

Atomic structure

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.

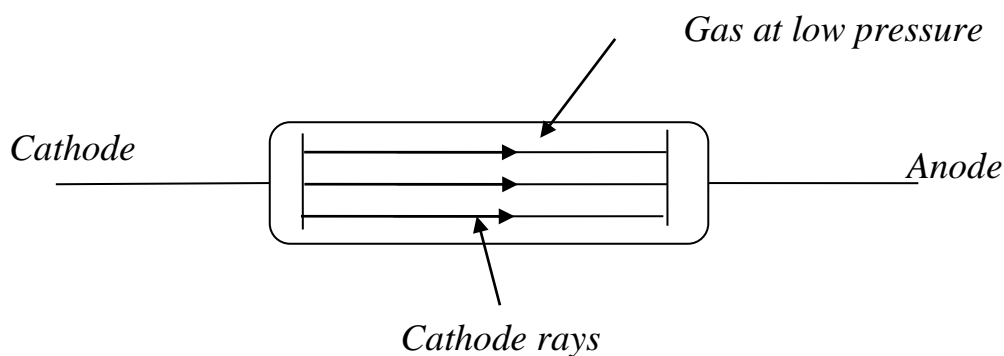


Figure 1: Cathode ray tube with anode directly opposite the cathode

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.

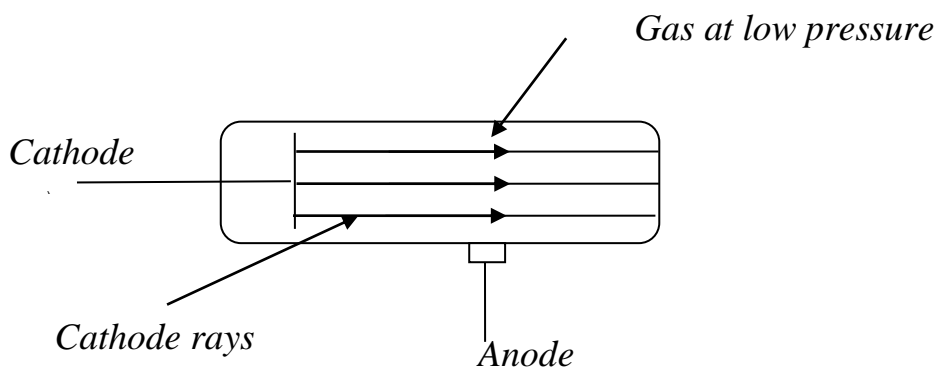


Figure 2: Cathode ray tube with the anode at the side of the tube

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

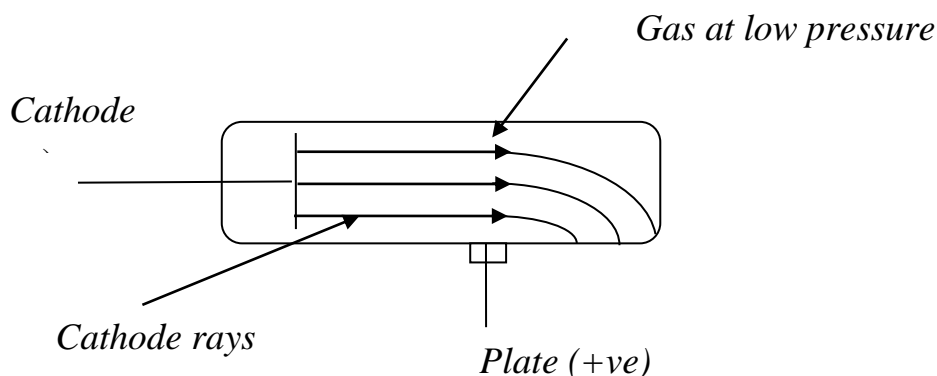


Figure 3: Cathode ray tube with an electromagnetic field.

This 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 fluoresces 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 a perforated cathode is used, positively charged particles are observed to move in a direction opposite to the electrons.

Using hydrogen gas resulted in the 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

Geiger and 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.

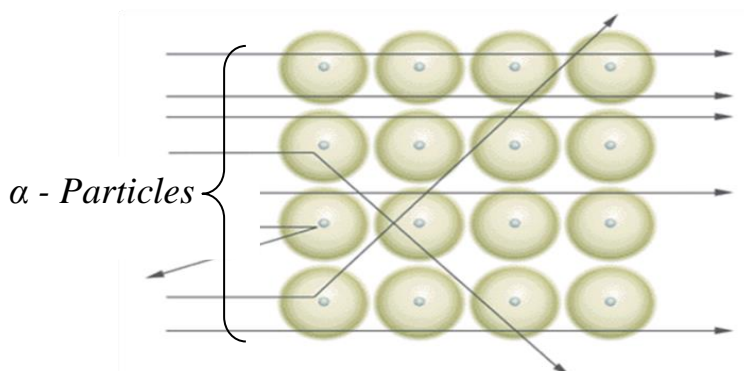
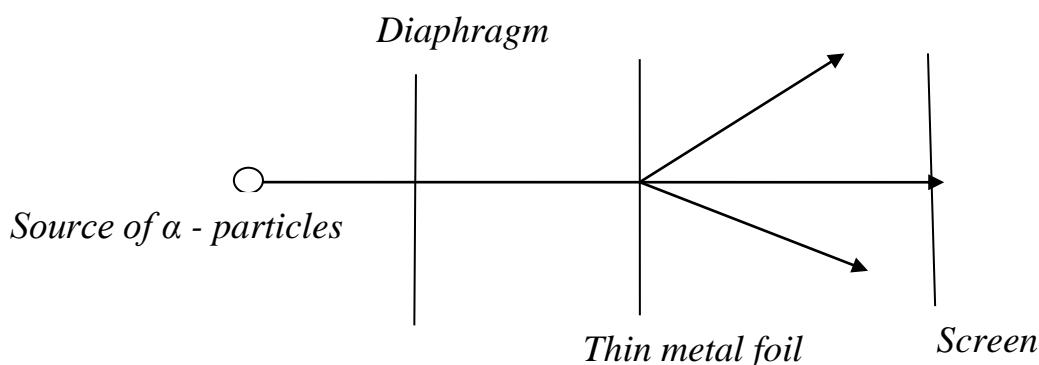
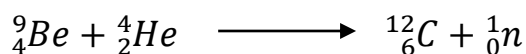


Figure 4: Rutherford's α – Particles scattering Experiment

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.

Neutrons

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



These were found to have no charge but had mass of the magnitude of the proton. These particles are also found within the nucleus.

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 **Balmer series**.

The 3 most prominent lines in these series are labeled $H\gamma$, $H\beta$ and $H\alpha$.

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's constant,

n_1 and n_2 are simple whole numbers indicating the quantum shell.

Where $n_1=1$, and $n_2=2, 3, 4$ etc

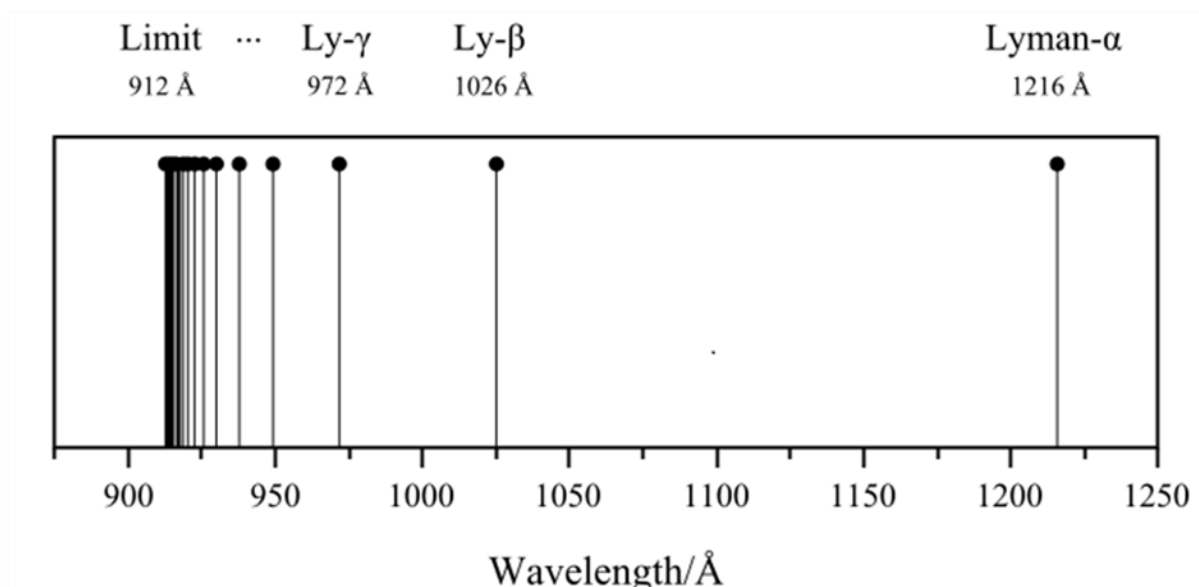


Figure 5: Hydrogen Spectral lines

Explanation

(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

$$E_1 - E_2 = h\nu$$

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

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

Where c is the velocity of light in a vacuum

$$\text{Therefore } E_1 - E_2 = \frac{hc}{\lambda}$$

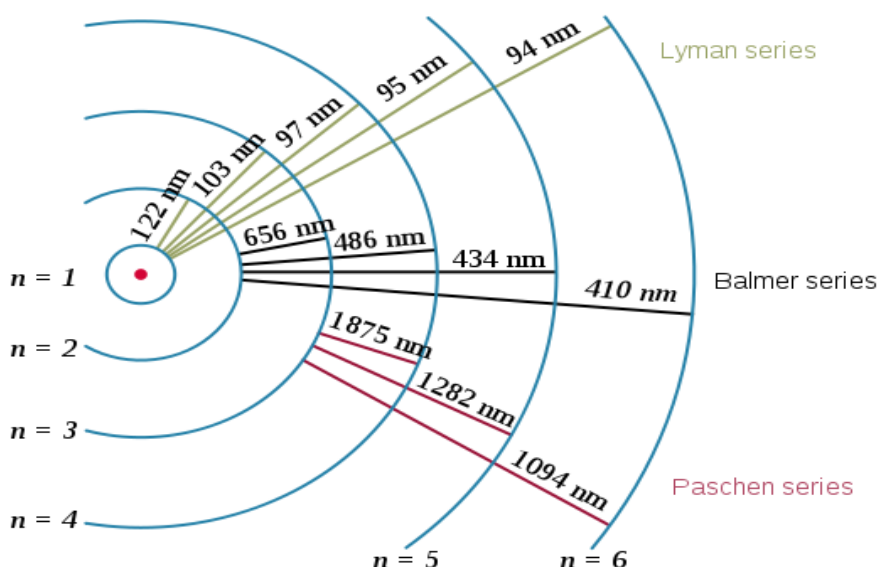


Figure 6: Hydrogen spectral series

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.

Significance of line spectrum of hydrogen

The line spectrum gives the fact that within atoms, there exist different energy levels (subshells, 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.

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 *l* 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.

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

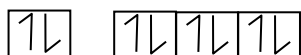


Therefore when full the 1st shell has 2 electrons.

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.

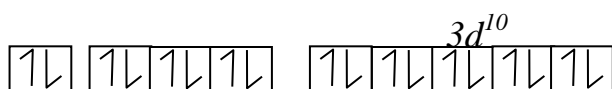


Therefore the maximum number of electrons that can be accommodated within the 2nd shell of any atom is 8.

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.



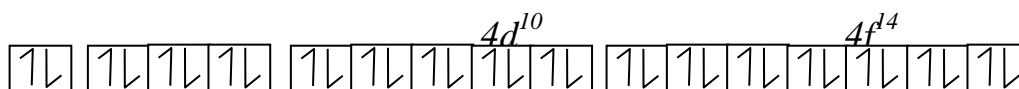
The 4th energy level has 4 sub shell given denoted by $4s$, $4p$, $4d$ and $4f$.

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.



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.

Rules/principles for writing electronic configurations of atoms

Pauli Exclusion Principle

It states that an orbital can take a maximum of two electrons on condition that the electrons have parallel and opposite spins.

Hund's Rule of maximum multiplicity

It 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.

Aufbau pattern of filling energy level

It 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.

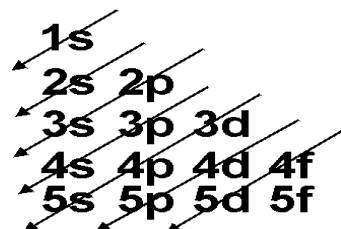


Figure 7: Aufbau pattern of filling energy levels

The modern periodic table of elements

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.

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

Atomic radius

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.

Variation in Atomic radius cross the period in the periodic table

Trend

Atomic radius decreases across the period.

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 outer-most 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.

Consider period 2 elements

<i>Elements</i>	<i>Li</i>	<i>Be</i>	<i>B</i>	<i>C</i>	<i>N</i>	<i>O</i>	<i>F</i>	<i>Ne</i>
<i>At. Number</i>	3	4	5	6	7	8	9	10
<i>Atomic radius /Å⁰</i>	1.52	1.13	0.83	0.77	0.71	0.66	0.71	1.60

Plot a graph of atomic radius against atomic number (03 marks)

Explain the shape of the graph (04 marks)

Note

The atomic radius of argon is higher than expected because its atoms do not form covalent bonds because they already have stable electronic configuration. Instead the atoms have inter atomic van der Waal's forces and inter nuclear distance between any neighboring argon atoms is therefore larger.

ii) ***Variation in atomic radius down a group in the periodic table***

Trend

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

Explanation

From one atom to the next one down a group, an extra proton is added to the nucleus and at the same time a new inner shell of electrons is being added.

As a result both the nuclear charge and screening effect increase but the increase in screening effect outweighs that due to nuclear charge.

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.

Example;

Consider Group IA elements (Alkali metals)

<i>Element</i>	<i>Atomic Number</i>	<i>Atomic radius /Å⁰</i>
Li	3	1.52
Na	11	1.54
K	19	2.27
Rb	37	2.48
Cs	55	2.65

State the variation in atomic radius of group(I) elements.

Explain your answer in (a) above.

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 is 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 to electron ratio decreases.

The nuclear attraction for the now increased number of electrons 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

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.

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

Ion	Al^{3+}	Mg^{2+}	Na^+	F^-
Ionic radius /nm	0.050	0.065	0.095	0.102

Ionisation Energy

Definition

Ionisation 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



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.



For example

For a sodium atom,



Second ionisation 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.



Example; for a sodium atom;



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.

Factors that determine the magnitude of 1st ionization energy

Nuclear charge of the atom

Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell

Atomic radius

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 first ionisation 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 first ionisation 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 first ionisation 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 first ionisation energy.

If the radius of an atom is large, the outer most electrons are further away from the nucleus and hence experience a low nuclear attraction leading to low first ionisation 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 first electron leading to a high first ionisation energy.

But if the first 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 first electron from such an atom i.e. the first ionisation energy value is low.

Note an orbital is thermodynamically stable if it is **half way or completely filled up**.

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

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. first ionisation energy generally decreases.

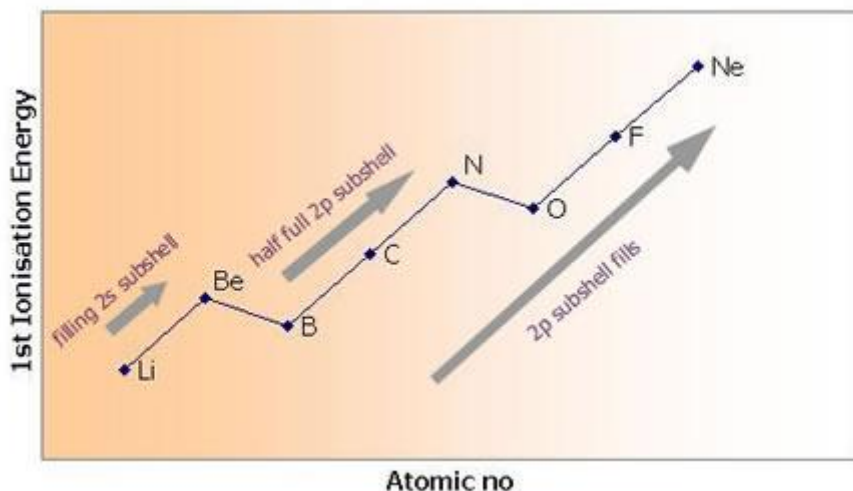
For example: Consider group (I) elements.

Element	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>
Atomic number	3	11	19	37	55
First ionisation energy/ KJmol^{-1}	513	496	418	403	376

- State the trend in first ionisation energy of group(I) elements.
- Explain your answer in (a) above.

Variation in first ionisation energy across the period

Consider across period 2 elements;



Trend

Ionisation 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 1st ionisation energy.

Beryllium, $1s^2 2s^2$ has a higher first 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 ionisation 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.

Note:

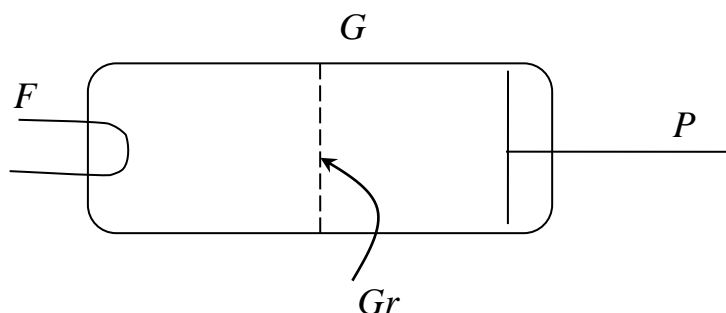
In every period, noble gases have the highest first ionization energy. This is because noble gases have full outer most sub shells and thus thermodynamically stable.

Helium: $1s^2$ has the highest first ionisation energy of all atoms.

This is because Helium atom has the smallest atomic radius therefore electrons in its outer most shell are closer to the nucleus and are attracted more strongly.

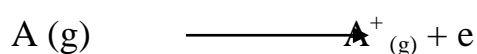
Also its outermost electronic configuration is thermodynamically stable.

Determination of ionisation energies of an atom of an element



The valve is evacuated by means of a vacuum pump and the gaseous atoms of the element whose ionisation energies are required are introduced into the valve and the inlet closed. The filament F is heated by passing an electric current through it and it emits 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 ionise according to the equation below



The electron emitted by A is attracted to the grid G while positive ions, A^+ move to plate P. The circuit is then completed and current thus flows and the minimum grid potential for the current to just flow is noted and it is the first ionization potential or energy, measured in electron volts (eV). $1\text{eV}=1.6\times 10^{-19}\text{ J}$

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 ionisation potentials of A are then measured.

Trend

Ionisation 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 ionisation energies of Beryllium in KJmol^{-1}

Electron number	1 st	2 nd	3 rd	4 th
Ionisation energy(kJmol^{-1})	900	1768	14905	21060

Explanation

The ***second ionisation*** is greater than the ***first*** 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 loss of a second electron require more energy.

Note:

Still for Beryllium

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

The largest difference between successive ionization energies is 13137 kJmol^{-1} and occurs between the 3^{rd} and 2^{nd} I.Es. This means the shells from which the two electrons bringing about the largest difference in I.Es come from are different shell i.e. the shell from which the 3^{rd} electron is removed is different from the shell from which the 2^{nd} electron was removed. The first two electrons in Beryllium therefore were removed from the same outer most shell before removing a 3^{rd} electron from another shell. Beryllium therefore belongs to group II in the periodic table.

Importance of ionisation energies in understanding the chemistry of atoms of elements

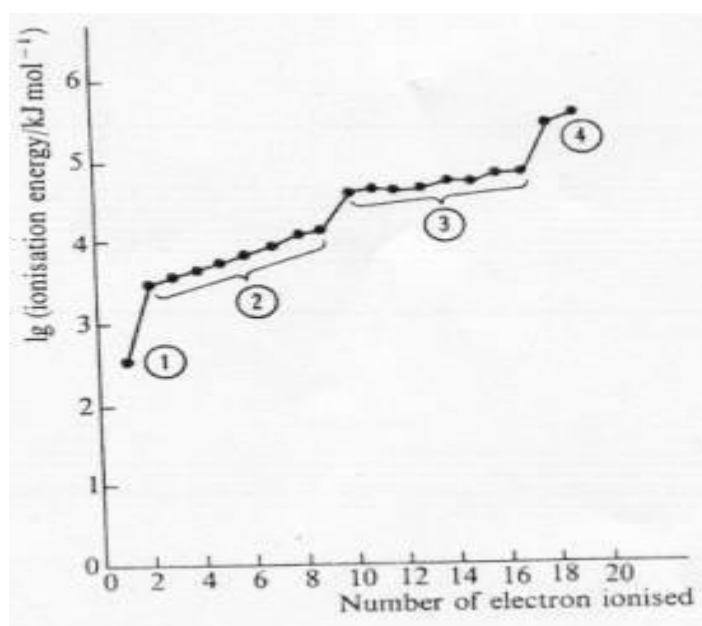
Ionization energy provides a basis for understanding the chemistry of elements. The following information is provided:

Atomic number of the element

This is given by the number of successive ionisation energies of an atom e.g. sodium with 11 successive ionization energies has atomic number 11.

The arrangement of electrons in the shells and distribution of energy level

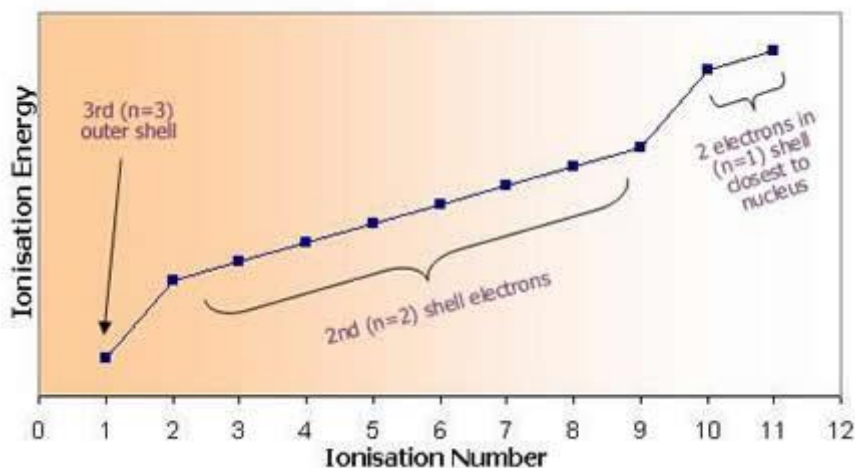
A plot of successive ionization energies of potassium shows distinct breaks. The arrangement starts with two electrons with fairly similar ionization energies which are both near the nucleus and difficult to remove. These are followed by 8 electrons with fairly similar variation in ionization energies. 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.



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.



Note

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

A careful plot of successive ionisation 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:

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

Determination of metallic or non-metallic character of an atom of an element

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

The first ionisation energies of metals are all nearly below 800kJ per mole while those of non-metals are all nearly above 800kJ per mole.

Example:

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

<i>Elements</i>	<i>Ionization energies in kJ/mol</i>		
	<i>First</i>	<i>Second</i>	<i>Third</i>
<i>A</i>	780	1500	7730
<i>B</i>	500	4560	6900
<i>C</i>	580	1815	4620
<i>D</i>	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 ionisation energy near 800kJ/mol also would show some metallic properties.

Moving from second to third ionisation 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 in 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 ionisation energies and an increase of about $1\frac{1}{2}$ 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 1, therefore it would react by giving away one electron in 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 $2\frac{1}{2}$ times. Therefore there is similar rise in ionisation energy. This implies that the three electrons in C 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 ionisation energy well over 800kJmol^{-1} is a non-metal.

Exercise

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

1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}	6^{th}	7^{th}	8^{th}
----------	----------	----------	----------	----------	----------	----------	----------

78	158	323	436	1600	2000	2360	MK 2910
6	0	0	0	0	0	0	0

Plot a graph of ionization energies against ionization number.

Explain the shape of the graph.

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

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

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

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

Which element belongs to;

Group I

Group II.

Give a reason for your answer in b(i) and (ii).

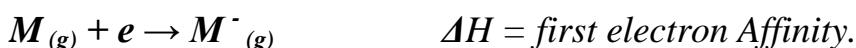
Penetrating power of electrons

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.

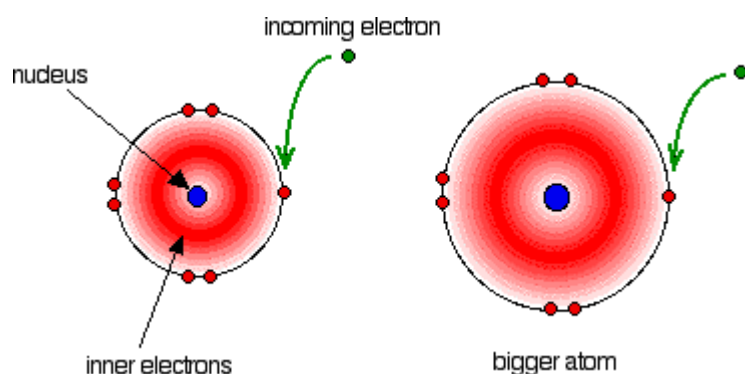
Electron affinity

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



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 ionisation 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.



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

It 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.



Note

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.

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 sign.

Factors determining the value of first electron affinity of an atom of an element

Nuclear charge of the atom

Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell

Atomic radius

Electronic configuration of the atom

Explanation

Nuclear charge

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 and less energy will be released on gaining an electron. This leads 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 the 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

Across period the in the periodic table

Trend

First electron affinity generally increases from one atom to the next one across the period.

Explanation

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 remains almost constant.

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

Example Consider the table below

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

- i) State and explain the variation in electron affinity of the period 3 elements.
- ii) Explain why the electron affinity of Magnesium is endothermic.

Down a group in the periodic table

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

Explanation

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 first electron affinity.

Example

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

<i>Element</i>	<i>Fluorine</i>	<i>Chlorine</i>	<i>Bromine</i>	<i>Iodine</i>
<i>first electron affinity</i>	-328	-349	-325	-295

Plot a graph of electron affinity against atomic number. (3 marks)

Explain the shape of the graph. (4 marks)

Electronegativity

This is the tendency by an atom in a covalent bond to attract the bonding electrons 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: $\text{H}^{\delta+} - \text{Cl}^{\delta-}$, $\text{H}^{\delta+} - \text{F}^{\delta-}$, $\text{O}^{\delta-} = \text{C}^{\delta+} = \text{O}^{\delta-}$, H_2O , NH_3 etc.

Factors determining electronegativity values

Nuclear charge of the atom

Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell

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 a result, they 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 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.

Variation in electronegativity

Across the period

Trend

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

Explanation

From one element to the next one, an additional electron is added to same shell. As a result, the nuclear charge increases progressively while the screening effect of the inner shells of electrons remains almost unchanged since electrons in the same shell screen each other poorly.

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.

Consider across period 3 elements

	MK						
<i>Element</i>	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>	<i>P</i>	<i>S</i>	<i>Cl</i>
<i>Electronegativity</i>	<i>0.9</i>	<i>1.2</i>	<i>1.5</i>	<i>1.8</i>	<i>2.1</i>	<i>2.5</i>	<i>3</i>

- i) Plot a graph of electronegativity against atomic number of the elements. (03 marks)
- ii) Explain the shape of the graph. (03 marks)

Down a group

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.

Example

Consider the table below

<i>Element</i>	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
<i>Electronegativity</i>	<i>4.0</i>	<i>3.0</i>	<i>2.8</i>	<i>2.5</i>

- i) State and explain the trend in the electronegativity of the elements.
- ii) State how you would expect the radius of the atoms above to vary.
- iii) Explain your answer in ii) above.

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.

Factors affecting electropositivity value of an atom of an element

Nuclear charge of the atom

Shielding/Screening effect of the electrons in the inner shells on the electrons in the outer shell

Atomic radius

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 is 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 electropositivity.

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 loss 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

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.

Across the period

Trend

Electropositivity decreases in moving across a period.

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. Electrons in the same shell screen each other poorly.

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 electropositivity.

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.

Factors determining melting point

Among metals

The melting points of metals depend on the following factors:

The number of electrons available for metallic bonding (number of delocalised 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.

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.

The crystal structure of the element

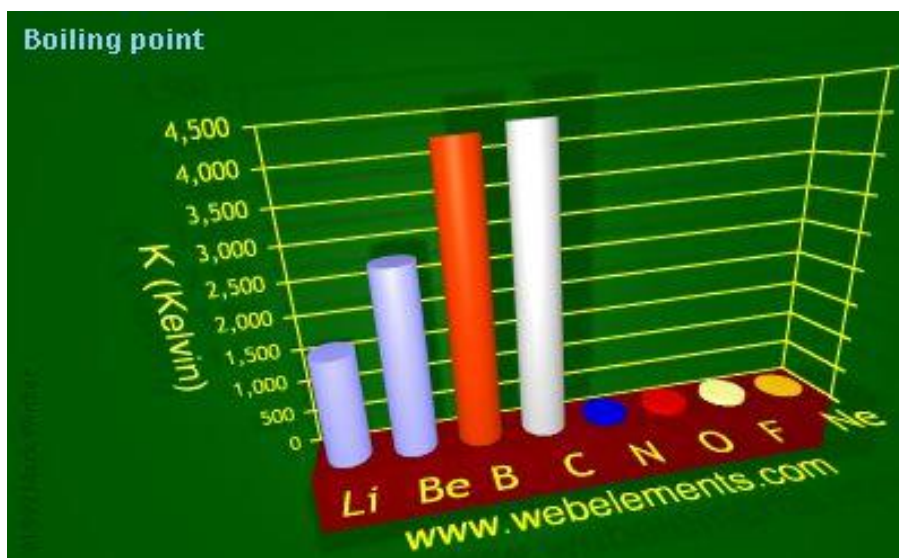
Among non-metals (Molecular substances)

Melting points of non-metals depend on:

- i) Molecular mass
- ii) Shape of molecules
- iii) Type of intermolecular forces of attraction

Trends in melting point across period 2

Trend



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

Explanation

The increase in melting point or boiling point from Li to C is attributed to the;

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.

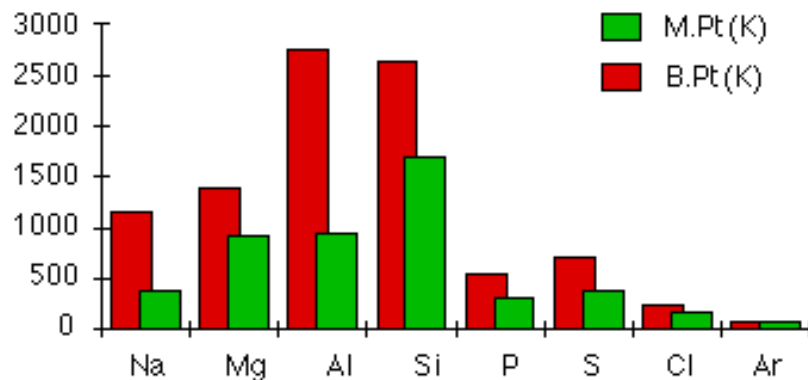
Change in the crystal structure of the elements across the period. Lithium has a body centered cubic (b.c.c) structure which has its atoms less efficiently packed than Beryllium with hexagonal closed packed (h.c.p).

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

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.

Trends in melting points across period 3

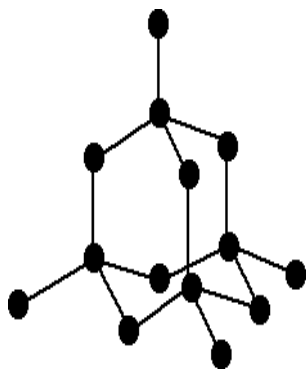
The chart shows how the melting and boiling points of the elements change as you go across the period. The figures are plotted in Kelvin rather than °C to avoid having negative values.



The melting points increase from sodium to silicon and drops abruptly for the non-metallic elements from 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.

Phosphorus contains smaller P_4 molecules. To melt phosphorus you don't have to break any covalent bonds - just the much weaker van der Waals forces between the molecules.

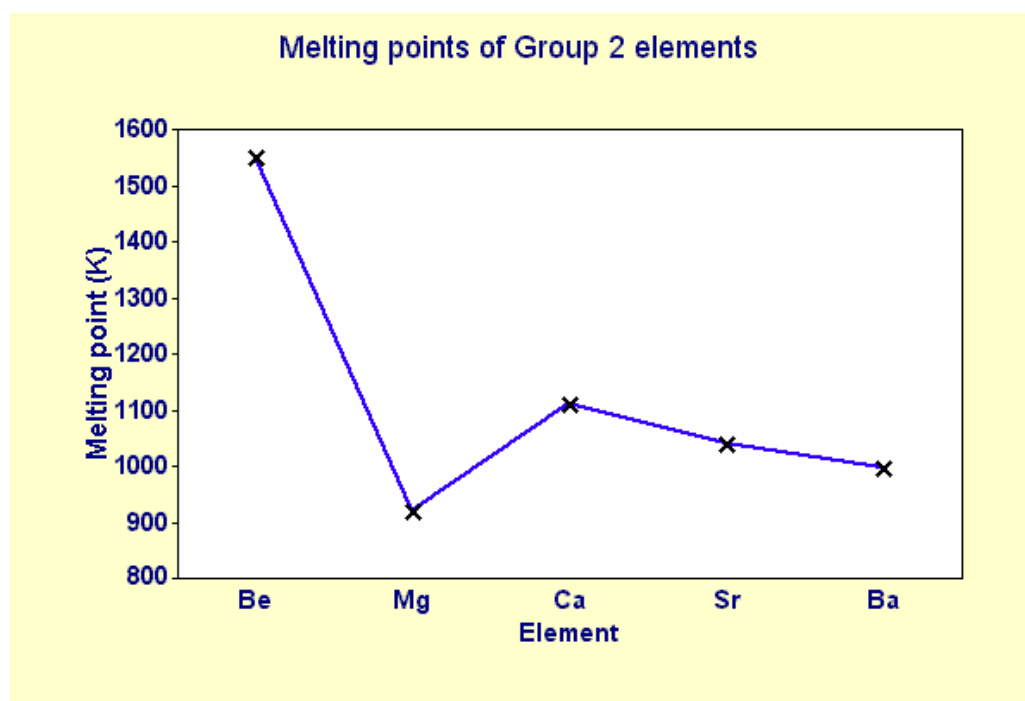
Sulphur consists of larger S_8 rings of atoms. The molecules are bigger than phosphorus molecules, and so the van der Waals forces of attractions will be stronger, leading to a higher melting and boiling point.

Chlorine, 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.

Trend in melting points of Group II elements

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

Graph of physical data



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 delocalised electrons. Therefore going down Group II:

The number of delocalised electrons remains the same, charge on each metal cation stays the same, but the atoms become larger so that the positive nucleus gets further away from the delocalised electrons.

So the force of attraction between the delocalised 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)

<i>Element</i>	<i>Molecular mass</i>	<i>Melting point /°C</i>	<i>Boiling point /°C</i>
<i>Fluorine</i>	38	-220	-188
<i>Chlorine</i>	71	-101	-34
<i>Bromine</i>	160	-7	58
<i>Iodine</i>	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

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

Hydride	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
boiling point / $^{\circ}C$	-161	-112	-90	-52	-12

State and explain the trend in the boiling points of the hydrides.

Revision questions

1. a) Explain what is meant by the term first **molar ionisation energy**. (2 Marks)
- b) Results obtained for the ionisation energies of boron are;

Electron number	1	2	3	4	5
Ionisation energy / kJ mol ⁻¹	800	2400	3700	25000	32800

- i) Plot log (ionisation energy) against the number of electrons removed.
- ii) Using your graph, deduce the most likely formula of boron chloride.

Question 2

- a) Define the term **first electron affinity**.

(1 mark)

- b) State **three** factors that affect the value of the first electron affinity. (1 mark)
- c) Explain why;
- first electron affinity of magnesium is positive. (2 marks)
 - first electron affinity for phosphorus is much lower than for silicon. (2 marks)

The first ionisation energy of sodium is $+500 \text{ kJmol}^{-1}$. Write an equation to show this change. (1 mark)

SOLUBILITY OF IONIC SALTS

Solubility of ionic salts in water depends on two energy term.

Lattice energy

Hydration (solvation) energy

Lattice energy

This is the amount of energy required to break one mole of an ionic salt into its constituent gaseous ions at standard conditions.



Or

This is the amount of energy released when one mole of an ionic salt is formed from its constituent gaseous ions at standard conditions.



Hydration energy

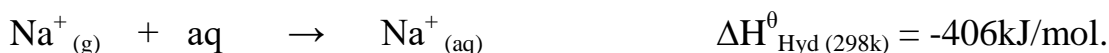
This is the amount of energy released when one mole of gaseous ions is fully dissolved in water at a given temperature.



Hydration energy has a negative sign because it involves attraction between a charge and water molecule which releases energy.

Note that

1. Each ion has its own hydration energy.



Therefore the $\Delta H^{\theta}_{\text{Hyd (298k)}}$ of NaCl = $(-406 + -377) = -783 \text{ kJ/mol}$ and that of $\text{MgCl}_2 = (-696 + 2 \times -377) = -1450 \text{ kJ/mol}$.

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

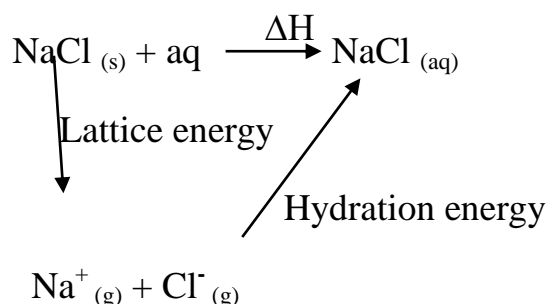
2. Water is a suitable solvent for dissolving ionic salts because:

It is a polar solvent, has a high dielectric constant.

It has a large dipole moment, so that ion-dipole interaction is high. If the solvation energy of a substance is greater than its lattice energy, the substance will dissolve exothermically in the solvent. If the solvation 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.

$\Delta H_{\text{solution}}$ is defined as the heat change that occurs when 1 mole of an ionic salt is fully dissolved in water at a given pressure.



ΔH = Enthalpy of solution.

Figure above shows *Born-Haber cycle for solubility of NaCl*.

$$\Delta H_{\text{solution}} = \Delta H_{\text{lattice}} + \Delta H_{\text{hydration}}$$

Note that

Whenever this formula is being applied in calculation, the value of $\Delta H_{\text{lattice}}$ must be positive. This is because the formula is only **valid** when the salt is being decomposed as shown in the cycle above.

Revision questions

Question 1

The lattice and hydration energies of MgCl_2 are -2644 kJ/mole and -2653 kJ/mole respectively.

- i) Draw a *Born-Haber cycle* for the solubility of MgCl_2 and indicate the energy changes that occur. (02 marks)
- ii) Calculate the enthalpy of solution of the salt. (03 marks)

Question 2

- i) Using potassium iodide, draw a Born Haber Cycle to show the energy changes that occur during solubility of an ionic salt in water. (02 marks)
- ii) The enthalpy of solution and lattice energy of potassium iodide are $+21 \text{ kJ/mol}$ and -642 kJ/mol respectively. Calculate the hydration energy for potassium Iodide. (03 marks)

Factors that affect lattice energy

Ionic charge (charge on the ion e.g Na^+ , Mg^{2+} , Al^{3+})

Ionic radius (distance between the ions)

Crystal structure of a compound.

Explanation

Lattice energy is directly proportional to the ionic charge.

If ionic charge is large, the electrostatic forces of attraction between the opposite charges are stronger leading to high lattice energy.

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

Lattice energy is inversely proportional to ionic radius.

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

On the other hand if the distance between the ions is small, the electrostatic forces of attraction between the opposite charges are greater leading to high lattice energy.

Variation in Lattice & Hydration energies

a) Both lattice and hydration energies increase across the period.

Explanation

Across the period, the radius of ions becomes increasingly smaller and as such the charge density increases.

This implies that an ion is easily hydrated and also exerts stronger electrostatic forces of attraction.

b) Both lattice and hydration energies decrease on descending the group.

Explanation

Down the group, the radius of ions becomes increasingly larger. As such the charge density decreases and the ion is less hydrated and also exerts weaker electrostatic forces of attraction.

DIAGONAL RELATIONSHIP

A relationship within the periodic table by which certain elements in the second period have a close chemical similarity to their diagonal neighbors in the next group of the third period that are diagonally placed.

This is particularly noticeable with the following pairs.

Lithium and Magnesium

Beryllium and Aluminum

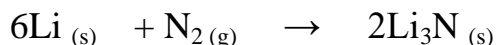
Boron and Silicon

Causes of diagonal relationship

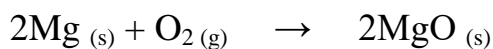
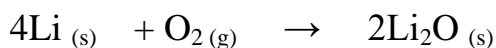
Similar electro negativities, atomic and ionic radius, hydration energies, electrode potentials, charge densities and polarizing powers, similar electropositivities.

Resemblance between Lithium and Magnesium

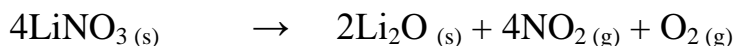
Both react directly with nitrogen to form nitrides on heating.



Both react with oxygen gas to form normal oxides only.



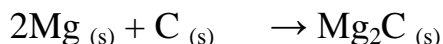
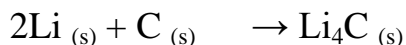
Both their nitrates decompose on heating to form normal oxide, nitrogen dioxide and oxygen gas.



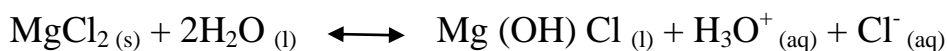
Both form carbonates that decompose on heating.



Both react with carbon when heated to form ionic carbide.



Both form chlorides and bromides that hydrolyze slowly and are soluble in ethanol;

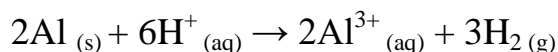
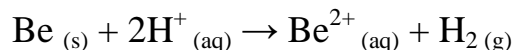
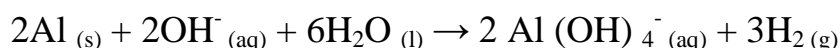
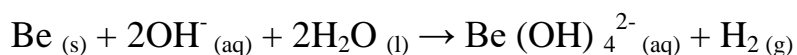


The oxonium ions produced makes the resultant solution acidic.

Resemblance between beryllium and aluminium

Both elements are passive to concentrated nitric acid.

Both react with conc. alkalis (to form complex) and mineral acids and hence they are regarded as amphoteric metals.

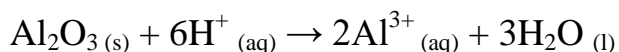
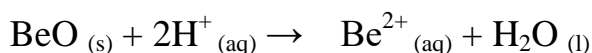


Both elements form chlorides which are partly covalent and exist as *dimmer*.

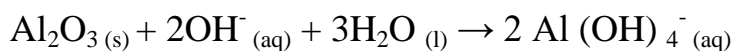
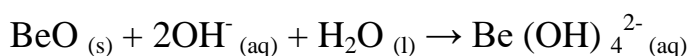
Their oxides are amphoteric as are their hydroxides.

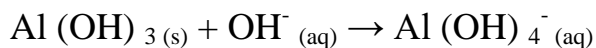
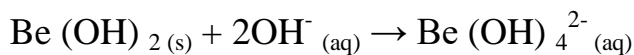
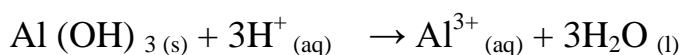
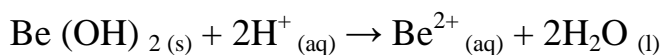
Oxides

With acids:

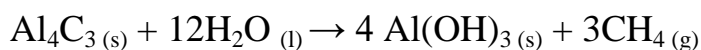
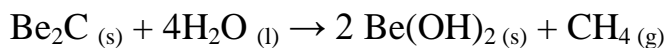


With bases:



Hydroxides**With bases:****With acids:**

Both their carbides hydrolyze in water to form methane gas.

**Reasons why the two elements (Li & Mg, Be & Al, B & Si) show resemblance in chemical properties**

The elements have similar electronegativity values, similar electrode potentials, similar hydration energies, similar ionization energies and their ions have similar charge densities and polarizing powers.

GROUP 2 ELEMENTS (alkaline earth metals)

(Be, Mg, Ca, Sr, Ba)

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 .

They have smaller atomic radii than corresponding group 1 metals.

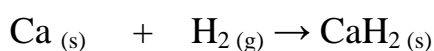
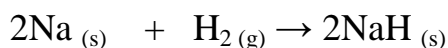
They have higher melting and boiling points than corresponding group 1 metals.

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

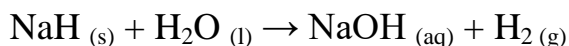
They are less electropositive, less reactive and form more covalent compounds than group 1.

Chemical properties of group 1& 2 metals**1. Reaction with Hydrogen**

The more electropositive metals of group 1 and 2 react with hydrogen to form ionic hydrides except beryllium and magnesium which form covalent hydrides.



The ionic hydrides are hydrolyzed by water to form hydroxides and hydrogen gas.

**2. Reaction with Water**

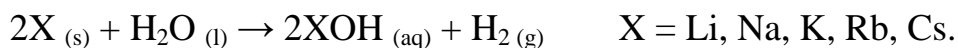
All group 1 metals react with water more vigorously than their group 2 counterparts to form corresponding hydroxides and hydrogen gas. The vigor of reaction increases down the group.

Explanation

These metals form positive ions in the course of their reaction. Group I elements lose one electron while group II elements lose two electrons. Therefore less energy is re-

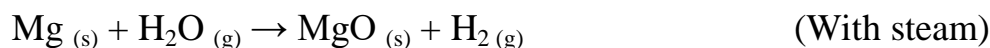
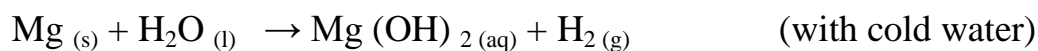
quired to remove one electron than two from the outer most shell hence group I metals react faster with water than corresponding metals of group II.

As the atomic radius increases down the group, ionisation energy decreases thereby increasing reactivity in each group. *The lower the ionisation energy the lower the activation energy for reaction and thus the faster the reaction.*

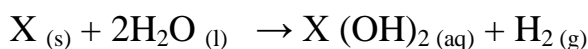


Be does not react with water.

Magnesium has a very slight reaction with cold water, but burns in steam to form white MgO and hydrogen gas.



Ca, Sr, and Ba react with increasing vigor with cold water to form corresponding hydroxides and hydrogen gas.



Note that

The hydroxides of Be & Mg have low solubility in water. However the solubility of hydroxides increase from $Ca(OH)_2$ through $Sr(OH)_2$ to $Ba(OH)_2$.

Explanation

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

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

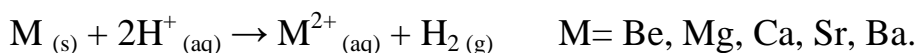
As such the lattice energy is easily superseded by the hydration energy thus facilitating solubility of the hydroxides.

Check

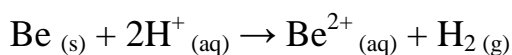
Question. State and explain the trend in solubility of the hydroxides.

3. Reaction with Acid.**i) Dilute and concentrated hydrochloric acid**

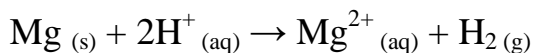
They react similarly with group 2 metals to form corresponding salt and liberating hydrogen gas.

**ii) Dilute sulphuric acid**

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



Mg reacts with cold dilute sulphuric acid to form salt and hydrogen gas.

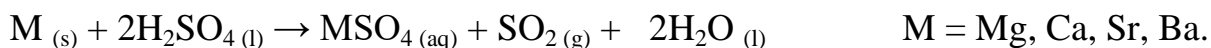


Ca, Sr & Ba react to form sparingly soluble sulphate which renders the reaction passive.

iii) Conc. sulphuric acid

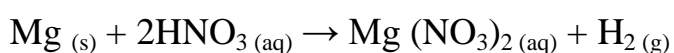
Be reacts in the same way as with dilute sulphuric acid.

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

**iv) Nitric acid**

Be does not react with nitric acid at all conditions.

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



Mg reacts with conc. nitric acid to form salt, nitrogen dioxide and water.



Ca, Sr & Ba react with nitric acid to form salt, nitrogen dioxide and water.



4. Reaction with Oxygen.

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

Normal oxide (O^{2-})

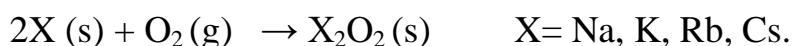
Peroxide (O_2^{2-})

Superoxide (O_2^-)

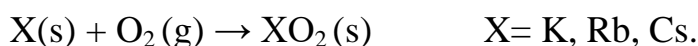
All group 1 metals form normal oxide with oxygen.



Elements Na to Cs in addition form peroxides of the type X_2O_2 .



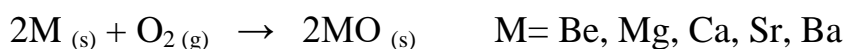
Elements K to Cs in addition form superoxide.



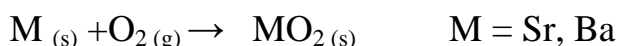
Note that

Lithium cannot form 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 2 metals when heated form normal oxide in oxygen.



The more electropositive metals form peroxides e.g Sr & Ba.

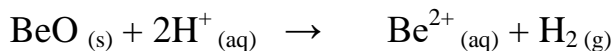
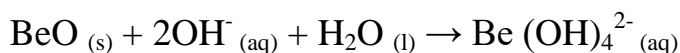


Note that

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 ion can easily be accommodated around the cation with least polarization forming stable lattice.

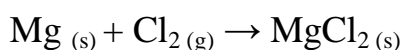
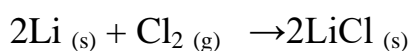
Beryllium oxide is amphoteric, shows both basic and acidic properties.



The other oxides are ionic and basic in nature.

(5) Reaction with halogens.

All the metals of group 1 & 2 combine directly under heat to form chlorides.



Compounds of group 1 & 2

Compounds of group (II) elements tend to be less ionic than those of group (I).

Explanation

The cations of group 2 have smaller ionic radius than corresponding group 1. Group 2 cations are doubly charged while those of group 1 are singly charged. Therefore cations of group 2 have higher charge density and more polarizing power than corresponding group 1. As such compounds of group 2 are less ionic than corresponding group 1 compounds. e.g. MgCl_2 is less ionic than NaCl .

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

Explanation

The cations of group 2 have smaller ionic radius than corresponding group 1.

Group 2 cations are doubly charged while those of group 1 are singly charged.

Therefore the lattice energy of group 2 salts is much higher than those of corresponding group 1 salts.

The higher lattice energy of group 2 salts makes them less soluble than their corresponding group 1 salts.

Sulphates of group 1 & 2

Sulphates of group 1 are white solids which are stable to heat and are readily soluble in water.

Sulphates of group 2 are white solids and sparingly soluble in water. Their solubility decreases 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 sulphates decreases more rapidly than the lattice energy down the group.

Note that solubility of the nitrates, carbonates and chromates are similar to those of the sulphates.

Carbonates of group 1 & 2

The carbonates of group 1 metals are white solids, readily dissolve in water and are stable to heat except lithium carbonate which decomposes on heating.

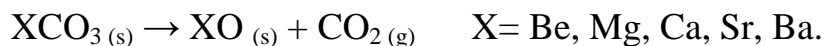


Explanation

Li^+ ion has a very small radius giving it a high charged density and a high polarizing power. As such the smaller oxide ion (O^{2-}) with a similar charged density approaches the Li^+ ion with least polarization thus forming a stable oxide.

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.



The thermal stability of the carbonates increases as the group is descended.

Carbonate	Decomposition temp. $^{\circ}\text{C}$
BeCO_3	100
MgCO_3	350
CaCO_3	900
SrCO_3	1290
BaCO_3	1350

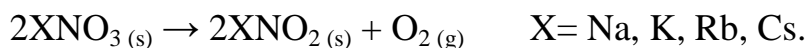
Explanation

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

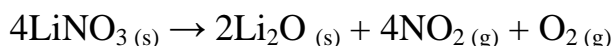
Since an oxide is smaller than a carbonate, the decomposition of metal carbonates becomes less energetically favorable down the group.

Nitrates of group 1 & 2

Group 1 nitrates (except lithium nitrate) decompose to form nitrites and oxygen.



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



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-}) with a similar charged density approaches the Li^+ ion more closely with least polarization 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 a relatively smaller nitrites. The decrease from nitrate to nitrite stabilizes the compound.

Complex formation by group 2 cations

Complex ion formation is favored by:

- i) Presence of empty orbitals on the cations to accommodate the lone pairs of electrons donated by ligands.
- ii) Small radius of the cation.
- iii) High charge on the cation.

Beryllium cation forms complex easily due to its very small ionic radius & high charge density. For example $Be(OH)_4^-$, $Be(H_2O)_4^{2+}$.

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.

Reactions in which Be resembles other group 2 elements

- i) All burn in air to form normal oxide.
- ii) All react with chlorine gas when heated to form chloride.
- iii) All react with dilute hydrochloric acid liberating hydrogen gas.

Reactions in which Be differs from other group 2 elements

Be reacts with conc. alkalis but others don't.

Beryllium oxide is amphoteric, reacts with both acid and alkalis. Other oxides of the group are basic in nature.

Be carbide reacts with water to form methane. Other members of the group don't.

Be forms chloride which is partly covalent and exist as dimmers. Other members form ionic chlorides.

Be forms only one type of oxide, the monoxide. Other members form more than one type of oxide.

Revision questions

Question 1

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

- i) Calculate the empirical formula of Z. (02 marks)
- ii) Determine the molecular formula of Z (vapor density of Z=80). (02 marks)
- iii) Write the structural formula of Z. (01mark)

Question 2

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

- i) Calculate the empirical formula of X. (02 marks)
- ii) Determine the molecular formula of X (vapor density of X= 133.5). (02 marks)
- iii) Write the structural formula of X. (02 marks)

Question 3

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

- i) Calculate the relative mass of iron chloride. (03 marks)
- ii) Determine the molecular formula of the iron chloride. (02 marks)
- iii) Write the structural formula of the iron chloride. (01 marks)

Question 4

- i) Compare the reaction of beryllium and barium with sulphuric acid under various conditions. (09 marks)

- ii) Explain how the solubility and basicity of the hydroxides of the elements of group 2 in the Periodic Table vary down the group. (05 marks)

Question 5

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

- i) Warm dilute sulphuric acid. (1½ marks)
 ii) Warm conc. sodium hydroxide. (1½ marks)

Question 6

The table below shows the atomic radii of elements of group (II) in the periodic table.

Element	Be	Mg	Ca	Sr	Ba
Atomic radius (nm)	0.112	0.160	0.197	0.215	0.221

State how the atomic radii of the elements vary in the group. (1 mark)

Explain your answer in (a) above. (3 marks)

Explain how the atomic radius affects the reactivity of group (II) elements with water. (2 marks)

Question 7

The elements beryllium, magnesium and barium belong to group II in the

periodic table.

Write the general outer electronic configuration of these elements. ($\frac{1}{2}$ mark)

State any **two** similar chemical properties shown by the elements. For each property, write an equation to illustrate your answer. (4 mark)

Beryllium differs in some of its properties from the rest of the elements in the group.

State any **two** properties in which Beryllium differs from the rest of the members of the group. (2 marks)

Give reasons why Beryllium shows different properties from the rest of the elements. (2 marks)

Name one reagent that can be used to distinguish between calcium ions and Barium ions.

Question 8

The following information is given;

Enthalpy of formation of magnesium oxide	= -642 KJ mol ⁻¹
Enthalpy of atomization of magnesium	= +148 KJ mol ⁻¹
First ionization energy of magnesium	= + 738 KJ mol ⁻¹
Second ionization energy of magnesium	= +1452 KJ mol ⁻¹
Bond dissociation energy of oxygen	= +496 KJ mol ⁻¹
First electron affinity of oxygen	= -152 KJ mol ⁻¹
Second electron affinity of oxygen	= +798 KJ mol ⁻¹

Calculate the lattice energy of magnesium oxide. (04marks)

State whether magnesium oxide is stable or not. Give a reason. (1½ marks)

State the **two** factors that affect magnitude of lattice energy. (1 mark)

Question 9

State and explain the trend in thermal stability of the carbonates of group (II) elements. (3 marks)

14.78 g of a pure sample of a carbonate of an element, **Z** which belongs to either group (I) or group (II) was completely decomposed upon heating, producing exactly 4.48 dm^3 of carbon dioxide at 0°C and 1 atm pressure (101kPa).

Calculate the number of moles of carbon dioxide produced.

ii) Deduce the relative atomic mass of Z. Hence, using the periodic table, identify Z.

(The molar volume of an ideal gas at 0°C and 1 atm pressure (101kPa) is 22.4 dm^3)

(03 marks)

c) Write equation for the reaction between beryllium and;

i) Concentrated sodium hydroxide solution. (1½ marks)

ii) Dilute hydrochloric acid. (1½ marks)

d). 1.71 g of barium reacts with oxygen to form 2.11 g of an oxide, X.

i) Calculate the formula of X (2 marks)

ii) Give the formula of the anion present in X. (1 mark)

(Ba = 137, O = 16)

ALUMINIUM AND ITS COMPOUNDS

Ore of aluminium is called Bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

Impurities found in the ore are:

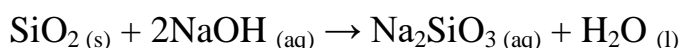
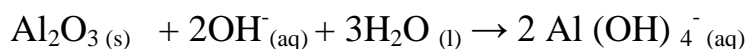
Silica, SiO_2

iron(III) oxide, Fe_2O_3

In order to obtain pure aluminium, the ore must first be refined to eliminate the impurities stated above.

a) **Purification of bauxite**

The ore is roasted and then crushed to powder. Conc. sodium hydroxide is added to dissolve the amphoteric oxide, Al_2O_3 and the acidic oxide SiO_2 .



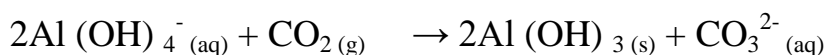
The impurity, Fe_2O_3 (basic), is eliminated by filtering off.

Aluminium is then re-precipitated as $\text{Al}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ by either:

i) Adding a little prepared aluminium hydroxide to the filtrate.



ii) Bubbling CO_2 gas through the filtrate to remove the excess OH^- ions.



The hydroxide, $\text{Al}(\text{OH})_3$ is heated to form aluminium (III) oxide.

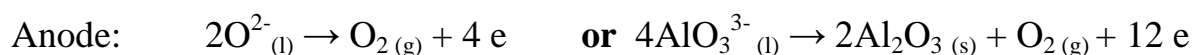
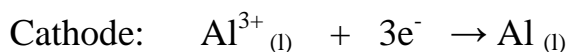


b) **Electrolysis of the fused ore**

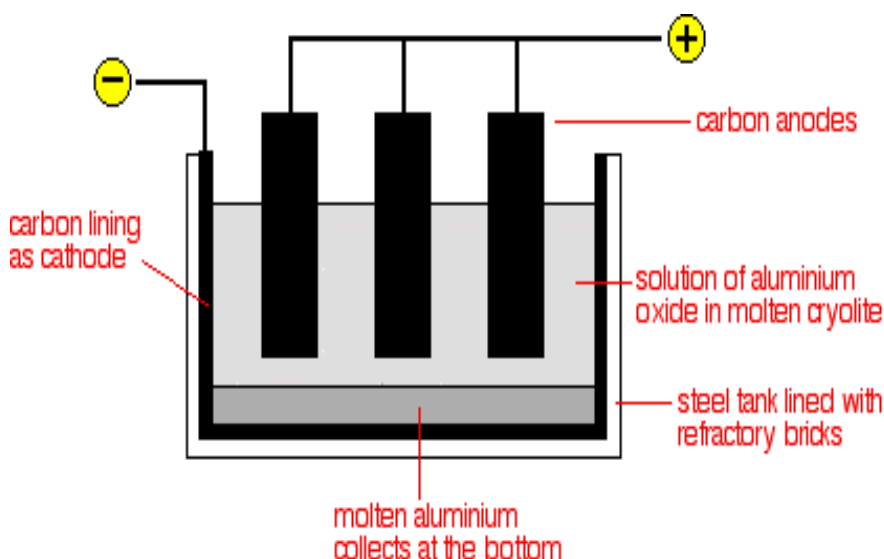
The pure oxide is first dissolved in molten cryolite (sodium aluminium fluoride - Na_3AlF_6) to lower its melting point.

The melt is then electrolyzed at a temperature between $800\text{--}900^\circ\text{C}$ at a high current density between graphite electrodes.

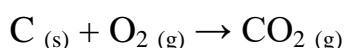
Molten aluminium sinks to the bottom at the cathode where it is tapped off while oxygen is liberated at the carbon anode.



The electrolysis cell is shown below



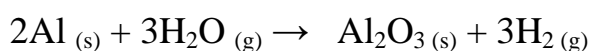
Note that the anode needs to be replaced from time to time because the oxygen produced reacts with it (graphite), oxidizing it to carbon dioxide gas hence it keeps on reducing in size.



Reactions of aluminium

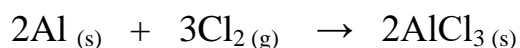
a) Reaction with water

Aluminium does not react with cold but reacts slowly with steam to form the oxide and hydrogen gas.



b) Reaction with chlorine

Aluminium when heated reacts with dry chlorine to form a chloride which sublimes. The chloride is predominantly covalent.



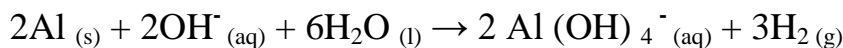
Explanation

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 polarisation. Therefore the large chloride ion is polarised greatly and as such a covalent character is induced.

The chloride forms dimer, Al_2Cl_6 , at high temperature with a chloride bridge structure. Aluminium bromide & iodide have similar structures.

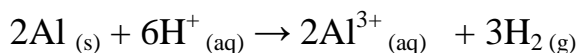
c) Reaction with solution of alkalis (NaOH & KOH)

Aluminium is an amphoteric metal. It reacts with concentrated alkalis to form aluminates complex and hydrogen gas.

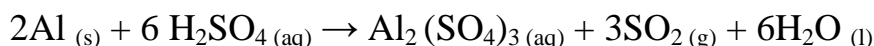


d) Reaction with acids

With dilute mineral acids except nitric acid, aluminium forms salt and hydrogen gas.



With hot conc. H_2SO_4 , aluminium forms salt, sulphur dioxide gas and water.

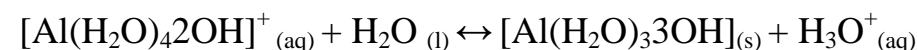
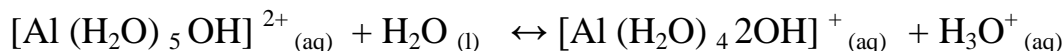
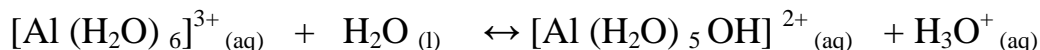


Aluminium does not react with dilute nitric acid. The metal is rendered passive due to the formation of an impervious layer of oxide.

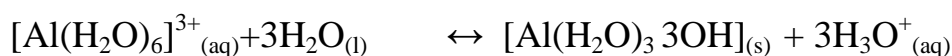
The acidity of the hexa - aqua ions

In aqueous solution, soluble salts of aluminium i.e. AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$ etc exist as $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

The resultant solution is acidic due to hydrolysis reactions



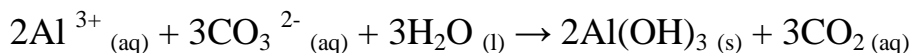
Overall equation:



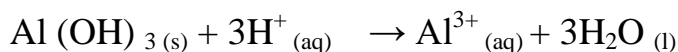
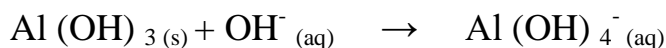
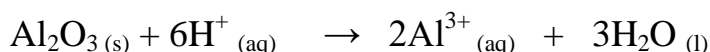
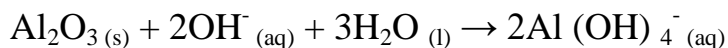
White precipitate

The hydroxonium ions produced make the resultant solution acidic with PH 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. Alkalies and dilute acids.



Some uses of aluminium include

Aluminium is used for	Because
1. Aircraft	light, strong, resists corrosion
2. other transport equipment 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

GROUP (IV) ELEMENTS

(C, Si, Ge, Sn, and Pb)

General features of group (IV) elements

All group (IV) elements have four electrons in their outermost shell with a general outer configuration of ns^2np^2 , $n=2$ for C, $n=3$ for Si, $n=4$ for Ge, $n=5$ for Sn $n=6$ for Pb etc

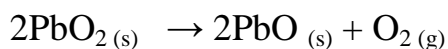
Metallic character increases down the group as the radius of the atoms become larger. Carbon and Silicon are non-metal, Germanium is a metalloid i.e it exhibits properties characteristics of metals and non-metals. While Tin & Lead are weak metals.eg they form amphoteric oxides

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 i.e they are powerful reducing agents.

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 +2 oxidation state.eg



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 covalence 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.

However, all the elements exhibit a covalence 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 that

Carbon, however, being the most electronegative 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 of 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, alkanes, alkenes, alkynes etc due to catenation. 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 on descending the group, atomic radius increases, electrons between the atoms become more distant from the nuclei making the bond weaker and unstable.

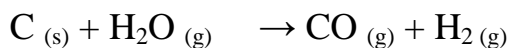
The melting points of group (IV) elements decrease as the group is descended.

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.

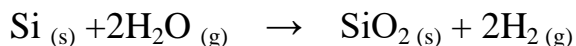
Chemical properties of group (IV) elements

Reaction with water

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

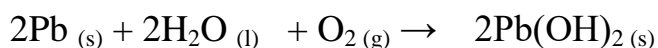


Silicon reacts with steam when heated to form silicon dioxide and hydrogen gas.



Germanium and Tin do not react with water at any condition.

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



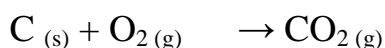
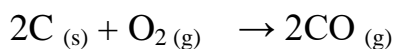
Note that

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

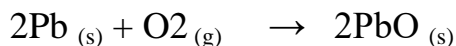
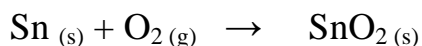
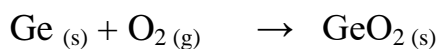
Reaction with Oxygen (air)

a) Carbon

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



b) When the rest of the elements are heated with oxygen, they form dioxides except lead which forms lead (II) oxide.



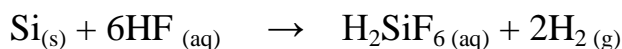
Reaction with acids

a) Carbon is attacked by all oxidizing acids e.g hot conc. Sulphuric acid and hot conc. Nitric acids.

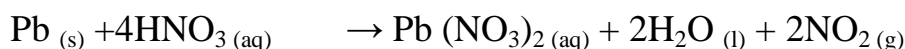
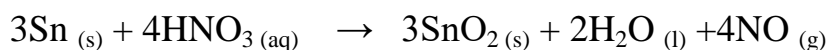




b) Silicon is resistant to all acids except hydrofluoric acid (HF)

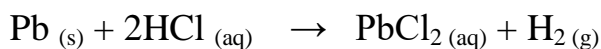


c) Germanium, Tin and Lead are oxidized by hot conc. nitric acid

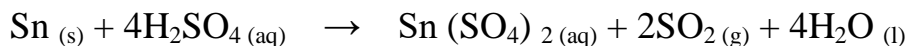


Lead is rendered passive in both cold dilute hydrochloric and sulphuric acids due to formation of insoluble salt of lead (II) chloride & lead (II) sulphate respectively.

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



Tin reacts with hot conc. Sulphuric acid to form tin (IV) sulphate.



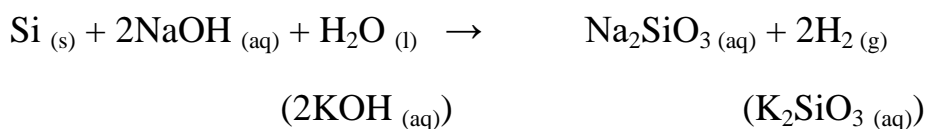
Lead reacts with hot conc. Sulphuric acid to form lead (II) sulphate, sulphur dioxide and water.



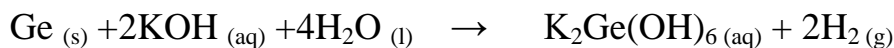
This reaction is similar to Aluminium & Chromium.

Reaction with Alkalis

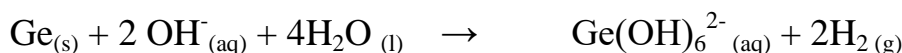
Carbon is resistant to alkalis but silicon dissolves in conc. Solution to form silicate.



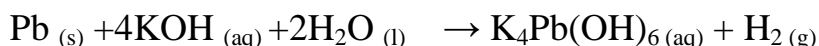
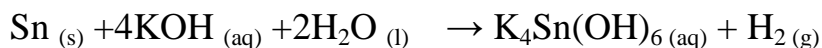
Germanium dissolves in conc. Alkalis to form hexa-hydroxo-germinate (IV)



Ionicly:



Tin and lead dissolve slowly in hot conc. Solution of alkalis to form hexahydroxystannate (II) and plumbate (II) respectively.



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 4

These elements form oxides of the type XO, where the element shows an oxidation state of +2 and also of the type XO₂, where the element shows an oxidation state of +4.

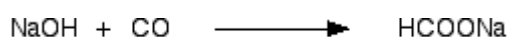
The oxides of the elements at the top of Group 4 are acidic, but acidity of the oxides falls as you go down the Group. Towards the bottom of the Group, the oxides become more basic - although without ever losing their acidic character completely.

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

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

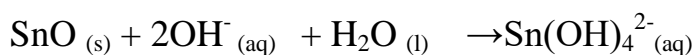
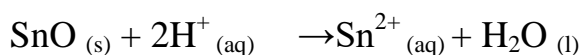
Monoxides

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.



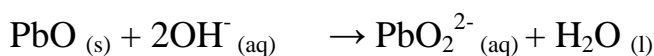
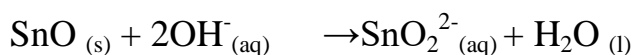
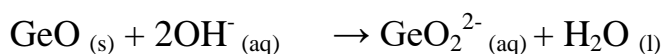
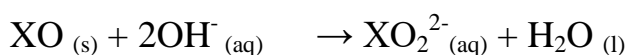
The fact that the carbon monoxide reacts with the basic hydroxide ion shows that it must be acidic

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



Similar reactions are undergone by GeO & PbO.

Alternatively:



They all react with concentrated hydrochloric acid.

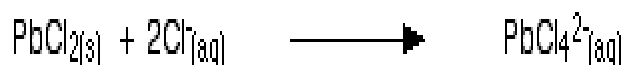


Where X can be Ge and Sn, but unfortunately needs modifying a bit for lead.

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.



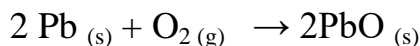
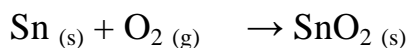
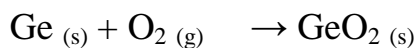
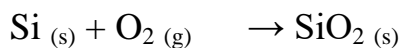
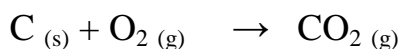
However, using concentrated hydrochloric acid, large excess of chloride ions in the concentrated acid react with the lead (II) chloride to produce a yellow soluble complex PbCl_4^{2-} .



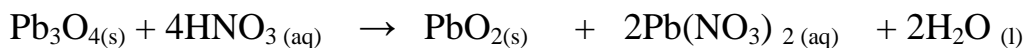
Dioxides

Preparation

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



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



Lead (IV) oxide is brown in colour.

With warm conc. HCl, red lead reacts according to the equation:

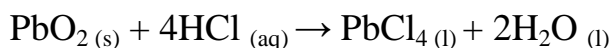


Yellow solution

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

In the case of lead (IV) oxide, the reaction has to be done with ice-cold hydrochloric acid. If the reaction is done any warmer, the lead (IV) chloride decomposes to give lead (II) chloride and chlorine gas. This is an effect of the preferred oxidation state of lead being +2 rather than +4.

Here the acid should be cold and concentrated.

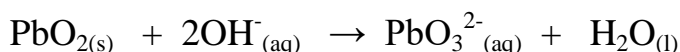
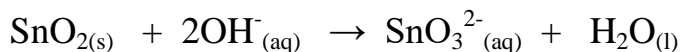
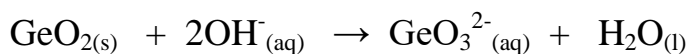


If the reaction is carried out at elevated temperature, lead (IV) oxide oxidizes hot conc. hydrochloric acid to chlorine gas.



The acidic nature of the dioxides

The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complexes of the form XO_3^{2-} .



The halides of group 4

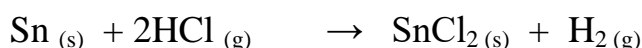
+2 halides

Preparation

Carbon and Silicon do not form +2 halides. Those of Ge, Sn and Pb can be prepared by heating the tetra-chlorides with the free metal.



Tin (II) chloride may be prepared in anhydrous form by passing dry HCl gas over heated tin.



Lead (II) chloride can also be prepared either by action of hot conc. HCl over lead (IV) oxide or by passing dry hydrogen chloride gas or chlorine over heated metal.



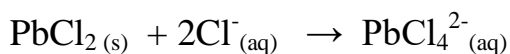
Conditions: hot/ conc. Acid.

Note that Lead (II) chloride is more soluble in concentrated hydrochloric acid than in water. This observation is explained below.

Lead (II) chloride has a high lattice energy which is not overcome 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 a soluble complex tetra- chloroplumbate (II) ions.



Yellow solution

+4 halides

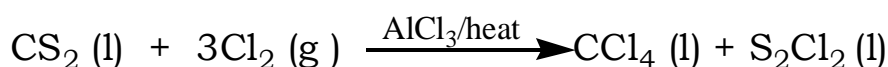
All the elements form tetra chlorides of the type XCl_4 , which are covalently bonded and are volatile liquids.

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.



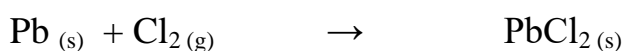
The two liquids are separated by fractional distillation.

SiCl_4 , GeCl_4 & SnCl_4 s

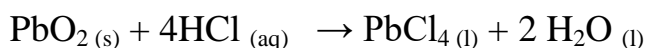
These are prepared by passing a stream of dry chlorine over the heated metal.



If a stream of chlorine is passed over heated lead, only lead (II) chloride is formed.

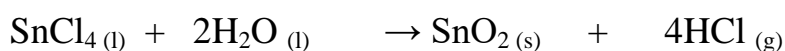
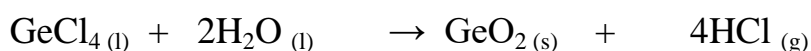
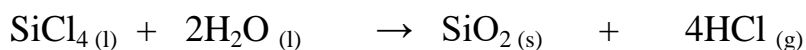
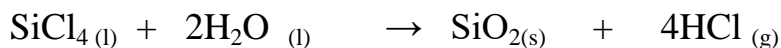


To prepare lead (IV) chloride, use ice cold conc. HCl on lead (IV) oxide.



Hydrolytic behavior of the tetrachloride

CCl_4 does not undergo hydrolysis in water. This is attributed to absence of the empty/vacant d-orbitals. However, other tetrachlorides undergo hydrolysis in water. This is attributed to availability of the empty d-orbitals thereby allowing the elements to expand their octet and show a covalency of more than +4. These empty d-orbitals accept lone pairs of electrons from the oxygen atom of water molecule thus facilitating the hydrolysis of the tetra chlorides.



Note that in each case white fumes of hydrogen chloride gas are formed.

Stability of the tetrachlorides

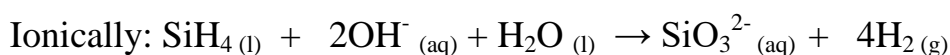
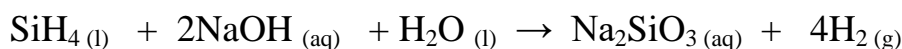
The tetrachlorides of carbon, silicon, and germanium are stable to heat, but those of tin and lead decompose on heating to form di-chlorides.



Hydrides of group 4 (CH_4 , SiH_4 , GeH_4 , SnH_4 and PbH_4)

The boiling points of the hydrides increase from methane down to stannane. This is due to increase in relative molecular mass. Thus the Van der Waals forces of attraction which bind the molecules together become progressively stronger as the relative molecular mass increases.

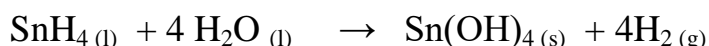
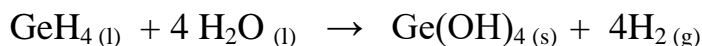
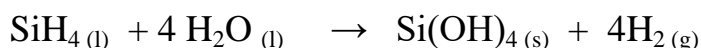
Methane, germane and stannane do not react with sodium hydroxide, but silane reacts with dilute sodium hydroxide to form sodium silicate and hydrogen gas.



Hydrolytic behavior of hydrides of group 4

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

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



Carbon differs from other group 4 elements in the following ways

Its covalence is limited to 4 is but others can have a maximum of 6. This is due to absence of vacant d-orbitals in carbon but others have.

Its unique ability to form multiple bonds such as: $\text{-C}\equiv\text{C-}$, $\text{-C}=\text{C-}$ etc

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 tetrachloride does not hydrolyze in water but tetra chlorides of other elements hydrolyse. Due to absence of vacant d-orbitals.

Carbon is the only element in group 4 which *forms only gaseous oxides*.

Why carbon differs from other elements in group 4

Very small atomic radius of carbon atom.

High electro- negativity of carbon atom.

Absence of vacant d-orbitals.

Inability to show the inert pair effect.

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, the precipitate formed dissolves forming a colourless solution. Explain this behavior and write ionic equation for the reaction.

GROUP (VII) ELEMENTS

(F, Cl, Br, I)

Physical properties

States at room temperature:

Fluorine, F_2 - yellow gas

Chlorine Cl_2 - yellow-green gas

Bromine Br_2 - red-brown liquid

Iodine I_2 - black (dark purple) solid - sublimes to a purple vapour.

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 with other elements.

All the elements have 7 electrons in their outer most shells with general outer most electronic configuration of ns^2np^5 $n=2,3,4 \text{ \& } 5$

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 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 the halogens to exist as liquid and solid respectively. However, in fluorine and chlorine, the forces are not strong enough and as a result they exist as gases.

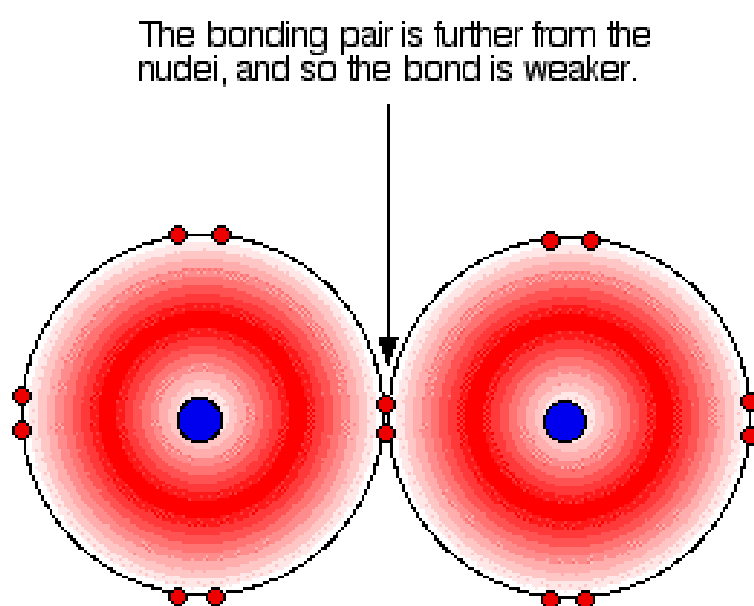
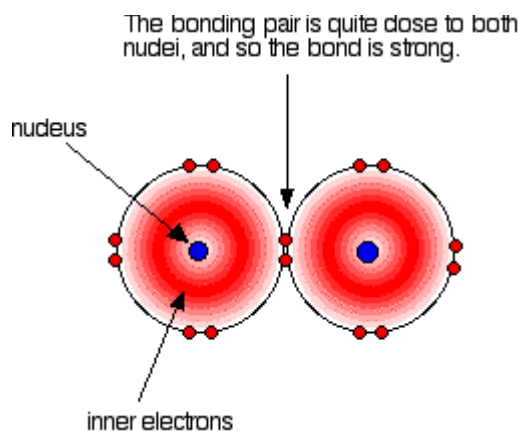
Bond dissociation energy of the halogens

Bond energy is the energy required to break a bond between two atoms.

Or it is the energy released when a bond is formed between two atoms.

Bond dissociation energy of the diatomic molecules decreases down the group from chlorine to iodine. However, F_2 has abnormally low bond dissociation energy. This is due to small atomic radius of fluorine atom, the non-bonding p- electrons present in F_2 molecule are closer to one another as such repel each other strongly thus weakening the F-F bond.

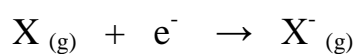
The decrease in B.D.E from Cl_2 to I_2 is attributed to increase in atomic radius as the group is descended; the bonding electrons in the halogen-halogen bond are far from the nuclei of the halogens and are attracted less strongly due to the screening effect of the inner complete shells of electrons thus weakening the bond progressively.



Note that the high reactivity of fluorine may be attributed to its low B.D.E.

Electron affinity of halogens

Electron affinity 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.



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 and there

by attain a noble gas like structure.

The electron affinity decreases numerically from Chlorine to Iodine. The atomic radius increases down the group, the electron being added experiences a greater repulsion from the electrons that are already present than the attraction experienced from the nucleus due to the screening effect of the inner complete shells of electrons.

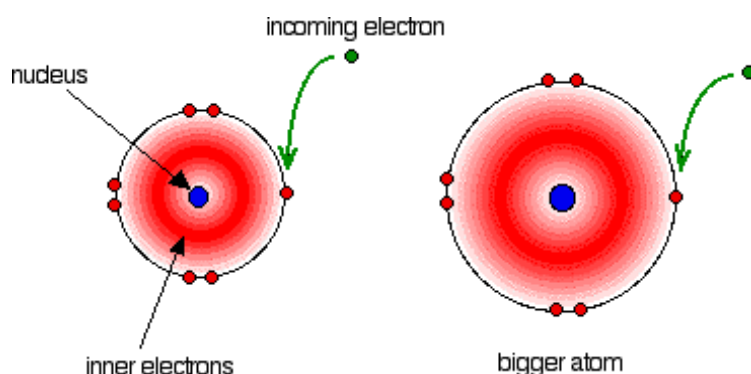
Fluorine, however, has a low value for its electron affinity, numerically less than that for chlorine.

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 a greater repulsive force from the electrons already present than the attraction from the nucleus.

The electron affinity is a measure of the attraction between the incoming electron and the nucleus.

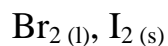
The higher the attraction, the higher the electron affinity.



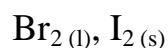
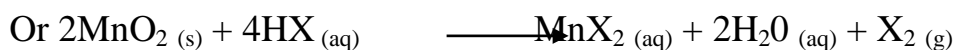
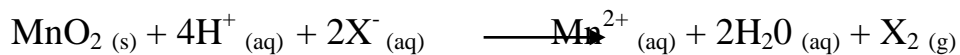
General methods of preparing halogens (excluding fluorine)

Reacting potassium manganate (II) solution with concentrated hydrogen halide.

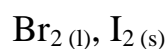
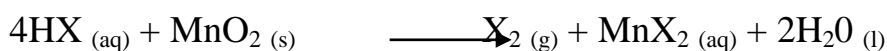
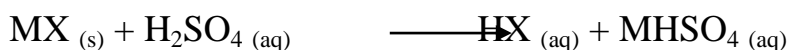




Heating manganese (IV) oxide with concentrated hydrogen halide.



Heating a mixture of an alkali metal halide with concentrated sulphuric acid in presence of manganese (IV) oxide.



Or



Reactivity of halogens

Reactivity of halogens decreases down the group as the size of the atoms

increase. Fluorine is exceptionally reactive compared to the rest of the elements in the group. This is attributed to its low bond dissociation energy between its atoms.

This is due to the smaller atomic radius of the fluorine atom resulting in greater repulsion between the non-bonding electrons in fluorine molecule and this consequently weakens the bond.

Some metallic fluorides are ionic while the corresponding halides are covalent for

example AlF_3 is ionic while AlCl_3 is covalent. This is because the chloride ion is bigger compared to the fluoride ion, its electron cloud is easily polarised by the small and highly charged ion forming a highly covalent compound. This is not the case with the small fluoride ion.

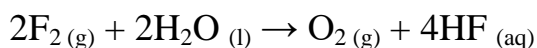
Chemical properties of halogens (reactions of halogens)

In all their reactions the halogens act as oxidising agents. Hence, their reactivity decreases down the group

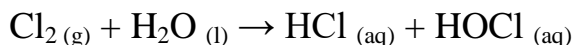
Reaction with water

Fluorine oxidises water to oxygen gas in a very exothermic reaction.

Hydrofluoric acid is also formed.



b) Chlorine reacts with water to form 'chlorine water' which is a mixture of two acids, Hydrochloric acid and hypochlorous acid.

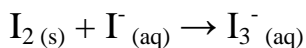


Bromine is only slightly soluble in water.



Iodine is virtually insoluble in water (It does not react with water).

It is however soluble in potassium iodide solution due to the formation of a soluble complex, the tri-iodide anion.



Iodine is sparingly soluble in water because the energy involved in disrupting the weak van der Waals 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.

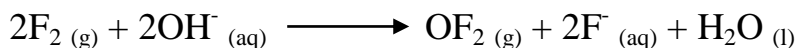
Note that

All halogens are more soluble in non-polar solvents such as CCl_4 . Cl_2 gives a colour-

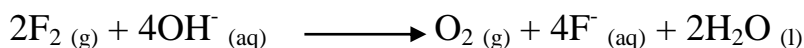
less solution. Bromine, a red solution and Iodine, a violet one.

Reaction with alkalis

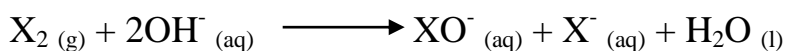
Fluorine reacts with cold dilute alkali to give oxygen difluoride gas, a fluoride and water.



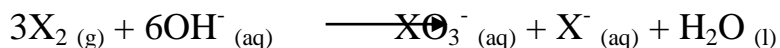
Fluorine reacts with hot concentrated alkalis to give oxygen gas, a fluoride and water.



Other halogens react with cold dilute alkalis to give halite (I) ion, a halide and water.

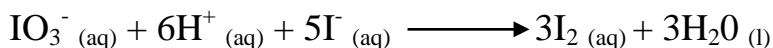
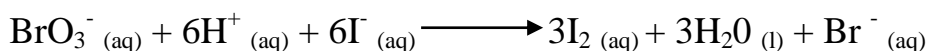
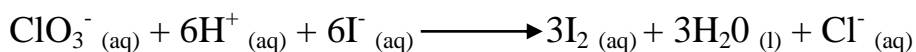


They react with hot concentrated alkalis to give halite (V) ion, a halide and water.

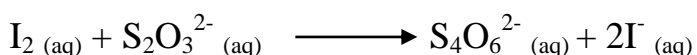


Cooling after evaporation deposits crystals of MXO_3 which is less soluble at room temperature than MX .

Halate (V) e.g ClO_3^- , BrO_3^- or IO_3^- is used in volumetric analysis to liberate iodine. They oxidise acidified potassium iodide solution to give iodine.



In order to determine the concentration of ClO_3^- , BrO_3^- or IO_3^- , the liberated iodine above is titrated against standard sodium thiosulphate solutions. Iodine reacts with sodium thiosulphate solution according to the equation:



Reactions of halogens with metals

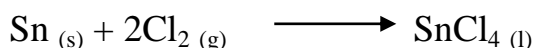
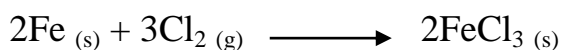
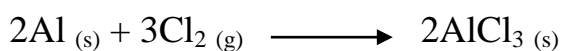
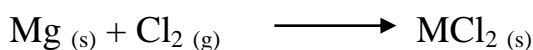
They are very reactive with metals. The vigour of reaction depends on:

The position of the metal in the reactivity series.

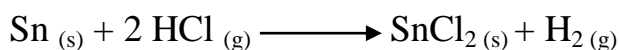
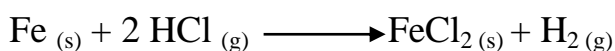
The nature of the halogen itself since reactivity of halogens decrease down the group.

Fluorine combines readily and directly with all metals whereas iodine reacts slowly even at high temperature.

Reaction of chlorine. Heated metals react with dry chlorine to form metal chlorides.



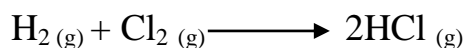
If the metal has variable oxidation states, the lower chloride is prepared by heating the metal in dry hydrogen chloride.



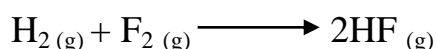
Reactions of halogens with some non-metals

Hydrogen

Chlorine reacts with hydrogen to form hydrogen chloride gas. The reaction is slow in diffused light but explosive in sunlight or ultraviolet radiation.

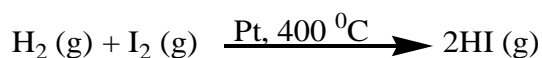
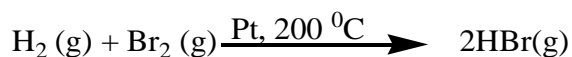


Fluorine can even react in darkness to form hydrogen fluoride gas.



Other halogens (I, Br) react with hydrogen in presence of a catalyst and at higher

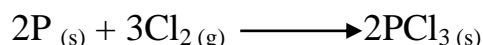
temperatures to give corresponding hydrides.



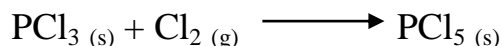
Note that the reactivity decreases down the group.

Reaction with phosphorus.

The halogens react with heated phosphorus to form phosphorus trihalides.

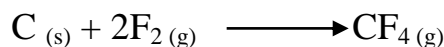


However if excess halogen, phosphorus pentahalides are formed though the tendency to form pentahalides is lowest with iodine.



Reaction with carbon

It is only fluorine that reacts with carbon to form carbon tetrafluoride.



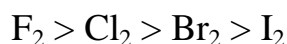
Oxidising properties of halogens

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.



The standard electrode potential (E^θ) becomes less positive as the group is descended and so oxidising power decreases down the group.



Oxidation states of halogens

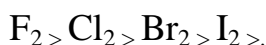
They all exhibit oxidation state of -1 by gaining an extra electron to complete their octet.

Fluorine is always univalent due to absence of vacant d-orbitals.

Other elements can show higher oxidation states due to availability of vacant d - orbitals which allows them to expand their octet.

Oxidising reactions of halogens

The oxidising property is based on standard electrode potential values. The more positive it is, the more oxidising that species is therefore the oxidising power is in the order



The oxidising reactions include:

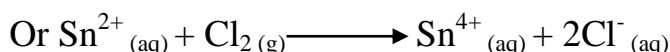
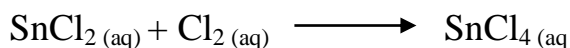
1. Displacement reactions. Chlorine displaces bromide ions from solution.



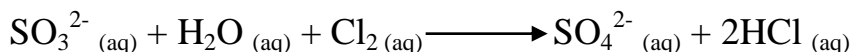
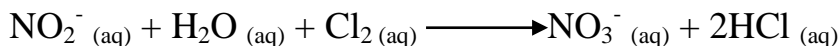
Similarly, bromine displaces iodine aqueous solutions.



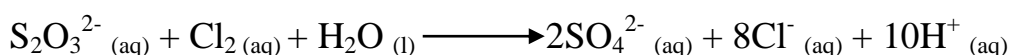
2. They oxidise the following metals in their lower oxidation states to higher oxidation states.



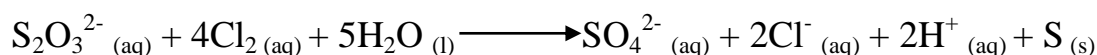
They oxidise aqueous solution of nitrite ions to nitrates. They as well oxidise sulphur dioxide gas in solution (SO_3^{2-}) to sulphuric acid (SO_4^{2-}).



Chlorine and bromine oxidise thiosulphate ions to sulphate ions.

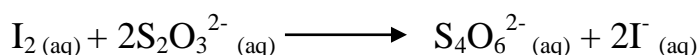


Or



Note that similar equations apply for bromine.

Iodine is a weaker oxidising agent. It oxidises the thiosulphate ions to tetrathionate ions.



The above equation is used to estimate amount of iodine in volumetric analysis.

Hydrides of group (VII)

HF is a liquid while other hydrogen halides are gases at room temperature. This is due to the strong hydrogen bonds between H-F 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 and charge density of the small F^- ion.

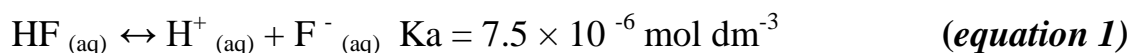
Fluorine forms hydride with the highest boiling point in aqueous solution due to extensive hydrogen bonds.

The acidity of the hydrides is in the order $\text{H-F} < \text{H-Cl} < \text{H-Br} < \text{H-I}$.

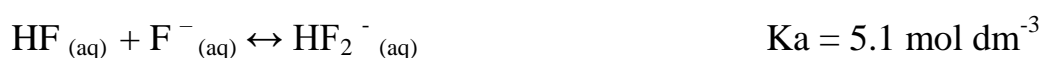
H-F is the weakest acid because the H-F bond is very strong as a result of small atomic radius and high electronegativity of Fluorine atom. It is weakly dissociated in solution releasing fewer H^+ ions. In addition, the presence of hydrogen bonding be-

tween 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.

Note that HF is a very weak acid and ionises in solution as follows:



The strength of the acid increases with increase in concentration. In concentrated solution, the reaction is:



Removal of fluoride ions in form of HF_2^{-} ions displaces the equilibrium of the equation (1) to the right making the more of the hydrogen ions to ionize in solution hence increasing the concentration of H^{+} ions in solution. Hence the K_{a} increases.

Bond energy of the hydrides

Bond energy/ enthalpy of the hydrides generally decreases in moving from HF to HI i. e $\text{H-F} > \text{H-Cl} > \text{H-Br} > \text{H-I}$.

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.

The boiling point of the hydrides increase down the group due to increasing size of the halogens giving them higher Van der Waal's forces of attraction.

Note that the hydrides are covalent but when dissolved in water, their aqueous solutions are good conductors because of the ions they produce.

Differences in the chemistry of Fluorine from other members of its group

Fluorine is always monovalent, others show higher oxidation state. This because fluorine lacks empty d-orbitals but others have.

Why does Fluorine show a difference?

Most electronegative in the group.

Low bond dissociation energy.

High positive value of standard electrode potential.

Smallest atomic radius, F^- ion has very high charge density, high polarising power, and high enthalpy of hydration.

Absence of vacant d-orbitals.

Oxy-acids & Oxy-ions

1. Chlorate(I) acid, $HClO$, (Chloric(I) acid)

2. Chlorate(III) acid, $HClO_2$, (Chloric(III) acid)

3. Chlorate(V) acid, $HClO_3$, (Chloric(V) acid)

4. Chlorate(VII) acid, $HClO_4$, (Chloric(vii) acid)

The acidity of the oxy-anions of chlorine increases with increase in the number of oxygen atoms attached to chlorine atom. Oxygen being more electronegative than chlorine, withdraws electrons from the O-Cl bond more towards itself. This weakens the O-H bond in the oxy-acid. The greater the number of oxygen atoms attached the stronger the effect and the stronger the acid.

Question 1

Work out the oxidation state of chlorine in each of oxyacids above.

2. Draw the molecular structure of each oxyacid.

Question 2

Fluorine and chlorine belong to group (VII). Discuss the reactions of the elements with;

Water (5marks)

Sodium hydroxide solution. (6 marks)

TRANSITION (d-block) elements

A d-block element is one in which the inner 'd' orbital (which has a higher energy) is in the process of filling up after the outermost 's' sub-shell (which has a lower energy) has been filled first. 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 has partially filled d-orbitals either in the free atom in its ground state or in one of its ions. The sub shells are filled up in order of increasing energy and so the 4s- orbitals are filled first before the 3d-orbitals.

Note that

For chromium, the electronic configuration of $[\text{Ar}] 3d^5 4s^1$ is a more stable arrangement than $[\text{Ar}] 3d^4 4s^2$.

This is because the former configuration has more **unpaired electrons** than the latter and therefore more stable owing to half-filled 3d-orbitals. Unpaired electrons experience minimum repulsion between each other.

For copper, the configuration $3d^{10} 4s^1$ is a more stable arrangement than $3d^9 4s^2$. The explanation is because the 3d-subshell is full therefore it is energetically stable.

Configuration of selected ions

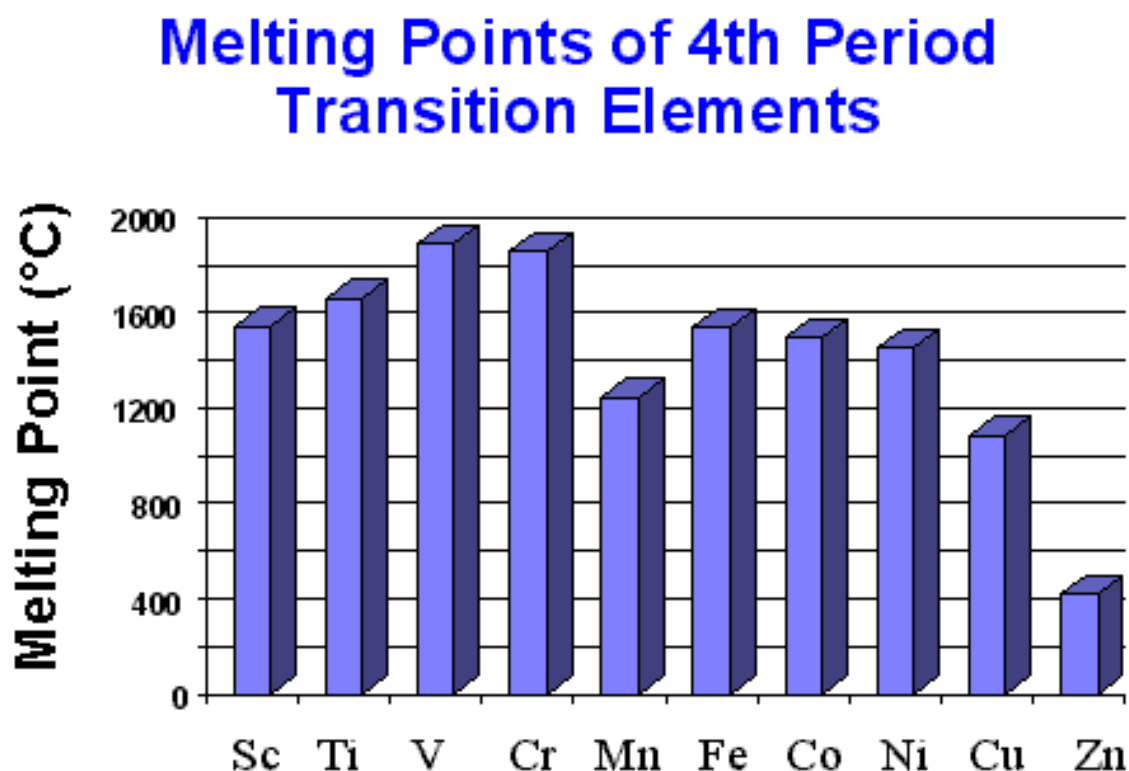


When a transition metal atom loses electrons to form ions, the 4s-electrons are lost first before 3d-electrons. This is because the 3d sub -shell is situated closer to the nucleus than the 4s sub shell. Thus when the 3d sub shell is occupied, the electrons in it repel the 4s-electrons further from the nucleus thereby increasing their energies than 3d-electrons and they are lost first.

General characteristics of transition elements

High melting and boiling points

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 the metallic bond formation. The greater the number of electrons contributed to the metallic bonds, the higher the melting point. Hence they have high melting and boiling points.



The melting points of these metals rise to a maximum value and then decrease with increase in atomic number.

A dip in the melting point is observed at manganese $[\text{Ar}] 4s^2 3d^5$. This is attributed to the stability of a half-filled 3d-orbitals, electrons therefore being less available for bond formation.

Zinc $[\text{Ar}] 4s^2 3d^{10}$ with a full 3d-orbitals uses only the outer most 4s-electrons in metallic bond formation as such has the lowest melting point.

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.

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					

Check: 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) $\text{Cr}_2\text{O}_7^{2-}$
- v) K_2CrO_4
- vi) $\text{Fe}(\text{CN})_6^{3-}$

Catalytic activity

Transition metals and their compounds behave as catalysts due to the presence of partially filled d-orbitals

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 thereby reducing the activation energy.

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:

Haber process in the manufacture of ammonia, finely divided iron is used.

Contact process in the manufacture of sulphuric acid, vanadium pent oxide is used.

Decomposition of hydrogen peroxide, manganese (IV) oxide is used.

Hydrogenation of alkenes and alkynes, nickel metal is used.

Note: 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 while **anionic com-**

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

plexes are those that carry an overall negative charge.

Neutral complexes are those that carry no charge for example;

$\text{Ni}(\text{CO})_4$, Tetracarbonylnickel(O)

$\text{Fe}(\text{CO})_5$, Pentacarbonyliron(O)

Qn. Give the name, coordination number, and the oxidation state of the metal ions in the following complexes:

i) $\text{Cr}(\text{H}_2\text{O})_6\text{Br}_3$ ii) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ iii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$

iv) $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}\text{SO}_4^{2-}$ v) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$.

Form colored compounds

Transition metal ions are colored because they have partially filled d 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.

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 metal ions possess some number of unpaired electrons

CHROMIUM AND ITS COMPOUNDS

(Atomic number = 24)

The electronic configuration of chromium is $1S^2 2S^2 2P^6 3S^2 3P^6 3d^5 4S^1$.

Note that

Chromium adopts the above electronic configuration rather than the expected $1S^2 2S^2 2P^6 3S^2 3P^6 3d^4 4S^2$ because the 3d is half filled unlike in the expected configuration therefore it is more energetically stable.

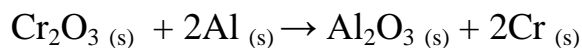
Occurance, extraction and uses of chromium

It occurs naturally as chromite, $FeCr_2O_4$ which is a mixture of Iron (II) oxide and chromium (III) oxide, $FeO \cdot Cr_2O_3$.

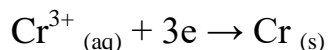
Extraction

By thermit process

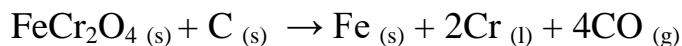
Chromium (III) oxide is reduced by aluminium i.e



By electrolytic process where Cr^{3+} ions are discharged at the cathode.



By carbon reduction process.



Uses of chromium

It is used in electroplating.

It is a component of alloy used to make stainless steel.

Physical properties of chromium

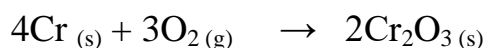
It is a hard, malleable and metal.

It has a melting point of 189°C .

Chemical properties of chromium

With Air (oxygen)

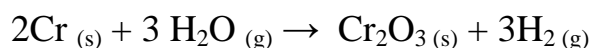
Chromium does not react with oxygen at room temperature, when heated it forms green chromium (III) oxide.



green solid

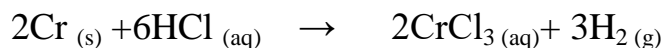
With water.

Chromium does not react with cold water but reacts with steam to form a green solid, chromium (III) oxide and hydrogen gas.



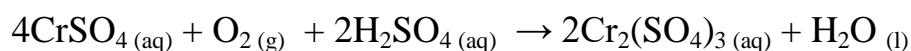
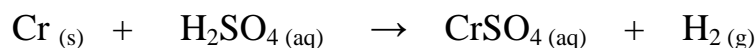
With acids.

Chromium reacts with dilute hydrochloric acid forming green chromium (III) chloride solution and liberating hydrogen gas.

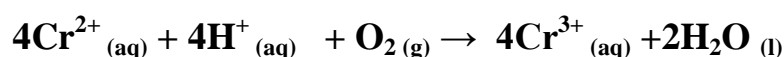
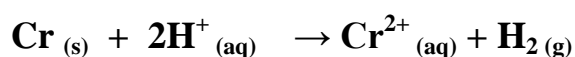


Chromium reacts with dilute sulphuric acid forming blue solution of chromium (II) sulphate and liberating hydrogen gas.

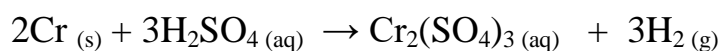
The blue solution turns to green when exposed to air. This is due to aerial oxidation of Cr^{2+} to Cr^{3+} ions.



Ionicallly:



Chromium reacts with dilute sulphuric acid on heating to form chromium (III) sulphate and hydrogen gas



Chromium reacts with hot conc. sulphuric acid to form chromium (III) sulphate, sulphur dioxide and water.

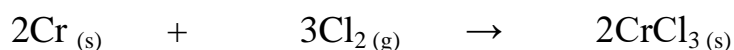


Note that chromium does not react with nitric acid due to the formation of a thin layer of chromium (VI) oxide which renders it passive towards nitric acid.

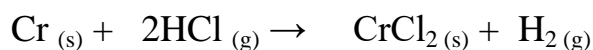
With non-metals

With chlorine

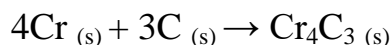
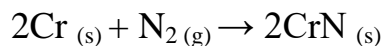
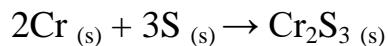
If chlorine gas is passed over heated chromium, green solid of chromium (III) chloride is formed.



Note that if hydrogen chloride is used instead, chromium (II) chloride is formed.



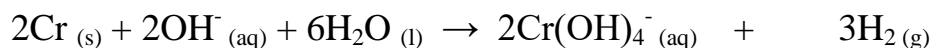
Heated chromium also reacts with sulphur, nitrogen and carbon.



V) With sodium hydroxide solution.

Chromium dissolves to give:

a colorless gas that burns with a pop sound and a green solution is formed.



Question 1

Discuss any 5 similarities in chemistry of chromium and aluminium.

Support your answers with equations where necessary. (08 marks)

Compounds of Chromium

Chromium shows principle oxidation states of +2, +3, & +6. The most stable oxidation state of chromium is +3.

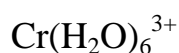
Compounds in + 2 oxidation state are not very important since they are less stable. Chromium (II) oxide is black while Chromium (II) hydroxide is yellow.

Chromium in + 3 oxidation state

In aqueous solution, chromium (III) is the most stable oxidation state of chromium. It exists as $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, hexaaquachromium(III) ion which is violet in colour.

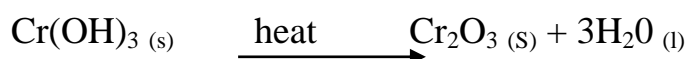
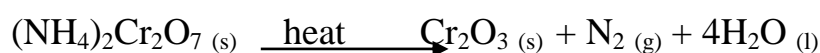
It is often green because of partial replacement of water molecules by other ligands.

Stable octahedral complexes of chromium are:



Chromium (III) oxide

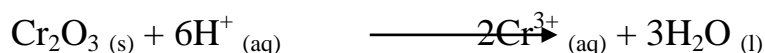
It is a green solid and can be obtained by heating ammonium dichromate, chromium (II) hydroxide or chromium (III) sulphate.



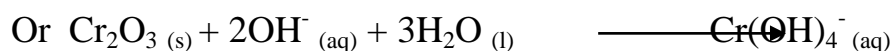
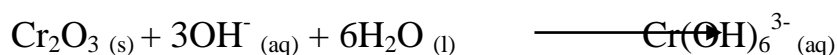
Chromium (III) oxide is stable and resists reduction by hydrogen or carbon monoxide gas.

It is amphoteric, reacts with both acids and bases.

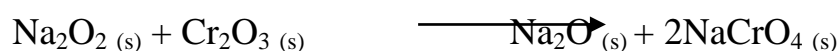
With acids, a salt and water are formed.



With alkalis, chromate (III) ion is formed.



Chromium (III) oxide can be oxidised to chromium (VI) e.g. fusion of chromium (III) oxide with sodium peroxide oxidises the oxide to sodium chromate (VI) which is yellow.

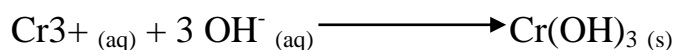


Also fusion of chromium (III) oxide with an alkali in air oxidises the oxide to chromate (VI).



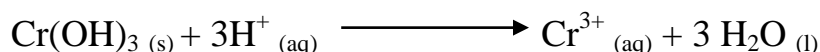
Chromium (III) hydroxide

This exists as a grey - green solid. It may be obtained by adding a little sodium hydroxide solution or ammonia solution to a chromium (III) salt solution.

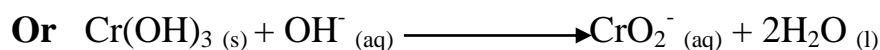
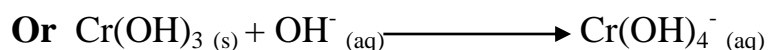
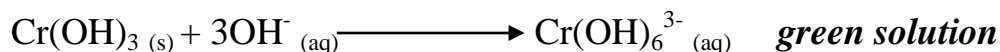


It is amphoteric, therefore reacts with both bases and acids.

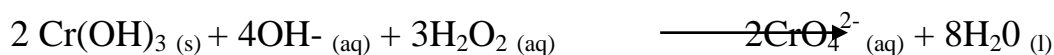
With acids, a salt and water are formed.



With alkalis, a solution of chromate (III) ions is formed.



Note that in presence of an alkali, chromium (III) hydroxide is oxidised to yellow chromate (VI) solution by chlorine, bromine, hydrogen peroxide or sodium peroxide.



The reaction is used to identify chromium (III) ions in qualitative analysis.

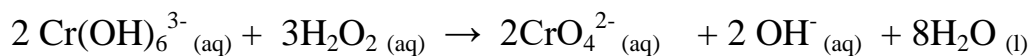
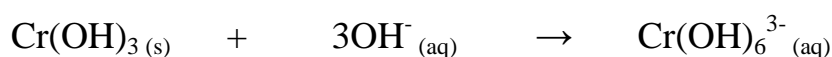
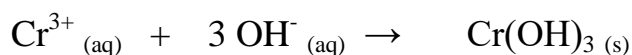
Question 2

Explain what is observed when sodium hydroxide is added to a solution containing Cr^{3+} ions and to the resultant solution, hydrogen peroxide added and boiled. How can the anion produced at the end of the reaction be confirmed? (06 marks)

Answer

Observation

A green precipitate soluble in excess, forming green solution. The solution turns yellow on addition of hydrogen peroxide.



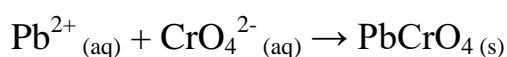
The presence of the chromate ions produced can be confirmed by.

Addition of Lead (II) ethanoate or Lead (II) nitrate solution.

Observation

A yellow precipitate is formed.

Equation

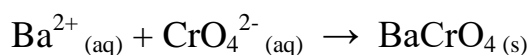


Addition of Barium nitrate or Barium chloride solution.

Observation

A yellow precipitate is formed.

Equation

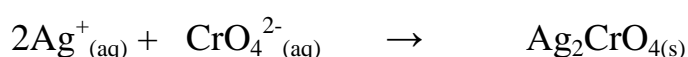


Addition of silver nitrate solution.

Observation

A brick red precipitate is formed.

Equation



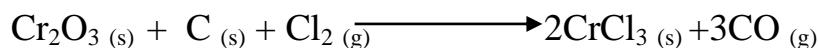
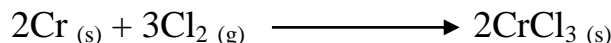
Addition of a little amyl alcohol (e. g pentan-1-ol) followed by dilute sulphuric acid.

Observation

A blue color is observed in the organic layer.

Chromium (III) chloride

It is obtained by passing dry chlorine over heated chromium metal or over a mixture of chromium (III) oxide and carbon at red heat.

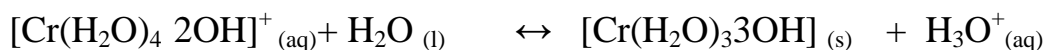


Note that chromium (III) salts are hydrolysed by water.

The acidity of the hexaaquachromium (III) ions

In aqueous solution, soluble salts of chromium in +3 oxidation state i.e. CrCl_3 , $\text{Cr}(\text{SO}_4)_3$ etc exist as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

The resultant solution is acidic due to hydrolysis reaction.



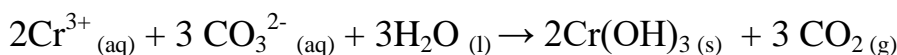
Over all equation:



(Green ppt)

The hydroxonium ions produced make the resultant solution acidic with pH less than 7 and a green solid is formed.

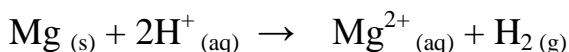
Note that if sodium carbonate solution is bubbled through aqueous solution of chromium (III) salts, bubbles of a colorless gas that turns lime water milky are given off.



If magnesium ribbon is added to aqueous chromium (III) salt, a colorless gas that burns with a pop sound is liberated.



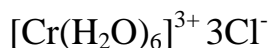
or



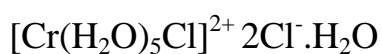
Similar reactions occur with aqueous solution of aluminium salts & iron (III) salts.

Hydrated Chromium(III) Chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

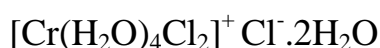
This salt of chromium exhibits hydration isomerism i.e existence of compounds with the same molecular formula but different structural formula. The following are the isomers of hydrated chromium(III) chloride:



(Hex-aqua-chromium(III) chloride),



(Chloropentaquachromium (III) chloride monohydrate).



(Dichlorotetra-aqua chromium (III) chloride dihydrate).

Identification/test of the isomers

1. *Using silver nitrate solution*

The first isomer precipitates 3moles of silver chloride because all the 3Cl^- ions are not directly bonded to the central metal cation.

The 2nd isomer precipitates 2moles of silver chloride.

The 3rd isomer precipitates 1mole of silver chloride.

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. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and 3Cl^-

The 2nd isomer contains 3moles of conducting ions i.e. $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ and 2Cl^-

The 3rd isomer contains 2moles of conducting ions i.e. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ and Cl^-

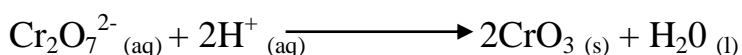
Compounds of chromium in +6 oxidation states

Because of the high charge density of Cr^{6+} ion, it can only exist as Oxo - ions. eg , CrO_3 , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$

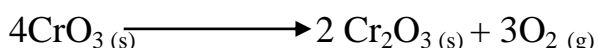
Chromium in +6 oxidation state

Chromium (VI) oxide

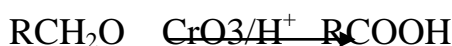
It is prepared by treating a saturated solution of potassium dichromate (VI) with conc. Sulphuric acid and the mixture cooled. Dark red crystals of chromium (VI) oxide are formed.



It decomposes at 257°C to chromium (III) oxide and oxygen gas.



It is soluble in propanone or ethanoic acid. Its solution in the acid is used as an oxidising agent in organic chemistry. i.e



It is deliquescent and very soluble in water. It dissolves in water to give chromic (VI) acids. The two most important acids it forms are chromic (VI) acid, H_2CrO_4 and dichromic (VI) acid, $\text{H}_2\text{Cr}_2\text{O}_7$.

Salts of chromium (VI) are yellow and those of dichromic (VI) acid are orange.

Chromate (VI) ion, CrO_4^{2-}

Chromates are salts of chromic acid, they have a characteristic yellow color e.g K_2CrO_4 and Na_2CrO_4 . It (the ion) has a tetrahedral structure.

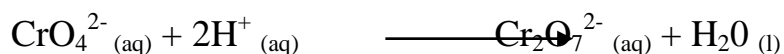
Chromates are obtained when an alkaline solution is added to a solution of dichromate ions.



Orange

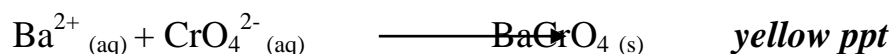
yellow

Chromates are stable in alkaline medium, however Chromates react with acids to form dichromate.



Note that sodium chromate and potassium chromate are both soluble, however potassium chromate is preferred to sodium chromate because it is not deliquescent.

There are several insoluble chromate (VI) salts and can be obtained by adding potassium chromate solution to any solution of corresponding metal salt. e.g



Similar observation with Pb^{2+} , but with Ag^+ , a red ppt is formed

ALUMS

Alums are double sulphate salts with general formula $\text{M}_2\text{SO}_4 \cdot \text{M}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

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:

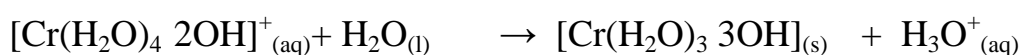
Chrome alum, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Its solution in water is acidic because the chromium (III) ions undergo hydrolysis leaving the solution acidic.

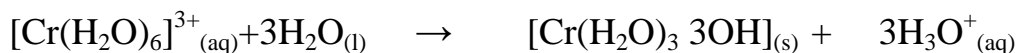
The complex ion is acting as an acid by donating a hydrogen ion to water molecules in the solution.

The water is, of course, acting as a base by accepting the hydrogen ion.



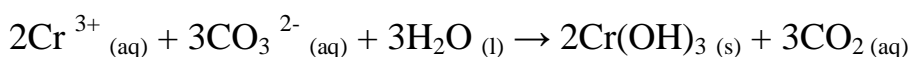


Over all equation



The accumulation of hydroxonium ions renders the resultant solution acidic.

If aqueous sodium carbonate is added, an effervescence of a colorless gas which turns lime water milky is formed and a green solid.

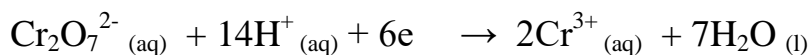
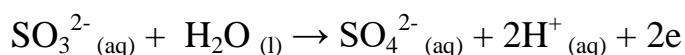
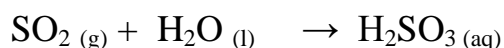


2) *Potash alum*, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

3) *Ammonium alum*, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Preparation of Chrome Alum

By bubbling sulphurdioxide gas into a solution of acidified potassium dichromate, chrome alum is formed.



The ions present after the above reactions are in the correct proportion for the formation of chrome alum on crystallizing.

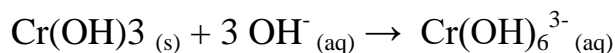
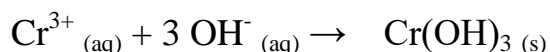
Test for Cr^{3+} ions in solution

Use of sodium hydroxide solution

Observation

Dark green precipitate, soluble in excess to form deep green solution.

Equations

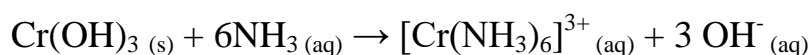
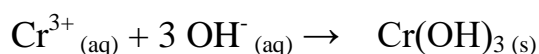


Use of aqueous ammonia solution

Observation

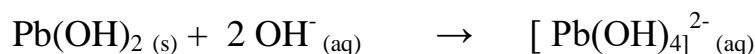
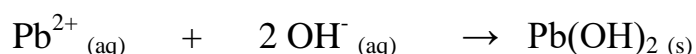
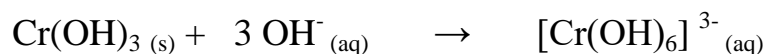
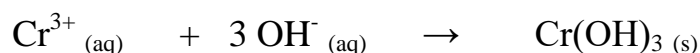
Green precipitate slowly dissolves in excess concentrated ammonia solution to form a purple solution.

Equations

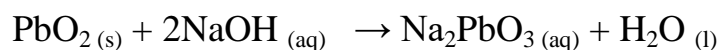
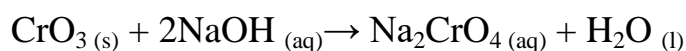


Similarities in the chemistry of chromium & lead

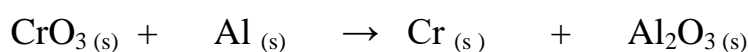
Cr^{3+} and Pb^{2+} form complex with sodium hydroxide solution.



Both their oxides in higher oxidation states are acidic.



Their oxides in higher oxidation states are strong oxidizing agents.



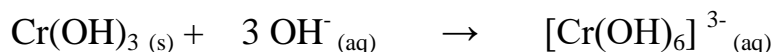
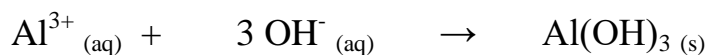
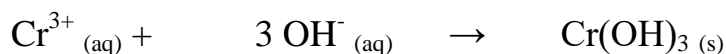
They both form compounds with variable oxidation states i.e

Lead :+2 & +4 and Chromium: +2, +3 & +6

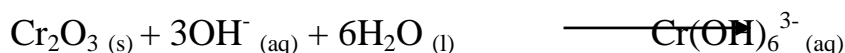
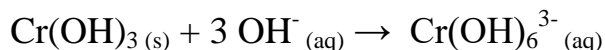
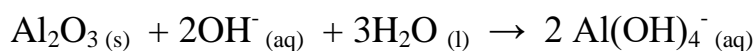
Chromium and Lead in higher oxidation states Cr^{6+} and Pb^{4+} form covalent compounds e.g PbCl_4 and CrCl_6

Similarities in the chemistry of Chromium & Aluminium

Cr^{3+} and Al^{3+} form complex with sodium hydroxide solution.



Their hydroxides and oxides react with alkalis.



Question 1

Write the electronic configuration of the following species (Cr= 24).

Cr

Cr^{2+}

Cr^{3+}

Cr^{6+}

State the common oxidation states of chromium.

Aqueous sodium hydroxide was added drop wise to a solution containing Cr^{3+} , state

what was observed and write equation for the reaction that took place.

d) Discuss using equations where applicable the reactions of chromium with:

air

water

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 that

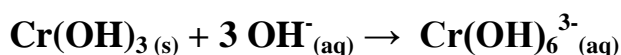
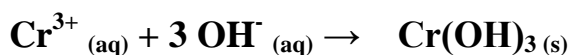
Chromium adopts the above electronic configuration rather than the expected $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$ because the 3d is half filled unlike in the expected configuration therefore it is more energetically stable.

b) +2, +3, +6

c) Observation

Green precipitate, soluble in excess to form deep green solution.

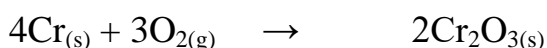
Equations



d)

i) With Air (oxygen)

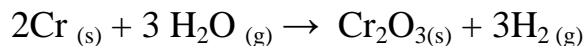
Chromium does not react with oxygen at room temperature, when heated it forms green chromium (III) oxide.



green solid

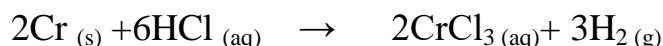
ii) With water.

Chromium reacts with steam to form green chromium (III) oxide and hydrogen gas.



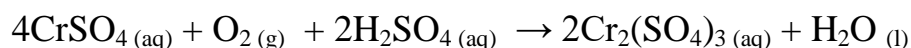
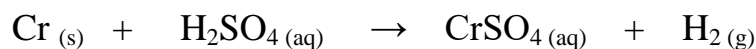
iii) With acids.

Chromium reacts with dilute hydrochloric acid forming green chromium (III) chloride solution and liberating hydrogen gas.

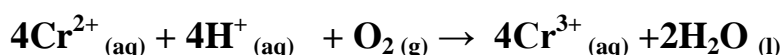
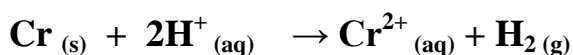


Chromium reacts with dilute sulphuric acid forming blue solution of chromium (II) sulphate and liberating hydrogen gas.

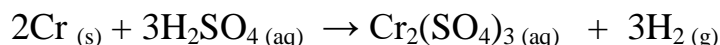
The blue solution turns to green when exposed to air. This is due to aerial oxidation of Cr^{2+} to Cr^{3+} ions.



Ionicallly:



Chromium reacts with dilute sulphuric acid on heating to form chromium (III) sulphate and hydrogen gas



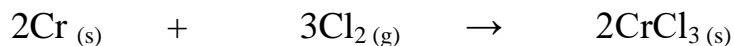
Chromium reacts with hot conc. sulphuric acid to form chromium (III) sulphate, sulphur dioxide and water.



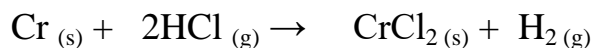
Note that chromium does not react with nitric acid due to the formation of a thin layer of chromium (VI) oxide which renders it passive towards nitric acid.

iv) With chlorine

If chlorine gas is passed over heated chromium, green solid of chromium (III) chloride is formed.

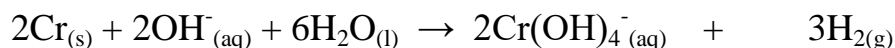


Note that if hydrogen chloride is used instead, chromium (II) chloride is formed.

**V) With sodium hydroxide solution.**

Chromium dissolves to give:

a colorless gas that burns with a pop sound and a green solution is formed.

**ZINC AND ITS COMPOUNDS**

(Atomic number = 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, ZnCO_3

Extraction process from sulphide ore

The ore contains traces of lead sulphide and silica as impurities.

Concentration process

The ore is first crushed and mixed with water and oil (a frothing agent) so as to remove

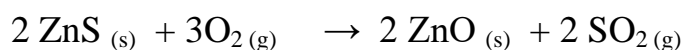
the unwanted earthly materials. The oil wets the sulphide particles and the water wets the impurities.

Air is then blown through the mixture producing a 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.



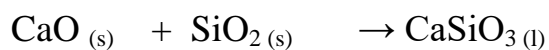
Reduction

Zinc oxide, limestone (CaCO_3) and excess coke are then heated in a blast furnace.

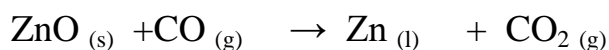
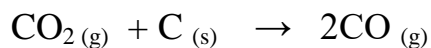
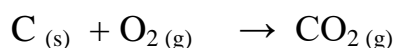
Limestone decomposes into calcium oxide and carbon dioxide gas.



The calcium oxide reacts with silica, one of the impurities to form calcium silicate (slag).



Coke burns to carbon dioxide, which is reduced by unburnt coke to carbon monoxide. The carbon monoxide reduces zinc oxide to zinc.



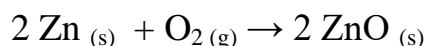
The slag sinks to the bottom and can be removed whereas the zinc produced leaves as vapor at the top of the blast furnace where it is cooled and allowed to solidify.

Reactions of zinc

a) With air

On exposure to air, zinc develops a thin layer of zinc oxide. This layer prevents further reaction with the oxygen present in air.

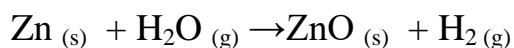
Zinc burns in air (oxygen) to form zinc oxide.



(yellow when hot and white on cooling)

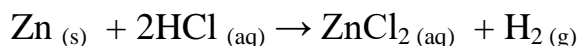
b) With water

Zinc (red hot) reacts with steam to form zinc oxide and hydrogen gas.

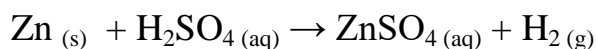


c) With acid

Zinc reacts with both dilute and conc. hydrochloric acid forming salt and hydrogen gas.



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



Reaction of zinc with conc. H_2SO_4 produces Zinc sulphate, sulphurdioxide and water as the products.

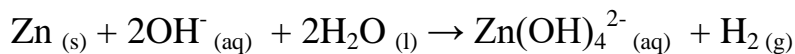


Note that

The products for the reaction with nitric acid (both dilute and conc.) are not easily defined.

d) With alkalis

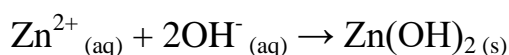
Zinc react with aqueous alkalis to form zincates' complex and hydrogen gas.



Compounds of zinc

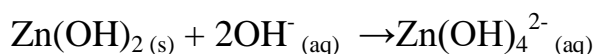
Zinc hydroxide

It is prepared as a white precipitate on addition of a little sodium hydroxide or aqueous ammonia to a solution containing zinc ions.

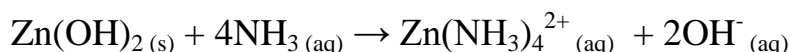


White ppt

The hydroxide is amphoteric. It dissolves in excess sodium hydroxide to form sodium zincates complex.



In aqueous ammonia, zinc hydroxide dissolves forming a colorless solution of tetra amine zinc ion.



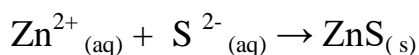
Zinc sulphide

This is prepared as a white precipitate on passing hydrogen sulphide through a solution of zinc ions.

When H₂S gas is passed through a solution of a metallic salt, a metallic sulphide is formed but if the H₂S is passed through an acidic solution of a metallic salt, the sulphide may not be formed.

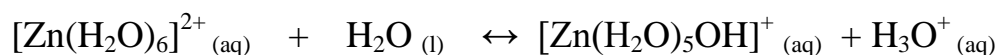
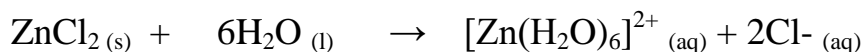
Explanation





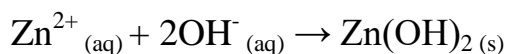
If before bubbling hydrogen sulphide the solution is acidified, the excess H^+ ions present suppresses the formation of sulphide ions in 1st equation above and therefore the concentration of sulphide ions will be too low to precipitate zinc sulphide.

Aqueous solution of zinc chloride is acidic due to hydrolysis of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ complex.



Test for zinc ions in solution

1) Addition of aqueous sodium hydroxide drop wise to a solution of Zn^{2+} ions produces a white ppt which dissolves in excess to form a colorless solution.

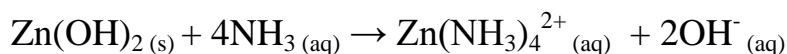
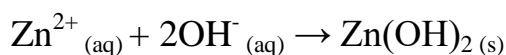


White ppt



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) Addition of potassium ferrocyanide solution to a solution of Zn^{2+} ions produces a white precipitate soluble in sodium hydroxide.

- 4) Addition of ammonium sulphide solution produces a white ppt soluble in dilute HCl acid.
- 5) Using disodium hydrogen phosphate, white ppt is formed with zinc ions.

Uses of zinc

Making alloys e.g. Brass is alloy of zinc and copper.

Galvanizing iron since zinc is higher than iron in electrochemical (reactivity) series.

Note that 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 ZnO which prevents further attack.

IRON AND ITS COMPOUNDS

(Atomic number: 26)

Ores of iron

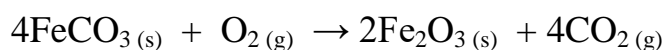
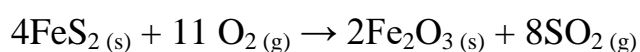
Haematite , Fe_2O_3

Magnetite , Fe_3O_4

Iron Pyrite , FeS_2

Siderite , FeCO_3

The first two ores are used directly but the last two must be first roasted in air to convert them to stable iron (III) oxide. e.g



Extraction of iron

Iron is extracted from its ore called haematite (Fe_2O_3) in a blast furnace.

The raw materials used in the extraction are:

The ore, Haematite

Coke

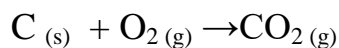
Limestone (calcium carbonate)

Hot air

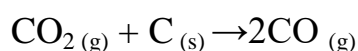
The hot blast of air enters the blast furnace through narrow pipes called Tuyeres located at the lower part of the furnace. The other materials are fed into the furnace from the top.

Reactions taking place in the blast furnace

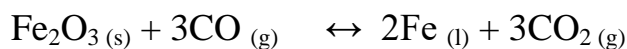
In the presence of hot air coke burns to produce carbon dioxide gas.



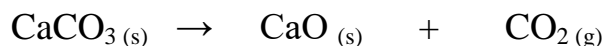
As the carbon dioxide ascends, it reacts with unburnt coke to form carbon monoxide.



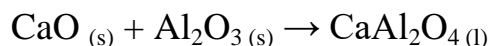
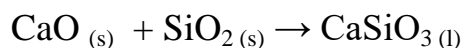
The carbon monoxide produced reduces the ore to iron.



The role of the limestone is to remove impurities like silica (SiO_2).



The quick lime then combines with silica and alumina present as impurities to form slag.



Molten iron and slag both sink to the bottom of the furnace and they can be tapped off separately. The molten iron is at the bottom covered by slag to prevent further re-oxidation.

The molten iron solidifies on cooling to form PIG iron.

Properties of pig iron:

Low melting point.

Impure e.g. 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

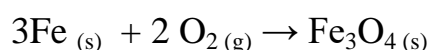
The Bessemer process

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.

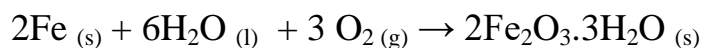
Reactions of iron

a) With air

Iron combines with oxygen when heated to form black solid of tri-iron tetra oxide.

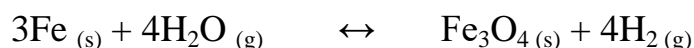


Iron reacts with moist cold air to form brown hydrated iron (III) oxide or rust.



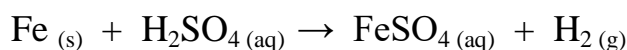
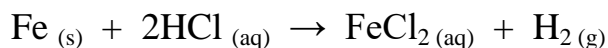
b) With water

Heated iron reacts with steam to form black triiron tetraoxide.



c) With acid

Iron reacts with dilute acids (HCl & H₂SO₄) to form hydrogen gas and iron (II) salts.

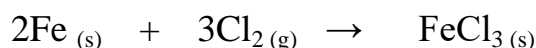


Hot conc. sulphuric acid oxidizes iron to iron (III) sulphate, sulphur dioxide and water.



d) With halogens

Heated iron reacts with dry chlorine gas to form iron (III) chloride.



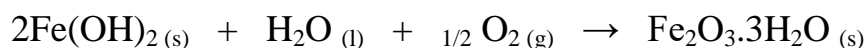
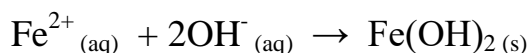
Compounds of iron

+2 oxidation state

In aqueous solution exists as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ which is a green solution. It undergoes hydrolysis making the resultant solution acidic.

a) Iron (II) hydroxide

It is 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.



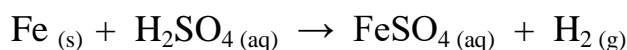
Note that

Similar reaction occurs on addition of ammonia solution to aqueous Fe^{2+} solution.

b) Hydrated iron (II) sulphate. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

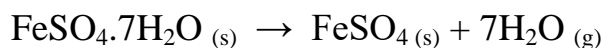
It is prepared by heating iron fillings with dilute sulphuric acid and crystallizing the salt from solution.

During the crystallization process, hydrated iron (II) sulphate forms as green crystals.

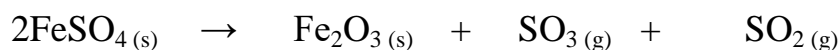


Action of heat on hydrated iron (II) sulphate

On gentle heating



On further heating



If conc. nitric acid is added to iron (II) sulphate, the green solution turns to yellow/brown due to formation of iron (III) ions.

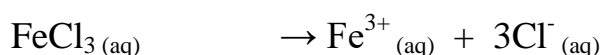
+3 oxidation state

This is the most stable oxidation state of iron.

The soluble salts in this oxidation state exist as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and undergo hydrolysis in water making resultant solution acidic.

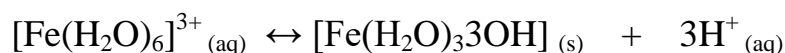
e.g. a solution of iron (III) chloride turns blue litmus red.

The Fe^{3+} ion is small and highly charged. It undergoes hydrolysis in aqueous solution to release hydrogen ions or hydroxonium ions that make the resultant solution acidic.



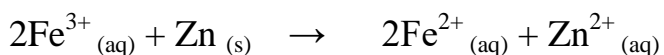
Brown ppt

or

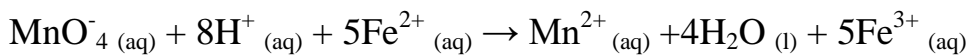


On addition of zinc powder to a brown/ yellow solution of iron (III), the color of the

solution changes to green.



The resultant solution can now be titrated with acidified solution of standard potassium permanganate.

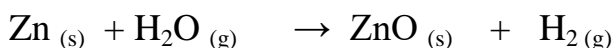


On bubbling hydrogen sulphide gas to a solution containing Fe^{3+} ions, the color of the solution changes from brown to green with formation of a yellow solid.

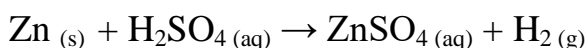
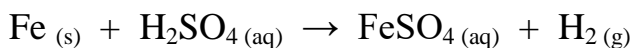


Similarities in the chemistry of Zn and Fe

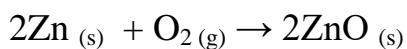
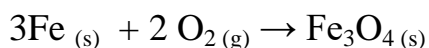
Both metals when heated (red hot) react with steam to form oxide and hydrogen gas.



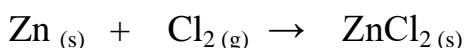
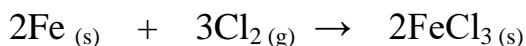
Both react with dilute acid (HCl & H_2SO_4) to liberate hydrogen gas.



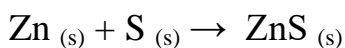
Both metal when heated react with oxygen to form oxide.

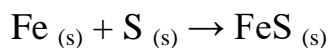


Both metals when heated react with chlorine to form chloride.



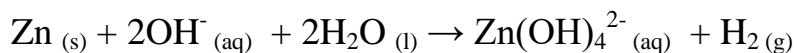
Both elements react with sulphur to form sulphide.





Differences in the chemistry of Zn & Fe

Zn dissolves in conc. alkalis forming hydrogen gas but iron does not.



2. Zn shows a single valence of +2 while iron exhibits variable valences of +2 & +3.
3. Zn forms compounds that are white in color whereas 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 .
- 6) Zinc does not react with cold moist air. Iron reacts with moist air to form hydrated iron (III) oxide (rust).

Qn. State the similarities in the chemistry of zinc & magnesium.

COPPER AND ITS COMPOUNDS

(Atomic number: 29)

Electronic configuration: $1S^2 2S^2 2P^6 3S^2 3P^6 3d^{10} 4S^1$

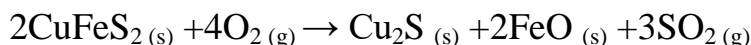
Ores of copper

1. copper pyrite, $CuFeS_2$
2. malachite, $CuCO_3 \cdot Cu(OH)_2$

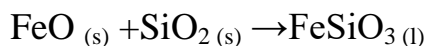
Extraction of copper (from pyrite ore)

The ore is first ground to powder. The finely divided ore is then mixed with water and oil (frothing agent). The earthly materials sink at the bottom because of their high density whereas the ore particles float on top, where they are removed, washed and dried.

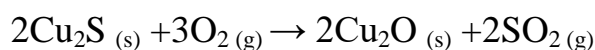
The ore is roasted to convert the copper pyrite to copper (I) sulphide, iron (II) oxide and sulphur dioxide.



The solid product is transferred into a blast furnace and silica added. On strong heating, the iron (II) oxide reacts with silica to form slag.

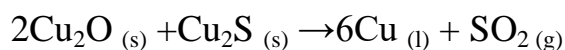


The copper (I) sulphide reacts with air forming copper (I) oxide.



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.



The copper formed solidifies on cooling and is called blister copper and contains impurities. The last process in the extraction is purification of blister copper.

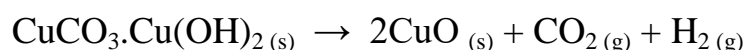
Extraction from malachite

Concentration process.

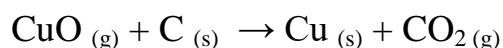
The ore is ground to powder. The finely divided ore particles is mixed with water and oil and shaken for a while.

The earthly materials (high density) sink at the bottom whereas the ore particles (low density) float on the surface, where they are removed, washed and dried.

The ore is roasted to form copper (II) oxide.

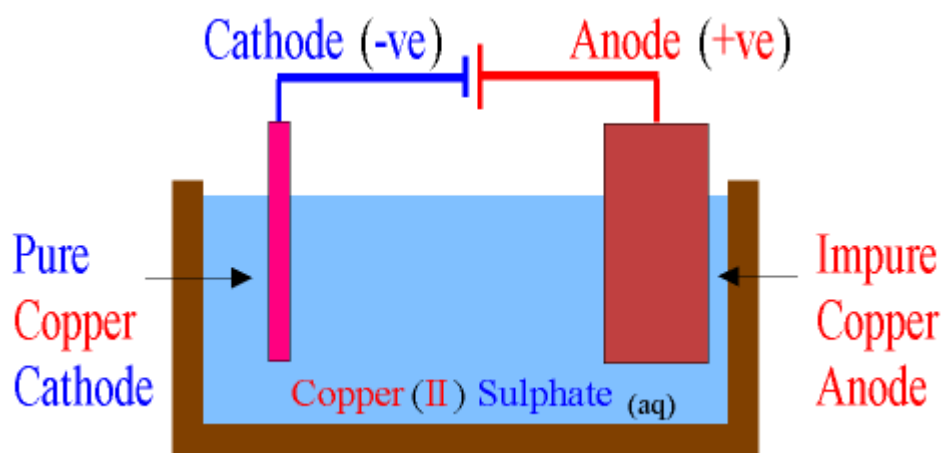
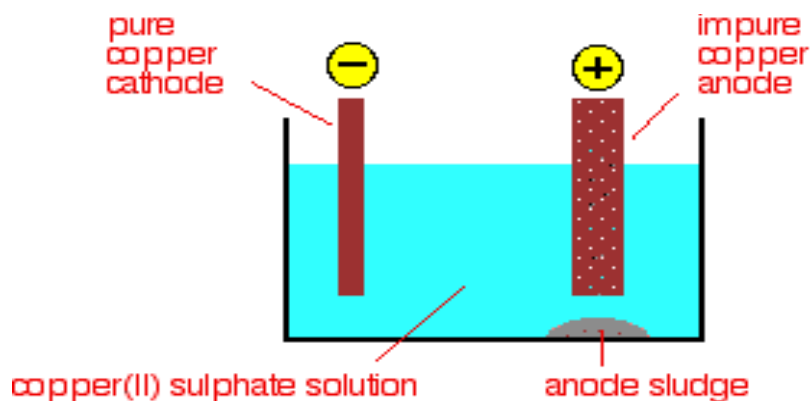


The copper (II) oxide is reduced with carbon on heating to copper.



The copper formed is then purified by method of electrolysis.

Purification of Copper –Electrolysis



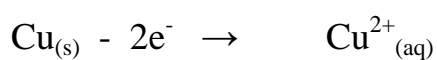
The anode is a block of impure copper.

The cathode is a thin piece of pure copper.

The electrolyte is copper (II) sulphate solution.

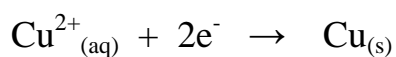
At the anode

Copper is dissolved by oxidation, Cu^{2+} ions go into solution.



At the cathode

Copper is deposited by reduction.



As copper ions move from the anode to the cathode, the anode gets smaller and the

cathode gets bigger.

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.

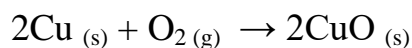
Coinage. Copper-colored coins, "silver" coins are also copper alloys - this time with nickel. These are known as cupronickel alloys. UK pound coins and the gold-colored bits of euro coins are copper-zinc-nickel alloys.

Reactions of copper

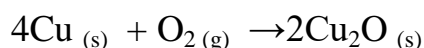
a) With air

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.

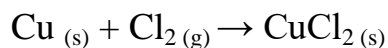


At very high temperature > 800 °C, copper reacts with oxygen to form copper (I) oxide.



b) With halogens.

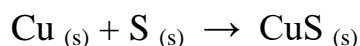
Heated copper reacts with halogen to form copper (II) halide.



However copper reacts with iodine to form copper (I) iodide.

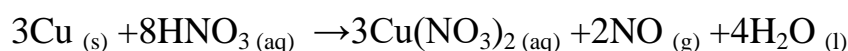
c) With sulphur.

When heated, copper forms a sulphide.

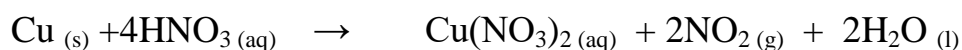


d) With acids.

i) Dilute nitric acid reacts with copper to form copper (II) nitrate, nitrogen monoxide and water.



ii) Copper reacts with concentrated nitric acid to form copper (II) nitrate, nitrogen dioxide gas and water.



iii) Copper reacts with concentrated sulphuric acid to form copper (II) sulphate, sulphur dioxide and water.



Compounds of copper

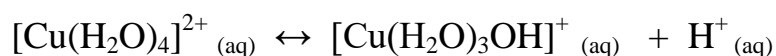
Copper shows 2 oxidation states of +1 and +2, however compounds in +1 oxidation state are unstable.

Compounds in +2 oxidation states

This is the most stable oxidation state of copper and in aqueous solution exists as

$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ which is a blue solution.

It slowly undergoes hydrolysis forming acidic solution.



Determination of copper (II) ions in copper (II) salts

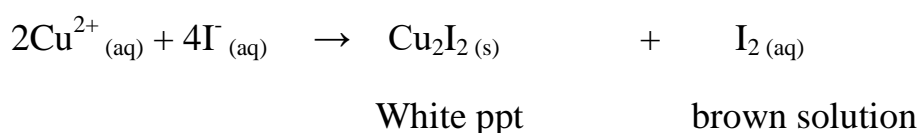
Method1

Applicable to any soluble salt of copper.

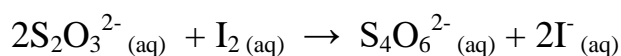
(starting from copper ore, dissolve the ore in dilute sulphuric acid)

Procedure

To a solution containing copper (II) ions is added excess potassium iodide solution, a white precipitate of copper (II) iodide is formed which is stained brown by the liberated iodine.



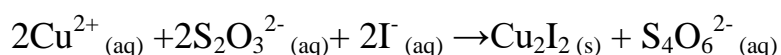
The amount of iodine liberated is then determined by titrating the resultant solution with a standard solution of sodium thiosulphate using starch indicator.



The volume of thiosulphate solution used is noted.

Treatment of results

The overall equation of reaction is obtained by adding the two equations above :



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.

MANGANESE AND ITS COMPOUNDS

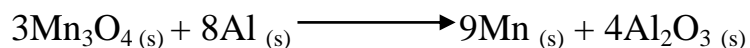
(Atomic number: 25)

The electronic configuration of manganese is $1S^2 2S^2 2P^6 3S^2 3P^6 4S^2 3d^5$.

It is a hard grey metal that occurs naturally as *pyrolusite* (impure MnO_2).

Extraction

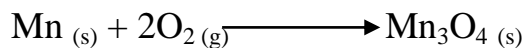
It is extracted by electrolysis of Manganese (II) salts or by thermit process using Mn_3O_4 and aluminium.



Chemical properties of manganese

Reaction with air

Heated manganese burns in air (oxygen) to give red trimangnesetetroxide.



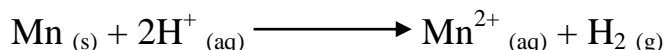
Reaction with water

Manganese reacts with hot water to form manganese(II) oxide.

Reaction with acids

With dilute acids.

Manganese displaces hydrogen from dilute hydrochloric acid and dilute sulphuric acid to form corresponding manganese (II) salts.

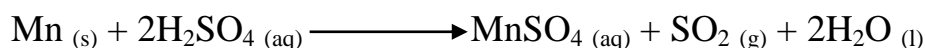


With concentrated acids.

Manganese reacts with concentrated nitric acid to give Manganese (II) nitrate, nitrogen dioxide and water.

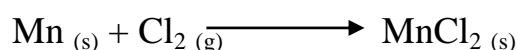
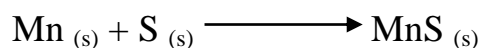
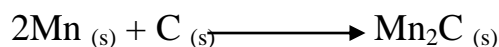
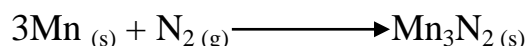


It reacts with concentrated sulphuric to form manganese (II) sulphate, sulphur dioxide and water.



Reaction with non-metals.

It reacts with non-metals on heating to give corresponding manganese (II) salts.



Compounds of manganese

Manganese can exist in +2, +3, +4, +6 and +7 oxidation states.

Manganese in +2 oxidation state

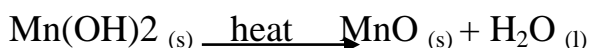
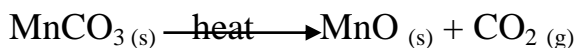
In +2 oxidation state, the two 4s electrons are lost leaving a half filled 3 d orbital which is stable. Therefore the Mn^{2+} ion is the most stable ion of manganese.

Compounds

Manganese (II) oxide

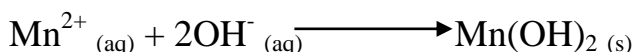
It is a grey - green solid obtained by heating manganese (II) carbonate, manganese (II)

oxalate or manganese (II) hydroxide.



Manganese (II) hydroxide

It is a white solid precipitated by addition of aqueous alkali, the ppt readily turns brown due to oxidation by air to form hydrated manganese (IV) oxide.



White ppt

On exposure to air,

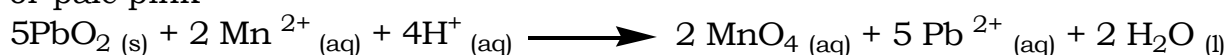
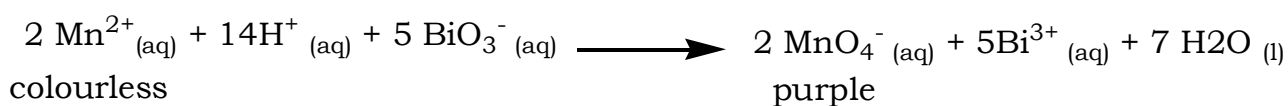


Brown solid

Manganese(II) salts

The chlorides, nitrates and sulphates of manganese(II) salts are pale pink when hydrated. They dissolve in water giving a pale pink solution. The solutions of manganese(II) salts can be oxidised to purple manganate(II) ions by either sodium

bismuthate(V) or lead(IV) oxide in presence of concentrated nitric acid.



The above reactions are used to confirm the presence of M^{2+} ions in solution.

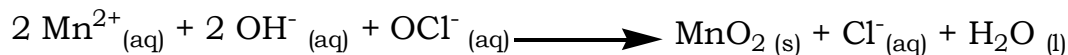
Manganese in + 4 oxidation state

Manganese(IV) oxide

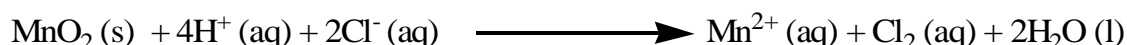
Manganese(IV) oxide is a black solid when anhydrous, brown when hydrated. It occurs naturally or as pyrolusite and can be prepared by heating manganese(II) nitrate at about 280°C .



It can as well be obtained by alkaline oxidation of manganese(II) salts by sodium hypochlorite.



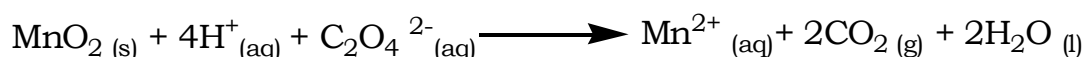
Manganese(IV) oxide oxidises conc. HCl on heating to give chlorine gas.



It oxidises iron(II) to iron(III) in presence of hot dilute sulphuric acid.



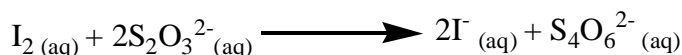
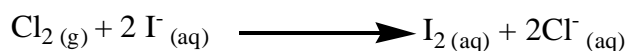
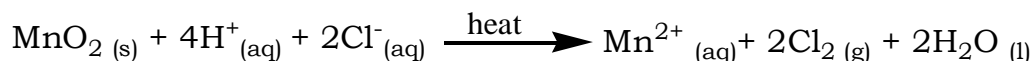
It also oxidises oxalic acid to carbon dioxide in presence of dilute sulphuric acid on heating.



Any of the above reactions can be used to estimate the percentage of manganese(IV) oxide in its minerals(pyrolusite).

Determination of percentage of manganese(IV) oxide in its mineral using $\text{S}_2\text{O}_3^{2-}$ solution

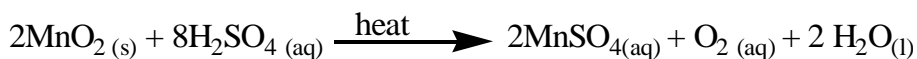
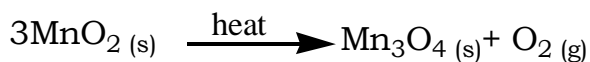
A weighed sample is treated with hot conc. HCl and the liberated chlorine is passed through excess potassium iodide solution. The liberated iodine is titrated against standard sodium thiosulphate solution in presence of starch indicator.



Overall equation



Manganese(IV) oxide liberates oxygen when strongly heated. i.e



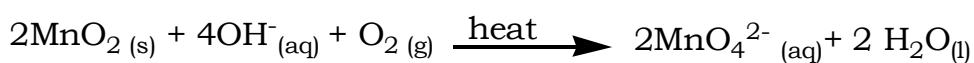
Note that manganese(IV) oxide is amphoteric. It can react with both acids and bases.

Compounds of manganese in the +6 oxidation state

Consider manganate(VI) ion, MnO_4^{2-}

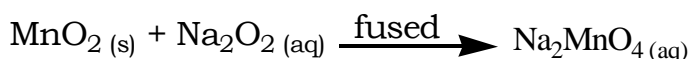
Potassium manganate(VI)

It is prepared by fusing manganese(IV) oxide and potassium hydroxide in air.

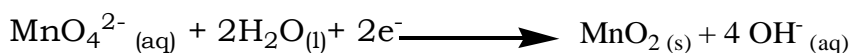


Sodium manganate(VI)

It can be prepared in the same way or by fusing manganese(IV) oxide with sodium peroxide.

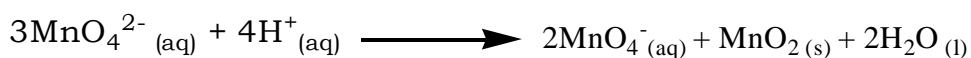


Manganate (VI) is quite a powerful oxidising agent. It is stable in alkaline solutions. i.e



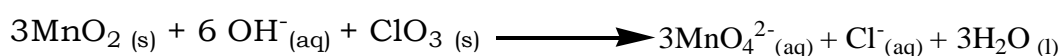
In acidic or neutral medium, the solution turns from green to purple with dark brown precipitate because manganate(VI) ion disproportionates in acidic or neutral medium.

In acidic medium:



Compounds of manganese in the +7 oxidation state

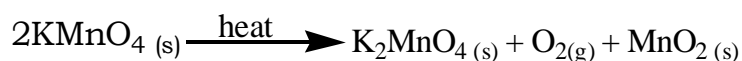
Potassium permanganate. It is prepared by fusing manganese(IV) oxide with potassium hydroxide and an oxidising agent added to give green manganate(VI). Potassium manganate(VI) is then extracted with water and oxidised to potassium manganate(VII) using chlorine.



Properties of potassium permanganate

The crystals are dark blue and relatively soluble in water to give a purple solution containing manganate(VII) ions.

Potassium manganate(VII) decomposes on heating to oxygen, potassium manganate(VI) and manganese(IV) oxide.

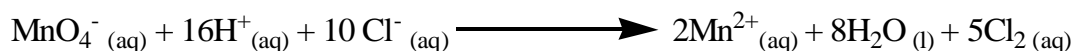


Oxidising action

Potassium manganate(VII) is used in dilute sulphuric acid. Under these conditions, it is reduced to manganese(II) ions.



Hydrochloric acid is not used since the chloride ions from the acid are oxidised by the permanganate ions to chlorine which is greenish yellow gas and its colour interferes with the endpoint.



Nitric acid cannot be used to acidify manganate(VII) solutions because it is a strong oxidising agent and will compete with the permanganate ions during the reaction.

Examples of oxidation reactions involving potassium permanganate

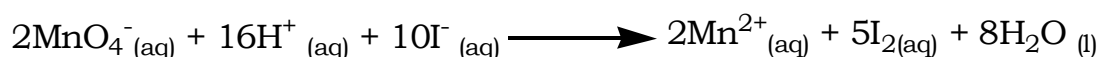
It oxidises iron(II) to iron(III) ions making the colour of solutions change from green to yellow.



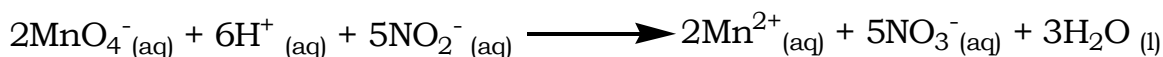
It oxidises ethanedioate ions (oxalate) ions to carbon dioxide.



It oxidises iodide ions to iodine.



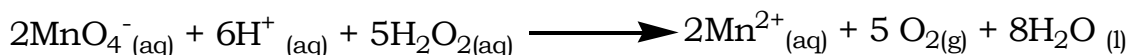
It oxidises nitrite ions to nitrate ions.



It oxidises sulphite ions to sulphate ions.



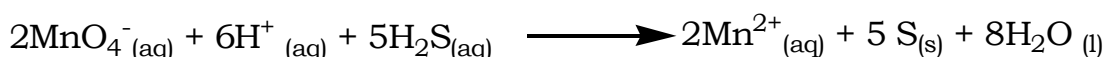
It oxidises hydrogen peroxide to oxygen.



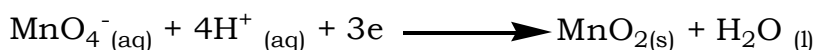
Question

Hydrogen sulphide was passed through a solution containing acidified potassium permanganate. State what was observed and write equation for the reaction that took place.

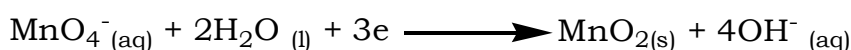
Solution: Purple solution turned colourless and a yellow solid was deposited.



Note that in neutral or alkaline solution, permanganate ions are reduced to manganese(IV) oxide.



In faintly alkaline solution,



In slightly acidic solution, permanganate decomposes to manganese(IV) oxide and oxygen gas.



Potassium permanganate is not used as a primary standard in volumetric analysis because it decomposes to give manganese(IV) oxide.

Question

a) Write the electronic configuration of the following species

i) Mn



b) i) State the most stable oxidation state of Manganese. Give a reason for your answer.

ii) State the possible oxidation states of manganese.

iii) Explain why manganese show variable oxidation states.

c) 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.

d) i) Give a formula of a compound or ion containing Mn in an oxidation state of +7

ii) How do you account for the existence of the +7 oxidation state?

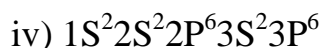
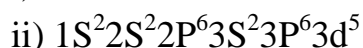
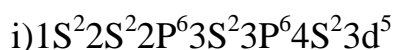
e) Write equation to show the reduction of MnO_4^- in

i) alkaline medium.

ii) acidic medium.

f) Discuss the chemistry of manganese and magnesium showing similarities.

Answers



i) 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.

ii) +2, +3, +4, +5, +6, +7.

Acidity of the oxide of manganese increases with the increasing oxidation state.

iii) The variable oxidation state of manganese is due to the fact that both the 4s and the

3d- electrons take part in bond formation.

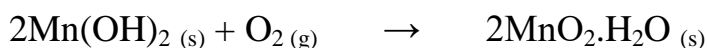
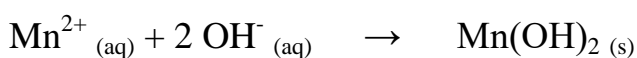
This is because electrons are being removed from energetically similar 4s and 3d- orbitals.

For +2 oxidation state, 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.

c) **Observation**

White precipitate, insoluble in excess and rapidly turns brown due to aerial oxidation.

Equation

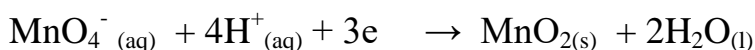
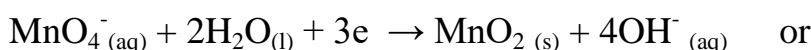


Note that similar observation and reaction occurs with aqueous ammonia solution.

d) i) MnO_4^{-}

ii) Manganese $1\text{S}^2 2\text{S}^2 2\text{P}^6 3\text{S}^2 3\text{P}^6 4\text{S}^2 3\text{d}^5$, shows an oxidation state of +7 by using both the 4s and 3d- electrons in the bond formation because they are energetically similar.

e)i)



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



Note that KMnO_4 has a wide applications in the laboratory as an oxidizing agent which include the following:

As an indicator in volumetric analysis to show end points of titrations.

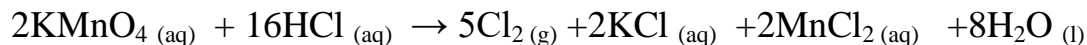
To test for reducing agents e.g. sulphurdioxide.

Estimating iron (II) salts and oxalates.

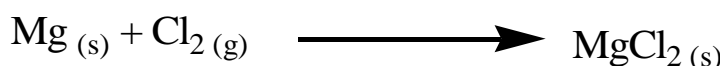
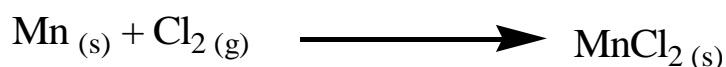
Preparation of gases e.g. chlorine gas is liberated when conc. hydrochloric acid is reacted with it.

Note that

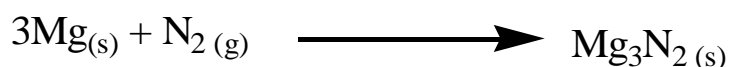
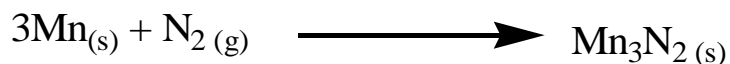
Hydrochloric acid is not used to acidify KMnO_4 during titration because KMnO_4 is a very strong oxidising agent, oxidises Cl^- ions from hydrochloric acid to chlorine which colors the whole solution pale green and makes it difficult to estimate end point.



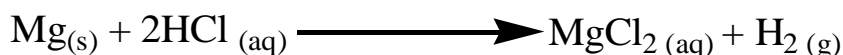
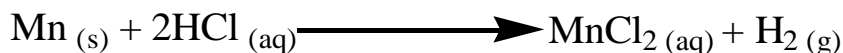
f) They both react with chlorine to form chloride when heated.



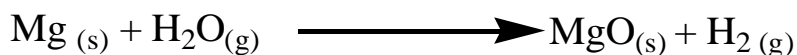
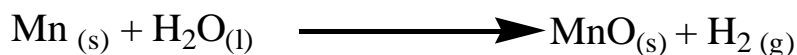
They both react directly with nitrogen to form similar nitrides



They both react with dilute hydrochloric acid to liberate hydrogen gas.



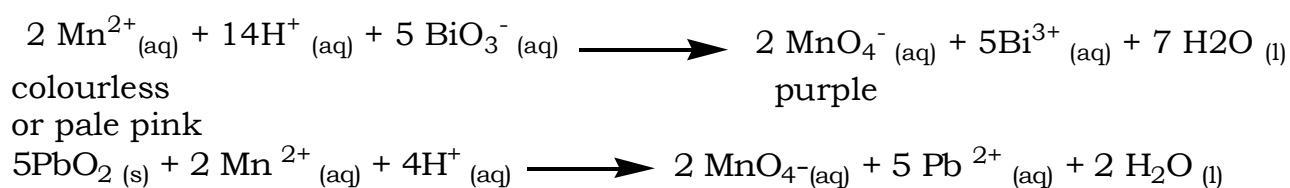
Manganese reacts with hot water to form oxide. Magnesium react with steam in the same way.



Confirmatory test of Manganese, Mn^{2+} ions in solution

To solid manganese (II) salt is added concentrated nitric acid and little solid lead (IV) oxide or sodium bismuthate solution and the mixture boiled. A purple solution forms if

Mn²⁺ ions are present.



Question 1

a) Write the electronic configuration for each of the following transition metal atoms and ions.

i) Cu

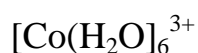
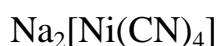
ii) Mn³⁺

iii) Ni²⁺

iv) Co

b) Indicate the coordination number and the oxidation number of the metal in each of the following coordination compounds and complexes.

c) Give the correct IUPAC name for each of the following coordination compounds.

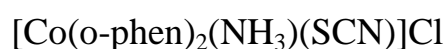


Question 2

Give the indicated isomers for each of the following coordination compounds and complexes.

Structural formula for the linkage isomer of $[\text{Cr}(\text{H}_2\text{O})_5(\text{NO}_2)]\text{I}$

Structural formula for the coordination-sphere isomer of



Question 3

For each of the following sets, state the coordination number and oxidation state of the central metal atom.

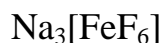
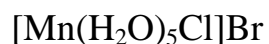
**Question 4**

Write the electronic configuration for each of the following transition metal atoms and ions.



Give the coordination and oxidation numbers for the transition metal atom in each of the following coordination compounds.

Name each of the following coordination compounds using the IUPAC rules.



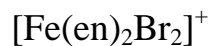
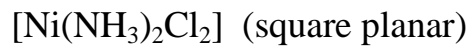
Write the correct structural formula for the isomers indicated for each of the following coordination compounds. (*Note that a structural formula is a chemical formula that shows how the atoms are bonded to one another in a molecule. For example $\text{Na}[\text{FeCl}_4]$ is a structural formula*).

linkage isomer of $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}$

ionization isomer of $[\text{Fe}(\text{NH}_3)_5\text{I}]\text{Br}_2$

Question 5

Draw all possible stereoisomers for each of the following complexes.



Describe briefly how the following metals can be extracted.

Zinc

Copper

Iron

For each of the compounds given, state the co-ordination number and oxidation state of the central atom and then give the name.

