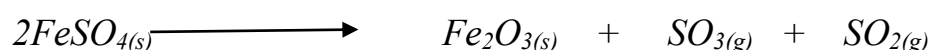
<div align="center">White acidic fumes</div>

If conc. nitric acid is added to iron (ii) sulphate, the green solution turns to yellow/ brown due to formation of iron (iii) ions.

Ammonium Ferrous Sulphate (Ammonium Iron (ii) sulphate) $(NH_4)_2SO_4.FeSO_4.6H_2O$

By mixingequimolar concentrated solutions of iron (ii) sulphate and ammonium sulphate, ammonium ferrous sulphate is formed.

It is a green double salt preferred to iron (ii) sulphate in volumetric analysis because it is not efflorescent and also not easily oxidized.

+3 oxidation state

This is the most stable oxidation state of iron.

The soluble salts in this oxidation state exist as $[Fe(H_2O)_6]^{3+}$ and undergo hydrolysis in water making resultant solution acidic.

e.g.a solution of iron (iii) chloride turns blue litmus red.

The Fe^{3+} ion is small and highly charged. It undergoes hydrolysis in aqueous solution to release hydrogen ions or hydroxonium ions which make the resultant solution acidic.

$FeCl_{3(aq)} \rightarrow Fe^{3+}_{(aq)} + 3Cl^-_{(aq)}$

$Fe^{3+}_{(aq)} + 6H_2O_{(l)} \rightarrow [Fe(H_2O)_6]^{3+}_{(aq)}$

$[Fe(H_2O)_6]^{3+}_{(aq)} + 3H_2O_{(l)} \rightleftharpoons [Fe(H_2O)_3(OH)_3]_{(s)} + 3H_3O^+_{(aq)}$

Brown ppt

Or

$[Fe(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Fe(H_2O)_3(OH)_3]_{(s)} + 3H^+_{(aq)}$
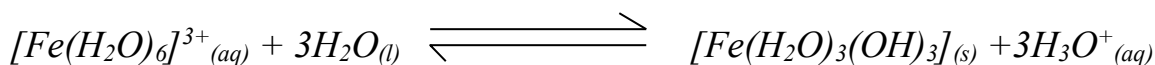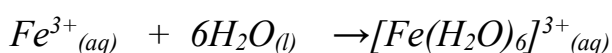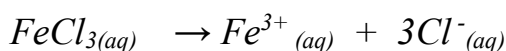
On addition of zinc powder to a brown/ yellow solution of iron (iii), the color of the solution changes to green.

$2Fe^{3+}_{(aq)} + Zn_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Zn^{2+}_{(aq)}$
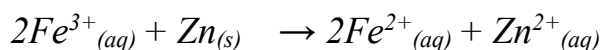
The resultant solution can now be titrated with acidified solution of standard potassium permanganate.

$$MnO_4{}^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}{}_{(aq)}$$
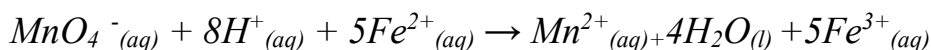
On bubbling hydrogen sulphide gas to a solution containing Fe^{3+} ion, the color of the solution changes from yellow to green with formationof a yellow solid.
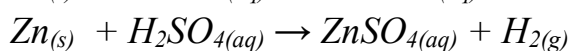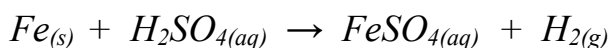
$$H_2S_{(g)} + 2Fe^{3+}{}_{(aq)} \rightarrow 2H^+{}_{(aq)} + 2Fe^{2+}{}_{(aq)} + S_{(s)}$$
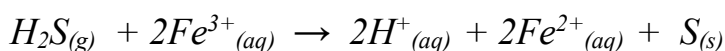
8.4.1. Similarities in the chemistry of zinc and iron

1) Both metals when heated (red hot) react with steam to form oxide and hydrogen gas.
$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

$$Zn_{(s)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)}$$
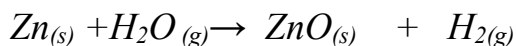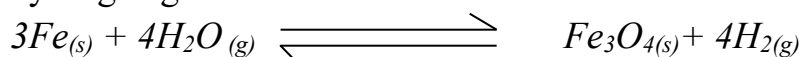
2) Both react with dilute acid (HCl& H_2SO_4) to liberate hydrogen gas.

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

3) Both metal when heated react with oxygen to form oxide.
$$3Fe_{(s)} + 2O_{2(g)} \rightarrow Fe_3O_{4(s)}$$
$$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$$
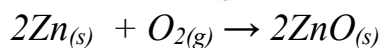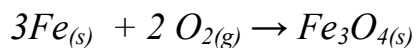
4) Both metals when heated react with chlorine to form chloride.
$$2Fe_{(s)} + 3Cl_{2(g)} \rightarrow 2FeCl_{3(s)}$$
$$Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(s)}$$
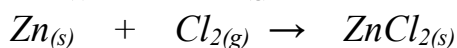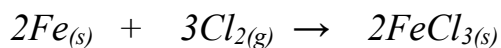
5) 5)Both elements react with sulphur to form sulphide.
$$Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)}$$
$$Fe_{(s)} + S_{(s)} \rightarrow FeS_{(s)}$$
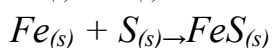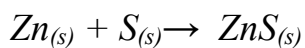
### 8.4.2. Differences in the chemistry of Zinc & Iron

1) Zn dissolves in conc. alkalis forming hydrogen gas but iron does not react with alkalis.

$$Zn_{(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}_{(aq)} + H_{2(g)}$$
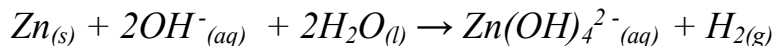
2) Zn shows a single valency of $+2$ while iron exhibits variable valencies of $+2, +3$ and $+6$

3) Zn forms compounds that are white in color where as Fe forms compounds which are colored.

Fe^{2+} -green

Fe^{3+} -brown

4) Iron is paramagnetic(due to unpaired electrons in the 3d-subshell) while Zn is diamagnetic(due to paired electrons in its 3d-subshell)

5) Fe forms dimeric chloride, $Fe_2Cl_6.$

Cl   ClCl

Fe   Fe

Cl   ClCl
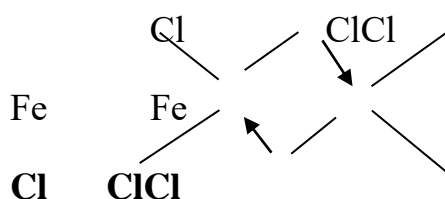
6) Zinc does not react with cold moist air. Iron reacts with moist air to form hydrated iron(iii) oxide (rust).

8.4.3. Test for Iron (ii) and Iron (iii) ions in aqueous solution

a) Test for Ferrous ions (Fe^{2+})

Use of sodium hydroxide solution / aqueous ammonia solution

Procedure

To the solution containing the unknown cation is added dilute sodium hydroxide solution or aqueous ammonia dropwise until in excess.

Observation

In the presence of Iron (ii) ions, a green precipitate of Iron (ii) hydroxide is formed. The precipitate turns brown due to aerial oxidation to iron (iii) hydroxide.

Equation

$$Fe^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \longrightarrow Fe(OH)_{2(s)}$$
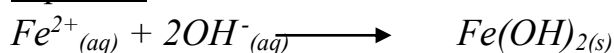
Use of Potassium hexacyanoferrate (iii) solution

Procedure

To the solution containing the unknown cation is added potassium hexacyanoferrate (iii) solution.

Observation

A dark blue precipitate (turnbull's blue) is formed.

Equation

$$K^{+}{}_{(aq)} + [Fe\,(CN)_6]^{3-}{}_{(aq)} + Fe^{2+}{}_{(aq)} \longrightarrow K[Fe(Fe(CN)_6]_{(s)}$$
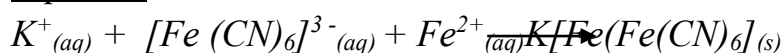
Test for Iron (iii) ions in solution

Use of sodium hydroxide solution/ aqueous ammonia solution

Procedure

To the solution containing the unknown cation is added dilute sodium hydroxide or aqueous ammonia solution dropwise until in excess.

Observation

A reddish brown precipitate of iron (iii) hydroxide is produced. The precipitate is insoluble in excess sodium hydroxide/ aqueous ammonia.

Equation

$$Fe^{2+}{}_{(aq)} + 3OH^{-}{}_{(aq)} \longrightarrow Fe(OH)_{3(s)}$$
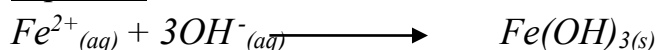
Use of potassium hexacyanoferrate (ii) solution

Addition of a few drops of potassium hexacyanoferrate (ii) solution to solution containing iron (iii) ions produces a dark blue precipitate (Prussian blue).Equation

$$K^{+}{}_{(aq)} + [Fe\,(CN)_4]^{4-}{}_{(aq)} + Fe^{3+}{}_{(aq)} \longrightarrow K[Fe(Fe(CN)_6]_{(s)}$$
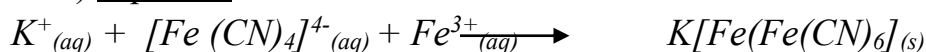
Use of potassium thiocyanate solution

Procedure

Addtidion of potassium thiocyanate solution to a solution containing Fe^{3+}ions produces a blood red coloration of thiocyanatopenta aqua iron(III)complex ion.

$$[Fe(H_2O)_6]^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \longrightarrow [Fe(H_2O)_5SCN]^{2+}{}_{(aq)} + H_2O_{(l)}$$
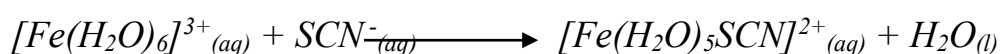
Question.

State the similarities in the chemistry of zinc & magnesium.

8.5. COBALT

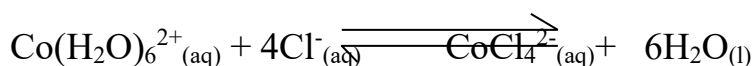### 8.5.1. Reaction of Cobalt (II) ion, Co^{2+}

The *+2* oxidation state is the most stable for simple cobalt salts.

Cobalt (ii) compounds are colored pink. The simplest ion that cobalt forms in solution is the hexa aqua cobalt (II) ion - *[Co(H₂O)₆]²⁺.which is pink in colour*

A ligand exchange reaction involving chloride ions

If you add concentrated hydrochloric acid to a solution containing hexa aqua cobalt(II) ions, the solution turns from its original pink colour to arich blue. The six water molecules are replaced by four chloride ions.

The reaction taking place is reversible.

$Co(H_2O)_6^{2+}$ (aq) + 4Cl⁻(aq) $\rightleftharpoons$ $CoCl_4^{2-}$(aq) + 6H₂O(l)

If you add water to the blue solution, it turns back to the pink colour due to the formation of hydrated cobalt (ii) ions.

a) Reaction of cobalt (ii) ions with sodium hydroxide solution
A blue precipitate formed insoluble in excess and turns pink on standing
Co^{2+}*(aq) + 2OH⁻(aq)→Co(OH)₂(s)*
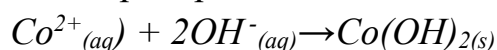
With sodium hydroxide solution and hydrogen peroxide
Rather than relying on oxidation by the air, you can add an oxidizing agent such as hydrogen peroxide
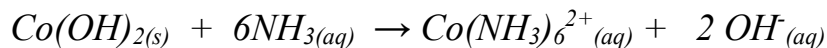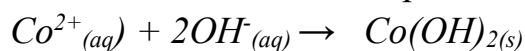You get the cobalt (II) hydroxide complex when you add the sodium hydroxide solution.
Addition of hydrogen peroxide produces lots of bubbles of oxygen and a dark chocolate brown precipitate. The final precipitate contains cobalt in the +3 oxidation state.
4Co (OH)₂(s) + 2 H₂O₂(aq) $\longrightarrow$ 4 Co(OH)₃(s)
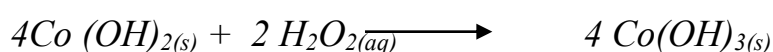
b) <u>Reaction of cobalt (ii) ions withammonia solution</u>
A blue precipitate formed which dissolves in excess to form a brown solution and turns to a deep red -brown solution on standing in air.

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

$Co(OH)_{2(s)} + 6NH_{3(aq)} \rightarrow Co(NH_3)_6^{2+}_{(aq)} + 2OH^-_{(aq)}$

$Co(NH_3)_6^{2+}_{(aq)} \rightarrow Co(NH_3)_6^{3+}_{(aq)} + e$
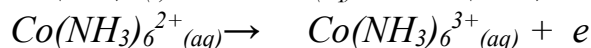
c) <u>With ammonia solution and hydrogen peroxide</u>
Rather than relying on oxidation by the air, you can add an oxidizing agent such as hydrogen peroxide
The reaction with ammonia solution followed by hydrogen peroxide produces the same dark reddish-brown solution as before only that the reaction is faster this time.
The equation for the oxidation of the ammine complex is:

$2Co(NH_3)_6^{2+} + H_2O_2(aq) \longrightarrow 2Co(NH_3)_6^{3+}_{(aq)} + 2OH^-_{(aq)}$
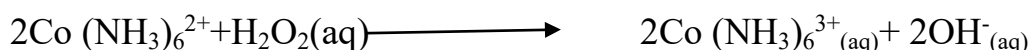
8.6. NICKEL

8.6.1. Test for Nickel (II) Ion, Ni²⁺ in solution

a) <u>Use of of dilute sodium hydroxide solution</u>
A green precipitate insoluble in excess formed.

$Ni^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Ni(OH)_{2(s)}$
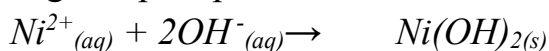
b) <u>Use of aqueous ammonia Solution</u>
A green precipitate formed which dissolves in excess to form a blue solution

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

$Ni(OH)_{2(s)} + 6NH_{3(aq)} \rightarrow (Ni(NH_3)_6^{2+}_{(aq)} + 2OH^-_{(aq)}$
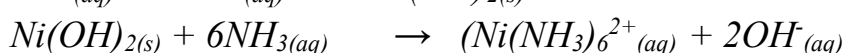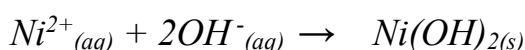
Note

The initial pale green precipitate of Ni(OH)$_2$ is frequently not seen if Ni^{2+} solution is dilute.

c) <u>Use of dimethylglyoxime</u>

Procedure

To the solution containing Ni^{2+} is 1stadded aqueous ammonia solution drop-wise until in excess followed by a drop of dimethylglyoxime solution.

<u>Observation</u>

A green pptsoluble in excess ammoniaforming a blue solution. On addition of dimethylglyoxime, a red precipitate of nickel dimethylglyoxime complex is formed .

8.7. COPPER

Atomic number is 29

Electronic configuration:$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Ores of copper

1. copper pyrite $CuFeS_2$

2. malachite $CuCO_3.Cu(OH)_2$

Extraction of copper

Copper is commonly extracted from its ore called copper pyrite.

The ore is 1st crushed to powder form. The finely divided ore is then mixed with water and frothing agent such as pine oil is added. The earthly materials sink to the bottom because of their high density whereas the ore particles float on top from where they are removed, washed and dried.

The ore is then roasted to convert the copper pyrite to copper (i) sulphide, iron(ii) oxide and sulphur dioxide.

$2CuFeS_{2(s)} + 4O_{2(g)} \rightarrow Cu_2S_{(s)} + 2FeO_{(s)} + 3SO_{2(g)}$
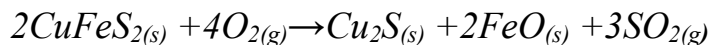
The solid product is transferred into a blast furnace and silica added.

On strong heating, the iron(ii)oxide reacts with silica to formslag.

$FeO_{(s)} + SiO_{2(s)} \rightarrow FeSiO_{3(l)}$
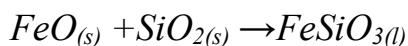
The copper (i) sulphide reacts with air forming copper (i) oxide.

$2Cu_2S_{(s)} + 3O_{2(g)} \rightarrow 2Cu_2O_{(s)} + 2SO_{2(g)}$
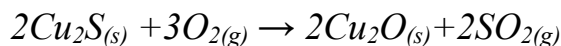
The copper(i)oxide produced and the unroasted copper (i) sulphide react in the heat of the blast furnace with limited air supply to form copper.

$2Cu_2O_{(s)} + Cu_2S_{(s)} \rightarrow 6Cu_{(l)} + SO_{2(g)}$
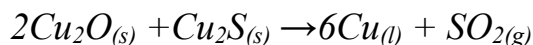
The copper formed solidifies on cooling and is called blister copper and contains impurities. The last process in the extraction is purification of blistercopper.

8.7.1. Extraction from malachite

<u>Concentration process</u>

The ore is ground to powder. The finely divided ore particles is mixed with water and frothing agent such as pine oil and shaken for a while.

The earthly materials because of their high density sink to the bottom whereas the ore particles because of their low density float on the surface, where they are removed, washed and dried.
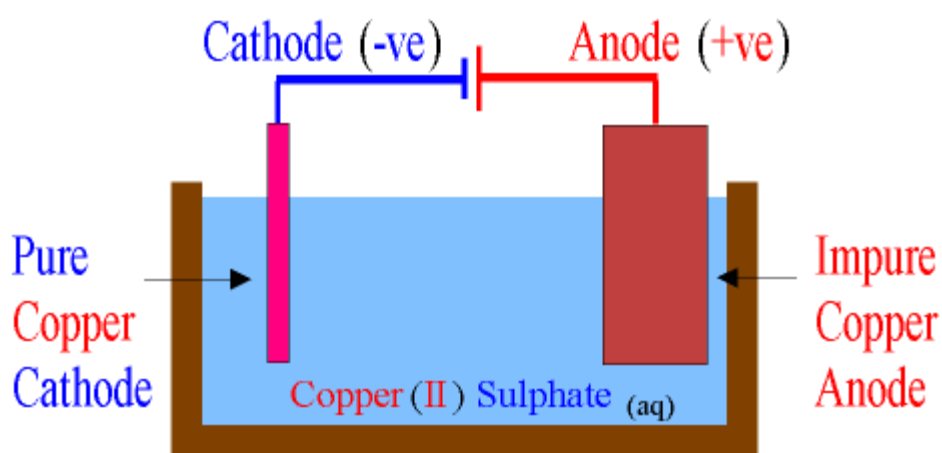
The ore is roasted to form copper(ii) oxide.

$$CuCO_3.Cu\,(OH)_{2(s)} \rightarrow 2CuO_{(s)} + CO_{2(g)} + H_{2(g)}$$
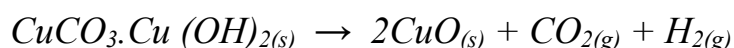
The copper(ii) oxide is reduced with carbon on heating to copper.

$$CuO_{(s)} + C_{(s)} \rightarrow Cu_{(s)} + CO_{2(g)}$$
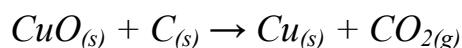
The copper formed is then purified by electrolysis.

<u>Purification of Copper</u>

–Electrolysis

- The anode is a block of made of the impure copper to be purified.

- The cathode is a thin piece of pure copper

- The electrolyte is copper (ii) sulphate solution.

- When electricity is passed through the cell,

At the Anode

Copper is dissolved by oxidationi.e Cu^{2+}ionsgo into solution.

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

At the cathode,

- copper is deposited by reduction.

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

- As copper ions move from the anode to the cathode the anode gets smaller as the cathode gets bigger

8.7.2. Uses of copper

Amongst other things copper is used for:

- Electrical wiring. It is a very good conductor of electricity and is easily drawn out into wires.

- Domestic plumbing. It doesn't react with water, and is easily bent into shape.

- Boilers and heat exchangers. It is a good conductor of heat and doesn't react with water.

- Making brass. Brass is a copper-zinc alloy. Alloying produces a metal harder than either copper or zinc individually.

- Bronze is another

- Copper alloy - this time with tin.

- Coinage. Copper-colored coins, "silver" coins are also copper alloys - this time with nickel. These are known as cupronickel alloys.

- UK pound coins and the gold-colored bits of euro coins are copper-zinc-nickel alloys.
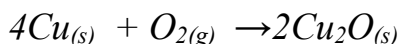
8.7.3. Reactions of copper

1) <u>With air</u>

Copper reacts with moist air to form a green outer layer of copper (ii) carbonate (protective layer).

Heated copper reacts with oxygen enriched air (below 800 °C) to form black copper (ii) oxide.
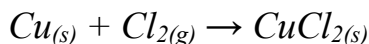
$2Cu_{(s)} + O_{2(g)} \rightarrow 2CuO_{(s)}$
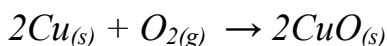
At very high temperature> 800 °C, copper reacts with oxygen to form copper (i) oxide.

$4Cu_{(s)} + O_{2(g)} \rightarrow 2Cu_2O_{(s)}$

2) <u>With halogens</u>.

Heated copper reacts with halogen to form copper (ii) halide.

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

However copper reacts with iodine to form copper (i) iodide.

3) <u>With sulphur</u>.

When heated, copper forms a sulphide .

$Cu_{(s)} + S_{(s)} \rightarrow CuS_{(s)}$
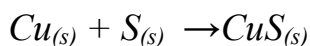
4) <u>With acids</u>

a. Dilute nitric acid reacts with copper to form copper (ii) nitrate, nitrogen monoxide and water.

$3Cu_{(s)} + 8HNO_{3\ (aq)} \rightarrow 3Cu\ (NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$
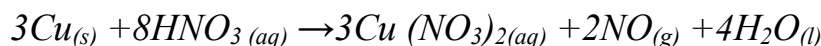
b. Copper reacts with concentrated nitric acid to form copper(ii)nitrate, nitrogen dioxide gas and water.

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

    c. Copper reacts with concentrated sulphuric acid to form copper (ii) sulphate, sulphur dioxide and water.

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

8.7.4. Compounds of copper

Copper shows 2 oxidation states of +1 and +2, however compounds in +1 oxidation state are unstable.
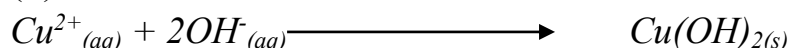
Compounds in +2 oxidation states

This is the most stable oxidation state of copper and in aqueous solution exists as $[Cu(H_2O)_4]^{2+}$ which is a blue solution.

It slowly undergoes hydrolysis forming acidic solution.

$$[Cu\,(H_2O)_4]^{2+}{}_{(aq)} \rightleftharpoons [Cu(H_2O)_3OH]^{+}{}_{(aq)} + H^{+}{}_{(aq)}$$

1) Copper(ii) hydroxide

It's a blue ppt formed when aqueous sodium hydroxide is added to copper (ii) ions.

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

Copper (ii) hydroxide does not dissolve in excess sodium hydroxide. However dissolves in excess ammonia solution to form a deep bluesolution.

$$Cu(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]^{2+}{}_{(aq)} + 2OH^{-}(aq)$$
<div align="center">Tetraamminecopper (ii) ions</div>
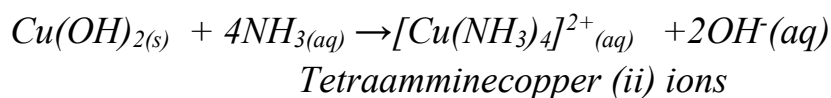
2) Copper (ii) chloride.

It's prepared by adding a stream of dry chlorine gas over heated copper metal.

$$Cu_{(s)} + Cl_{2(g)} \rightarrow CuCl_{2(s)}$$
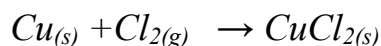
In aqueous solution, it exists as $[Cu\,(H_2O)_4]^{2+}$.

<div align="center">141</div>

It slowly undergoes hydrolysis forming acidic solution.

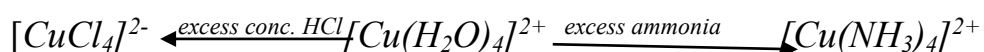$$[Cu(H_2O)_4]^{2+}{}_{(aq)} \rightleftharpoons [Cu(H_2O)_3OH]^{+}{}_{(aq)} + H^{+}{}_{(aq)}$$
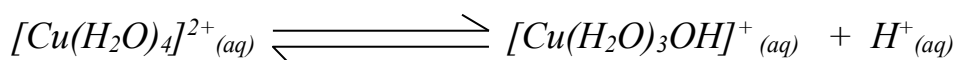
Copper(ii) chloride dissolves in conc. hydrochloride acid to form a yellow solution of tetrachlorocuprate(ii) ions $[CuCl_4]^{2-}$

Note:

A complex ion may undergo ligand exchange whereby all its ligands are replaced by a different ligand which is more willing to donate the pair of electrons more readily. Altering a ligand around a central metal ion brings about a marked color change.

E.g. $[Cu(H_2O)_6]^{2+}$

$$[CuCl_4]^{2-} \xleftarrow{\text{excess conc. HCl}} [Cu(H_2O)_4]^{2+} \xrightarrow{\text{excess ammonia}} [Cu(NH_3)_4]^{2+}$$

Yellow   Blue Deep blue

8.7.5. Determination of copper (ii) ions in copper (ii) salts
Method1

Applicable to any soluble salt of copper.

(starting from copper ore, dissolve the ore in dilute sulphuric acid)

Procedure:

To a solution containing copper(ii) ions is added excess potassium iodide, a white precipitate of copper(i) iodide is formed which is stainedbrown by the liberated iodine.

$$2Cu^{2+}{}_{(aq)} + 4I^{-}{}_{(aq)} \rightarrow Cu_2I_{2(s)} + I_{2(aq)}$$
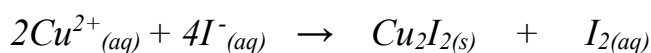
White ppt   brown soln

The amount of iodine liberated is then determined by titrating the resultant solution with a standard solution of sodium thiosulphate using starch as indicator.

$$2S_2O_3{}^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$
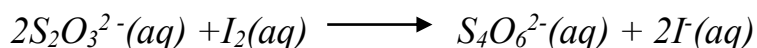
The volume of thiosulphate solution used is noted.

Treatment of results

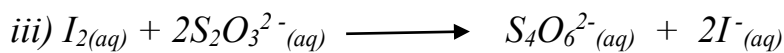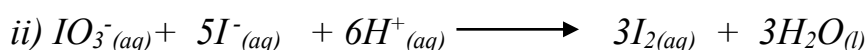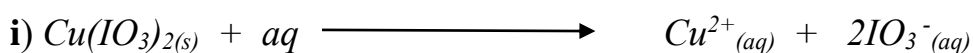The overall equation of reaction is obtained by adding the two equations above:

$$2Cu^{2+}{}_{(aq)} + 2S_2O_3{}^{2-}{}_{(aq)}\, 2I^-{}_{(aq)} \longrightarrow Cu_2I_{2(s)} + S_4O_6{}^{2-}{}_{(aq)}$$
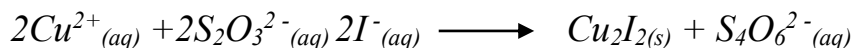
2moles of thiosulphate ions react with 2moles of Cu^{2+} ions.

Thus knowing the moles of thiosulphate ions that reacted, that of copper ions present in the solution can be determined.

Method2

This method applies to copper (ii) iodate only Cu $(IO_3)_2$

i) $Cu(IO_3)_{2(s)} + aq \longrightarrow Cu^{2+}{}_{(aq)} + 2IO_3{}^-{}_{(aq)}$

ii) $IO_3{}^-{}_{(aq)} + 5I^-{}_{(aq)} + 6H^+{}_{(aq)} \longrightarrow 3I_{2(aq)} + 3H_2O_{(l)}$

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

To a solution containing copper (ii) iodate is added excess potassium iodide solution followed by dilute sulphuric acid.

Iodine is liberated according to the equations above. The liberated iodine is then titrated with a standard solution of sodium thiosulphate usingstarch as indicator. The volume of thiosulphate used is noted.

8.7.6. Test for Copper(II) ions.

Use of Sodium Hydroxide solution

Procedure:

To the solution containing the cation is added sodium hydroxide dropwise till in excess.

Observation

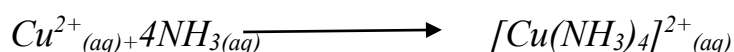A blue precipitate of $Cu(OH)_2$ insoluble in excess sodium hydroxide is formed.

$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Cu(OH)_{2(s)}$$
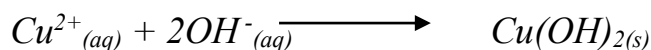
The precipitate turns black on heating due to the formation of copper(II)oxide.

Use of aqueous ammonia solution

Observation

A blue precipitate of copper(II)hydroxide soluble giving a deep blue solution Tetraammine copper(II)ions complex.
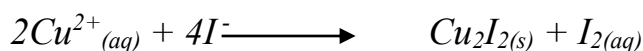
$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]^{2+}_{(aq)}$$

Use of potassium Iodide Solution

Procedure

To the solution containing copper(II)ions is added Potassium Iodide Solution.

Observation:

A white precipitate of copper (I) iodide and a brown solution of Iodine is produced.

$$2Cu^{2+}_{(aq)} + 4I^- \longrightarrow Cu_2I_{2(s)} + I_{2(aq)}$$

Use of Potassium hexacyanoferrate(II) solution

Procedure

To the solution containing copper (II) ions is added Potassium hexacyanoferrate(II) Solution.

A brown precipitate of copper hexacyanoferrate(II)

$$Cu^{2+}_{(aq)} + [Fe(CN)_6]^{4-}_{(aq)} \longrightarrow Cu_2[Fe(CN)_6]_{(s)}$$
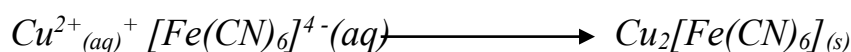
8.8.   ZINC AND ITS COMPOUNDS

Atomic number is 30.

Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Ores of Zinc

- *Zinc blende :ZnS*

- *Zinc calamine:ZnCO₃*

8.8.1. Extraction process from sulphide ore

The ore contains traces of lead sulphide and silica as impurities which should be removed.

Concentration of the ore

The ore is first crushed and mixed with water and oil (a frothing agent) so as to remove the unwanted earthly materials.

The oil wets the sulphide particles and the water wets the impurities.

Air is then blown through the mixture producing froth. The oiled sulphide particles float on the surface while the impurities sink to the bottom.The ore is collected, washed and dried.

Roasting

The concentrated ore is then heated strongly in air to form zinc oxide.

$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$
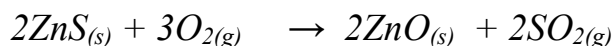
Reduction

Zinc oxide, limestone ($CaCO_3$) and excess coke are then heated in a blast furnace.

Limestone decomposes into calcium oxide and carbon dioxide.

$$CaCO_{3(s)} \quad \rightarrow \quad CaO_{(s)} \quad + \quad CO_{2(g)}$$

The calcium oxide reacts with silica, one of the impurities to form calcium silicate (slag).

$$CaO_{(s)} \quad + SiO_{2(s)} \quad \rightarrow CaSiO_{3(l)}$$
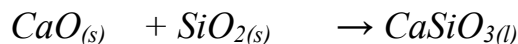
Coke burns to carbon dioxide, which is reduced by unburnt coke to carbon monoxide. The carbon monoxide reduces zinc oxide to zinc.
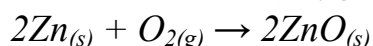
$$C_{(s)} + O_{2(g)} \quad \rightarrow \quad CO_{2(g)}$$

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

$$ZnO_{(s)} + CO_{(g)} \quad \rightarrow \quad Zn_{(l)} \quad + \quad CO_{2(g)}$$
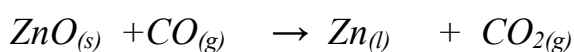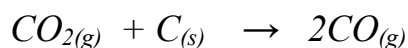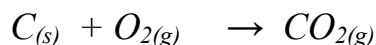
The slag sinks to the bottom and can be removed whereas the zinc produced leaves as vapour at the top of the blastfurnace where its cooled and allowed to solidify.

8.8.2. Reactions of zinc

a) <u>With air</u>
On exposure to air, zinc develops a thin layer of zinc oxide. This layer prevents further reaction with the oxygen present in air.
Zinc burns in air (oxygen) to form zinc oxide.
$$2Zn_{(s)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$$
(Yellow when hot and white on cooling)

b) <u>With water</u>
Zinc (red hot) reacts with steam to form zinc oxide and hydrogen gas.
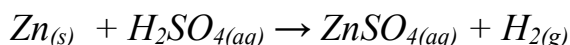$$Zn_{(s)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)}$$
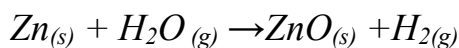
c) <u>With acid</u>
Zinc reacts with both dilute and conc. hydrochloric acid forming salt and hydrogen gas.
$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$
Zinc reacts with dilute sulphuric acid to form salt and hydrogen gas.
$$Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$$
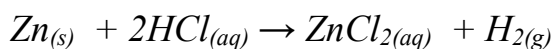
d) Reaction of zinc with conc. H_2SO_4

Produces zinc sulphate, sulphur dioxide and water as the products.

$Zn_{(s)} + 2H_2SO_{4\ (aq)} \rightarrow ZnSO_{4\ (aq)} + 2\ H_2O_{\ (aq)} + SO_{2(g)}$
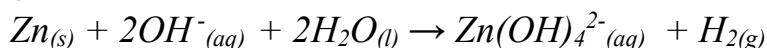
NB:

The products for the reaction with nitric acid (both dilute and conc.) are not easily defined.

e) **With alkalis**

Zinc reacts with aqueous alkalis to form zincates' complex and hydrogen gas.

$Zn_{(s)} + 2OH^-_{\ (aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}_{\ (aq)} + H_{2(g)}$

8.8.3. Compounds of zinc

1) Zinc hydroxide

It is prepared as a white precipitate on addition of a little sodium hydroxide or aqueous ammonia to a solution containing zinc ions.

$Zn^{2+}_{\ (aq)} + 2OH^-_{\ (aq)} \rightarrow Zn(OH)_{2(s)}$
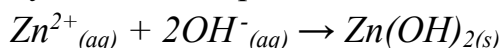
White ppt

The hydroxide is amphoteric. It dissolves in excess sodium hydroxide to form sodium zincates' complex.

$Zn(OH)_{2(s)} + 2OH^-_{\ (aq)} \rightarrow Zn(OH)_4^{2-}_{\ (aq)}$
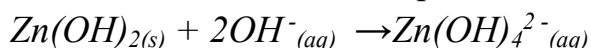
In aqueous ammonia, zinc hydroxide dissolves forming a colorless solution of tetra amine zinc ion.

$Zn(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow Zn(NH_3)_4^{2+}_{\ (aq)} + 2OH^-_{\ (aq)}$
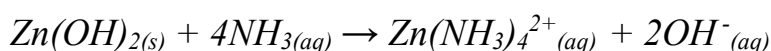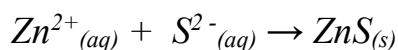
2) Zinc Sulphide

This is prepared as a white ppt on passing hydrogen sulphide through a solution of zinc ions.

When H_2S gas is passed through a solution of a metallic salt, a metallic sulphide is formed but if the H_2S is passed through an acidic solution of a metallic salt, the sulphide may not be formed.
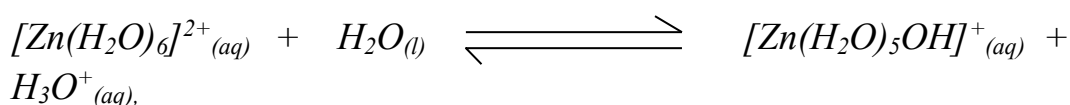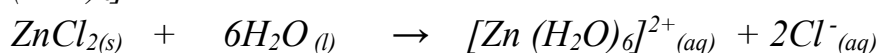
Explanation:

$H_2S_{(g)} + aq \rightleftharpoons 2H^+_{\ (aq)} + S^{2-}_{\ (aq)}$

$$Zn^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \rightarrow ZnS_{(s)}$$
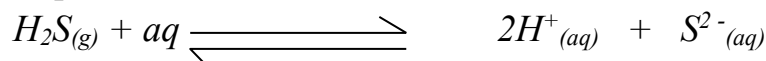
If before bubbling hydrogen sulphide the solution is acidified, the excess H+ ions present suppresses the formation of sulphide ions in 1st equation above and therefore the concentration of sulphide ions will be too low to precipitate zinc sulphide.
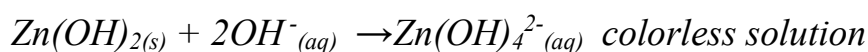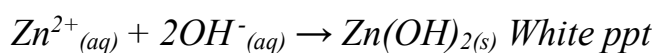
Note

Aqueous solution of zinc chloride is acidic due to hydrolysis of $[Zn(H_2O)_6]^{2+}$
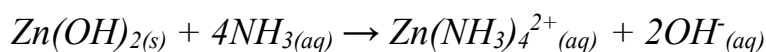
$$ZnCl_{2(s)} + 6H_2O_{(l)} \rightarrow [Zn(H_2O)_6]^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$

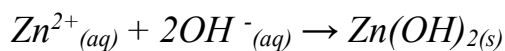$$[Zn(H_2O)_6]^{2+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Zn(H_2O)_5OH]^+{}_{(aq)} + H_3O^+{}_{(aq),}$$

8.8.4. Test for zinc ions

1) Addition of aqueous sodium hydroxide drop wise to a solution of zinc ions produces a white ppt which dissolves in excess alkali to form acolourless solution.

$$Zn^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Zn(OH)_{2(s)} \ White \ ppt$$

$$Zn(OH)_{2(s)} + 2OH^-{}_{(aq)} \rightarrow Zn(OH)_4{}^{2-}{}_{(aq)} \ colorless \ solution$$

2) Addition of ammonia solution drop wise to a solution of zinc ions produces a white ppt soluble in excess to form a colorless solution.
3)

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

$$Zn(OH)_{2(s)} + 4NH_{3(aq)} \rightarrow Zn(NH_3)_4{}^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$$

4) Addition of potassium ferrocyanide solution to a solution of Zinc ions produces a white ppt soluble in sodium hydroxide.

5) Addition of ammonium sulphide solution produces a white precipitate soluble in dilute hydrochloric acid.

6) Using disodium hydrogen phosphate forms white ppt with zinc ions.

8.8.5. Uses of zinc

- Making alloys e.g. Brass is alloy of zinc and copper.

- Galvanizing iron.

Zinc is higher than iron in electrochemical (reactivity) series.

If a galvanized piece of iron developed a small scratch and the iron is exposed, iron does not rust.

This is because the zinc in the neighborhood of the exposed iron undergoes oxidation in preference to iron forming a thin layer of Zinc oxide formed which prevents further attack

The simplified version of inorganic chemistry by SSERWADDA Walter