OXIDATION AND REDUCTION REACTIONS

Oxidation is the removal of electrons from a substance while reduction is the addition of electrons to a substance.

An oxidation reaction is a reaction in which electrons are removed from a substance.

For example;

$$\mathbf{Zn(s) \longrightarrow Zn^{2+}(aq) + 2e}$$

$$\mathbf{Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e}$$

A reduction reaction is a reaction in which electrons are added to a substance.

For example;

$$\mathbf{Cu^{2+}(aq) + 2e \longrightarrow Cu(s)}$$

$$\mathbf{Cl_2(g) + 2e \longrightarrow 2Cl^-(aq)}$$

An oxidizing agent is a substance which removes electrons from another substance. It is also called an electron acceptor.

Examples of oxidizing agents include;

- Oxo ions of transition elements such as;
  - ✓ Manganate(VII) ion, also known as permanganate- MnO_4-
  - ✓ Dichromate(VI) ion – $Cr_2O_7^{2-}$
- Highly reactive non-metals like fluorine, chlorine
- Oxo ions of halogens for example
  - ✓ Iodate(V) ion IO_3^-
  - ✓ Chlorate(V) ion ClO_3^-
- Hydrogen peroxide H_2O_2
- Manganese(IV) oxide MnO_2

A reducing agent is a substance which adds electrons to another substance. It is also known as an electron donor.

Examples of reducing agents include;

- Highly reactive metals such as potassium, sodium, etc.
- Halides like iodide I^-, bromide Br^-
- Cations of transition and other multivalent elements in lower oxidation states such as;
  - ✓ Fe^{2+}
  - ✓ Sn^{2+}
  - ✓ Mn^{2+}
  - ✓ E.t.c

REDOX REACTIONS

A redox reaction is a reaction in which oxidation and reduction occur simultaneously.

It occurs between a reducing agent and an oxidising agent, hence the name *redox.*

The oxidising agent removes electrons from the reducing agent (while the reducing agent adds (donates) electrons to the oxidising agent), the oxidising agent becomes reduced while the reducing agent becomes oxidised.

OXIDATION STATES (OXIDATION NUMBER)

Oxidation state/number of an element is the charge which an atom of an element attains when all the atoms of other elements in the compound are removed (with the more electronegative element taking all the bonding electrons)

NOTE

A substance is said to be charged if its oxidation state changes from a lower value (a more negative or less positive value) to a higher value (a more positive value or less negative value)

Examples

1. In each of the following changes, state whether oxidation or reduction has taken place

a) Fe^{2+} to Fe^{3+}

Oxidation

b) Cl^- to Cl_2

----

c) Cu^{2+} to Cu

Reduction

d) MnO_4^- to Mn^{2+}

Rules for assigning oxidation states

1. The oxidation state of an element in its uncombined form is zero (0), examples

Element	**Oxidation state**
Cl_2	**0**
Zn	**0**
P	**0**

2. The oxidation state of a single ion of an atom is equal to the charge of the ion, for example;

Ion	**Oxidation state**
Fe^{2+}	**+2**
Fe^{3+}	**+3**
O^{2-}	**-2**
Cr^{3+}	**+3**

3. The oxidation state of oxygen its compounds is -2, except in;
   a) Peroxides like hydrogen peroxide (H_2O_2) and sodium peroxide (Na_2O_2) where it is -1
   b) Oxygen difluoride (OF_2) where it is +2
   c) Super oxides for example sodium super oxide (NaO_2) and potassium super oxide (KO_2) where it is -0.5 (-1/2)
4. The oxidation state of hydrogen in its compounds is +1 except in metallic hydrides like magnesium hydride (MgH_2), sodium hydride (NaH), e.t.c where it is -1
5. The oxidation states of all elements in a compound are equal to the overall charge of the compound or ion.
6. For elements or atoms bonded together, the oxidation state is arbitrarily given as 0, e.g the oxidation state for O_2 is 0

   Other compounds with 0 oxidation state include;
   - Carbonyl CO
   - Aqua H_2O
   - Amine NH_3
   - E.t.c

Group(I) elements have an oxidation state of +1

Group(II) elements have an oxidation state of +2

Group(III) elements have an oxidation state of +3

Group(IV) elements have oxidation states of +4 and -4

Group(V) elements have oxidation states of +5 and -3

Group(VI) elements have oxidation states of +6 and -2

Group(VII) elements have oxidation states of +7 and -1

Examples

1. Calculate the oxidation state of the following

a) Fluorine in fluorine molecule

....

b) Chlorine in chloride

....

c) Manganese in potassium permanganate ($KMnO_4$)

Solution

Let the oxidation state of manganese be = Y

$(1X1) + (1XY) + (4X\text{-}2) = 0$

$1 + Y + \text{-}8 = 0$

$Y - 8 = -1$

$Y = -1 + 8$

$Y = +7$

The oxidation state of manganese is +7

d) Chlorine ClO_3^-

Solution

Let the oxidation state of manganese be = p

$(1xp) + (3x\text{-}2) = -1$

$P - 6 = -1$

$P = +5$

The oxidation state of chlorine is +5

e) Chromium in $Cr_2O_7^{2-}$

Solution

Let the oxidation state of chromium be = t

$(tx2) + (7x\text{-}2) = -2$

$2t - 14 = -2$

$2t = -2+14$

$2t = +12$

$t = +6$

EXERCISE

Calculate the oxidation state of the underlined elements in the compounds given below.

a) $H\underline{N}O_3$
b) $\underline{Cu}(OH)_2$
c) $\underline{Al}(H2O)_3.3OH$
d) $\underline{Pb}(OH)_4^{2-}$
e) $\underline{Zn}(NH_3)_4^{2+}$
f) $\underline{Cr_2}O_3$
g) $\underline{Cr}O_4^{2-}$
h) $(\underline{Cu}(H_2O)_4.2Cl).2H_2O$
i) $\underline{Fe}(CO)_5$

WRITING REDOX EQUATIONS

A redox equation is conveniently written by combining two half equations.

A half equation represents the reaction in which an oxidising agent accepts electrons or a reaction in which a reducing agent donates electrons. There are two types of half equations i.e.

- The oxidation half equation
- The reduction half equation

a) The oxidation half equation

This illustrates a reaction in which a reducing agent donates electrons during a redox reaction , for example;

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

$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e$

b) The reduction half equation

This illustrates a reaction in which an oxidising agent accepts electrons during a redox reaction, for example;

$Cl_2(g) + 2e \longrightarrow 2Cl^-(aq)$

$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+(}aq) + 4H_2O(l)$

How to write half reactions

Guiding question

Write the half equation for the dichromate(VI) ion

Steps taken

1. Identify the major products formed when the oxidising agent is reduced or when the reducing agent is oxidised.

$Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+(}aq)$

The table below shows the major products formed when some of the common oxidising agents are reduced, and the colour changes involved.

Oxidising agent	Colour of oxidising agent	Product formed on reduction	Colour of the final product
Manganate(VII) ion MnO_4^-	Purple	Mn^{2+}	Colourless
Dichromate(VI) ion $Cr_2O_6^{2-}$	Orange	Cr^{3+}	Green
Chromate ion CrO_4^{2}-	Yellow	Cr^{3+}	Green
Chlorate(V) ion ClO_3^-	Colourless	Cl^-	Colourless
Iodate(V) ion IO_3^-	Colourless	I^-	Colourless
Chlorate(I) ion ClO^-	Yellow	Cl^-	Colourless

Manganese(IV) oxide MnO_2	Black (solid)	Mn^{2+}	Colourless/faint pink
Chlorine Cl_2	Greenish yellow (gas)	Cl-	Colourless
Iodine I_2	Red (liquid) Grey/black (solid) Purple (gas/vapour)	I^-	Colourless
Hydrogen peroxide H_2O_2	Colourless	H_2O	Colourless

Table 1.0, oxidising agents and their reduction products and colour

For reducing agents, they undergo oxidation reactions, the table below shows the major products formed when some of the common reducing agents are oxidised, and the colour changes involved.

Reducing agent	**Colour of the reducing agent**	**Product formed on oxidation**	**Colour of the final product**
Iron(II) ion Fe^{2+}	Green	Fe^{3+}	Brown
Oxalate ion $C_2O_4^{2-}$	Colourless	CO_2	Colourless gas
Iodide ion I-	Colourless	I_2	Brown
Nitrite ion NO_2^-	Colourless	NO_3^-	Colourless
Sulphite ion SO_3^{2-}	Colourless	SO_4^{2-}	Colourless
Thiosulphate ion $S_2O_3^{2-}$	Colourless	$S_4O_6^{2-}$	Colourless
Tin(II) ion Sn^{2+}	Colourless	Sn^{2+}	Colourless
Hydrogen peroxide H_2O_2	Colourless	O_2	Colourless

Table 1.1, reducing agents and their reduction products and colour

2. Balance the number of atoms starting with atoms other than oxygen and hydrogen.
   $\mathbf{Cr_2O_7^{2-}(aq) \longrightarrow 2\,Cr^{3+}(aq)}$
3. Balance the number of oxygen atoms by adding a water molecule to the side lacking oxygen.
   $\mathbf{Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$
4. Balance each hydrogen atom by adding a hydrogen ion to the side lacking it.
   $\mathbf{Cr_2O_7^{2-}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$
5. Balance the charges by adding the appropriate number of electrons to the side which has excess positive charges.
   $\mathbf{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$

EXERCISE

Write the half equation for permanganate ion.

How to obtain the overall equation from the half equations

Guiding questions

1. *Write the overall equation for the reaction between a solution of acidified potassium permanganate and nitrous acid.*

Steps taken

1. Assemble the two half equations. One of the half equations must be reduction equation and the other one must be an oxidation one. ie

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

$$NO_2^-(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + 2H^+(aq) + 2e$$

2. Multiply each half equation by the number of electrons on the other half equation such that the total number of electrons in one half equation is the same as those in the other half equation.

$$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)\ /X2$$

$$NO_2^-(aq) + H_2O(l) \longrightarrow NO_3\text{-}(aq) + 2H^+(aq) + 2e\ /X5$$

➡

$$2MnO_4^-(aq) + 16H+(aq) + 10e \longrightarrow 2\,Mn^{2+}(aq) + 8H_2O(l)$$

$$5NO_2^-(aq) + 5H_2O(l) \longrightarrow 5NO_3^-(aq) + 10H^+(aq) + 10e$$

3. Add the two half equations and cross out the electrons.

$$2MnO_4^-(aq) + 16H^+(aq) + \cancel{10e} + 5NO_2^-(aq) + 5H_2O(l) \longrightarrow 2Mn^{2+(}aq) + 8H_2O(l) + 5NO_3\text{-}(aq) + 10H^+(aq) + \cancel{10e}$$

4. Eliminate or balance out any substances which are recurring

$$2MnO_4^-(aq) + (16\text{-}10)H^+(aq) + 5NO_2^-(aq) + \cancel{5H_2O(l)} \longrightarrow 2Mn^{2+}(aq) + (8\text{-}5)\cancel{H_2}O(l) + 5NO_3^-(aq) + \cancel{10H^+(aq)}$$

5. Now write the remaining components of the above equation

Overall

$$2MnO_4^-(aq) + 6H^+(aq) + 5NO_2^-(aq) \longrightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5\,NO_3^-(aq)$$

Observation

Purple solution turns to a colourless solution.

2. CrO_4^{2-} and SO_3^{2-}

$$CrO_4^{2-}(aq) + 8H^+(aq) + 3e \longrightarrow Cr^{3+}(aq) + 4H_2O(l)\ /X2$$

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e\ /X3$$

⇒

$$2CrO_4^{2-}(aq) + (16\text{-}6)H^+(aq) + \cancel{6e} + 3SO_3^{2-}(aq) + \cancel{3H_2O(l)} \longrightarrow 2Cr^{3+}(aq) + (8\text{-}3)H_2O(l) + 3SO_4^{2-}(aq) + 6\cancel{H^+}(aq) + \cancel{6e}$$

Overall equation

$$2CrO_4^{2-}(aq) + 10H^+(aq) + 3SO_3^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 5H_2O(l) + 3SO_4^{2-}(aq)$$

Observation

Yellow solution turns to a green solution.

3. **I_2 and $S_2O_3^{2-}$**

$I_2(aq) + 2e \longrightarrow 2I^-(aq)$

$2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2e$

Overall equation

$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

4. **MnO_4^- and $C_2O_4^{2-}$**

$MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ /x2

$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e$ /x5

$\Longrightarrow$

Overall equation

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

Observation

Purple solution turns to a colourless solution and bubbles of a colourless gas which form a white precipitate with calcium hydroxide solution are given off.

Application of redox reactions

- In volumetric/quantitative analysis
- In qualitative analysis

a) In qualitative analysis

The colour changes which occur when oxidising agents are reduced or when reducing agents are oxidised can be used to give information about the likely contents on some unknown samples.

Guiding questions

1. State what is observed and write equations for the reaction that would take place when;
   a) Sodium oxalate solution is added in excess to acidified potassium permanganate solution.
      Observation
      Purple solution turns colourless and bubbles of a colourless gas are given off.

Equation

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2}\text{-}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

b) Sodium nitrite is added to a solution of acidified potassium dichromate(VI) solution

Observation

Orange solution turns to a green solution

Equation

$$3NO_2^-(aq) + Cr_2O_7^{2-}(aq) + 16H^+(aq) \longrightarrow NO_3^-(aq) + 2Cr^{3+}(aq) + 8H_2O(l)$$

c) Hydrogen peroxide is added to acidified potassium dichromate(VI) solution

Observation

Orange solution turns to a green solution

Equation

$$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2O_2(l) \longrightarrow 2Cr^{3+}(aq) + 7H_20(l) + 3O_2(g)$$

d) *Sodium iodate solution and acidified potassium nitrite solution.*

Observation

………

Equation

………

b) In volumetric analysis

Using the mole ratio from a well-balanced (stoichiometric) redox equation, the amount of concentration of unknown substances can be determined during redox titration.

Guiding questions

1. 25cm^3 of 0.2M potassium dichromate solution required 22cm^3 of solution iron(II) sulphate solution to reach end point. Determine the molarity of iron(II) sulphate solution.

Solution

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Cr^{3+}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$$

Mole ratio of $Cr_2O_7^{2-} : Fe^{2+}$ = *1:6*

1000cm^3 of solution contains 0.2 moles of potassium dichromate

25cm^3 of solution will contain $\frac{0.2x25}{1000}$ *moles*

= *0.00025 moles*

1 mole of potassium dichromate solution react with 6 moles of iron(II) sulphate solution

0.00025 moles of potassium dichromate solution will react with $\frac{6 \text{ X } 0.00025}{1}$

= *0. 003 moles*

22cm^3 of iron(II) sulphate solution contain 0.003 moles

1000cm^3 of iron(II) sulphate solution will contain $\frac{0.003 \text{ X } 1000}{22}$ moles

= 0.136M

Therefore the molarity of iron(II) sulphate solution is 0.136M

2. 25cm3 of iodine solution required 25.5cm3 of 0.1M sodium thiosulphate solution for complete reaction using starch indicator. Calculate the concentration of iodine solution in;

a) Moles per litre

Solution

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

1000cm3 of solution contains 0.1 moles of sodium thiosulphate

25.5cm3 of solution will contain $\frac{0.1 \text{ X } 25.5}{1000}$ moles

= 0.0025 moles

Mole ratio of $S_2O_3^{2-} : I_2$ = 2:1

2 moles of sodium thiosulphate react with 1 mole of iodine

0.0025 moles of sodium thiosulphate will react with $\frac{1 \text{ X } 0.0025}{2}$ moles of iodine

= 0.001275 moles of iodine

25cm3 of sodium thiosulphate solution contain 0.001275 moles

1000cm3 of sodium thiosulphate solution will contain $\frac{0.001275 \text{ X } 1000}{25}$

= 0.051M

The concentration of iodine solution is 0.051 mol^{-1}

b) Grams per litre

Solution

Rfm of iodine I_2 = 2 X 127

= 254

1 mole of iodine weighs 254 gl^{-1}

0.051 moles of iodine will weigh 254 X 0.051g

=12.954gl^{-1}

The concentration of iodine solution is 12.954gl^{-1}

ARRANGEMENT OF ELECTRONS IN AN ATOM

(Electronic configuration)

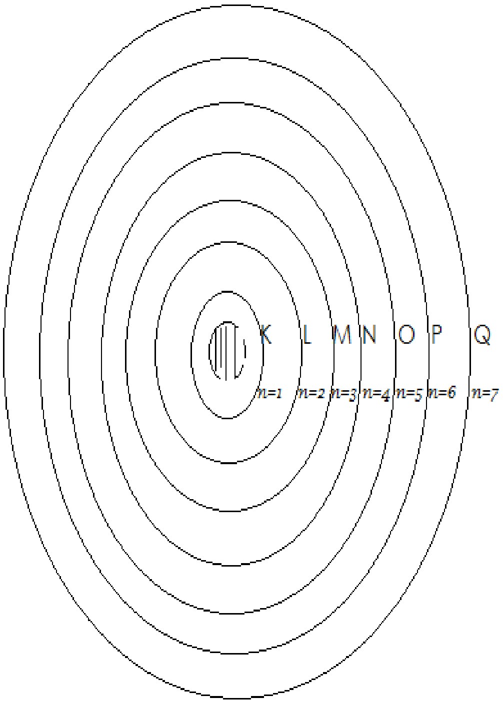
An atom of an element of an atom is made up of a nucleus which is made up of protons and neutrons. The number of protons in the nucleus of an atom of an element is known as atomic number.

The sum of the number of neutrons and protons in the nucleus of an atom of an atom of an element is known as mass number.

Outside the nucleus of an atom consists of *shells*, these shells are labelled as follows;

- K shell
- L shell
- M shell
- N shell
- O shell
- P shell
- E.t.c

Consider the figure below; showing arrangement of shells.



Each shell is further labelled with a *principle quantum number (n)* as shown below.

Shell	**Principle quantum number (n)**
K	**1**
L	**2**
M	**3**
N	**4**
O	**5**
P	**6**
Q	**7**

These shells are also called *energy levels.* Shells far away from the nucleus have a higher energy level than those near the nucleus, thus the energy in the shells is in order K<L<M<N<O<P<Q.

Within a shell, there are subshells. These subshells include;

- s subshell
- p subshell
- d subshell
- f subshell

Each subshell is labelled with a *Subsidiary Quantum number (l)* also called *Azimuthal quantum number (l).* The values of *l* range from **0-3** as shown in the table below.

Sub shell	**Subsidiary/ Azimuthal Quantum number**
s	**0**
p	**1**
d	**2**
f	**3**

The sub shells within each shell differ in energy status, those which are far from the nucleus have a higher energy content than those which are near to it.

The K shell has one sub shell- the *s*-subshell

The L shell has two sub shells – the *s*-subshell and *p*-subshell

The M shell has three sub shells- the *s*-subshell and *p*-sub-shell and *d*-subshell

The N shell has four sub shells- the *s*-subshell, *p*-subshell, *d*-subshell and *f*-subshell.

To distinguish between a subshell which belongs to different shells but having the same subsidiary quantum number, the principle quantum number of the shell is written together with the symbol of the subshell, for example the M-shell (n=3) is described as 3*s*-subshell, to distinguish it from another s-subshell which belongs to the N-shell (n=4), described as 4*s*-subshell.

Note

Both the 3s and the 4s-subshells have the same subsidiary quantum number $\ell=0$

ORBITALS

Within a subshell, there are orbitals, each orbital is labelled with a magnetic quantum number

$m\ell = -\ell----0----+\ell$

Each orbital has a magnetic quantum number, consider the table below.

Subshell	**Mℓ values**	**Number of orbitals in the shell**
s (l=0)	0	1
p (l=1)	-1, 0, +1	3
d (l=2)	-2,-1,0,+1,+2	5
f (l=3)	-3, -2, -1, 0, +1, +2, +3	7

The number of mℓ values of a subshell is equal to the number of orbitals in that subshell.

Each orbital can accommodate a maximum of two(2) electrons, thus

Subshell	**Number of orbitals**	**Maximum number of electrons**
s	**1**	**2**
p	**3**	**6**
d	**5**	**10**
f	**7**	**14**

Spin quantum number

Within an orbital, there are two electrons (maximum) each with a spin quantum number m_s. The m_s values for the two electrons in an orbital are $-1/2$ and $+1/2$

Electrons within an orbital spin about their axes in opposite directions, a spining electron creats/generates a magnetic field because it's a moving charged particle since the two electrons in the orbital spin in opposite directions (i.e have opposite spins). The magnetic fields they create have opposite polarities and hence attract each other. This minimises the repulsion between them as a result of having similar charge.

Electron box diagram

These provide an over simplified way of representing orbitals within shells. The actual shapes of orbitals are quite complicated.

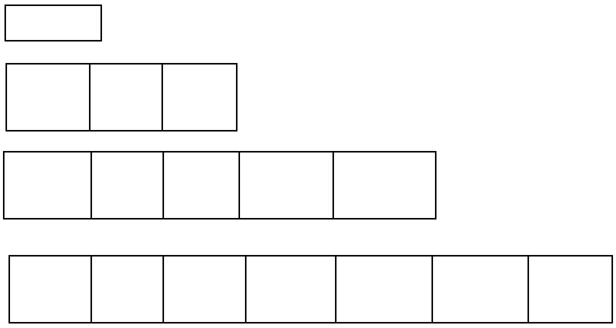
Subshell electron box diagram

s-subshell

p-subshell

d-subshell

f-subshell



Filling electrons in atoms

During filling of electrons in an atom, the following rules are followed.

1. **Afbau principle(Building principle)**
   Its states that electrons fill atomic orbitals, subshells and shells in order of increasing energy. This means that subshells and shells closer to the nucleus (those with low energy) are filled first.
2. **Pauli exclusion principle**
   It states that two electrons in any one atom may be described by the same set of the four quantum numbers.
   The two electrons in the same orbital also differ in spin quantum number.
3. **Hund's rule of maximum multiplicity**
   It states that are filled in orbitals of equal energy singly before pairing.
   It applies when filling electrons in orbiatls of equal energy i.e orbitals of a subshell.

Illustration

Filling electrons in a p-subshell

a) 2 electrons

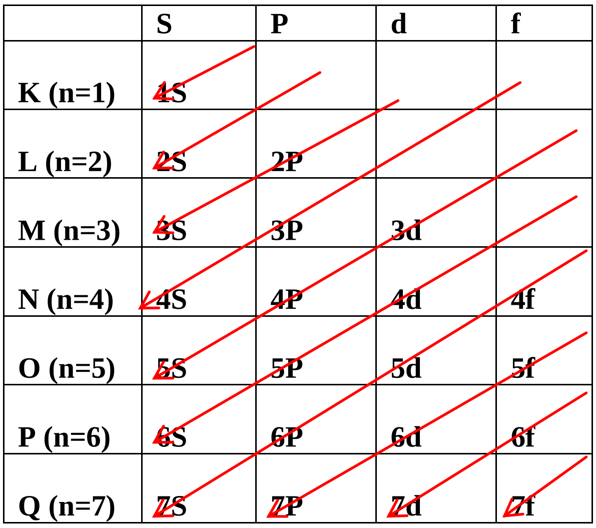
b) 4 electrons

1⇂	1	1

c) 5 electrons

1⇂	1⇂	1

Electronic configuration can be easily written following the criteria summarised below;



	S	P	d	f
K (n=1)	1S			
L (n=2)	2S	2P		
M (n=3)	3S	3P	3d	
N (n=4)	4S	4P	4d	4f
O (n=5)	5S	5P	5d	5f
P (n=6)	6S	6P	6d	6f
Q (n=7)	7S	7P	7d	7f

Fig 1.2

Overlap of subshells

Shells of low principle quantum numbers cover energy ranges which differ fairly considerably from one another.

However, after the first two shells, the energy rangesof succeeding shells begin to overlap.

Expected order	Actual order
6f	5d
6d	5f
6p	7s
6s	6p
5f	5d
5d	4f
5p	6s
5s	5p
4f	4d
4d	5s
4p	4p
4s	3d
3d	4s
3p	3p
3s	3s
2p	2p
2s	2s

1s	1s

The actual order can be obtained using figure 1.2 above.

Stability of the subshells

The nucleus of sny stom is said to be stable if its outermost energy level is;

- Full with electrons, for example magnesium has atomic number of 12, its electronic configuration is $1S^2 2S^2 2P^6 3S^2$
- Half full with electrons for example phosporus has atomic number of 15, its electronic configuration is $1S^2 2S^2 2P^6 3S^2 3P^3$

If the outermost subshell is neither fully filled nor half full, it is described as being partially filled and hence unstable

Guiding questions

1. *Write the electronic configuration of the following elements.*
   a) Aluminium
   $1S^2 2S^2 2P^6 3S^2 3P^1$
   b) Sulphur
   $1S^2 2S^2 2P^6 3S^2 3P^4$
   c) Berryllium
   $1S^2 2S^2$
   d) Fluorine
   $1S^2 2S^2 2P^5$
   e) Chlorine
   $1S^2 2S^2 2P^6 3S^2 3P^5$
   f) Argon
   $1S^2 2S^2 2P^6 3S^2 3P^6$
2. *Write the electronic configuration of the following elements.*
   a) ^{29}Cu
   Expected E.C
   $1S^2 2S^2 2P^6 3S^2 3P^6 4S^2 3d^9$ *this is unstable because the outermost subshell is partially filled therefore an electron is promoted from* $4S^2$ *to the* $3d^9$ *to give* $4S^1$*(which is half full hence relatively stable) and* $3d^{10}$ *(which is full and stable) to give;*

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

   b) ^{24}Cr
   $1S^2 2S^2 2P^6 3S^2 3P^6 4S^1 3d^5$

   c) ^{26}Fe
   $1S^2 2S^2 2P^6 3S^2 3P^6 3d^6 4S^2$
   d) ^{30}Zn

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

Note:

The above principle(s) is/are usually applied when writing the electronic configuration(s) of transition elements and other d-block elements.

Electronic configuration of ions

Ions are formed when atoms lose or gain electrons. When an atom loses electrons, it forms a positively charged ion called a cation, metal atoms react by loss of electrons. The electrons lost are those in the outermost energy level

When an atom gains electrons, it forms a negatively charged ion called an anion, non metal atoms react by gain of electrons. The electrons gained are added to the outermost energy level.

For transition elements, electrons are lost from inner S-subenergy level followed by those in the inner 3-subenergy level.

Examples

1. Write the electronic configuration of the following ions
   a) Fe^{3+}
   $1S^2 2S^2 2P^6 3S^2 3P^6 3d^5 4S^0$
   b) Cu^+
   $1S^2 2S^2 2P^6 3S^2 3P^6 4S^0 3d^{10}$
   c) Cu^{2+}
   $1S^2 2S^2 2P^6 3S^2 3P^6 4S^0 3d^9$
   d) Cr^{3+}
   $1S^2 2S^2 2P^6 3S^2 3P^6 4S^0 3d^3$
   e) Na^+
   $1S^2 2S^2 2P^6 3S^0$

Exercise

Write the electronic configuration of the following ions.

a) Mn^{2+}
b) Fe^{2+}
c) Zn^{2+}
d) Al^{3+}
e) Co^{2+}
f) V^{3+}

Determination of the block, group and period of an element in the periodic table.

Given that we can now conviniently and easily write the electronic configuration of ions and elements, we can use that information to easily determine the block, group and period to which an element belongs in the periodic table. The following guidelines maybe used to the above effect;

- The block is got from the outermost energy level
- The group is got from the sum of electrons in the outer/last s and p-subenergy levels.
- The period is got from the greatest energy level.

Examples

Determine the block, group and period to which the following elements belong.

a) ^{7}N
   $1S^22S^22P^3$
   Block P, group(V) and period 2
b) ^{15}P
   $1S^22S^22P^63S^23P^3$
   Block P, group(V) and period 3
c) ^{34}Se
   $1S^22S^22P^63S^23P^64S^23d^{10}4P^4$
   Block P, group(VI) and period 4
d) ^{35}Br
   $1S^22S^22P^63S^23P^64S^23d^{10}4P^5$
   Block P, group(VII) and period 4
e) ^{26}Fe
   $1S^22S^22P^63S^23P^64S^23d^6$
   Block d, - and period 4

Exercise

Determine the block, group and period to which the following elements belong.

a) Magnesium
b) Chlorine
c) Argon
d) Potassium
e) Boron
f) Silicon
g) Nitrogen
h) Sulphur

3.0 THE PERIODIC TABLE

The periodic table is a compilation fo elements arranged in order of increasing atomic number. Elements with similar chemical properties are grouped together in *groups* (verticle coloumns). The position of an element in a group depends on its *atomic number.*

The periodic table consists of four divisions known as *blocks* , these blocks include;

- S-block
- P-block
- d-block
- f-block

The to which an element belongs is determined by the subshell in which the last electrons of that element are placed, therefore the s-block consists of elements whose outermost electrons are in the s-subshell.

a) **TheS-block**
This consists of elements whose outermost electrons are found in the s-subshell. It includes elements in group(I) and group(II), these are electropositive metals because they lose electrons to form positively charged ions.

b) **The P-block**
This consists of elements whose outermost electrons are found in the p-subshell. It includes elements in the following groups;
    - Group(III)
    - Group(IV)
    - Group(V)
    - Group(VI)
    - Grouip(VII)
    - Group(VIII)

c) **The d-block**
This consists of all elements between group(II) and group(III) of the periodic table. Their outermost electrons are in the d-subenergy level.

Elements in the S and P block levels are known as *main group elements* while those in d and f-blocks are known as *transition elements* because they form a transition between the S and P blocks.

All (most) elements in the S, d and f blocks are metals. Most of the P block elements are non-metals, however, some P block elements like *aluminium, lead and tin* are metals. All elements in group(VIII) are known as noble gases, inert gases, rare gases or group(0) elements.

d) **d-block elements**
These include elements whose outermost electrons are found in the d-subenergy level. Most of them form a partially filled 3d-subenergy level and hence are known as transition metals (except scandium and zinc).

Characteristics of transition metals

- They have variable oxidation states
- They form coloured ions/compounds in solution
- They form complexes e.g $Cu(NH_3)_4^{2+}$
- They act as catalysts
- They have magnetic properties i.e they are paramagnetic.

Characteristics of transition metals

- Most of them form compounds in one oxidation state except group(IV) elements
- They usually form non coloured compounds with the solid being white and the solutions being colourless. However, few form coloured compounds such as;
  - ✓ Sodium peroxide
  - ✓ Lead(II) oxide
- They have limited capacity to form complexes although lead and beryllium form complexes.

3.1 PERIODICITY

The properties of elements in the periodic table keep on repeating themselves with increase inn atomic number as the periodic table is traversed from metals through non-metals.

These properties include;

- Nuclear charge
- Screening (shielding effect)
- Effective nuclear charge

Definitions

a) **Nuclear charge**
This is the positive charge of the nucleus due to protons.

b) **Screening (shielding effect)**
This is the repulsion which an outer electron experiences from electrons in the inner shells and subshells.

c) **Effective nuclear charge**
This is the resulatnt attraction which the electron experiences from the nucleus.

Variation of nuclear charge

a) **Across the period**
Across the period, nuclear charge increases due to increase in the number of protons.

b) **Down the group**
Down the group, nuclear charge increases due to increase in the number of protons

Variation of screening effect

a) **Across the period**

Across the period, screening effect increases slightly due to addition of an electron to the same energy level.
It follows that the increase in screening effect is less than the increase in nuclear charge.

b) Down the goup
Down the group, screening effect increases due to increase in the number of electrons.
In this case, a full inner energy level of electrons is added, therefore the increase in screening effect down the group is always great.

Variation of effective nuclear charge

a) Across the period
Across the period, nuclear charge increases due to increase in the number of protons
Screening effect increases but slightly due to addition of an electron to the same energy level.
The increase in nuclear charge outweighs the increase in screening effect, therefore the effective nuclear attatraction increases.

b) Down the group
Down the group, nuclear charge increases due to increase in the number of protons
Also, screening effect increases due to addition of a full inner energy level of electrons
The increase in screening effect outweighs the increase in nuclear charge, therefore the effective nuclear attatraction decreases.

3.11 ATOMIC RADIUS

The size of atoms elements can be describe in terms of atomic radius where an atom is assumed to be spherical.

It is defined as the distance of closest approach of one atom to another in a given bonding situation. At this distance, the inter-nuclear repulsions just balance the nuclear electronic attration.

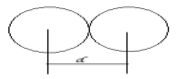
Atomic radius is expressed in four different ways namely;

- Covalent radius
- Metallic raius
- Van der Waal's radius
- Ionic radius

a) Covalent radius
This is half the distance between the nuclei of two identical atoms bonded together a single covalent bond.

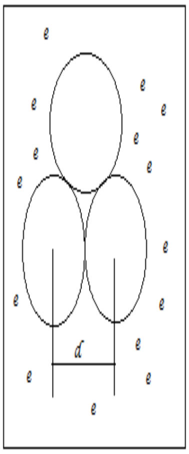
d- distance between the nuclei

covalent radius r=$^{d}/_{2}$



b) Metallic radius

This is half the distance between the nuclei of two adjacent individual atoms of a metal in its crystal lattice.



Metallic radius

$r = {}^{d}/_{2}$

c) Van der Waal's radius

This is half the distance between the nuclei of two identical atoms held by van der waal's bond.

d) Ionic radius

This is half the distance between two nuclei of identical atoms held together by an ionic bond.

Factors affecting atomic radius

- Nuclear charge
- Screening effect

a) Nuclear charge

When nuclear charge is high, the atomic radius becomes small, this is because the outer electrons experience great attraction from the nucleus bringing them closer to it and consequently atomic radius decreases.

When nuclear charge is low, the atomic radius becomes large, this is because the outer electrons experience less attraction from the nucleus making them to be far from it and consequently atomic radius increases.

b) **Screening effect**

Atomic radius increases with increase in screening effect. This is because when screening effect is high, electrons in the outer shells experience great repulsion from those near the nucleus and are thus far from the nucleus.

However, when screening effect is low, it means that the outer electrons experience greater nuclear attraction and are thus closer to the nucleus, consequently the atomic radius reduces.

Variation of atomic radius

a) **Across the period**

Period 2						
Element	**Li**	**Be**	**B**	**C**	**O**	**F**
Atomic radius (nm)	**0.123**	**0.089**	**0.082**	**0.07**	**0.066**	**0.064**

Period 3							
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**P**
Atomic radius (nm)	**0.156**	**0.136**	**0.125**	**0.117**	**0.110**	**0.104**	**0.09**

Trend

Atomic radius decreases across the period.

Explanation

Across the period, nuclear charge increases due to increase in the number of protons.

Similarly, screening increases but slightly due addition of electrons to the same energy level

The increase in nuclear charge outweighs the increase in screening effect and the effective nuclear charge (attraction) increases leading to a decrease in atomic radius.

b) **Down the group**

Group (II) elements					
Element	**Be**	**Mg**	**Ca**	**Sr**	**Ba**
Atomic radius (nm)	**0.110**	**0.160**	**0.197**	**0.215**	**0.221**

Trend

Atomic radius increases down the group

Explanation

Down the group, nuclear charge increases due to increase in the number of protons.

Similarly, screening increases due addition of a full inner energy level electrons

The increase in screening effect outweighs the increase in nuclear charge and therefore the effective nuclear charge (attraction) reduces leading to an increase in atomic radius.

Note

For metals which react by loss of electrons, increase in atomic radius increases reactivity and for non-metals which react by gain of electrons, increase in atomic radius reduces reactivity.

Ionic radius

Ions have their respective sizes; these sizes are expressed as ionic radius. The ions include cations and anions.

a) Cations

Cations are formed when atoms lose electrons

When cations are formed, the screening effect decreases while the nuclear charge remains constant, consequently effective nuclear charge increases, the same nuclear charge now attracts the remaining fewer electrons strongly and closely to the nucleus.

It follows that therefore, the ionic (cationic) radius of an ion is smaller than the atomic radius of its parent atom.

The more electrons an atom/ion loses, the more its screening effect decreases but since since nuclear charge remains constant, the effective nuclear charge increases and thus the remaining fewer electrons become more strongly attracted by the same nuclear charge to the nucleus hence reduction in ionic radius.

For example,

$Mg^{+} > Mg^{2+} > Mg^{3+}$ **or** $Mg^{3+} < Mg^{2+} < Mg^{+}$

Guiding question

Explain why potassium atom is bigger than potassium ion.

b) Anions

Anions are formed when atoms gain electrons. This leads to an increase in screening effect while the nuclear charge remains constant. The effective nuclear charge decreases and the same (constant) nuclear charge now weakly attracts the increased (many) electrons, therefore these electrons even move far away from the nucleus, this consequently leads to an increase in ionic radius. It implies therefore that an ion has a bigger ionic (anionic) radius than the atomic radius of its parent atom, i.e; $Cl<Cl^-$ or $Cl^- >Cl$

The more electrons an atom/ion gains, the more the increase in screening effect while the nuclear charge remains constant. Effective nuclear charge decrease and many electrons become weakly (less strongly) attracted by the same nuclear charge hence increase in anionic radius.

Guiding question

Compare and explain the following ionic radii

a) $N^-<N^{2-}<$

b) $Fe^{2+}>Fe^{3+}$

IONISATION ENERGY (I.E)

When an atom loses electrons, it is that electron which is most loosely held that is lost (removed first) i.e the electron in the outermost shell or subshell.

Since electrons are attracted to the nucleus, heat energy is therefore required to remove them, implying that ionization is a thermal process which is endothermic. The removal of electrons occurs in steps and each step requires a specific amount of energy, this energy is known as ionization energy. It is measured in $KJMol^{-1}$

Ionization energy is the minimum amount of energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions.

Equation

$$M(g) \longrightarrow M^+(g) + e$$

Or

Ionization energy is the minimum amount of energy required to remove an electron from a gaseous atom to form a monopositvely or unipositively charged gaseous ion.

Equation

$$M(g) \longrightarrow M^+(g) + e$$

First ionization energy

This is the minimum amount of energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of monopositively/unipositively charged gaseous ions.

Equation

$$M(g) \longrightarrow M^+(g) + e$$

Or

It is the minimum amount of energy required to remove an electron from a gaseous atom to form a monopositvely or unipositively charged gaseous ion.

Equation

$$M(g) \xrightarrow{\hspace{3cm}} M^{+}(g) + e$$

Second ionization energy

This is the minimum amount of energy required to remove one mole of electrons from one mole of monopositively/unipositively charged gaseous ions to form one mole of dipositively charged gaseous ions.

Equation

$$M^{+}(g) \xrightarrow{\hspace{3cm}} M^{2+}(aq) + e$$

Or

It is the minimum amount of energy required to remove an electron from a unipositively gaseous ion to form a dipositively charged gaseous ion

Equation

$$M^{+}(g) \xrightarrow{\hspace{3cm}} M^{2+}(aq) + e$$

Third ionization energy

This is the minimum amount of energy required to remove one mole of electrons from one mole of dipositively charged gaseous ions to form one mole of tripositively charged gaseous ions.

$$M^{2+}(g) \xrightarrow{\hspace{3cm}} M^{3+}(aq) + e$$

Note

One mole of an electron contains $6.02X10^{-23}$ *particles*

Factors affecting ionization energy

These include;

- Atomic radius
- Nuclear charge
- Screening effect
- Penetrating power
- Electronic configuration
- Net charge on the ion

a) **Atomic radius**

When atomic radius is small, the outermost electrons are nearer the nucleus and experience greater nuclear attraction thus require high energy to remove them leading to high ionization energy

When atomic radius is large, the outermost electrons are far from the nucleus and experience less nuclear attraction thus require little energy to remove them leading to low ionization energy

b) **Nuclear charge**

When the nuclear charge is high, the nuclear attraction on the outermost electrons is high and ionization energy will be also high.

When the nuclear charge is low, the nuclear attraction on the outermost electrons is small and ionization energy will be low.

c) **Screening effect**

When screening effect is high, electrons are far from the nucleus and ionization energy will be low.

When screening effect is low, electrons are close to the nucleus and ionization energy will be high.

d) **Penetrating power**

This is the ability of electrons in the outer energy levels to come nearer to the nucleus than those in the inner energy levels.

This therefore means that when penetrating power is high, electrons are nearer to the nucleus and hence experience greater nuclear attraction, this leads to high ionization energy.

This also follows that when penetrating power is low, ionization will be low

Penetrating power is in order: ***S>P>d>f***

e) **Electronic configuration**

When the electron to be removed is coming from a sub-energy level which is full, the ionization energy will be high because the atom is stable and a lot of energy is required to remove an electron.

When the electron to be removed is coming from a sub-energy level which is partially filled, the ionization energy will be low because the atom is unstable and little energy is required to remove an electron.

f) **Net charge on the particle**

Ionization energy decreases with increase in the net charge of the positive ion

This is because the bigger the net positive charge, the more strongly are the remaining fewer electrons attracted and hence great energy will be required to remove them.

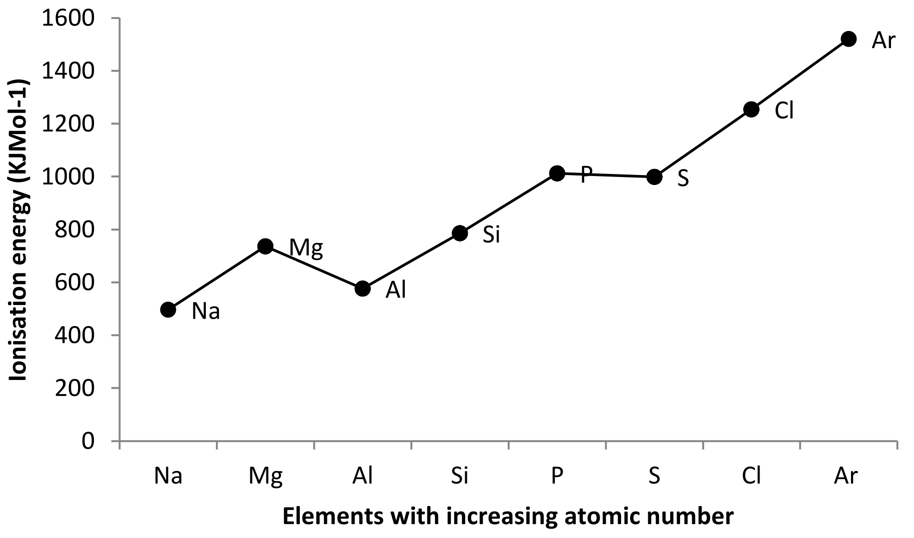
This is due to the fact that when an electron is removed, the screening effect decreases while nuclear charge remains constant, effective nuclear charge increases and outer electrons become more strongly attracted to the nucleus. This explains why the magnitude of ionization energy increases with increase in number of electrons removed, i.e;

1st I.E < 2ND I.E < 3rd I.E < 4th I.E

Variation in ionization energy

a) Across the period

Period 3								
Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
1st Ionisation energy ($JKMol^{-1}$)	**497**	**737**	**577**	**786**	**1012**	**999**	**1255**	**1521**



Trend

Generally, first ionisation energy increases across the period with an abnormal behavior shown by magnesium and phosphorus.

Explanation

Across the period, nuclear charge increases due to increase in the number of protons.

Similarly, screening increases but slightly due addition of electrons to the same energy level

The increase in nuclear charge outweighs the increase in screening effect and the effective nuclear charge (attraction) increases leading to a decrease in atomic radius and consequently the ionisation energy increases.

However, the first ionisation energy of magnesium is higher than that of aluminium;

This is because the first ionisation energy of magnesium involves removal of an electron from a $3S^2$ sub-energy level which is full and stable hence requires high amount of energy.

$^{12}Mg: 1S^22S^22P^63S^2$

The first ionisation energy of phosphorus involves removal of an electron from a $3P^1$ sub-energy level which is partially filled and hence unstable therefore requires little amount of energy.

$^{13}Al: 1S^22S^22P^63S^23P^1$

Also the first ionisation energy of phosphorus is higher than that of Sulphur

$^{15}P: 1S^22S^22P^63S^23P^3$

This is because the first ionisation energy of phosphorus involves removing an electron from a $3P^3$ sub-energy level which is half-full and hence relatively stable therefore requires high amount of energy.

$^{16}S: 1S^22S^22P^63S^23P^4$

The first ionisation energy of sulphur involves removing an electron from a $3P^4$ sub-energy level which is partially filled and hence unstable therefore requires little amount of energy.

b) Down the group

Group (II)					
Element	**Be**	**Mg**	**Ca**	**Sr**	**Ba**
First ionisation energy **(KJMol-1)**	**899**	**737**	**590**	**549**	**503**

Trend

First ionisation energy decreases down the group

Explanation

Down the group, nuclear charge increases due to increase in number of protons.

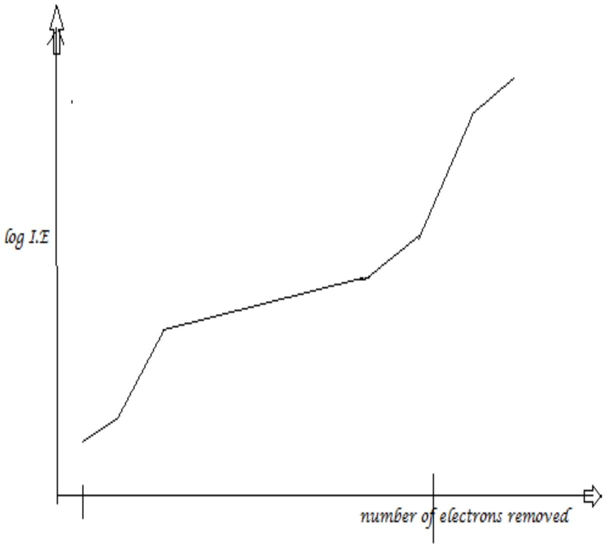
Also screening effect increases due to addition of a full inner energy level of electrons.

The increase in screening effect outweighs the increase in nuclear charge, the effective nuclear charge decreases and atomic radius increases, consequently, ionisation energy reduces since electrons will be weakly attracted to the nucleus.

Importance of ionisation energy

- The number of successive ionisation energies indicates the number of electrons in an atom, magnesium with 12 ionisation energies has 12 electrons.
- Metallic/non-metallic character. The magnitude of first ionisation energy is used as a measure of metallic or non-metallic character of an element; for example; the first ionisation energy of metals is nearly 800KJMol^{-1} while that of non-metals is nearly above 800KJMol^{-1}

The graph below shows a graph of successive ionisation energies for magnesium against the number of electrons removed.



Comments

- The element belongs to group(II) of the periodic table, this is because there is a very big difference between the second and third ionisation energies compared to the first and second ionisation energies, this means that the third electron is coming from sub-energy which is full and stable.
- There is a general increase in successive ionisation energies, this is because as electrons are successively removed, the constant nuclear attracts the remaining fewer electrons more strongly hence making it increasingly more difficult to remove them. Also ionic radius decreases and this enhances the nuclear attraction for the remaining few electrons.

Example

The table below shows the first four ionisation energies of elements A, B, C, D and E in KJMol^{-1}

Element	**1st**	**2nd**	**3rd**	**4th**	**Group**
A	**500**	**4600**	**6900**	**9500**	*(I)*
B	**740**	**1500**	**7700**	**10500**	*(II)*
C	**650**	**1600**	**3000**	**4800**	*(IV)*
D	**900**	**1800**	**14800**	**21000**	*(II)*
E	**580**	**1800**	**2700**	**11600**	*(III)*

QUESTION

Explain why the elements belong to the groups as stated above

ELECTRON AFFINITY (E.A)

When an electron is added to a gaseous atom, an energy (enthalpy) change occurs, this enthalpy change is known as electron affinity.

Electron affinity is defined as the energy change which occurs when one mole of electrons is added to one mole of gaseous atoms to form one mole of uninegatively charged ions.

It is measured in $KJMol^{-1}$

Equation

$$X(g) + e \longrightarrow X^{-}(g)$$

It can also be defined as the energy change which occurs when an electron is added to a gaseous atom to form a uninegatively charged ion.

Equation

$$X(g) + e \longrightarrow X^{-}(g)$$

First electron affinity

It is defined as the energy change which occurs when one mole of electrons is added to one mole of gaseous atoms to form one mole of uninegatively charged ions.

First electron affinity has a negative value (enthalpy) because the incoming electron is strongly attracted by the greater nuclear charge and consequently a lot of energy is given out/released.

Equation

$$X(g) + e \longrightarrow X^{-}(g) \quad \Delta \text{-ve}$$

It can also be defined as the energy change which occurs when an electron is added to a gaseous atom to form a uninegatively charged ion.

Equation

$$X(g) + e \longrightarrow X^{-}(g) \quad \Delta \text{-ve}$$

Second electron affinity

It is defined as the energy change which occurs when one mole of electrons is added to one mole of uninegatively charged ions to form one mole of a dinegatively charged gaseous ions.

$$X^{-}(g) + e \longrightarrow X^{2-}(g) \quad \Delta \text{+ve}$$

Second electron affinity is positive (+) because after gaining the first electron, the ion formed possesses a negative charge and since the incoming electron also bears a negative charge, there will be a force of repulsion between the incoming electron and the already charged ion, therefore to overcome the repulsive force, energy must be applied and the overall process becomes endothermic.

Note:

- *Formation of a divalent anion is an endothermic process showing that the univalent anion is more stable than the divalent one.*
- *The more negative the electron affinity is, the more stable is the anion formed.*

Factors affecting electron affinity

These include;

- Atomic radius
- Nuclear charge
- Screening effect
- Electronic configuration
- Net charge

a) Atomic radius

First electron affinity increases with a decrease in atomic radius; this is because small atomic radius means electrons are firmly attached to the nucleus and thus a lot of energy is required to add an electron to the atom.

b) Nuclear charge

First electron affinity increases with increase in nuclear charge, when nuclear charge is high, the incoming electron is strongly attracted by the nucleus and hence a lot of energy is given out

c) Screening effect

First electron affinity decreases with increase in screening effect, this is because the incoming electron will be strongly repelled by the existing electrons in the inner energy levels and little energy will be given out, sometimes energy is absorbed.

d) Electronic configuration

First electron affinity decreases with increase in the stability of the subshell to which an electron is being added.

If a shell or subshell is full or half, is described as being stable or relatively (moderately) stable respectively, therefore energy is required to add an electron to such a shell or subshell.

However, when the incoming electron is being added to sub-energy level which is partially filled, energy will be given out and electron affinity will be high.

This explains why the electron affinity of group(II) and group(VII) elements is positive.

e) Net charge

Electron affinity decreases with increase in the negative charge of the ion.

This is because when at atom gains an electron, it attains a negative charge and the screening effect increases, nuclear charge remains constant, effective nuclear attraction decreases and the incoming electron becomes more strongly repelled hence energy is required to another electron

Variation of first electron affinity

a) Across the period

Period 2							
Element	Li	Be	B	C	N	O	F
Electron affinity ($KJMol^{-1}$)	-57	-66	-16	-123	131	-141	-353
Period 3							
Element	Na	Mg	Al	Si	P	S	Cl
Electron affinity ($KJMol^{-1}$)	-20	+67	-30	-135	-60	-200	-348

Trend across period 3

Generally, electron affinity increases across the period, however, the first electron affinity of magnesium is positive.

Explanation

Across the period, nuclear charge increases due to increase in the number of protons
Screening effect increases slightly due to addition of an electron to the same energy level
The increase in nuclear charge outweighs the increase the screening effect, therefore the effective nuclear charge increases and the incoming electron is strongly attracted to the nucleus thus a lot of energy is given out.

The first electron affinity of magnesium is positive; this is because it involves addition of an electron to a $3S^2$ sub-energy level which is full and stable, therefore the incoming electron is strongly repelled away, to overcome this repulsion, energy must be applied and overall process becomes endothermic.
E.C of $^{12}Mg = 1S^2 2S^2 2P^6 3S^2$

Question

State an explain the trend in first electron affinity across period 2

b) Down the group

Group(VII)

Element	F	Br	Cl	I
Electron affinity ($KJMol^{-1}$)	-333	--348	-328	-295

Trend

Generally, electron affinity decreases down the group; however, the electron affinity of fluorine is abnormally lower than expected.

Explanation

Down the group, nuclear charge increases due to addition of protons to the nucleus from one element to the next.

Similarly, screening effect increases due to addition of a full inner energy level of electrons. The increase in screening effect outweighs the increase in nuclear charge; therefore the effective nuclear attraction for incoming electrons decreases thus a decrease in electron affinity.

Fluorine is a small atom (has a very small atomic radius) with a high electron density in the outermost energy level so these electrons tend to repel the incoming electrons (reduce nuclear attraction for incoming electrons) leading to very low energy given out thus low electron affinity.

Question

Explain why the electron affinity of fluorine is lower than that of chlorine

ELECTRONEGAVITY

Electronegativity is defined as the tendency of an atom of an element to attract bonding electrons towards itself when covalently bonded to another atom of another element.

It can also be defined as the tendency of an atom of an element to withdraw bonding electrons from another atom with which it forms a covalent bond.

In a covalent bond, the more electronegative atom attracts the electrons to itself more strongly and it attains a partial negative charge leaving the other one with a partial positive charge.

The difference between electronegativity is used to determine the ionic character or polarity of a covalent bond. If two bonded atoms are similar, then the difference in electronegativity becomes zero (0) and the bond becomes purely non-polar.

However if the two bonded atoms are different, then the bond becomes polar, the degree of polarity depends on the relative electronegativities of the bonded atoms.

Factors affecting electronegativity

These include;

- Atomic radius
- Nuclear charge
- Screening effect

a) **Atomic radius**
Electronegativity increases with a decrease in atomic radius, this is because when the atomic radius is small, the bonding electrons are close to the nucleus and therefore strongly attracted to it but when atomic radius is large, electronegativity decreases, this is because when the atomic radius is large, the bonding electrons are far from the nucleus and therefore weakly attracted

b) **Nuclear charge**
The higher the nuclear charge, the greater are the bonding electrons strongly attracted and electronegativity will be high.
The lower the nuclear charge, the less are the bonding electrons attracted and electronegativity will be low.

c) **Screening effect**
The greater the screening effect, the less strongly are the bonding electrons attracted and electronegativity will be low
The lower the screening effect, the more strongly will the bonding electrons be attracted and electronegativity will be high.

Variation of electronegativity

a) **Across the period**

Trend

Electronegativity increases across the period

Explanation

Across the period, nuclear charge increases due to increase in the number of protons
Screening effect increases slightly due to addition of an electron to the same energy level
The increase in nuclear charge outweighs the increase the screening effect, therefore the effective nuclear charge increases and the incoming electron is strongly attracted to the nucleus thus increase in electronegativity.

b) **Down the group**

Trend

Electronegativity decreases down the group.

Explanation

Down the group, nuclear charge increases due to addition of protons to the nucleus from one element to the next.
Similarly, screening effect increases due to addition of a full inner energy level of electrons.
The increase in screening effect outweighs the increase in nuclear charge; therefore the effective nuclear attraction for incoming electrons decreases thus a decrease in electronegativity.

ELECTROPOSITIVITY

This is the measure of the ease with which atoms of elements can lose electrons so as to form positive ions (cations).

It can also be defined as the tendency of an atom in gaseous state to lose an electron to form a positively charged ion.

The easier it is for an atom to lose electrons, the more electropositive it is and consequently the stronger the metallic character. It is the opposite of electronegativity.

Highly reactive metals like potassium, sodium are highly electropositive while the highly reactive non-metals like fluorine, oxygen and chlorine are highly electronegative.

Factors affecting electronegativity

These include;

- Atomic radius
- Nuclear charge
- Screening effect

a) **Atomic radius**
Electropositivity increases with a increase in atomic radius, this is because when the atomic radius is large, the bonding electrons are far from the nucleus and therefore weakly attracted to it so are easily lost but when atomic radius is small, electropositivity decreases, this is because when the atomic radius is small, the bonding electrons are close to the nucleus and therefore strongly attracted to it so not easily lost.

b) **Nuclear charge**
The higher the nuclear charge, the greater are the bonding electrons strongly attracted to the nucleus and electropositivity will be low.
The lower the nuclear charge, the less are the bonding electrons attracted to the nucleus and electropositivity will be high since they can easily be lost.

c) **Screening effect**
The greater the screening effect, the less strongly are the bonding electrons attracted to the nucleus and electropositivity will be high.
The lower the screening effect, the more strongly will the bonding electrons be attracted to the nucleus and electropositivity will be low.

Variation of electropositivity

a) **Across the period**
Trend
Electropositivity decreases across the period
Explanation
Across the period, nuclear charge increases due to increase in the number of protons
Screening effect increases slightly due to addition of an electron to the same energy level
The increase in nuclear charge outweighs the increase the screening effect, therefore the effective nuclear charge increases and the incoming electron is strongly attracted to the nucleus thus a decrease in electropositivity

b) **Down the group**

Trend

Electronegativity increases down the group

Explanation

Down the group, nuclear charge increases due to addition of protons to the nucleus from one element to the next.

Similarly, screening effect increases due to addition of a full inner energy level of electrons. The increase in screening effect outweighs the increase in nuclear charge; therefore the effective nuclear attraction for incoming electrons decreases thus an increase in electropositivity.

MELTING POINT

Melting point is the constant temperature at which the solid state of a substance changes to a liquid state when the two are in equilibrium.

The melting point of a substance depends on;

- The number of electrons available for bonding
- The atomic radius i.e the element to element bond length and consequently its bond strength
- The crystal structure

Trends in melting point

a) **Across period 2**

Element	Li	Be	B	C	N	O	F	Ne
Melting point (^{0}C)	180	1283	2037	3700	-270	-219	-220	-249
Atomic number	3	4	5	6	7	8	9	10

Trend

Melting point increases from lithium to carbon, then after decreases to neon.

Explanation

Melting point increases from lithium to boron because the number electrons available for bonding increase from 1 in lithium through 2 in beryllium to 3 in boron hence the strength of the bond increases and also the atomic radius decreases from lithium to carbon; the inter-atomic bonds become shorter and stronger, thirdly there is change in crystal structure from giant ionic in lithium and beryllium to giant covalent in boron; thus the increasing melting point.

In carbon, each atom is bonded to four other carbon atoms through strong covalent bonding, this gives diamond a 3-dimenional network of bonds which are very strong to break thus the very high melting point.

The non-metallic substances nitrogen, oxygen, and fluorine form molecular structures which are held by weak Van der Waal's forces of attraction whose strength and magnitude increases with increase in molecular weight due to increased polarization, consequently melting point decreases.

b) Across period 3

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Melting point (0C)	98	650	660	1423	44	119	-101	-189
Atomic number	11	12	13	14	15	16	17	18

Trend

Melting point increases from sodium to silicon, and then thereafter decreases to argon.

Explanation

The increase in melting point from sodium to aluminium due to increase in number of electrons contributed towards bonding increases from 1 on sodium through 2 in magnesium to 3 in aluminium.

However the melting point of aluminium is not very high from that of magnesium because aluminium does not appear to contribute all the 3 electrons towards the metallic bonding.

Silicon has a giant covalent structure in which each silicon atom is bonded to four other silicon atoms giving silicon a 3-dimension (3-D) network of bonds which are very strong and therefore its melting point is very high.

The rest of the molecules phosphorus, Sulphur, and chlorine form simple molecular structures where the molecules are held by weak Van der Waal's forces of attraction whose strength and magnitude increases with increase in molecular weight due to increased polarization.

Phosphorus forms P_4 and P_2 molecules while Sulphur forms S_2 and S_8 molecules, the molecular weight of S8 is greater than that of the P_4 molecules therefore the S_8 molecules are held by strong Van der Waal's forces than the P_4, consequently the melting point of Sulphur is greater than that of phosphorus.

Chlorine forms Cl2 molecules with a very small molecular weight and thus weak Van der Waal's forces, leading to a very low melting point.

c) Down the group

Group(II)

Element	Be	Mg	Ca	Sr	Ba
Melting point (^{0}C)	1283	650	840	768	714
Atomic number	4	12	20		

Trend

Melting point generally decreases down the group. However, the melting point of calcium is higher than that of magnesium.

Explanation

Down the group, atomic radius increases thus the bonds formed are longer and weaker, therefore the melting point decreases.

Calcium has a body centered cubic arrangement in which atoms are closely packed giving it a high melting point than that of magnesium with hexagonal close parked arrangement.

PERIOD 2 ELEMENTS

These include the following elements;

- Lithium Li
- Beryllium Be
- Boron B
- Carbon C
- Nitrogen N
- Oxygen O
- Fluorine F
- Neon

They undergo reactions with the following

- ✓ Water
- ✓ Sodium hydroxide solution
- ✓ Acids
- ✓ Air
- ✓ Halogens

When describing chemical properties (reactions) of an element; mention the names of reactants and products and write a well-balanced (stoichiometric equation) equation for the reaction that took place. State all the necessary conditions for the reaction to proceed.

The following reactions shall be studied;

a) **Reaction with water**

The elements react with water as follows;

Lithium

Lithium reacts slowly with cold water forming lithium hydroxide and hydrogen gas

Equation

$$2Li(s) + 2H_2O(l) \longrightarrow 2LiOH(aq) + H_2(g)$$

On heating, lithium reacts vigorously with steam form lithium oxide and hydrogen gas

Equation

$$Li(s) + H_2O(g) \longrightarrow Li_2O(s) + H_2(g)$$

Beryllium does not react with water

Boron

Boron reacts with steam on heating to form boron oxide and hydrogen gas.

Equation

$$2B(s) + 3H_2O(g) \longrightarrow B_2O_3(s) + 3H_2(g)$$

Carbon

Carbon does not react with cold water but reacts with steam on heating forming carbon monoxide and hydrogen gas. A mixture of carbon monoxide and hydrogen gas is referred to as a water gas.

Equation

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

The carbon monoxide formed is very unstable and is readily oxidised by air to form carbon dioxide as shown in the below equation.

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

Nitrogen and oxygen do not react with water

Fluorine

Fluorine is a strong oxidising agent and readily reacts with water to form oxygen gas and hydrogen fluoride.

Equation

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

b) Reaction with sodium hydroxide solution

Lithium does not react with sodium hydroxide solution because it is basic

Beryllium

Beryllium reacts with hot concentrated sodium hydroxide solution forming sodium beryllate and hydrogen gas.

Equation

Molecular

$Be(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow Na_2Be(OH)_4(aq) + H_2(g)$

Ionic

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

Boron

Boron reacts with hot concentrated sodium hydroxide solution forming sodium borate and hydrogen gas.

Equation

Molecular

$2B(s) + 6NaOH(aq) \longrightarrow 2Na_3BO_3(aq) + 3H_2(g)$

Ionic

$2B(s) + 6^-OH(aq) \longrightarrow 2BO_3^{3-}(aq) + 3H_2(g)$

Nitrogen and oxygen does not react with sodium hydroxide solution.

Fluorine reacts with sodium hydroxide solution according conditions of concentration and temperature; i.e;

With cold dilute sodium hydroxide solution

Fluorine reacts with cold dilute sodium hydroxide solution forming sodium fluoride, oxygen difluoride and water.

Equation

Molecular

$2NaOH(aq) + F_2(g) \longrightarrow 2NaF(aq) + OF_2(g) + H_2O(l)$

Ionic

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

With hot concentrated sodium hydroxide solution

Fluorine reacts with hot concentrated sodium hydroxide solution forming sodium fluoride, oxygen and water

Equation

Molecular

$2NaOH(aq) + F_2(g) \longrightarrow 2NaF(aq) + O_2(g) + H_2O(l)$

Ionic

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

c) Reaction with acids

With sulphuric acid

Lithium reacts with dilute sulphuric acid forming lithium sulphate and hydrogen gas

Equation

$2Li(s) + H_2SO_4(aq) \longrightarrow Li_2SO_4(aq) + H_2(g)$

Beryllium reacts with warm dilute suphuric acid to form beryllium sulphate and hydrogen gas.

Equation

$Be(s) + H_2SO_4(aq) \longrightarrow BeSO_4(aq) + H_2(g)$

Beryllium reacts with hot concentrated sulphuric acid to form beryllium sulphate, Sulphur dioxide gas and water.

Equation

$Be(s) + 2H_2SO_4(aq) \longrightarrow BeSO_4(aq) + SO_2(g) + 2H_2O(g)$

Carbon reacts with hot concentrated sulphuric acid to carbon dioxide gas, Sulphur dioxide gas and water.

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

Nitrogen, oxygen and fluorine do not react with dilute and even hot concentrated sulphuric acid.

With nitric acid

Lithium reacts with dilute nitric acid forming lithium nitrate, nitrogen monoxide and water.

$Li(s) + 2HNO_3(aq) \longrightarrow LiNO_3(aq) + NO(g) + 2H_2O(l)$

Nitrogen monoxide formed is very unstable and easily oxidised by air to nitrogen dioxide

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Beryllium does not react with nitric acid.

Finely divided boron reacts with concentrated nitric acid forming boric acid, nitrogen dioxide.

$B(s) + 3HNO_3(aq) \longrightarrow H_3BO_3(aq) + 3NO_2(g)$

Carbon reacts with hot concentrated nitric acid to form carbon dioxide, nitrogen dioxide and water.

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

Observation

Brown fumes are given off

With hydrochloric acid

Lithium reacts with dilute hydrochloric acid forming lithium chloride and hydrogen gas

$Li(s) + 2HCl(aq) \longrightarrow 2LiCl(aq) + H_2(g)$

Beryllium also reacts with dilute hydrochloric acid forming lithium chloride and hydrogen gas

$Be(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + H_2(g)$

d) Reaction with air.

Lithium reacts with air on heating to form lithium oxide and lithium nitride.

$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$

$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$

Beryllium reacts with air forming beryllium oxide

$2Be(s) + O_2(g) \longrightarrow 2BeO(s)$

Boron reacts with dry air on heating forming boron oxide

$2B(s) + 3O_2(g) \longrightarrow 2B_2O_3(s)$

Carbon reacts with dry oxygen gas on strong heating to form carbon dioxide gas

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

e) Reaction with halogens

Lithium reacts with halogens forming lithium halides.

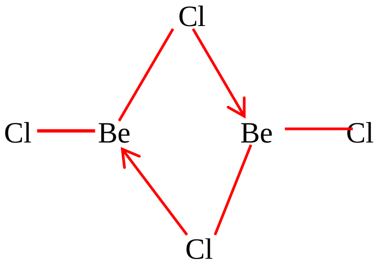
$Li(s) + X_2(g) \longrightarrow 2LiX(s)$

Where X= F, Cl, Br, I

Beryllium reacts with chlorine and bromine to form beryllium chloride and beryllium bromide.

$Be(s) + X_2(g) \longrightarrow BeX_2(s)$ X= Cl, Br

Beryllium chloride dimerises in vapour phase as shown below to form a dimer



Compounds of period 2 elements

These include basically the oxides and the chlorides.

a) The oxides

Element	Li	Be	B	C	N	O	F
Formula of oxide	Li_2O	BeO	B_2O_3	CO_2	NO_2	O_2	OF_2
Structure of oxide	Giant ionic	Giant ionic	Giant covalent	Simple molecular	Simple molecular	Simple molecular	Simple molecular

Types of structures

Giant ionic structure

This is an ionic compound which consists of ions arranged in a regular way resulting in a compound with a giant 3-dimensional structure. Such a compound has a high melting point due to strong ionic bonds, is soluble in water and insoluble in organic solvents, and conducts electricity in aqueous or molten state but not in solid state.

Giant covalent structure

This is a covalent compound made of atoms joined by strong covalent bonds resulting into a 3-dimensional giant structure such as silicon(IV) oxide. Such a compound has very high melting and boiling points because the covalent bonds are very strong.
It is not soluble in any solvent and does not conduct electricity because there are no free electrons.

Simple molecular structure

The structure is made up of simple molecules which are held by weak Van der Waal's forces of attraction. Such a compound has a very low melting and boiling point. Many are gases, liquids at room temperature.

These oxides undergo the following reactions

Reaction with water

Lithium oxide is basic and reacts with water forming lithium hydroxide

$Li_2O(s) + H_2O(l) \longrightarrow 2LiOH(aq)$

Beryllium oxide does not react with water because it is amphoteric.

Boron oxide is acidic and reacts with water forming boric acid.

$B_2O_3(s) + 3H_2O(l) \longrightarrow 2H_3BO_3(aq)$

Carbon dioxide is acidic and reacts with water forming a weak carbonic acid

$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$

Nitrogen dioxide reacts with water forming nitric acid and nitrous acid

$2NO_2(g) + H_2O(l) \longrightarrow HNO_3(aq) + HNO_2(aq)$

Oxygen and oxygen difluoride do not react with water.

Reaction with sodium hydroxide solution

Lithium oxide does not react with sodium hydroxide solution because it is a basic oxide

Beryllium oxide is amphoteric and therefore reacts with sodium hydroxide solution forming sodium beryllate.

$BeO(s) + 2NaOH(aq) + H_2O(l) \longrightarrow Na_2Be(OH)_4(aq)$

Or

$BeO(s) + 2^-OH(aq) + H_2O(l) \longrightarrow Be(OH)_4^{2-}(aq)$

Boron oxide reacts with sodium hydroxide solution to form sodium borate.

$B_2O_3(s) + 6NaOH(aq) \longrightarrow 2Na_3BO_3(aq) + 3H_2O(l)$

Or

$B_2O_3(s) + 6^-OH(aq) \longrightarrow 2BO_3^{3-}(aq) + H_2O(l)$

Carbon monoxide reacts with sodium hydroxide solution forming sodium methanoate.

$CO(g) + NaOH(aq) \longrightarrow HCOONa(aq)$

Carbon dioxide reacts with sodium hydroxide solution forming sodium carbonate and water.

$CO_2(g) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$

Nitrogen dioxide reacts with sodium hydroxide solution forming sodium nitrate and sodium nitrate and water.

$2NaOH(aq) + 2NO_2(g) \longrightarrow NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$

Oxygen and oxygen difluoride do not react with sodium hydroxide solution.

b) The chlorides

Element	Li	Be	B	C	N	O
Formula of the chloride	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2 Cl_2O_7
Structure	Giant ionic	Giant ionic	Simple molecular	Simple molecular	Simple molecular	Simple molecular

Reaction with water

Lithium does not react with water

Beryllium chloride is partially ionized in water to form an acidic solution i.e pH less than 7. This is because beryllium chloride is a soluble salt hence in water it is ionized to give beryllium ions and chloride ions.

$BeCl_2(s) \longrightarrow Be^{2+}(aq) + 2Cl^-(aq)$

The beryllium ion formed has a high ionic charge and a small ionic radius giving it a high charge density hence in water it is heavily hydrated.

$\mathbf{Be^{2+}(aq) + 4H_2O(l) \longrightarrow Be(H_2O)_4^{2+}(aq)}$

The $Be(H_2O)_4^{2+}$ formed undergoes hydrolysis as follows;

$\mathbf{Be(H_2O)_4^{2+}(aq) \rightleftharpoons [Be(H_2O)_3.OH]^{+}(aq) + H^{+}(aq)}$

Or

$\mathbf{Be(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons [Be(H_2O)_3.OH]^{+}(aq) + H_3O^{+}(aq)}$

The hydrogen/hyroxonium ions formed are responsible for the acidic nature of the resultant solution.

Explain why a solution of chromium(III) sulphate is highly acidic.

State what is observed and write an equation for the reaction that takes place when sodium carbonate is added to aluminium chloride in water.

A white precipitate and bubbles of a colourless gas which turn moist blue litmus paper red and form a white precipitate with calcium hydroxide solution

$\mathbf{2Al^{3+}(s) + 3CO_3^{2-}(aq) + 3H_2O(l) \longrightarrow 2Al(OH)_3(s) + CO_2(g)}$

Boron trichloride reacts with water to form hydrochloric acid and boric acid.

$\mathbf{BCl_3(s) + 3H_2O(l) \longrightarrow 3HCl(aq) + H_3BO_3(aq)}$

Carbon tetrachloride does not react with water or its not hydrolysed by water.

Explanation

^{6}C, E.C = $1S^22S^22P^2$

Carbon does not have vacant 3-d orbitals to accept/accommodate the lone pairs of electrons from the water ligands hence in water, it is not hydrolysed.

Nitrogen trichloride is hydrolysed as follows;

$\mathbf{NCl_3(g) + 3H_2O(l) \rightleftharpoons NH_3(g) + 3HOCl(aq)}$

Oxygen dichloride reacts as below;

$\mathbf{OCl_2(g) + H_2O(l) \rightleftharpoons 2HOCl(aq)}$

Also

$\mathbf{Cl_2O_7(g) + H_2O(l) \rightleftharpoons 2HClO_4(aq)}$

PERIOD 3 ELEMENTS

These elements include;

- ✓ Sodium Na
- ✓ Magnesium Mg
- ✓ Aluminium Al
- ✓ Silicon Si
- ✓ Phosphorus P
- ✓ Sulphur S
- ✓ Chlorine Cl
- ✓ Argon Ar

The melting points of the elements were generally discussed on pages 38,39 and 40, so we will now focus on their chemical properties.

Chemical properties of period 3 elements

When describing chemical properties (reactions) of an element; mention the names of reactants and products and write a well-balanced (stoichiometric equation) equation for the reaction that took place. State all the necessary conditions for the reaction to proceed.

The following are the common reactions of period 3 elements.

a) Reaction with water

Sodium

Sodium melts into a silvery ball, dirts the surface of water, reacting vigorously producing hydrogen gas fumes and sodium hydroxide solution. Also the size of sodium reduces in size until it finished up.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

Magnesium

Magnesium with water in two ways as discussed below

It reacts slowly with cold water at room temperature forming magnesium hydroxide and hydrogen gas.

$$Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + H_2(g)$$

However, when heated, magnesium reacts readily with steam forming magnesium oxide and hydrogen gas.

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g)$$

Aluminium

Aluminium does not react with cold water, but when heated, it reacts with steam forming amphoteric aluminium oxide and hydrogen gas. The aluminium used in this case should be clean and fresh because once exposed to air; aluminium sometimes reacts forming an insoluble aluminium oxide which would prevent its reaction with water.

$$2Al(s) + 3H_2O(l) \longrightarrow Al_2O_3(s) + 3H_2(g)$$

Silicon

Silicon reacts with steam on heating to form silicon(IV) oxide.

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

Phosphorus

Heated phosphorus reacts with steam to form phosphorus acid and hydrogen gas.

$$2P(s) + 6H_2O(l) \longrightarrow 2H_3PO_3(aq) + 3H_2(g)$$

Or

$$P_4(s) + 12H_2O(l) \longrightarrow 4H_3PO_3(aq) + 6H_2(g)$$

Sulphur does not react with water

Chlorine

Chlorine reacts with water to form a mixture of hydrochloric acid and hypochlorous acid.

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

Hydrochloric acid (chlorine water) formed is a pale yellow solution, when exposed to sunlight, it turns colourless and gives off a colourless gas which relights a glowing splint.

$$2HOCl(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Argon does not react with water at any condition.

Describe the reactions of period 3 elements with water.

b) **Reaction with air**

Air consists of mainly oxygen and nitrogen, and so we shall be looking at reactions with either nitrogen or oxygen or both.

Sodium

Sodium burns in limited air with a bright yellow flame forming basic sodium oxide which is a white solid.

$$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$$

However, in excess air sodium burns with a bright yellow flame forming sodium peroxide which is a yellow solid

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

Magnesium

Magnesium burns in air forming a mixture of magnesium oxide and magnesium nitride both of which are white solids (ashes)

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

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

Aluminium

Aluminium reacts with air when heated to form aluminium oxide and aluminium nitride as shown in the equations below.

$$Al(s) + O_2(g) \longrightarrow Al_2O_3(s)$$

$$2Al(s) + N_2(g) \longrightarrow 2AlN(s)$$

Phosphorus

Phosphorus reacts with oxygen present in the air to form phosphorus trioxide and phosphorus pentaoxide depending on the amount of oxygen, when the amount of oxygen is limited, phosphorus trioxide is formed. But when the oxygen is in excess, phosphorus pentaoxide is formed.

The equations can be written in any of the following ways;

For limited oxygen;

$$P_4(s) + 3O_2(g) \longrightarrow 2P_2O_3(s)$$

Or

$P_4(s) + 3O_2(g) \longrightarrow P_4O_6(s)$ dimerised form of phosphorus(III) oxide

For excess oxygen

$$P_4(s) + 5O_2(g) \longrightarrow 2P_2O_5(s)$$

Or

$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$ dimerised form of phosphorus(V) oxide

Silicon

Silicon burns in oxygen on heating forming silicon(IV) oxide

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

Sulphur

Sulphur burns in air with a bright blue flame forming white fumes containing Sulphur dioxide and Sulphur trioxide.

Limited oxygen

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

Excess oxygen

$$2S(s) + 3O_2(g) \longrightarrow 2SO_3(g)$$

Chlorine

Chlorine reacts with limited air forming dichlorine oxide.

$$2Cl_2(g) + O_2(g) \longrightarrow 2Cl_2O(g)$$

It reacts with excess oxygen forming dichlorine heptaoxide

$$2Cl_2(g) + 7O_2(g) \longrightarrow 2Cl_2O_7(l)$$

c) **Reaction with aqueous alkalis**

These aqueous alkalis include sodium hydroxide and potassium hydroxide solutions, any of them used gives the same product(s)

Sodium and magnesium do not react with alkalis because they are basic in nature.

Aluminium

Aluminium is amphoteric; it therefore reacts with hot concentrated sodium/potassium hydroxide solution forming sodium/potassium aluminate and hydrogen gas.

Molecular equation

$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2NaAl(OH)_4(aq) + 3H_2(g)$

Ionic equation

$2Al(s) + 2^{-}OH(aq) + 6H_2O(l) \longrightarrow 2Al(OH)_4^{-}(aq) + 3H_2(g)$

Silicon

Silicon reacts with hot concentrated sodium/potassium hydroxide solution forming sodium/potassium silicate and hydrogen gas

Molecular equation

$Si(s) + 2NaOH(aq) + H_2O(l) \longrightarrow Na_2SiO_3(aq) + 2H_2(g)$

Ionic equation

$Si(s) + 2^{-}OH(aq) + H_2O(l) \longrightarrow SiO_3^{2-}(aq) + 2H_2(g)$

Phosphorus

Phosphorus reacts with hot concentrated sodium/potassium hydroxide solution forming sodium/potassium hypophosphite (phosphonate) and phosphine gas

$P_4(s) + 3NaOH(aq) + 3H_2O(l) \longrightarrow 3NaH_2PO_2(aq) + PH_3(g)$

OR

$P_4(s) + 3^{-}OH(aq) + 3H_2O(l) \longrightarrow 3H_2PO_2^{-}(aq) + PH_3(g)$

Sulphur

Sulphur reacts with hot concentrated sodium/potassium hydroxide solution forming sodium/potassium sulphide, sodium/potassium thiosulphate and water.

$3S(s) + 6NaOH(aq) \longrightarrow 2Na_2S(aq) + Na_2SO_3(aq) + 3H_2O(l)$

Or

$3S(s) + 6^{-}OH(aq) \longrightarrow 2S^{2-}(aq) + SO_3^{2-}(aq) + 3H_2O(l)$

Chlorine

Chlorine reacts with sodium/potassium hydroxide solution when cold dilute and also when hot and concentrated.

Cold dilute sodium hydroxide solution

Chlorine reacts with cold dilute sodium hydroxide solution forming sodium chloride, sodium hypochloride (sodium chlorate(I)) and water.

$Cl_2(g) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$

Or

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

Hot concentrated sodium hydroxide solution

Chlorine reacts with hot concentrated sodium hydroxide solution forming sodium chloride, sodium chlorate (sodium chlorate(V)) and water.

$$3Cl_2(g) + 6NaOH(aq) \longrightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$$

Or

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

Argon does not react with sodium hydroxide solution.

d) **Reaction acids**

Acids are described as being cold and dilute, cold and moderately (50%) concentrated and hot concentrated.

Reaction with cold and dilute hydrochloric acid

Sodium reacts with cold and dilute hydrochloric acid to form sodium chloride and hydrogen gas.

$$Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$$

Magnesium reacts with cold and dilute hydrochloric acid to form magnesium chloride and hydrogen gas

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

Aluminium reacts with cold and dilute hydrochloric acid to form aluminium chloride and hydrogen gas

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

Silicon, phosphorus, Sulphur and chlorine do not react with hydrochloric acid.

Reaction with cold dilute sulphuric acid

Sodium reacts with cold dilute sulphuric acid forming sodium sulphate

$$2Na(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2(g)$$

Magnesium reacts with cold dilute sulphuric acid forming magnesium sulphate and hydrogen gas.

$$Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$$

Aluminium reacts with cold dilute sulphuric acid forming aluminium sulphate and hydrogen gas.

$$2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

Silicon, phosphorus, Sulphur and chlorine do not react with dilute sulphuric acid.

Reaction with concentrated sulphuric acid

When sulphuric acid is concentrated, it reacts as an oxidising agent with magnesium, aluminium and Sulphur.

Magnesium

Magnesium reacts with hot concentrated sulphuric acid forming magnesium sulphate and the acid is reduced to Sulphur dioxide gas and water.

$$Mg(s) + 2H_2SO_4(aq) \longrightarrow MgSO_4(aq) + 2H_2O(l) + SO_2(g)$$

Aluminium

Aluminium reacts with hot concentrated sulphuric acid forming aluminium sulphate and the acid is reduced to Sulphur dioxide gas and water

$$2Al(s) + 6H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 6H_2O(l) + 3SO_2(g)$$

Phosphorus

Hot concentrated sulphuric acid oxidises phosphorus to phosphoric acid, and the acid is itself reduced to sulphur dioxide and water

$$P_4(s) + 10H_2SO_4(aq) \longrightarrow 4H_3PO_4(aq) + 10SO_2(g) + 4H_2O(l)$$

Sulphur

Sulphur is oxidised by hot concentrated sulphuric acid forming sulphur dioxide gas and the acid is reduced to water

$$S(s) + 2H_2SO_4(l) \longrightarrow 3SO_2(g) + 2H_2O(l)$$

The reaction between sodium and is highly exothermic and should not be tried in ordinary laboratories.

Reaction with dilute nitric acid

Sodium reacts with dilute nitric acid forming sodium nitrate and hydrogen gas

$$2Na(s) + 2HNO_3(aq) \longrightarrow 2NaNO_3(aq) + H_2(g)$$

Magnesium reacts with cold moderately concentrated nitric acid forming magnesium nitrate, nitrogen monoxide gas and water.

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

Aluminium reacts with dilute nitric acid forming aluminium nitrate and hydrogen gas

$$2Al(s) + 6HNO_3(aq) \longrightarrow 2Al(NO_3)_3(aq) + 3H_2(g)$$

Reaction with concentrated nitric acid

Sodium

Sodium reacts explosively with nitric acid forming sodium nitrate, nitrogen dioxide gas and water.

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

Magnesium

Magnesium reacts with hot concentrated nitric acid forming magnesium nitrate, nitrogen dioxide gas and water.

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

Observation

Brown fumes of a gas are given off

Guiding question

State what is observed and write equations for the reactions between magnesium, copper and nitric acid.

Solution

Magnesium and copper react with cold moderately concentrated nitric acid forming corresponding nitrates, nitrogen monoxide gas and water

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

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

Observation

For copper, the brown solid dissolved forming a blue solution and brown fumes are given off.

For magnesium, grey solid dissolved forming a colourless solution and brown fumes of a gas are given off.

Magnesium and copper react with hot concentrated nitric acid forming corresponding nitrates, nitrogen dioxide gas and water.

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

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

Observation

For copper, the brown solid dissolved forming a blue solution and brown fumes of a gas are given off.

For magnesium, grey solid dissolved forming a colourless solution and brown fumes of a gas are given off.

Aluminium is rendered passive by hot concentrated nitric acid because it forms a coating of aluminium nitrate which prevents further reaction.

Phosphorus

Hot concentrated nitric acid oxidises phosphorus to phosphoric acid, and the acid is itself reduced to nitrogen dioxide and water.

$$P_4(s) + 20HNO_3(aq) \longrightarrow 4H_3PO_4(aq) + 20NO_2(g) + 4H_2O(l)$$

Silicon does not react with nitric acid

Carbon

Carbon reduces hot concentrated nitric acid to nitrogen dioxide, and itself is oxidised to carbon dioxide.

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

Sulphur

Sulphur is oxidised by hot concentrated nitric acid to sulphuric acid, and the acid is reduced to nitrogen dioxide and water.

$$S(s) + 6HNO_3(l) \longrightarrow H_2SO_4(aq) + 6NO_2(g) + 2H_2O(l)$$

Fluorine, oxygen, nitrogen and chlorine do not react with nitric acid because they are themselves oxidising agents.

e) Reaction with hydrofluoric acid

Only silicon is able to react with hydrofluoric acid forming hyxafluorosilicic acid.

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

f) Reaction with chlorine

Sodium

Sodium reacts with dry chlorine gas on heating to form white fumes of sodium chloride

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

Magnesium

Heated magnesium reacts with dry chlorine gas to form anhydrous magnesium chloride.

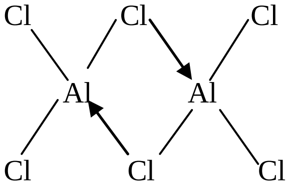
$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

Aluminium

When dry chlorine gas is passed over heated aluminium foil, it forms aluminium chloride. This reaction is usually applied in direct synthesis of aluminium chloride. Aluminium chloride sublimes on heating.

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

Aluminium chloride formed can dimerise in vapour phase to form a dimer as shown below.



Silicon

When heated silicon is reacted with a stream of dry chlorine gas, silicon tetrachloride which is a volatile covalent liquid is formed.

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

Phosphorus

Heated phosphorus reacts with dry chlorine gas forming white fumes of mainly mixture of phosphorus(III) chloride and phosphorus(V) chloride.

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(s)$$

$$P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(s)$$

Sulphur

When a stream of dry chlorine is passed over some heated sulphur, an orange (red) evil-smelling volatile liquid known as disulphur dichloride is formed.

$$2S(s) + Cl_2(g) \longrightarrow S_2Cl_2(l)$$

Chlorine does not react with itself; argon too has no reaction with chlorine because it is inert.

Compounds of period 3 elements

Period 3 elements react with other elements and reagents, some of the common compounds under consideration here include

- ✓ Chlorides
- ✓ Oxides
- ✓ Hydrides

a) The chlorides

The table below shows a summary of period 3 elements, their structures, physical states at room temperature, type of bonding, and boiling points.

	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5/PCl_3	S_2Cl_2
State at room temperature	Solid			Liquid	Liquid Gas	Liquid
Bonding	Ionic		Covalent			
Structure	Giant ionic		Layer covalent	Simple molecular		
Melting point (^{0}C)	808	713	193	-68	**160- PCl_5 --** **90 PCl_3**	-78

Preparation of the chlorides

Sodium chloride

It is prepared by heating sodium in dry chlorine gas.

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

Magnesium chloride

It is prepared by passing dry chlorine gas over heated magnesium.

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

Aluminium chloride

It is prepared by passing dry chlorine gas over heated aluminium foil.

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

Silicon tetrachloride

It is prepared by passing dry chlorine gas over a hot mixture of silicon dioxide and carbon (coke).

$$SiO_2(s) + C(s) + 2Cl_2(g) \longrightarrow SiCl_4(l) + CO_2(g)$$

Phosphorus trichloride

It is prepared by heating phosphorus in limited chlorine gas. It is also known as phosphorus(III) chloride.

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

Or

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(g)$$

Phosphorus pentachloride

It is prepared by heating phosphorus in excess chlorine gas. It is also known as phosphorus(V) chloride.

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

Or

$P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(g)$

Disulphur dichloride

It is prepared by passing a stream of dry chlorine is passed over some heated sulphur. It is a volatile red liquid with a weird smell.

$2S(s) + Cl_2(g) \longrightarrow S_2Cl_2(l)$

Sulphur dichloride

It is formed when disulphur dichloride is passed over excess chlorine.

$S_2Cl_2(l) + Cl_2(g) \longrightarrow 2SCl_2(l)$

Chemical properties of the chlorides

Reaction with water

Sodium chloride is strongly ionic and does not undergo hydrolysis, and their solutions are neutral. This is because the sodium ion in sodium chloride has a large ionic radius giving it a low charge density and low polarizing power and hence does not strongly attract water molecules.

Magnesium chloride

Magnesium chloride is partially hydrolysed in cold water to form basic magnesium chloride and hydrogen chloride gas.

$MgCl_2(s) + H_2O(l) \longrightarrow Mg(OH)Cl(aq) + HCl(g)$

Magnesium chloride is fully hydrolysed in warm water to form basic magnesium oxide and hydrogen chloride gas.

$MgCl_2(s) + H_2O(l) \longrightarrow MgO(s) + 2HCl(g)$

Aluminium chloride

Aluminium chloride is strong electrolyte, therefore it fully ionizes forming aluminium ions Al^{3+}

$AlCl_3(s) \longrightarrow Al^{3+}(aq) + 3Cl^-(aq)$

Aluminium ions Al^{3+} formed has a high charge and a small ionic radius therefore in water, it becomes heavily hydrated as follows

$Al^{3+}(aq) + 6H_2O(l) \rightleftharpoons Al(H_2O)_6^{3+}(aq)$

The hexaaquaaluminium ion formed undergoes hydrolysis as follows.

$Al(H_2O)_6^{3+}(aq) \rightleftharpoons [Al(H_2O)_5.OH]^{2+}(aq) + H^+(aq)$

Or

$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5.OH]^{2+}(aq) + H_3O^+(aq)$

The hydrogen/hydroxonium ions formed make the resultant solution acidic.

Note, for stepwise hydrolysis;

$Al(H_2O)_6^{3+}(aq) \rightleftharpoons [Al(H_2O)_5.OH]^{2+}(aq) + H^+(aq)$
$[Al(H_2O)_5.OH]^{2+}(aq) \rightleftharpoons [Al(H_2O)_4.2OH]^+(aq) + H^+(aq)$
$[Al(H_2O)_4.2OH]^+(aq) \rightleftharpoons Al(H_2O)_3.3OH(aq) + H^+(aq)$

Or

$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5.OH]^{2+}(aq) + H_3O^+(aq)$
$[Al(H_2O)_5.OH]^{2+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_4.2OH]^+(aq) + H_3O^+(aq)$
$[Al(H_2O)_4.2OH]^2+(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_3.3OH(aq) + H_3O^+(aq)$

Explain why a solution containing aluminium chloride has a pH less than 7.

State what is observed and write an equation for the reaction that would take place when sodium carbonate is added to aluminium chloride in water.

Solution

A white precipitate is formed and bubbles of a colourless gas which turn lime water milky are given off.

$Al^{3+}(aq) + 3H_2O(l) \rightleftharpoons Al(OH)_3(s) + 3H^+]X2$ (i)
$CO_3^{2-}(aq) + 2H^+(l) \rightleftharpoons CO_2(g) + H_2O(l)]X3$ (ii)
Combining equation (i) and (ii) gives the below equation.
$2Al^{3+}(aq) + 3CO_3^{2-}(aq) + H_2O(l) \longrightarrow 2Al(OH)_3(s) + 3CO_2(g)$

Silicon(IV) chloride

Silicon(IV) chloride is hydrolysed in water to form hydrated silicon dioxide and fumes of hydrogen chloride gas.

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

Phosphorus trichloride

Phosphorus trichloride is hydrolysed in water to form phosphorous acid and fumes of hydrogen gas.

$PCl_3(g) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(g)$

Phosphorus pentachloride

Phosphorus trichloride is hydrolysed in water to form phosphorous acid and fumes of hydrogen gas

$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(g)$

Disulphur dichloride

Disulphur dichloride hydrolyses in water forming a weak sulphurous acid and fumes of hydrogen chloride gas, a yellow solid of sulphur is also deposited.

$$2S_2Cl_2(l) + 3H_2O(l) \longrightarrow H_2SO_3(aq) + 3S(s) + 4HCl(g)$$

b) Oxides of period 3 elements

Oxide	Na_2O Na_2O_2	MgO	Al_2O_3	SiO_2	P_2O_3 P_2O_5	SO_2 SO_3	Cl_2O Cl_2O_7
Melting point	1257	2827	2007	1607	560	30	-91
Bond type	Ionic bond		Ionic	Covalent			
Type of structure	Giant ionic		Giant ionic	Giant covalent	Simple molecular		
Nature of oxide	Basic oxide		Amphoteric Oxide	Acidic oxide			

Note

Oxides of metals have higher melting points than those of corresponding chlorides.

Explanation

Oxygen is more electronegative than chlorine, the oxide ion is small therefore not easily polarized like a cation, this makes the oxides highly ionic with strong ionic bonds which require a lot of energy to break.

On the other hand, chloride ions are big and therefore easily polarized by cations, this makes the chlorides attain a covalent character with weaker ionic bonds which require less energy to break.

Trends

The melting points increase from sodium oxide to magnesium oxide and the decreases to dichlorine heptaoxide

Explanation

Sodium oxide, magnesium oxide and aluminium oxide ionic oxides with giant ionic structures, these ionic bonds require a lot of energy to break hence they have high melting points.

Melting point increases from sodium oxide to magnesium oxide due to increase of charge density of the cation which leads to increase in strength of the ionic bond and hence a lot of energy to break the bond.

Melting point decreases from magnesium oxide to aluminium oxide, this is due to the very charge density of aluminium which is highly polar, and this makes aluminium oxide which is slightly covalent with a weaker ionic bond which requires less energy to break the bonds.

Silicon(IV) dioxide has a high melting point, this is because it has a giant covalent structure with an infinite 3-dimensional tetrahedral arrangement of strong silicon-oxygen covalent bonds which require a lot of energy to break.

Phosphorus(V) oxide, sulphur trioxide and oxides of chlorine have lower melting points. This is because they have simple molecular structures with weak inter-molecular forces of attraction which requires less heat energy to break.

From phosphorus pentachloride to sulphur trioxide, there is a decrease in melting point due to decrease in molecular weight which leads to decrease in strength of Van der Waal's forces of attraction and hence decrease in energy required to break them.

From sulphur trioxide to dichlorine dichloride, there is decrease in strength in Van der Waal's forces of attraction as a result, melting point decreases.

Preparation of the oxides

Sodium oxide

It is prepared by burning sodium in limited air where it burns with a bright yellow flame.

$$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$$

However, in excess air sodium burns with a bright yellow flame forming sodium peroxide which is a yellow solid

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

Magnesium oxide

Magnesium oxide is prepared by burning magnesium in plentiful oxygen.

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

Aluminium oxide

Aluminium oxide is made by burning aluminium in oxygen gas.

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

Phosphorus oxides

Phosphorus reacts with oxygen present in the air to form phosphorus trioxide and phosphorus pentaoxide depending on the amount of oxygen, when the amount of oxygen is limited, phosphorus trioxide is formed. But when the oxygen is in excess, phosphorus pentaoxide is formed.

The equations can be written in any of the following ways;

For limited oxygen;

$P_4(s) + 3O_2(g) \longrightarrow 2P_2O_3(s)$

Or

$P_4(s) + 3O_2(g) \longrightarrow P_4O_6(s)$ dimerised form of phosphorus(III) oxide

For excess oxygen

$P_4(s) + 5O_2(g) \longrightarrow 2P_2O_5(s)$

Or

$P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$ dimerised form of phosphorus(V) oxide

Silicon dioxide

Silicon dioxide is made by burning in silicon in excess oxygen.

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

Sulphur dioxide

Sulphur dioxide is prepared by heating sulphur in limited oxygen where it burns with a bright blue flame forming white fumes. It is also made by reacting any hydrogensulphite with a dilute mineral acid

$H^+(aq) + HSO_3^-(aq) \longrightarrow SO_2(g) + H_2O(l)$

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

Sulphur dioxide

It is made by heating sulphur in excess oxygen.

$2S(s) + 3O_2(g) \longrightarrow 2SO_3(g)$

It can also be made by combining sulphur dioxide with oxygen in presence of vanadium pentaoxide at a temperature of 450 0C at a pressure of one atmosphere.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Dichlorine oxide

It is obtained by heating chlorine with limited air forming.

$2Cl_2(g) + O_2(g) \longrightarrow 2Cl_2O(g)$

Dichlorine heptaoxide

Dichlorine heptaoxide is made by heating excess oxygen with chlorine.

$$2Cl_2(g) + 7O_2(g) \longrightarrow 2Cl_2O_7(l)$$

Chemical properties of the oxides of period 3 elements

a) **Reaction with sodium hydroxide solution**

Sodium oxide and magnesium oxide do not react with sodium hydroxide solution because they are basic oxides.

Aluminium oxide

It is an amphoteric oxide, therefore reacts with hot concentrated sodium hydroxide solution forming sodium aluminate.

$$Al_2O_3(s) + 2\,NaOH(aq) + 3H_2O(l) \longrightarrow 2NaAl(OH)_4(aq)$$

Or

$$Al_2O_3(s) + 2\,{}^{-}OH(aq) + 3H_2O(l) \longrightarrow 2Al(OH)_4^{-}(aq)$$

Silicon dioxide

Silicon dioxide is acidic in nature; it reacts with hot concentrated sodium hydroxide solution forming sodium silicate.

$$SiO_2(s) + 2\,NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

Or

$$SiO_2(s) + 2\,{}^{-}OH(aq) \longrightarrow SiO_3^{2-}(aq) + H_2O(l)$$

Phosphorus trioxide

Phosphorus trioxide reacts with hot concentrated sodium hydroxide solution forming sodium hydrogenphosphite and water.

$$P_4O_6(s) + 8NaOH(aq) \longrightarrow 4Na_2HPO_3(aq) + 2H_2O(l)$$

Or

$$P_4O_6(s) + 8\,{}^{-}OH(aq) \longrightarrow 4HPO_3^{2-}(aq) + 2H_2O(l)$$

Phosphorus pentaoxide

Phosphorus pentaoxide reacts with hot concentrated sodium hydroxide solution forming disodium hydrogenphosphate and water.

$$P_4O_{10}(s) + 8NaOH(aq) \longrightarrow 4Na_2HPO_4(aq) + 2H_2O(l)$$

Or

$$P_4O_{10}(s) + 8\,{}^{-}OH(aq) \longrightarrow 4HPO_4^{2-}(aq) + 2H_2O(l)$$

Also

$$P_2O_5(s) + 6NaOH(aq) \longrightarrow 2Na_3PO_4(aq) + 3H_2O(l)$$

Or

$$P_2O_3(s) + 6\,{}^{-}OH(aq) \longrightarrow 2PO_4^{3-}(aq) + 3H_2O(l)$$

Sulphur dioxide

Sulphur dioxide reacts with sodium hydroxide solution forming sodium sulphate, when excess sulphur dioxide is present, sodium hydrogen sulphite is formed.

$$NaOH(aq) + SO_2(g) \longrightarrow Na_2SO_3(aq) + H_2O(l) \text{ ....(i)}$$
$$Na_2SO_3(aq) + H_2O(l) + SO_2(G) \longrightarrow 2NaHSO_3(aq)\text{....(ii)}$$

When sodium hydrogensulphite formed is heated, the following reaction takes place.

$$4NaHSO_3(aq) \longrightarrow 2Na_2SO_4(aq) + SO_2(g) + 2H_2O(l) + S(s) \text{ ....(iii)}$$

Combining equations (i), (ii) and (iii) above gives

$$4NaOH(aq) + 3SO_2(g) \longrightarrow 2Na_2SO_4(aq) + 2H_2O(l) + S(s)$$

Observation

A yellow solid is deposited

Dichlorine oxide

It reacts with sodium hydroxide solution forming sodium chlorate(I) and water.

$$Cl_2O(g) + 2NaOH(aq) \longrightarrow 2NaOCl(aq) + H_2O(l)$$

Or

$$Cl_2O(g) + 2^{-}OH(aq) \longrightarrow 2^{-}OCl(aq) + H_2O(l)$$

Dichlorine heptaoxide

Dichlorine heptaoxide reacts with sodium hydroxide solution forming sodium chlorate(VII) and water.

$$Cl_2O_7(g) + 2NaOH(aq) \longrightarrow 2NaClO_4(aq) + H_2O(l)$$

Or

$$Cl_2O_7(g) + 2^{-}OH(aq) \longrightarrow 2ClO_4^{-}(aq) + H_2O(l$$

b) Reaction with water

Sodium oxide

Sodium oxide is basic; it reacts with water solution forming sodium hydroxide.

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

Magnesium oxide

Magnesium oxide is basic; it reacts with water solution forming magnesium hydroxide.

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

Aluminium oxide is amphoteric and does not react with water because it forms strong covalent bonds.

Silicon(IV) oxide

Silicon(IV) oxide is acidic and reacts with hot water under pressure to form silicic acid.

$$\mathbf{SiO_2(s) + H_2O(l) \longrightarrow H_2SiO_3(aq)}$$

Phosphorus(III) oxide

Phosphorus(III) oxide reacts with water forming phosphorus acid

$$\mathbf{P_2O_3(s) + 3H_2O(l) \longrightarrow 2H_3PO_3(aq)}$$

Phosphorus(V) oxide

Phosphorus(V) oxide reacts with water forming phosphoric acid

$$\mathbf{P_2O_5(s) + 3H_2O(l) \longrightarrow 2H_3PO_4(aq)}$$

Sulphur dioxide

Sulphur dioxide is acidic and reacts with water forming sulphurous acid.

$$\mathbf{SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)}$$

Sulphur trioxide

Sulphur trioxide is acidic and reacts with water forming sulphurous acid.

$$\mathbf{SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)}$$

Dichlorine oxide

Dichlorine oxide reacts with water forming hypochlorous/chloric(I) acid

$$\mathbf{Cl_2O(g) + H_2O(l) \longrightarrow 2HOCl(aq)}$$

Chlorine(VII) oxide

Dichlorine heptaoxide reacts with water forming chlorate(VII) acid

$$\mathbf{Cl_2O_7(g) + H_2O(l) \longrightarrow 2HCl\ O_4(aq)}$$

c) Reaction with acids

Sodium oxide

Sodium oxide is basic and reacts with dilute mineral acids forming sodium salts and water.

$$\mathbf{Na_2O(s) + 2H^+(aq) \longrightarrow 2Na^+(aq) + H_2O(l)}$$

Magnesium oxide

Sodium oxide is basic and reacts with dilute mineral acids forming magnesium salts and water.

$$\mathbf{MgO(s) + 2H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l)}$$

Aluminium oxide

Aluminium oxide is amphoteric and reacts with dilute mineral acids forming aluminium salts and water.

$$Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O(l)$$

The rest of the oxides are acidic and therefore do not react with acids.
However, silicon(IV) oxide is the only period 3 oxide which reacts with hydrofluoric acid forming silicon(V) fluoride and water.

$$SiO_2(s) + HF(aq) \longrightarrow SiF_4(l) + H_2O(l)$$

Hydrides of period 3 elements

These are compounds of hydrogen. Metals form ionic hydrides while non-metals form covalent hydrides.

Hydride	NaH	MgH2	AlH3	MgH2	PH3	H2S	HCl
Bond type	Ionic	Covalent					
Structure	Giant ionic	Simple molecular					

Preparation of the hydrides

Sodium hydride

It is prepared by passing dry hydrogen gas over hot sodium

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

Magnesium hydride

It is prepared by passing dry hydrogen gas over hot magnesium metal.

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

Aluminium hydride

It is prepare by heating a mixture of lithium hydride and aluminium chloride in ether.

$$3LiH(s) + AlCl_3(s) \longrightarrow AlH_3(s) + 3LiCl(s)$$

Silicon(IV) hydride (Silane)

It is prepare by reacting a mixture of lithium aluminium tetrahydride and silicon tetrachloride chloride.

$SiCl_4(l) + LiAlH_4(s) \longrightarrow SiH_4(g) + LiCl(s) + AlCl3(s)$

Phosphine

It is prepared by heating phosphorus with hot concentrated sodium hydroxide solution.

$P_4(s) + 3NaOH(aq) + 3H_2O(l) \longrightarrow 3NaH_2PO_2(aq) + PH_3(g)$

Hydrogen sulphide

It is prepared by reacting iron(II) sulphide with either dilute hydrochloric or sulphuric acid.

$FeS(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2S(g)$

Hydrogen chloride

Hydrogen chloride is prepared by reacting sodium chloride and concentrated sulphuric acid.

$NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(aq) + HCl(g)$

Chemical properties of the halides

a) Reaction with water (hydrolysis)

Sodium hydride

Sodium hydride reacts with water to form sodium hydroxide and hydrogen gas

$NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$

Magnesium hydride

Magnesium hydride reacts with water forming magnesium hydroxide and hydrogen gas.

$MgH_2(s0 + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + 2H_2(g)$

Aluminium hydride does not react with water/does not undergo hydrolysis.

Silane

Silicon tetrahydride reacts with hot water forming silicon dioxide and hydrogen gas, in this case, sodium hydroxide or dilute sulphuric acid may be used as a catalyst.

$SiH_4(g) + 2H_2O(l) \longrightarrow SiO_2(s) + 4H_2(g)$

However, it reacts with water forming silicic acid and hydrogen gas

$SiH_4(g) + 3H_2O(l) \longrightarrow H_2SiO_3(aq) + 4H_2(g)$

Silicon tetrahydride also reacts with water in presence of alkalis like sodium hydroxide solution forming sodium silicate and hydrogen gas.

$SiH_4(g) + H_2O(l) +2 NaOH \longrightarrow Na_2SiO_3(s) + 4H2(g)$

Phosphine does not react with water/undergo hydrolysis

Hydrogen sulphide

Hydrogen sulphide partially ionizes in water forming hydroxonium ions and sulphide ions according to the following equation;

$H_2S(g) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$

Hydrogen chloride

It ionises in water completely as follows;

$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

b) Reaction with sodium hydroxide solution

Sodium hydride, magnesium hydride, aluminium hydride and phosphine do not react with sodium hydroxide solution (alkalis)

Silane

Silane reacts with sodium hydroxide solution forming sodium silicate and hydrogen gas.

$SiH_4(g) + H_2O(l) + 2\ NaOH \longrightarrow Na_2SiO3(s) + 4H_2(g)$

Or

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

Hydrogen sulphide

Hydrogen sulphide reacts with sodium hydroxide solution forming sodium hydrogensulphide and water.

$H_2S(g) + NaOH(aq) \rightleftharpoons NaHS(aq) + H_2O(l)$

Hydrogen chloride

It reacts with sodium hydroxide solution forming a solution of sodium chloride and water.

$HCl(g) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

c) Reaction with acids

With nitric acid

Concentrated nitric acid oxidises hydrogen sulphide (a strong reducing agent) to sulphur and its self is reduced to nitrogen dioxide and water.

$H_2S(g) + 2HNO_3(aq) \longrightarrow S(s) + 2NO_2(g) + 2H_2O(l)$

With sulphuric acid

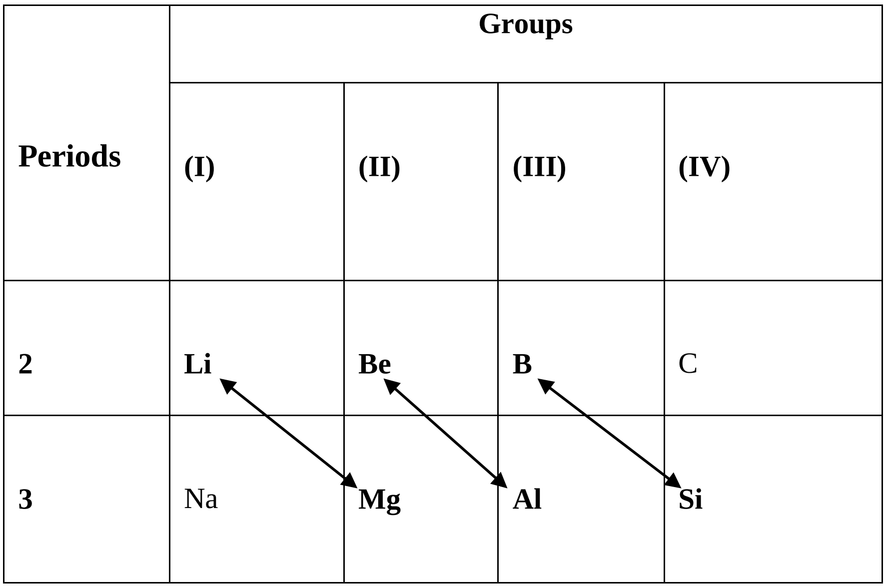
Concentrated sulphuric acid oxidises hydrogen sulphide (a strong reducing agent) to sulphur and its self is reduced to sulphur dioxide and water.

$$H_2S(g) + H_2SO_4(l) \longrightarrow S(s) + SO_2(g) + 2H_2O(l)$$

The rest of the hydrides do not react acids.

DIAGONAL RELATIONSHIP

Part of the periodic table is shown below;



Periods	**Groups**			
	(I)	**(II)**	**(III)**	**(IV)**
2	**Li**	**Be**	**B**	C
3	Na	**Mg**	**Al**	**Si**

Down the group in the periodic table, atomic radius increases while charge density, polarizing power and electronegativity decrease.

Across the period, atomic radius decreases while charge density, polarizing power and electronegativity increase.

A decrease in atomic radius, an increase in charge density, polarizing power and electronegativity across the period are offset by the an increase in atomic radius and a decrease in charge density, polarizing power and electronegativity down the group on moving from one element to another in a diagonal way. Therefore, elements which are diagonally opposite to each other have similar atomic radius, charge density, polarizing power and electronegativity, such elements therefore have similar chemistry and are described to have diagonal relationship.

From the above table, the two elements shown by the directional arrows are such that one is a period 2 element while the other is a period 3 element. It can also be noted that the pair of elements come from two adjacent groups and are diagonally neighbouring each other.

Diagonal relationship is the similarity (resemblance) in chemical properties between elements in period 2 of the periodic table and those elements that are diagonally adjacent to each other in neighbouring groups and are in period 3.

Diagonal relationship is shown by the following pairs of elements

- Lithium and magnesium
- Beryllium and aluminium
- Boron and silicon

Reasons why the elements show diagonal relationship (similar chemical properties)

- ✓ Their atoms have the same atomic radius
- ✓ The atoms of these elements have similar electronegativities
- ✓ Their cations have the same charge density
- ✓ Their cations have similar polarizing power
- ✓ Their cations have the same standard electrode potentials

Chemical properties of the elements that have diagonal relationship

a) **Lithium and magnesium**

Below are some of the reactions in which lithium resembles magnesium

Reaction with nitrogen

Lithium and magnesium react with nitrogen gas on heating to form corresponding ionic nitrides.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

Other group(I) elements have no similar reaction.

Reaction with oxygen

Lithium and magnesium react with excess oxygen gas on heating to form corresponding ionic oxides.

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$$

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

Other group(I) elements peroxides and super oxides with excess oxygen.

$$2Na(s) + O_2(g) \longrightarrow Na_2O2(s)$$

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

Action of heat on nitrates of the elements

Lithium nitrate and magnesium nitrate decompose to form their respective oxides, nitrogen dioxide gas and oxygen

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

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

The nitrates of other group(I) elements decompose forming a nitrite and oxygen gas

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

$$2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$$

Action of heat on carbonates of the elements

Lithium carbonate and magnesium carbonate decompose to form their respective oxides, and carbon dioxide gas.

$$Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$$

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$$

The carbonates of other group(I) elements do not decompose when heated i.e they are thermally stable.

Note

Lithium hydrogencarbonate and magnesium hydrogencarbonate can only exist in solution whereas the solid hydrogencarbonates of other group(I) elements can be prepared.

Action of heat on hydroxides of the elements

Lithium hydroxide and magnesium hydroxide decompose to form corresponding oxides, and water.

$$2LiOH(s) \longrightarrow Li_2O(s) + H_2O(l)$$

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

The hydroxides of other group(I) elements do not decompose when heated i.e they are stable to heat.

Solubility of the compounds of the elements

Phosphates, carbonates, fluorides and hydroxides of lithium are sparingly (slightly) soluble while corresponding compounds of other group(I) elements are much more soluble.

b) Beryllium and aluminium

Beryllium and aluminium show chemical similarities discussed below.

Reaction with alkalis

Both beryllium and aluminium react with hot concentrated solution of alkalis such as sodium hydroxide solution to form complexes of sodium beryllate and aluminium beryllate respectively and hydrogen gas.

Molecular for Be

$Be(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow Na_2Be(OH)_4(aq) + H_2(g)$

Ionic

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

Molecular for Al

$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2NaAl(OH)_4(aq) + 3H_2(g)$

Ionic equation

$2Al(s) + 2^-OH(aq) + 6H_2O(l) \longrightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$

Other group(II) elements do not react with alkalis

Reaction with nitric acid

Both beryllium and aluminium are rendered passive by concentrated nitric acid.

Other group(II) elements react with nitric acid according to conditions of temperature and concentration.

Magnesium reacts with cold moderately concentrated nitric acid forming magnesium nitrate, nitrogen monoxide gas and water

$3Mg(s) + 8HNO_3(aq) \longrightarrow 3Mg(NO3)_2(aq) + 2NO(g) + 4H_2O(l)$

Magnesium reacts with hot concentrated nitric acid forming magnesium nitrate, nitrogen dioxide gas and water.

$Mg(s) + 4HNO_3(aq) \longrightarrow Mg(NO3)_2(aq) + 2NO_2(g) + 4H_2O(l)$

Oxides of lithium and magnesium

The oxides of beryllium and aluminium are amphoteric and therefore react with both acids and alkalis.

With alkalis, beryllium and aluminium form beryllate and aluminate respectively

$BeO(s) + 2NaOH(aq) + H_2O(l) \longrightarrow Na_2Be(OH)_4(aq)$

Or

$BeO(s) + 2^-OH(aq) + H_2O(l) \longrightarrow Be(OH)4^{2-}(aq)$

And

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2NaAl(OH)_4(aq)$

Or

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

With acids, they form corresponding salts and water.

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

$Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O(l)$

The oxides of group(II) elements are basic, therefore react with acids but not bases

$MO(s) + 2H^+(aq) \longrightarrow M^{2+}(aq) + H_2O(l)$

The carbides of beryllium and aluminium

Carbides of beryllium and aluminium (contain C^{4-} ion) and hydrolyse in water giving methane gas and a corresponding hydroxide.

$Be_2C(s) + 4H_2O(l) \longrightarrow 2Be(OH)_2(aq) + CH_4(g)$

$Al_4C_3(s) + 14H_2O(l) \longrightarrow 4Al(OH)_3(aq) + 3CH_4(g)$

Carbides of other group(II) elements give alkynes on hydrolysis as follows

- ✓ Calcium carbide (contain $C{\equiv}C^{2-}$ ion)gives ethyne on hydrolysis

  $CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + HC{\equiv}CH(g)$

- ✓ Magnesium carbide (contain C_3^{4-} ion) on hydrolysis gives propyne

  $Mg_2C_3(s) + 4H_2O(l) \longrightarrow 2Mg(OH)_2(aq) + CH_3C{\equiv}CH(g)$

Beryllium and aluminium form fused chlorides with low melting points and low conductivity and the chlorides are easily hydrolysed in water as shown below. The resultant solution is acidic.

This is because; beryllium chloride is a soluble salt hence in water it is ionized to give beryllium ions and chloride ions.

$BeCl_2(s) \longrightarrow Be^{2+}(aq) + 2Cl\text{-}(aq)$

The beryllium ion formed has a high ionic charge and a small ionic radius giving it a high charge density hence in water it is heavily hydrated.

$Be^{2+}(aq) + 4H_2O(l) \longrightarrow Be(H_2O)_4^{2+}(aq)$

The $Be(H_2O)_4^{2+}$ formed undergoes hydrolysis as follows;

$Be(H_2O)_4^{2}+(aq) \rightleftharpoons [\,Be(H_2O)_3.OH]^+(aq) + H^+(aq)$

Or

$Be(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons [\,Be(H_2O)_3.OH]^+(aq) + H_3O^+(aq)$

The hydrogen/hyroxonium ions formed are responsible for the acidic nature of the resultant solution.

Aluminium chloride is strong electrolyte; therefore it fully ionizes forming aluminium ions Al^{3+}

$AlCl_3(s) \longrightarrow Al^{3+}(aq) + 3Cl\text{-}(aq)$

Aluminium ions Al^{3+} formed has a high charge and a small ionic radius therefore in water; it becomes heavily hydrated as follows

$Al^{3+}(aq) + 6H_2O(l) \rightleftharpoons Al(H_2O)_6^{3+}(aq)$

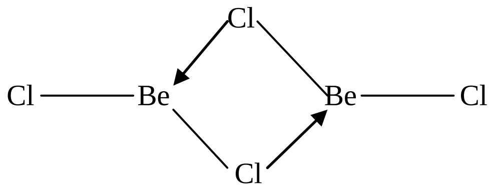
The hexaaquaaluminium ion formed undergoes hydrolysis as follows.

$Al(H_2O)_6^{3+}(aq) \rightleftharpoons [Al(H_2O)_5.OH]^{2+}(aq) + H+(aq)$
Or
$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5.OH]^{2+}(aq) + H_3O^+(aq)$

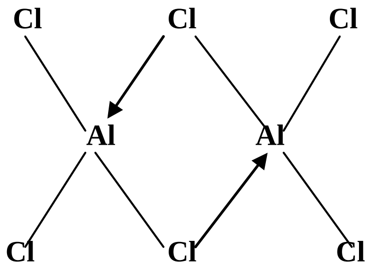
The hydrogen/hydroxonium ions formed make the resultant solution acidic.

Also, the chlorides dimerise in vapour phase and exist as dimers.

$2BeCl_2(g) \rightleftharpoons Be_2Cl_4(g)$



$2AlCl_3(g) \rightleftharpoons Al_2Cl_6$



The chlorides of other group(II) elements have high conductivity and boing points, they are ionic and not easily hydrolysed in water.

c) **Boron and silicon**

Below are some reactions in which the chemistry of boron and silicon are similar

Reaction with air

Silicon and boron react with dry oxygen on strong heating to form acidic oxides as shown below.

$2B(s) + 3O_2(g) \longrightarrow 2B_2O_3(s)$

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

Aluminium also forms an oxide when heated in dry oxygen, but the oxide formed is amphoteric.

Boron trichloride and silicon tetrachloride are covalent liquids at room temperature while aluminium chloride is partly ionic and a solid at room temperature.

Boron and silicon form hydrides which are covalent and volatile and readily ignite in air, while aluminium forms polymerized hydrides.

Boron and silicon form only covalent compounds while other group(III) elements like aluminium form ionic and covalent compounds.

Guiding question

a) Define the term diagonal relationship

b) State any three pairs of elements which exhibit the above property

c) Outline any four reason why the elements you have stated in (a) above show diagonal relationship

d) Describe any two properties in each case to show how the stated pair of elements are similar to each other.

GROUP CHEMISTRY

The elements in the periodic table are vertically in groups which include the following

- Group(I) elements
- Group(II) elements
- Group(III) elements
- Group(IV) elements

- Group(V) elements
- Group(VI) elements
- Group(VII) elements
- Group(VIII) elements

All elements in the same group have the same

- ✓ Chemical properties
- ✓ Number of electrons in the outermost shell/subshell, this forms basis for naming a given group for example all elements in group(I) have one electron in their outermost shell.

Elements in the same group are referred to as a chemical family.

a) GROUP(I) ELEMENTS

They are also called alkaline metals

They are very reactive and therefore kept under oil in the laboratory such that they do not come into direct contact with water and air.

They are highly electropositive and include the following;

- ✓ Lithium Li
- ✓ Sodium Na
- ✓ Potassium K
- ✓ Rubidium Rb
- ✓ Ceasium Cs

They have a general outer electronic configuration of nS^1 and they tend to lose electrons easily forming stable positive ions with a charge of +1 and therefore they are reducing agents.

Their ionisation energies are low and reduce down the group, the table below shows the ionisation energies of group(I) elements.

Element	**1st ionisation energy ($KJMol^{-1}$)**	**2nd ionisationenergy ($KJMol^{-1}$)**
Li	520	7300
Na	500	4600
K	420	3100
Rb	400	2700
Cs	320	2100

Comments

First ionisation energies decrease down the group, this because, down the group, nuclear charge increases due to increase in number of protons. Also screening effect increases due to addition of a full inner energy level of electrons. The increase in screening effect outweighs the increase in nuclear charge therefore the effective nuclear charge decreases leading to an increase in atomic radius thus the ionisation energy reduces.

There is a very big difference between the first and second ionisation energies (first ionisation energy is much lower than second ionisation energy). This is because; after losing the first electron for example in ^{3}Li, E.C= $1S^{2}2S^{1}$, from the $2S^{1}$ subshell, the remaining fewer electrons are strongly held by the constant nuclear charge, also the radius of the ion formed is smaller than that of its parent atom, and keeping in mind that the second electron is being removed from $1S^{2}$ sub-energy level which is full energy, these factors combined imply that the electron being removed is very strongly attracted to the nucleus and consequently a lot of energy is required to remove it, that is why the second ionisation energy is much greater than the first ionisation energy.

Physical properties of group(I) elements

- ✓ They have low melting and boiling points, and the melting points reduce down the group. This is due to the fact that each group(I) element contributes one electron towards the metallic bond and also the strength of the metallic bond reduces down the group due to increase in atomic radius.
- ✓ They are soft and can be easily cut by a knife, however, softness decreases down the group.
- ✓ They have shinny surfaces when freshly cut, but they soon tarnish when exposed to air with which they react to form oxides.
- ✓ They are good conductors of heat and electricity
- ✓ They have low densities, and no tensile strength
- ✓ They occur naturally as salts such as sodium chloride, potassium chloride and they are extracted by electrolysis.
- ✓ Their compounds are all white crystalline salts with high melting points due to the high degree of ionic character.
- ✓ They mainly form ionic compounds which are very stable to heat due to the low charge density of their ions.

Their nitrates decompose on heating to form nitrites and oxygen gas except lithium

$$NaNO_3(s) \longrightarrow NaNO_2(s) + O_2(g)$$

Lithium nitrate decomposes forming lithium oxide, nitrogen dioxide and oxygen gas

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

Their carbonates, sulphates and hydroxides do not decompose on heating except for lithium which decompose as follows;
Lithium carbonate decomposes when heated forming lithium oxide and carbon dioxide gas

$$Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$$

Lithium hydroxide decomposes on heating to form lithium oxide and water.

$$2LiOH(s) \longrightarrow Li_2O(s) + H_2O(l)$$

Their hydrogencarbonates exist as solids and decompose on heating tp form carbonates, carbon dioxide gas and water.

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

$$\mathbf{2KHCO_3(s) \longrightarrow K_2CO_3(s) + CO_2(g) + H_2O(l)}$$

Their compounds are soluble in water because the hydration energies of their solutions are slightly higher than the lattice energies therefore they are able to easily dissolve in water.
For lithium, it has a high enthalpy of hydration due to its small size, which gives it a higher charge density (polarizing power)

Question

1. When 20g of a mixture of anhydrous sodium carbonate and sodium hydrogencarbonate was heated and cooled, 13.8g of the mixture remained.
   Write an equation for the reaction that took place.
   $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$
   Calculate the percentage of sodium hydrogencarbonate in the mixture.

Solution

Loss in mass = (20-13.8)g
= 6.2g

Rfm of $NaHCO_3$ *= (1x23) + (1x1) + (3x16)*
= 84

Rfm of CO_2 *= (1x12) + (2x16)*
= 44

Rfm of H_2O *= (2x1) + (1x16)*
= 18

Rfm of H_2O *and* CO_2 *= (18+44) = 62*

62g is the loss in mass by 2x84g of sodium hydrogencarbonate

6.2g is loss in mass by $\frac{2x84}{62}$ *x 6.2*
= 16.8g

Percentage of sodium hydrogencarbonate

$= \frac{mass\ of\ sodium\ hydrogencarbonate}{rfm} x\ 100\%$

$= \frac{16.8}{20}$ *x 100%*

= 84%

b) Chemical properties of group(I) elements

Reaction with air

Lithium burns in air with a red flame forming a mixture of lithium oxide and lithium nitride

$$\mathbf{4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)}$$

$$\mathbf{6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)}$$

In limited air, sodium burns with a bright yellow flame forming a white solid of sodium oxide

$$2Na(s) + O_2(g) \xrightarrow{\qquad\qquad} 2Na_2O(s)$$

However in excess air, sodium forms a yellow solid of sodium peroxide.

$$2Na(s) + O_2(g) \xrightarrow{\qquad\qquad} Na_2O_2(s)$$

Potassium burn with a bright purple flame forming a white solid of potassium oxide

$$2K(s) + O_2(g) \xrightarrow{\qquad\qquad} 2K_2O(s)$$

However in excess air, sodium forms potassium peroxide.

$$2K(s) + O_2(g) \xrightarrow{\qquad\qquad} K_2O_2(s)$$

Potassium also forms potassium super oxide with excess oxygen

$$K(s) + O_2(g) \xrightarrow{\qquad\qquad} KO_2(s)$$

Structures

For peroxide

$$O^- - O^- \qquad (O_2^{2-})$$

For super oxide

$$[O \overset{- - - -}{\text{——}} O]^- \qquad (O_2^-)$$

NOTE

The affinity for oxygen by the elements increases down the group. Lithium has a charge of +1 and a small ionic radius giving it a very high charge density which polarizes the large peroxide and super oxide ions forming unstable lattices at room temperature which readily dissociate to form stable normal oxides.

Reaction with water

Lithium reacts very slowly with cold water at room temperature forming lithium hydroxide and hydrogen gas

$$2Li(s) + 2H_2O(l) \xrightarrow{\qquad\qquad} 2Li(OH) + H_2(g)$$

When heated, lithium reacts vigorously with steam forming lithium oxide and hydrogen gas

$$2Li(s) + H_2O(g) \xrightarrow{\qquad\qquad} Li_2O(s) + H_2(g)$$

Sodium reacts vigorously with cold water forming sodium hydroxide and hydrogen gas. It melts into a silvery ball, dirts the surface of water producing a hissing sound. The solution formed is hot, implying that the reaction is exothermic.

$$2Na(s) + 2H_2O(l) \xrightarrow{\qquad\qquad} 2NaOH(aq) + H_2(g)$$

Potassium also reacts with cold water but more vigorously than sodium, it dirts the water surface producing a purple (lilac) flame forming potassium hydroxide and hydrogen gas.

$$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$$

Sodium and potassium hydroxide solutions are the strongest alkalis known.

Reaction with halogens

Hot metals react with halogen vapours as follows;
Lithium reacts with dry chlorine gas when hot forming lithium chloride

$$2Li(s) + Cl_{2(}g) \longrightarrow 2LiCl(s)$$

Sodium reacts with dry chlorine gas forming sodium chloride

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

Potassium also reacts with chlorine in a similar way

$$2K(s) + Cl_2(g) \longrightarrow 2KCl(s)$$

Generally, the reaction between group(I) elements and halogens can be represented by the equation below;

$$2M(s) + X_2(g) \longrightarrow 2MX(s)$$

Where M = Li, Na, K and X = F, Cl, Br, I

Reaction with acids

Dilute hydrochloric acid

Lithium reacts with dilute hydrochloric acid forming lithium chloride and hydrogen gas

$$2Li(s) + 2HCl(aq) \longrightarrow 2LiCl(aq) + H_2(g)$$

Sodium reacts with vigously dilute hydrochloric acid forming sodium chloride and hydrogen gas

$$2Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$$

Potassium reacts violently with dilute hydrochloric acid forming potassium chloride and hydrogen gas

$$2K(s) + 2HCl(aq) \longrightarrow 2KCl(aq) + H_2(g)$$

With dilute sulphuric acid

Lithium reacts with dilute sulphuric acid forming lithium sulphate and hydrogen gas

$$2Li(s) + H_2SO_4(aq) \longrightarrow Li_2SO_4(aq) + H_2(g)$$

Sodium reacts with dilute sulphuric acid forming lithium sulphate and hydrogen gas

$2Na(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2(g)$

Potassium reacts with dilute sulphuric acid forming lithium sulphate and hydrogen gas

$2K(s) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + H_2(g)$

With concentrated sulphuric acid
The elements react explosively with concentrated sulphuric acid forming sulphates, sulphur dioxide gas and water.

$2Li(s) + 2H_2SO_4(aq) \longrightarrow Li_2SO_4(aq) + SO_2(g) + 2H_2O(l)$

$2Na(s) + 2H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + SO_2(g) + 2H_2O(l)$

$2K(s) + 2H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + SO_2(g) + 2H_2O(l)$

These reactions are very explosive and should not be tried out in ordinary laboratories

With nitric acid
The elements reacts with very dilute nitric acid forming nitrates and hydrogen gas

$2Li(s) + 2HNO_3(aq) \longrightarrow 2LiNO_3(aq) + H_2(g)$

$2Na(s) + 2HNO_3(aq) \longrightarrow 2NaNO_3(aq) + H_2(g)$

$2K(s) + 2HNO_3(aq) \longrightarrow 2KNO_3(aq) + H_2(g)$

When reacted with concentrated nitric acid, brown fumes of nitrogen dioxide gas are formed

$Li(s) + 2HNO_3(aq) \longrightarrow LiNO_3(aq) + NO_2(g) + H_2O(l)$

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

$K(s) + 2HNO_3(aq) \longrightarrow KNO_3(aq) + NO_2(g) + H_2O(l)$

Reaction with hydrogen
Lithium reacts with hydrogen on heating to form lithium hydride

$2Li(s) + H_2(g) \longrightarrow 2LiH(s)$

Sodium reacts with hydrogen on heating to form sodium hydride

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

Lithium reacts with hydrogen on heating to form lithium hydride

$$2K(s) + H_2(g) \longrightarrow 2KH(s)$$

Guiding question

State the type of bond formed when sodium reacts with hydrogen

Describe an experiment to identify the bond stated above

Solution

Solid sodium hydride is heated to its melting point and the molten solution is electrolysed using graphite electrodes

At the anode, the hydride ions are discharged producing hydrogen gas which burns with a pop sound

$$H^-(aq) \longrightarrow H_2(g) + 2e$$

The mass of the cathode increases due to the discharge of sodium ions forming sodium

$$Na^+(aq) + e \longrightarrow Na(s)$$

The formation of hydrogen gas and solid metal shows that sodium hydride is ionic.

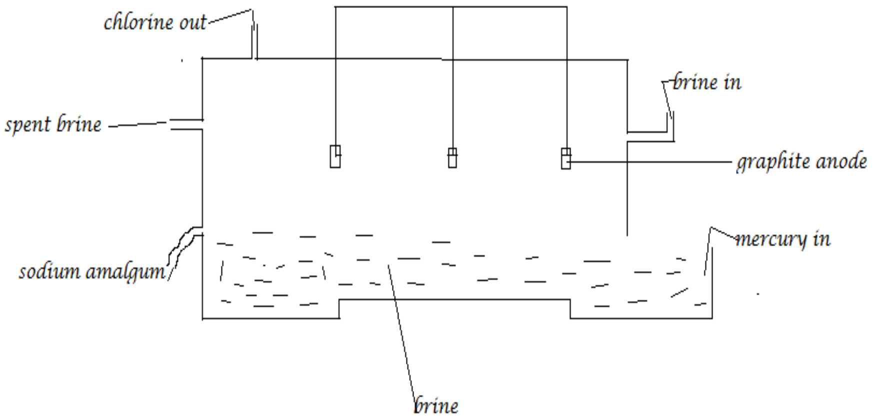
Compounds of group(I) elements

Salts of group(I) elements are more soluble in water than corresponding salts of group(II) elements due to relatively lower lattice energy. They include;

a) Hydroxides

The hydroxides of group(I) are strong alkalis, they are manufactured on large scale by electrolysis of concentrated solutions of chlorides for example concentrated sodium chloride (brine)

Manufacture of sodium hydroxide by electrolysis of brine using flowing mercury cathode and graphite anode



Brine gives a high concentration of sodium and chloride ions

$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$

At the anode, the chloride ions are discharged producing chlorine gas

Reaction at the anode
$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$

At the cathode, the sodium ions are discharged producing sodium metal

Reaction at the cathode
$Na^+(aq) + e \longrightarrow Na(s)$

The sodium formed reacts with mercury to form sodium amalgam

$Na(s) + Hg(l) \longrightarrow NaHg(l)$

The sodium amalgam formed reacts with water to form sodium hydroxide, mercury and hydrogen gas.

$2NaHg(l) + H_2O(l) \longrightarrow 2NaOH(aq) + Hg(l) + H_2(g)$

b) **Sodium thiosulphate $Na_2S_2O_3.5H_2O$**
Properties and uses

It reacts with dilute hydrochloric acids forming a yellow solid, and bubbles of a colourless gas. This is commonly used to obtain reaction rates of a particular reaction by varying the concentration of the acid

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$

With iodine, it forms tetrathionate and iodide

$$2S_2O_3^{2-}(aq) + I_2(aq \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

c) Carbonates and hydrogencarbonates

When sodium/potassium hydroxide is bubbled with carbon dioxide, sodium/potassium carbonate solution is formed; when the carbon dioxide is excess, sodium/potassium hydrogencarbonate which is a white precipitate is formed. These reactions are illustrated by the equations below;

$$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

$$2KOH(aq) + CO_2(g) \longrightarrow K_2CO_3(aq) + H_2O(l)$$

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

$$K_2CO_3(aq) + CO_2(g) + H_2O(l) \longrightarrow 2KHCO_3(s)$$

Sodium/potassium carbonate is stable to heat because the compound is more ionic and therefore does not decompose on heating.
Sodium/potassium hydrogencarbonate partially decomposes when heated to form sodium/potassium carbonate, carbon dioxide gas and water.

This reaction is used to test for presence of carbon dioxide.

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

$$2KHCO_3(s) \longrightarrow K_2CO_3(aq) + CO_2(g) + H_2O(l)$$

When a saturated solution of sodium carbonate is poured in a transparent glass beaker and a cotton thread inserted into it and removed to dry then placed back into the saturated solution, crystals begin forming around it and finally a large crystal is formed. This crystal is hydrated sodium carbonate $Na_2CO_3.10H_2O$ (sodium carbonate decahydrate), Hydrated sodium carbonate is efflorescent, it therefore loses its water of crystallization when exposed to the atmosphere.

d) Sulphates and hydrogensulphates

Sodium/potassium sulphate is formed by reacting dilute sulphuric acid and sodium/potassium hydroxide solution, a reaction known as neutralization.

These sulphates are soluble salts; the solid salt is obtained by warming the solution of the salt until a solid begins to form after which it is allowed to cool and the excess water poured off.

$$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$

$$2KOH(aq) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + 2H_2O(l)$$

Hydrogensulphates of sodium and potassium can be prepared by reacting a sodium or potassium halide and concentrated sulphuric acid.

$$NaCl(s) + \quad + H_2SO_4(l) \longrightarrow NaHSO_4(aq) + HCl(g)$$

$$KBr(s) + \quad + H_2SO_4(l) \longrightarrow KHSO_4(aq) + HBr(g)$$

Sodium also forms hydrated sodium sulphate $Na_2SO_4.10H_2O$ (sodium sulphate decahydrate) which is efflorescent.

e) **Nitrates**

The nitrates of sodium and potassium decompose on heating to form respective nitrites and oxygen gas.

$$NaNO_3(s) \longrightarrow NaNO_2(s) + O_2(g)$$

$$NaNO_3(s) \longrightarrow NaNO_2(s) + O_2(g)$$

Lithium nitrate decomposes forming lithium oxide, nitrogen dioxide and oxygen gas

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

GROUP(II) ELEMENTS

These are also called alkaline earth metals which include the following

- ✓ Beryllium Be
- ✓ Magnesium Mg
- ✓ Calcium Ca

- ✓ Strontium Sr
- ✓ Barium Ba

They have a general outer electronic configuration of nS^2

They mainly occur as carbonates, phosphates, silicates and sulphates

They mainly form ionic compounds

They are ductile, malleable and good conductors of both heat and electricity

Physical properties of group(II) elements

Element	Be	Mg	Ca	Sr	Ba
Atomic radius (nm)	112	160	197	215	260
Ionic radius (nm)	31	72	100	118	130
1st I.E ($KJMol^{-1}$)	899	738	590	550	500
2nd I.E ($KJMol^{-1}$)	1800	7700	1150	1080	770
Electronegativity	1.5	1.2	1.1	1.0	0.9
Melting point (^0C)	1287	649	839	768	674
Metallic structure	Hexagonal closely packed	Hexagonal closely packed	Body centered cubic	Cubic closely packed	Hexagonal close packing

Trends and explanations of the properties

a) **Atomic radius**

Trend

Atomic radius increases down the group

Explanation

Down the group, nuclear charge increases due to increase in the number of protons.
Similarly, screening effect increases due addition of a full inner energy level electrons
The increase in screening effect outweighs the increase in nuclear charge and the effective nuclear charge reduces leading to an increase in atomic radius.

b) **Ionic radius**

Trend

Ionic radius is smaller than atomic radius of the same element

Explanation

When cations are formed, the screening effect decreases due to loss of electrons while the nuclear charge remains constant, consequently effective nuclear charge increases, the same nuclear charge now attracts the remaining fewer electrons strongly and closely to the nucleus, this therefore makes ionic radius smaller than atomic radius of the same element.

c) **First ionisation energy**

Trend

First ionisation energy decreases down the group

Explanation

Down the group, nuclear charge increases due to increase in number of protons.

Also screening effect increases due to addition of a full inner energy level of electrons.

The increase in screening effect outweighs the increase in nuclear charge, the effective nuclear charge decreases and atomic radius increases; consequently, ionisation energy reduces since electrons will be weakly attracted to the nucleus.

d) Second ionisation energy

Trend

Second ionisation energy also decreases down the group but it is much higher than first ionisation energy

Explanation

After losing the first electron, screening effect decreases, nuclear charge remains constant meaning that effective nuclear charge increases, therefore the remaining fewer electrons are more strongly attracted by the constant nuclear charge and as a result, a lot of energy is required to remove the second electron thus second ionisation energy is much greater than first ionisation.

e) Electronegativity

Trend

Electronegativity decreases down the group

Explanation

Down the group(II), nuclear charge increases due to addition of protons to the nucleus from one element to the next.

Similarly, screening effect increases due to addition of a full inner energy level of electrons.

The increase in screening effect outweighs the increase in nuclear charge; therefore the effective nuclear attraction for incoming electrons decreases thus an increase in electropositivity.

f) Melting point

Trend

Melting point decreases down group(II) except that the melting point of magnesium is lower than expected.

Explanation

Down the group, atomic radius increases and also the distance between the delocalized electrons increase. Also each atom contributes two electrons towards the metallic bond therefore the strength of each atomic bond would be expected to be the same but that does not happen because as atomic radius increases, the bond becomes longer and weaker, thus the energy required to break it decreases with increasing atomic radius.

The melting point of magnesium is lower than that of calcium because magnesium has a hexagonal close packed structure which results into weaker inter metallic bonds that require less energy to break.

Chemical properties of group(II) elements

Group(II) elements lose two electrons in the outermost shell thereby losing being oxidised to +2 oxidation state, therefore they are reducing agents.

a) **Reaction with air**

When heated, group(II) elements react with air to form oxides and nitrides

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

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

$$2Sr(s) + O_2(g) \longrightarrow 2SrO(s)$$

$$2Ba(s) + O_2(g) \longrightarrow 2BaO(s)$$

The barium oxide is only formed when the amount of air is limited, but in excess oxygen, barium forms a peroxide.

$$Ba(s) + O_2(g) \longrightarrow BaO_2(s)$$

Also

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

$$3Ca(s) + N_2(g) \longrightarrow Ca_3N_2(s)$$

$$3Sr(s) + N_2(g) \longrightarrow Sr_3N_2(s)$$

$$3Ba(s) + N_2(g) \longrightarrow Ba_3N_2(s)$$

b) **Reaction with water**

Beryllium does not react with water at any condition, reactivity of the elements with water increases down the group.

Magnesium reacts slowly with cold water at room temperature forming magnesium hydroxide and hydrogen gas.

$$Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + H_2(g)$$

When heated, magnesium reacts vigorously with steam forming magnesium oxide and hydrogen gas.

$$Mg(s) + 2H_2O(g) \longrightarrow MgO\ (s) + H_2(g)$$

The rest of the elements react with cold water at room temperature forming hydroxides of the metal and hydrogen gas.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

$$Sr(s) + 2H_2O(l) \longrightarrow Sr(OH)_2(aq) + H_2(g)$$

$$Ba(s) + 2H_2O(l) \longrightarrow Ba(OH)_2(aq) + H_2(g)$$

c) **Reaction with acids**

With dilute hydrochloric acid

Group(II) elements react with dilute hydrochloric acid forming a chloride of the metal and hydrogen gas. The reaction with hydrochloric acid becomes more vigorous down the group.

$$Be(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + H_2(g)$$

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

$$Ca(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2(g)$$

$$Sr(s) + 2HCl(aq) \longrightarrow SrCl_2(aq) + H_2(g)$$

$$Ba(s) + 2HCl(aq) \longrightarrow BaCl_2(aq) + H_2(g)$$

With dilute sulphuric acid

The elements react with dilute sulphuric acid forming sulphates and hydrogen gas but the rate of reaction reduces down the group because of formation of insoluble sulphates which prevent further reaction.

$$Be(s) + H_2SO_4(aq) \longrightarrow BeSO_4(aq) + H_2(g)$$

Warming is necessary for beryllium to react.

$$Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$$

$$Ca(s) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + H_2(g)$$

$$Sr(s) + H_2SO_4(aq) \longrightarrow SrSO_4(aq) + H_2(g)$$

$$Ba(s) + H_2SO_4(aq) \longrightarrow BaSO_4(aq) + H_2(g)$$

With concentrated sulphuric acid

Hot concentrated sulphuric acid oxidises the metals to a metal sulphate and itself is reduced to sulphur dioxide gas.

$$Be(s) + H_2SO_4(aq) \longrightarrow BeSO_4(aq) + SO_2(g) + H_2O(g)$$

$$Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + SO_2(g) + H_2O(g)$$

$$Ca(s) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + SO_2(g) + H_2O(g)$$

$$Sr(s) + H_2SO_4(aq) \longrightarrow SrSO_4(aq) + SO_2(g) + H_2O(g)$$

$$Ba(s) + H_2SO_4(aq) \longrightarrow BaSO_4(aq) + SO_2(g) + H_2O(g)$$

With nitric acid

The elements react with very dilute nitric acid forming nitrates and hydrogen gas.

Beryllium is rendered passive by hot concentrated nitric acid

Magnesium reacts with nitric acid in two ways;
When the acid is cold and moderately concentrated, magnesium reacts with it forming magnesium nitrate, nitrogen monoxide gas and water.

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

The nitrogen monoxide formed is unstable and undergoes oxidation forming brown fumes of nitrogen dioxide gas

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

But when the acid is concentrated, magnesium reacts with it forming magnesium nitrate, nitrogen dioxide gas and water.

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

Note:

Copper also reacts with nitric acid in a similar way as magnesium

d) **Reaction with alkalis**

Beryllium reacts with hot concentrated sodium hydroxide solution forming sodium beryllate.

$$Be(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow Na_2Be(OH)_4(aq) + H_2(g)$$

Or

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

Other group(II) elements do not react with alkalis.

e) **Reaction with halogens**

All the elements in group(II) elements react with halogens to form respective halides, this reaction requires heat to proceed. The reaction can be summarized by the general equation below.

$$M(s) + X_2(g) \longrightarrow MX_2(s)$$

Where M = Be, Mg, Ca, Sr, Ba
X = F, Cl, Br, I

f) **Reaction with carbon**

Beryllium reacts with carbon on strong heating forming beryllium carbide

$$2Be(s) + C(s) \longrightarrow Be_2C(s)$$

Beryllium carbide contains C^{4-} and hydrolyses forming methane and beryllium hydroxide

$$\mathbf{Be_2C(s) + 4H_2O(l) \longrightarrow 2Be(OH)_2(aq) + CH_4(g)}$$

Calcium, strontium and barium react with carbon when heated to form corresponding carbides.

$$\mathbf{Ca(s) + 2C(s) \longrightarrow CaC_2(s)}$$

These carbides contain $C\equiv C^{2-}$ /C_2^{2-} anion and hydrolyse in water forming ethyne and hydroxide of the metal as shown by the reaction below;

$$\mathbf{CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g)}$$

Magnesium reacts with carbon on strong heating forming magnesium carbide

$$\mathbf{2Mg(s) + 3C(s) \longrightarrow Mg_2C_3(s)}$$

Magnesium carbide contain C_3^{4-} ion, on hydrolysis, it yields propyne.

$$\mathbf{Mg_2C_3(s) + 4H_2O(l) \longrightarrow 2Mg(OH)_2(aq) + CH_3C\equiv CH(g)}$$

g) Reaction with hydrogen

When reacted with hydrogen gas on heating, the elements form hydrides

$$\mathbf{Be(s) + H_2(g) \longrightarrow BeH_2(s)}$$

$$\mathbf{Mg(s) + H_2(g) \longrightarrow MgH_2(s)}$$

$$\mathbf{Ca(s) + H_2(g) \longrightarrow CaH_2(s)}$$

$$\mathbf{Sr(s) + H_2(g) \longrightarrow SrH_2(s)}$$

$$\mathbf{Ba(s) + H_2(g) \longrightarrow BaH_2(s)}$$

Beryllium hydride is covalent, magnesium hydride is ionic, while the hydrides if calcium, strontium and barium are highly ionic.

Compounds of group(II) elements

All group(II) compounds are white in colour and ionic in nature but less ionic than those of group(I), however, compounds of beryllium are partially covalent because.
Group(II) compounds become more ionic down the group because their cations have the same charge of +2 and cationic radius increases down the group and hence charge density decreases down the group and consequently the ionic character of the compounds increases.

The cations of group(II) are smaller in radius than those of group(I), also group(II) cations have a charge of +2 while those of group(I) have a charge of +1 therefore the cations of group(II) elements have a high charge density than those of group(I) and hence their compounds are less ionic than those of group(I).
They have higher melting and boiling points compared to corresponding group(I) compounds.

Solubility of group(II) compounds
Solubility can be looked at in terms of ability of a compound to dissolve in water.
The ability of a compound to dissolve in water/solution depends on the following factors

- Lattice energy
- Hydration energy
- Enthalpy of solution

These can be related by the relationship below

Enthalpy of solution = (lattice energy + hydration energy) KJMol^{-1}
For a compound to be soluble, the enthalpy of solution should be a negative value.

a) Lattice energy
This is the energy required to break one mole of crystal lattice of a compound into its constituent gaseous ions. The value of lattice energy is usually a positive value.
When lattice energy is high (more positive), the enthalpy of solution becomes positive and the compound is insoluble but when lattice energy is low (less positive), the enthalpy of solution becomes negative and the compound is soluble.
Lattice energy depends on;

- ✓ Charge on the ion
- ✓ Ionic radius

Ionic charge
If the charge on the ion is high, the forces of attraction between the ions and will be strong, the bond formed will also be strong and lattice energy will be high therefore solubility will be low.
If the ionic charge is small, then the oppositely charged ions will be attract each other less strongly (weakly), the bond formed will be weak and lattice energy will be low, hence solubility will be high.

Ionic radius
If the radius of the ion is small, then the oppositely charged ions approach/attract each other more closely and strongly and lattice energy will be high.
But if the radius of the ion is high, then the oppositely charged ions weakly approach/attract each other and lattice energy will be low.

Group(II) compounds have high lattice energies due to high ionic charge and small ionic radius, therefore their compounds are less soluble than those of group(I) elements.

b) Hydration energy

This is the energy change that occurs when one mole of a substance is completely surrounded by water molecules. It is usually an exothermic process i.e is has a negative value.

When the hydration energy high (more negative), the enthalpy of solution becomes negative and the compound is soluble.

When hydration energy is low (less negative/more positive), the enthalpy of solution is positive and solubility becomes low.

Hydration energy depends on;

- ✓ Charge on the ion
- ✓ Ionic radius

Charge on the ion

If the charge of the ion is high, the forces of attraction between the ions and water molecules will be high, and hydration energy will be high.

But if the ionic charge is low, the water molecules are loosely attracted by the ion and hydration energy will be low.

Ionic radius

Ions with a smaller ionic radius tend to attract water molecules more strongly and hydration energy will be high.

When the ionic radius is large, water molecules are loosely attracted implying that less energy is given out and thus low hydration energy.

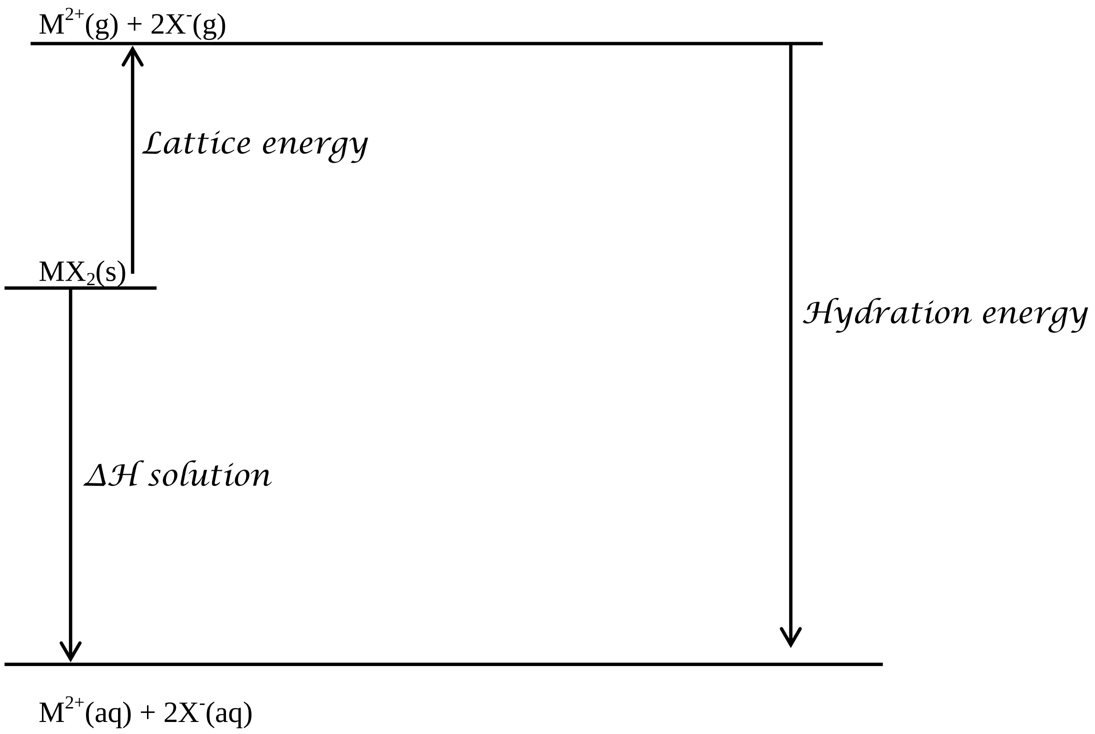
Note

For solubility to be high, the hydration energy must be greater (more negative) than lattice energy (less positive) such that the enthalpy of solution is high (more negative)

However, when the hydration energy is less (less negative) than lattice energy (more positive) then enthalpy of solution will be low (more positive/less negative) and solubility will also be low.

$$\begin{tikzcd}
MX_2(s) \arrow[rr, "\text{Enthalpy of solution}"] \arrow[d, "\text{Lattice energy(+)}"] & & M^{2+}(aq) + 2X^-(aq) \\
M^{2+}(g) + 2X^-(g) \arrow[urr, "\text{Hydration energy(-)}"'] & &
\end{tikzcd}$$

Enthalpy of solution = (Lattice energy(+ve) + Hydration energy(-ve))$KJMol^{-1}$



Enthalpy of solution = (Lattice energy(+ve) + Hydration energy(-ve))KJMol-1

Example

The table below shows enthalpies of hydration of magnesium and chloride ions.

Ion	**Hydration energy ($KJMol^{-1}$)**
Mg^{2+}	1891
Cl^-	381

a) State whether the values for the enthalpies of hydration are negative or positive

They are negative because hydration involves bond formation between ions and water molecules which is an exothermic process.

b) Calculate the enthalpy of hydration of magnesium chloride.

Equation

$$Mg^{2+}(aq) + 2Cl^-(aq) \longrightarrow MgCl_2(aq)$$

$$\text{Hydration energy} = \Delta H Mg^{2+} + 2\Delta Cl^-$$
$$= -1891 + 2(-381)$$
$$= -\ 2653KJMol^{-1}$$

a) **Hydroxides of group(II) elements**

Beryllium hydroxide

It is prepared by reacting a soluble salt of beryllium and ammonium hydroxide solution (alkali), a reaction known as precipitation.
The product is then filtered to obtain the residue

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

Magnesium hydroxide

It is prepared by reacting a soluble salt of magnesium and sodium hydroxide solution (alkali), a reaction known as precipitation.
The product is then filtered to obtain the residue

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

Calcium hydroxide, strontium hydroxide and barium hydroxide are prepared by reacting the oxide of the metal and water, a process known as slacking.

$$\mathbf{MO(s) + H_2O(l) \longrightarrow M(OH)_2(aq)}$$

Solubility of the hydroxides

The solubility of the hydroxides increases down the group.
This is because down the group, both lattice energy and hydration energy decrease while the nuclear charge remains constant and cationic radius increases, but lattice energy decreases much more rapidly than hydration energy therefore the hydration energy outweighs lattice energy and solubility increases down the group.

Note
Oxalates and chromates of group(II) elements have the same solubility trend as that of sulphates of the same group.

Thermal stability of the hydroxides

This is the resistance of a substance to thermal decomposition (due to heat)
A substance is said to have high thermal stability if it does not decompose easily or decomposes at high temperature, but if it easily decomposes when heated, then it is described as being unstable to heat.
When group(II) hydroxides are heated, they decompose forming corresponding oxides and water.

$$\mathbf{M(OH)_2(s) \longrightarrow MO(s) + H_2O(l)}$$

Where M = Be, Mg, Ca, Sr and Ba

Thermal stability of the hydroxides increases down the group, because ionic radius increases down the group while nuclear charge remains constant, therefore charge density decreases and the hydroxide ion becomes less polarized, the oxygen-hydrogen bond becomes stronger and hence the energy required to break it is high so thermal stability increases.

Chemical properties of the hydroxides

a) **Reaction with acids**

Group(II) hydroxides react with dilute nitric and hydrochloric acid forming nitrates and chlorides respectively and water.

With nitric acid;

$Be(OH)_2(s) + 2HNO_3(aq) \longrightarrow Be(NO_3)_2(aq) + 2H_2O(l)$

$Mg(OH)_2(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + 2H_2O(l)$

$Ca(OH)_2(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$

$Sr(OH)_2(s) + 2HNO3(aq) \longrightarrow Sr(NO_3)_2(aq) + 2H_2O(l)$

$Ba(OH)_2(s) + 2HNO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$

Or

$M(OH)_2(s) + 2H+(aq) \longrightarrow M^{2+}(aq) + 2H_2O(l)$

Where M = Be, Mg, Ca, Sr and Ba

With hydrochloric acid

$Be(OH)_2(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + 2H_2O(l)$

$Be(OH)_2(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + 2H_2O(l)$

$Be(OH)_2(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + 2H_2O(l)$

$Be(OH)_2(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + 2H_2O(l)$

$Be(OH)_2(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + 2H_2O(l)$

Or

$M(OH)_2(s) + 2H^+(aq) \longrightarrow M^{2+}(aq) + 2H_2O(l)$

Where M = Be, Mg, Ca, Sr and Ba

b) **Reaction with alkalis**

Only beryllium oxide reacts with alkalis such as sodium/potassium hydroxide solution forming sodium beryllate because it is an amphoteric oxide.
The rest of the hydroxides do not react with alkalis.

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

Sulphates of group(II) elements

These are salts of group(II) elements formed by a reaction with sulphuric acid.

Solubility of the sulphates

The solubility of the sulphates of group(II) elements decrease down the group. This is because down the group, both lattice energy and hydration energy while the nuclear charge remains constant and cationic radius increases, however hydration energy decrease much more rapidly than lattice energy and the enthalpy of solution becomes less negative, hence the solubility decreases.

Thermal stability of the sulphates

The sulphates of group(II) elements are stable to heat i.e they have very high thermal stabilities and are therefore not decomposed by heat.

Preparation of the sulphates

Beryllium sulphate and magnesium sulphate are soluble salts, they can be prepared by reacting dilute sulphuric acid with the metal, metal oxide, meta hydroxide or carbonate.

$$Be(s) + H_2SO_4(aq) \longrightarrow BeSO_4(aq) + H_2(g)$$

$$Mg(s) + H2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$$

Or

$$BeO(s) + H_2SO_4(aq) \longrightarrow BeSO4(aq) + H_2O(l)$$

$$MgO(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2O(l)$$

Or

$$Be(OH)_2(s) + H_2SO_4(aq) \longrightarrow BeSO_4(aq) + 2H_2O(l)$$

$$Mg(OH)_2(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + 2H_2O(l)$$

Or

$$BeCO_3(s) + H_2SO_4(aq) \longrightarrow BeSO_4(aq) + H_2O(l) + CO_2(g)$$

$$BeCO_3(s) + H_2SO_4(aq) \longrightarrow BeSO_4(aq) + H_2O(l) + CO_2(g)$$

Chlorides of group(II) elements

Preparation of the chlorides

Anhydrous chlorides can be prepared by direct synthesis i.e by heating the metal in dry chlorine or hydrogen chloride gas.

$$Be(s) + Cl_2(g) \longrightarrow BeCl_2(s)$$

$$Be(s) + 2HCl(g) \longrightarrow BeCl_2(s) + H_2(g)$$

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

$$Mg(s) + 2HCl(g) \longrightarrow MgCl_2(s) + H_2(g)$$

$$Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$$

$$Ca(s) + 2HCl(g) \longrightarrow CaCl_2(s) + H_2(g)$$

$$Sr(s) + Cl_2(g) \longrightarrow SrCl_2(s)$$

$$Sr(s) + 2HCl(g) \longrightarrow SrCl_2(s) + H_2(g)$$

$$Ba(s) + Cl_2(g) \longrightarrow BaCl_2(s)$$

$$Ba(s) + 2HCl(g) \longrightarrow BaCl_2(s) + H_2(g)$$

Hydrated chlorides can be prepared by action of hydrochloric acid on a metal or its oxide, hydroxide or carbonate. The resultant solution is then saturated by evaporation and allowed to cool forming a saturated solution from which crystals can be grown.

$$Be(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + H_2(g)$$

$$BeO(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + H_2O(l)$$

$$Be(OH)_2(s) + 2HCl(aq) \longrightarrow BeCl2(aq) + H_2O(l)$$

$$BeCO_3(s) + 2HCl(aq) \longrightarrow BeCl_2(aq) + H_2O(l) + CO_2(g)$$

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

$$MgO(s) +2\ HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$$

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$$

$$MgCO_3(s) +2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l) + CO_2(g)$$

$$Ca(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2(g)$$

$CaO(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$

$Ca(OH)2(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$

$CaCO3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

$Sr(s) + 2HCl(aq) \longrightarrow SrCl_2(aq) + H_2(g)$

$SrO(s) + 2HCl(aq) \longrightarrow SrCl_2(aq) + H_2O(l)$

$Sr(OH)2(s) + 2 HCl(aq) \longrightarrow SrCl_2(aq) + H_2O(l)$

$SrCO3(s) + 2HCl(aq) \longrightarrow SrCl_2(aq) + H_2O(l) + CO_2(g)$

$Ba(s) + 2HCl(aq) \longrightarrow BaCl_2(aq) + H_2(g)$

$BaO(s) + 2 HCl(aq) \longrightarrow BaCl_2(aq) + H_2O(l)$

$Ba(OH)_2(s) + 2HCl(aq) \longrightarrow BaCl_2(aq) + H_2O(l)$

$BaCO3(s) + 2HCl(aq) \longrightarrow BaCl_2(aq) + H_2O(l) + CO_2(g)$

Melting points of the chlorides

Chloride	$BeCl_2$	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Melting point (^0C)	405	714	782	875	962

From the above table, it can be noted that melting point increases down group(II) chlorides. This is because down the group, cationic radius increases while the ionic charge remains constant, this leads to a decrease in charge density and polarizing power of the cations thus the chloride ions become less polarized and hence less ionic (more covalent) with increasing stronger ionic bonds which require much energy to break thus the increase in melting points.

Chemical properties of the chlorides

Reaction with water

Group(II) chlorides are not easily hydrolysed, and hydrolysis decreases down the group. However, the following reactions of beryllium and magnesium chloride are discussed.

Beryllium chloride hydrolyses in water to form beryllium hydroxide and hydrogen chloride gas.

$$BeCl_2(s) + 2H_2O(l) \longrightarrow Be(OH)_2(s) + 2HCl(aq)$$

Magnesium chloride is partially hydrolysed in water forming basic magnesium chloride and hydrogen chloride gas.

$$MgCl_2(s) + H_2O(l) \longrightarrow Mg(OH)Cl(aq) + HCl(g)$$

The rest of the chlorides are not easily hydrolysed but dissociate in water forming ions. This is because they are formed by a reaction between a strong base and a strong acid therefore they do not undergo hydrolysis and the solutions formed are neutral.

$$CaCl_2(s) + aq \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

$$SrCl_2(s) + aq \longrightarrow Sr^{2+}(aq) + 2Cl^-(aq)$$

$$BaCl_2(s) + aq \longrightarrow Ba^{2+}(aq) + 2Cl^-(aq)$$

Nitrates of group(II) elements

Preparation of the nitrates

They are prepared by action of dilute nitric acid on the metal, metal oxide, metal hydroxide or carbonate.

$$M(s) + 2HNO_3(aq) \longrightarrow M(NO_3)_2(aq) + H_2(g)$$

Where M = Be, Mg, Ca, Sr and Ba

$$MO(s) + 2HNO_3(aq) \longrightarrow M(NO_3)_2(aq) + 2H_2O(l)$$

Where M = Be, Mg, Ca, Sr and Ba

$$M(OH)_2(s) + 2HNO_3(aq) \longrightarrow M(NO_3)_2(aq) + H_2O(l)$$

Where M = Be, Mg, Ca, Sr and Ba

$$MCO_3(s) + 2HNO_3(aq) \longrightarrow M(NO_3)_2(aq) + H_2O(g) + CO_2(g)$$

Where M = Be, Mg, Ca, Sr and Ba

Properties of the nitrates of group(II) elements

Thermal stability

All group(II) nitrates decompose on heating to form an oxide of the metal, brown fumes of nitrogen dioxide gas and oxygen. Thermal stability increases down the group.

$$2M(NO_3)_2(s) \longrightarrow 2MO(s) + 4NO_2(g) + O_2(g)$$

Where M = Be, Mg, Ca, Sr and Ba

Carbonates of group(II) elements

Preparation of the carbonates

Beryllium and magnesium carbonates are best prepared by heating a solution containing hydrogencarbonate for example sodium/potassium hydrogen carbonate and an aqueous solution of the metal ion.

$$Be^{2+}(aq) + 2HCO_3^-(aq) \longrightarrow BeCO_3(s) + CO_2(g) + H_2O(l)$$

$$Mg^{2+}(aq) + 2HCO_3^-(aq) \longrightarrow MgCO_3(s) + CO_2(g) + H_2O(l)$$

The rest of the carbonates are prepared by a reaction between a soluble solution of a carbonate such as sodium/potassium carbonate and a solution containing an ion of the element whose carbonate is to be prepared.

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MgCO_3(s)$$

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow SrCO_3(s)$$

$$Ba^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow BaCO_3(s)$$

Thermal stability of the carbonates

Thermal stability of the carbonates increases down the group.

This is because ionic radius increases down the group while ionic charge remains constant thus charge density and polarizing power decrease and therefore the carbonate ions become less polarized and hence the carbon-oxygen bonds become stronger and the energy required to break them increases.

However, on strong heating, the carbonates decompose to form oxides of the metal and carbon dioxide gas.

$$MCO_3(s) \longrightarrow MO(s) + CO_2(g)$$

Where M = Be, Mg, Ca, Sr and Ba

Oxides of group(II) elements

Preparation of the oxides

They are prepared by heating any of the following

- ✓ Hydroxide of the metal
- ✓ Nitrate of the metal
- ✓ Carbonate of the metal

a) **From the metallic hydroxide**

$$M(OH)_2(s) \longrightarrow MO(s) + H_2O(l)$$

Where M = Be, Mg, Ca, Sr and Ba

b) **From the metallic nitrate**

$$2M(NO_3)_2(s) \longrightarrow 2MO(s) + 4NO_2(g) + O_2(g)$$

Where M = Be, Mg, Ca, Sr and Ba

c) **From the metallic carbonate**

$\mathbf{MCO_3(s) \longrightarrow MO(s) + CO_2(g)}$
Where M = Be, Mg, Ca, Sr and Ba

Melting points of the oxides of group(II) elements

Oxide	BeO	MgO	CaO	SrO	BaO
Melting point(^{0}C)	2530	2852	2627	2531	1928

Trend
Generally, melting point of the oxides decrease down the group, however the melting point of beryllium oxide is lower than expected.

Explanation
Down the group, ionic radius increases while the charge remains constant, charge density decreases and the oxide ion is poorly polarized therefore the strength of the ionic bonds reduces and hence the amount of energy required to break them reduces.
For beryllium oxide, the beryllium ion has a high ionic charge and hence the charge density is also high, the oxide ion is strongly polarized, this creates some covalent character in beryllium character which reduces the strength of the ionic bond implying that the energy required to break it is lower.

Chemical properties of the oxides
Reaction with water
Beryllium oxide does not react with water because of covalent character in it. The rest of the oxides react with water forming hydroxides of the metal.

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

$\mathbf{CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)}$

$\mathbf{SrO(s) + H_2O(l) \longrightarrow Sr(OH)_2(aq)}$

$\mathbf{BaO(s) + H_2O(l) \longrightarrow Ba(OH)_2(aq)}$

Reaction with alkalis
Only beryllium oxide is amphoteric and reacts with sodium/potassium hydroxide solution forming a beryllate.
$\mathbf{BeO(s) + 2^{-}OH(aq) + H_2O(l) \longrightarrow Be(OH)_4{}^{2-}(aq)}$

Reaction with acids

All oxides of group(II) elements react with dilute (non oxidising) mineral acids like hydrochloric acid, sulphuric acid and nitric forming corresponding salts and water. The general equation below represents such reactions.

$$\mathbf{MO(s) + 2H^{+}(aq) \longrightarrow M^{2+}(aq) + H_2O(l)}$$

With sulphuric acid and calcium oxide, strontium oxide and barium oxide, there is formation of an insoluble sulphate which retards the reaction.

Carbides of group(II) elements

Beryllium carbide is covalent, the rest of the carbides are ionic both of which are prepared by heating the metal or its oxide in carbon.

$$\mathbf{2BeO(s) + 3C(s) \longrightarrow Be_2C(s) + 2CO(g)}$$

$$\mathbf{MO(s) + 3C(s) \longrightarrow MC_2(s) + CO(g)}$$

Where M = Mg, Ca, Sr and Ba

Complex ion formation in group(II) elements

A complex is an ion positive or negative in which atoms or groups of atoms (ligands) with a negative charge or a lone pair of electrons form coordinate bonds with the central metallic ion.

A ligand is either a neutral molecule or a negatively charged ion which has a lone pair of electrons and it uses the lone pair of electrons to form coordinate bonds with the central metallic ion.

Examples of neutral ligands include;

- ✓ Ammine NH_3
- ✓ Aqua H_2O
- ✓ Carbonyl CO
- ✓ Etc

Negatively charged ligands include;

- ✓ Fluoro F^-
- ✓ Chloro Cl^-
- ✓ Hydroxo ^-OH

For a complex to be formed,

- ➢ The metallic cation must have vacant d-orbitals to accommodate the lone pairs of electrons from the ligands.
- ➢ The cation must have a high charge and a small ionic radius to give it a high charge density to attract the lone pairs of electrons from the ligands.

Group(II) cations have a low tendency to form complexes and the tendency to form complexes decrease down the group.

Beryllium lacks vacant d-orbitals but is able to form a complex because of its small ionic radius and high charge giving it a high charge density.

Other group(II) elements have vacant d-orbitals but their cations have low charge density, this greatly affects their ability to form complexes.

Beryllium forms beryllate, the complex of magnesium occurs in chlorophyll; that of calcium occurs in EDTA, while the rest do not form complexes.

Qualitative analysis of group(II) cations

a) Using sodium hydroxide solution

Be^{2+}

White precipitate soluble in excess

Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}

White precipitate insoluble in excess

b) Using ammonia solution

White precipitate soluble in excess
But with Ca^{2+}, no observable change

c) Using sulphate (sodium sulphate, sulphuric acid)

No observable change with Mg^{2+} and Be^{2+}
With Ca^{2+}, Sr^{2+} and Ba^{2+}
White precipitate insoluble

d) Using sodium/ammonium oxalate followed by ethanoic acid

No observable change with Mg^{2+} and Be^{2+}
With Ca^{2+}, Sr^{2+}
White precipitate insoluble in the acid.
With Ba^{2+}
White precipitate soluble in the acid.

$$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow BaC_2O_4(s)$$

$$BaC_2O_4(s) + 2H^+(aq) \longrightarrow Ba^{2+}(aq) + H_2C_2O_4(aq)$$

e) Using sodium/potassium chromate solution followed by ethanoic acid

No observable change with Mg^{2+}, Be^{2+} , Ca2+, and Sr2+
With Ba^{2+}
Yellow precipitate insoluble in ethanoic acid.

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow BaCrO_4(s)$$

When the precipitate is dissolve in dilute nitric or hydrochloric acid, an orange solution is formed.

$$2BaCrO_4(s)+2H^+(aq) \longrightarrow 2Ba^{2+}(aq +Cr_2O_7^{2-}(aq) +H_2O(l)$$

Name a reagent that can be used to distinguish between the following pairs of ions

a) **Mg2+ and Ca2+**
Reagent: dilute sulphuric acid
Observations
Mg2+ : No observable change
Ca2+ : A white precipitate is formed

b) **Ba2+ and Ca2+**
Reagent: potassium chromate(VI) solution
Observations
Ba2+ : A yellow precipitate is formed
Ca2+ : No observable change

c) **Mg2+ and Ba2+**
Reagent: potassium chromate(VI) solution
Observations
Ba2+ : A yellow precipitate is formed
Mg2+ : No observable change

GROUP(III) ELEMENTS

These are the first members of the P block and they have 3 electrons in their outermost energy level.

Their general outer electronic configuration is nS^2nP^1, they have a fixed oxidation state of +3 and they include;

- ✓ Boron with atomic number 5
- ✓ Aluminium with atomic number 13

Boron is a non-metal; aluminium and the rest are metals and metallic character increases down the group.

Boron shows the following reactions;

a) **Reaction with air**

When heated to red hot, boron reacts with air to form boron oxide and boron nitride

$$4B(s) + 3O_2(g) \longrightarrow 2B_2O_3(s)$$

$$2B(s) + N_2(g) \longrightarrow 2BN(s)$$

b) **Reaction with water**

Boron does not react with cold water, but it reacts with steam on heating to form boron oxide and hydroxide gas.

$$2B(s) + 3H_2O(g) \longrightarrow B_2O_3(s) + 3H_2(g)$$

c) **Reaction with chlorine**

When heated, boron reacts with dry chlorine gas forming boron chloride

$$2B(s) + 3Cl_2(g) \longrightarrow 2BCl_3(s)$$

d) **Reaction with acids**

Boron does not react with cold dilute acids but only reacts with hot concentrated acids;

With hot concentrated nitric acid

Boron is reacts with hot concentrated nitric acid to form boric acid and brown fumes of nitrogen dioxide gas.

$$2B(s) + 6HNO_3(l) \longrightarrow 2H_3BO_3(aq) + 6NO_2(g)$$

With concentrated sulphuric acid

Boron is reacts with hot concentrated sulphuric acid to form boric acid and sulphur dioxide gas.

$$2B(s) + 3H_2SO_4(l) \longrightarrow 2H_3BO_3(aq) + 3SO_2(g)$$

e) Reaction with alkalis

Boron reacts with hot concentrated alkalis such sodium/potassium hydroxide solution to form sodium/potassium borate and hydrogen gas.

$$2B(s) + 6KOH(aq) \longrightarrow 2K_2BO_3(aq) + 3H_2(g)$$

$$2B(s) + 6NaOH(aq) \longrightarrow 2Na_2BO_3(aq) + 3H2(g)$$

f) Reaction as a reducing agent

Boron reduces silicon(IV) oxide to form silicon and boron oxide as shown by the reaction below;

$$3SiO_2(s) + 4B(s) \longrightarrow 2B_2O_3(s) + 3Si(s)$$

Compounds of boron

a) Boron oxide

Boron oxide is an acidic oxide with a giant covalent structure. It is acidic and does not react with acids but reacts with alkalis to form borates and water.

$$B_2O_3(s) + 6KOH(aq) \longrightarrow 2K_3BO_3(aq) + 3H_2O(l)$$

Or

$$B_2O_3(s) + 6\,^{-}OH(aq) \longrightarrow 2BO_3^{3-}(aq) + 3H_2O(l)$$

b) Boron halides

The halides of boron are covalent, the boron atom lacks an electron pair to have a full energy level therefore it acts as an electron acceptor when the halides react with ammonia to form additional products. For example;

$$BF_3(s) + HN_3(g) \longrightarrow BF_3.NH_3(s)$$

Or

$$BF_3(s) + HN_3(g) \longrightarrow H_3N \rightarrow BF_3(s)$$

The halides are also hydrolysed in aqueous phase to form acidic solutions.

$$BCl_3(s) + 3H_2O(l) \rightleftharpoons H_3BO_3(aq) + 3HCl(aq)$$

ALUMINIUM

Aluminium is a group(III) element with atomic number of 13, electronic configuration of **$1S^2 2S^2 2P^6 3S^2 3P^1$**

It occurs naturally as ores such as bauxite and cryolite from which a pure sample of aluminium can be extracted.

Physical properties of aluminium

It is a silvery white metal

It is a good conductor of both electricity and heat

It has a density of $2.96 gcm^{-3}$

It's very malleable and ductile therefore aluminium sheet (foil) and wire are easily available.

It has a melting point of 600^0C

Chemical properties of aluminium

a) **Reaction with air**

When pure aluminium is exposed to air, it develops a thin layer of basically aluminium oxide, this layer is a protective lining which prevents further reaction of aluminium with other chemicals.

When heated in air, aluminium burns forming aluminium oxide and aluminium nitride both of which are white solids. This reaction is shown by the equations below;

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

$$2Al(s) + N_2(g) \longrightarrow 2AlN(s)$$

b) **Reaction with water**

Aluminium shows no reaction with cold water at room temperature. This is because of the layer of aluminium oxide lining aluminium, this layer prevents reaction with water.

However, when aluminium is strongly heated, it reacts with steam forming aluminium oxide and hydrogen gas.

$$2Al(s) + 3H_2O(g) \longrightarrow Al_2O_3(s) + 3H_2(g)$$

c) **Reaction with acids**

Aluminium reacts very slowly with dilute hydrochloric acid, however when the acid is hot and concentrated, it reacts forming aluminium chloride and hydrogen gas.

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

Or

$$2Al(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2(g)$$

Aluminium does not easily react with dilute sulphuric acid because of the oxide film of aluminium which is insoluble in the dilute acid. However, when hot concentrated acid is used, aluminium reacts forming aluminium sulphate, sulphur dioxide gas and water.

$$2Al(s) + 6H_2SO_4(l) \longrightarrow Al_2(SO4)_3(aq) + 3SO_2(g) + 6H_2O(l)$$

Aluminium does not react with (is rendered passive by) nitric acid at any concentration, this is because nitric acid is a strong oxidising agent therefore it favours formation (build up) of the aluminium oxide, a protective oxide layer on the surface of aluminium which prevents further reaction.

d) Reaction with alkalis

Aluminium reacts with hot concentrated sodium hydroxide solution forming sodium aluminate and hydrogen gas.

$$2Al(s) + 2^-OH(aq) + 6H_2O(l) \longrightarrow 2Al(OH)_4^-(aq) + H_2(g)$$

Or

$$2Al(s) + 2^-OH(aq) + 2H_2O(l) \longrightarrow 2AlO_2^-(aq) + H_2(g)$$

When aluminium utensils are washed using soap, soap undergoes hydrolysis to form an alkaline solution which reacts with/corrodes the utensils, causing ware out and with continued use of soap, the utensils eventually develop holes and become useless, the following reactions show the events that take place.

$$RCOO^-(aq) + H_2O(l) \rightleftharpoons RCOOH(aq) + {}^-OH(aq)$$

Then,

$$2Al(s) + 2^-OH(aq) + 2H_2O(l) \longrightarrow 2AlO_2^-(aq) + H_2(g)$$

e) Reaction with non-metals

Aluminium reacts with oxygen when heated strongly to form aluminium oxide which is amphoteric in nature.

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

Aluminium reacts with sulphur when heated strongly to form aluminium sulphide.

$$2Al(s) + 3S(s) \longrightarrow Al_2S_3(s)$$

Aluminium reacts with chlorine on strong heating to form aluminium chloride.

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

When strongly heated in carbon, aluminium reacts forming aluminium carbide.

$$4Al(s) + 3C(g) \longrightarrow Al_4C_3(s)$$

With nitrogen gas, aluminium reacts on heating forming aluminium nitride.

$$2Al(s) + N_2(g) \longrightarrow 2AlN(s)$$

EXTRACTION OF ALUMINIUM

Aluminium is extracted from an ore known as bauxite (impure hydrated aluminium oxide $Al_2O_3.2H_2O$), also cryolite (impure trisodium haxafluoroaluminate Na_3AlF_6) is used.

It is widely found in form of aluminium silicates in rocks such as clays, micas and fieldspars.

An ore is a naturally occurring substance (rock material) from which an element can be extracted.

The extraction process

Aluminium is extracted from bauxite in two stages namely;

- Concentration (purification/dressing) of the ore
- Reduction of the purified ore by electrolysis to produce the metal.

Concentration of the ore

This involves removal of impurities from the ore, these impurities are iron(III) oxide are silicon dioxide (silica).

Bauxite is first roasted in air to convert any iron(II) oxide to iron(III) oxide and also to remove water from it.

$$\mathbf{4FeO(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)}$$

The roasted ore is then crushed (pulverized/ground) to a fine powder, and heated with excess concentrated sodium hydroxide solution under high pressure.

Aluminium oxide and silicon(IV) oxide dissolve in the alkali forming sodium aluminate and sodium silicate respectively.

The iron(III) oxide impurity present in the ore is basic and does not react with sodium hydroxide solution.

$$\mathbf{Al_2O_3(s) + 2^-OH(aq) + 3H_2O(l) \longrightarrow 2Al(OH)_4^-(aq)}$$

Or

$$\mathbf{Al_2O_3(s) + 6^-OH(aq) + 3H_2O(l) \longrightarrow 2[Al(OH)_6]^{3-}(aq)}$$

And

$$\mathbf{SiO_2(s) + 2^-OH(aq) \longrightarrow SiO_3^{2-}(aq) + H_2O(l)}$$

The solution is then filtered to remove iron(III) oxide which is insoluble and hence remains in the residue.

The filtrate now contains sodium silicate and sodium aluminate, but our interest is to obtain aluminium, therefore it is seeded with pure aluminium hydroxide (the crystals are added to the filtrate) to precipitate out aluminium hydroxide, this reaction leaves sodium silicate in solution.

$$\mathbf{Al(OH)_4^-(aq) \xrightarrow{Al(OH)_3(s)} Al(OH)_3(s) + {}^-OH(aq)}$$

Or

$$\mathbf{[Al(OH)_6]^{3-}(aq) \xrightarrow{Al(OH)_3(s)} Al(OH)_3(s) + 3^-OH(aq)}$$

Alternatively, aluminium hydroxide can be precipitated by bubbling carbon dioxide gas through the solution of the filtrate; this reaction also leaves sodium silicate in the solution.

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

Or

$$2[Al(OH)_6]^{3-}(aq) + 3CO_2(g) \longrightarrow 2Al(OH)_3(s) + 3CO_3^{2-}(aq) + 3H_2O(l)$$

The resulting solution is again filtered off to obtain the residue (aluminium hydroxide) which is then heated strongly to give pure aluminium oxide (alumina)

$$2Al(OH)_3(s) \longrightarrow Al_2O_3(s) + 3H_2O(l)$$

Reduction of the purified ore

The aluminium oxide obtained above is then dissolved in molten cryolite and electrolysed at carbon electrodes at 900^0C. The purpose of the molten cryolite is to lower the melting point of aluminium oxide which is 2045^0C. Carrying out electrolysis at this temperature would be very expensive.

At the cathode, aluminium ions Al^{3+} are discharged producing aluminium

$$Al^{3+}(aq) + 3e \longrightarrow Al(s)$$

At the anode, the oxide ions are discharged producing oxygen gas.

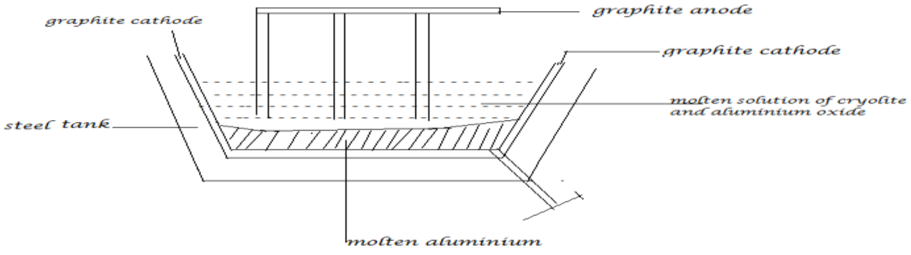
$$2O^{2-}(aq) \longrightarrow O_2(g) + 4e$$

Since the temperature is very high, the oxygen produced at the anode reacts with the anode itself forming carbon dioxide gas. This means that the anode has to be replaced from time to time.

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

Also, since the cryolite has fluoride ions, which can easily be discharged to fluorine, the voltage has to be kept low to avoid this, also this low voltage lowers the rate which oxygen and graphite react to form carbon dioxide.

The electrolysis of aluminium is only economical if there is cheap electricity from water power. Otherwise the process consumes a lot of electricity.



Uses of aluminium

- ✓ It is used to make electrical cables for conveying electricity because of its lower density and good electrical conductivity.
- ✓ It is used for making domestic cooking utensils like pans, kettles, because it has a bright appearance, light in weight, and non-poisonous in nature.
- ✓ Making light but strong alloys such as duralumin (Al, Mg, Cu, Fe, Si) and Magnalium (Al, Mg, Ca) used in the construction of air craft and ships because they are light.
- ✓ Aluminium is used to make door and window frames because it does not corrode (resists corrosion)
- ✓ It is used for handling or holding nitric acid because it is rendered positive by the acid.
- ✓ Aluminium foils is used as packing material for sweets, biscuits, chocolates and cigarettes because it is non-toxic.
- ✓ It is used to make heat exchangers in the chemical, oil and other industries because it is a good conductor of heat.
- ✓ Aluminium is used in roofing to insulate buildings because it is an excellent reflector of radiant energy.
- ✓ It is used as a reducing agent in the extraction of some metals such as chromium, because of its high affinity for oxygen. It will therefore reduce oxides of chromium, iron and manganese on strong heating.

$$\mathbf{2Al(s) + Cr_2O_3(s) \longrightarrow Al_2O_3(s) + 2Cr(s)}$$

$$\mathbf{2Al(s) + Fe_2O_3\ (s) \longrightarrow Al_2O_3(s) + 2Fe\ (l)}$$

$$\mathbf{3Mn_3O_4(s)\ +\ 8Al\ (s \longrightarrow 4Al_2O_3(s)\ +\ 9Mn(s)}$$

$$\mathbf{3Fe_3O_4(s)\ +\ 8Al\ (s) \longrightarrow 4Al_2O_3(s)\ +\ 9Fe(s)}$$

Compounds of aluminium

Aluminium forms both ionic and covalent compounds both of which are white in solid state and colourless in solution. However its ionization energy is high. Furthermore, the Al^{3+} ion has a very small ionic radius and has a high charge of +3. Therefore its charge density (i.e. the charge-to-radius ratio) is very high compared with other metal ions of period 3. Below in the table is a comparison;

Cation	**Charge**	**Ionic radius (nm)**	**Charge density**
Na^+	+1	0.095	10.5
Mg^{2+}	+2	0.065	30.8
Al^{3+}	+3	0.050	60.0

Consequently, the Al^{3+} ion is able to strongly polarize most anions –i.e its able to distort the electron clouds of anions(especially anions with large anionic radius) to form bonds with a high degree of covalent character. This explains why most compounds of aluminium are predominantly covalent.

Aluminium fluoride AlF_3 and aluminium oxide Al_2O_3 are predominantly ionic, this is because the fluoride ion, F^- and oxide ion, O^{2-} have very small ionic radii , hence they are weakly polarized by the aluminium ions Al^{3+} resulting into a high degree of ionic character in these compounds.

However, the chloride $AlCl_3$, bromide $AlBr_3$ and the iodide AlI_3 of aluminium are predominantly covalent, because the chloride, bromide and iodide ions have large ionic radii, so they are strongly polarized by the aluminium ion resulting into a large degree of covalence.

In aqueous solutions, the Al^{3+} is stabilized by the coordination of six water molecules or exists as a hydrated ion to form the hexaaquaaluminium(III) complex ion, $[Al(H_2O)_6]^{3+}$, which is octahedral in shape.

$$Al^{3+}(aq) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq)$$

Due to the high charge density and high polarizing power of the aluminium ion, it polarizes the lone pair of electrons on the water molecules, releasing hydrogen ions in solution that exist a hydroxonium ions.

The solution above, is acidic –i.e is a proton donor/an electron acceptor and so aqueous solutions containing the complex ion are acidic –i.e have a PH less than 7.

Explanation:

The hexaaquaaluminium(III) ion undergoes hydrolysis to form hydroxonium ions which make the solution acidic.

$$[Al(H_2O)_6]^{3+}(aq) \longrightarrow [Al(H_2O)_5.OH]^{2+}(aq) + H^+(aq)$$

Or

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \longrightarrow [Al(H_2O)_5.OH]^{2+}(aq) + H_3O^+(aq)$$

The hydrolysis of the complex ion is due to the very small ionic radius and high ionic charge on the central aluminium cation which gives it a high charge density such that it strongly polarises the coordinated water molecules thereby weakening the oxygen-hydrogen bonds much so that other water molecules in solution are able to abstract protons to form hydroxonium ions which are responsible for making the resultant solution acidic.

Revision questions

1. Aluminium chloride was dissolved in water and the solution tested with litmus
   a) State what was observed and explain your answer.

   Observation:

   Blue litmus turned red (or pink).

   Explanation:

   When dissolved in water aluminium sulphate forms hydrated aluminium ions which undergo hydrolysis to form hydrogen (or hydroxonium ions) which make solution acidic hence turning blue litmus paper red (or pink)

   $$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \longrightarrow [Al(H_2O)_5.OH]^{2+}(aq) + H_3O^{+}(aq)$$

   Or

   $$[Al(H_2O)_6]^{3+}(aq) + 2H_2O(l) \longrightarrow [Al(H_2O)_4(OH)2]^{2+}(aq) + 2H_3O^{+}(aq)$$

   Or

   $$[Al(H_2O)_6]3+(aq) \; + \; 3H_2O\,(l) \qquad Al(H_2O)_3(OH)3\,(s) \; + \; 3H_3O+\,(aq)$$

2. Sodium carbonate was added dropwise to a solution containing aluminium nitrate
   a) State what was observed

   Effervescence/bubbles of a colourless gas were given off and a white precipitate was formed.

   b) Explain your observation

   Aluminium nitrate is a strong electrolyte; it completely ionises forming aluminium ion and nitrate ion, the aluminium ion has a high charge and a small ionic radius therefore it undergoes hydrolysis and its solution contains hydrated aluminium ions which undergo hydrolysis to form hydrogen ions (or hydroxonium ions) which react with the carbonate ions in sodium carbonate solution to form carbon dioxide which bubbles out as a colourless gas and insoluble aluminum hydroxide which is a white precipitate.

$$Al^{3+}(aq) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3H^+(aq)$$

$$2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)$$

Or:

The overall equation below may be given instead of the two equations above.

$$2Al^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(l) \longrightarrow 2Al(OH)_3(s) + 2CO_2(g)$$

Alternative equations for the reactions reactions.

$$[Al(H_2O)_6]^{3+}(aq) + 3H_2O(l) \longrightarrow Al(H_2O)_3.3OH(s) + 3H_3O^+(aq)$$

$$2H_3O^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + 3H_2O(l)$$

Or:

The overall equation below may be given instead of the two equations above

$$2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \longrightarrow 2Al(H_2O)_3.3OH(s) + 3CO_2(g) + 3H_2O(l)$$

3. Magnesium ribbon was added to an aqueous solution of aluminium chloride solution

a) State what was observed.

The silvery grey solid dissolved with effervescence of a colourless gas, and a white solid.

b) Explain your observation in (a)

The hydrated aluminium ions in aluminium chloride solution undergo hydrolysis to form hydrogen ions which react with magnesium ribbon to form hydrogen gas which bubbles out as a colourless gas and insoluble aluminium hydroxide as a white solid.

$$Al^{3+}(aq) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3H^+(aq)$$

$$2H^+(aq) + Mg(s) \longrightarrow Mg^{2+}(aq) + H_2(g)$$

Or:

The overall equation below may be written instead of the two equations above.

$$2Al^{3+}(aq) + 3Mg(s) + 6H2O(l) \longrightarrow 2Al(OH)3(s) + 3Mg^{2+}(aq) + 3H_2(g)$$

Alternative equations

$$[Al(H_2O)_6]^{3+}(aq) + 3H_2O\ (l) \longrightarrow Al(H_2O)_3.3OH(s) + 3H_3O^+(aq)$$

$$2H_3O^+(aq) + Mg(s) \longrightarrow Mg^{2+}(aq) + H_2(g) + 2H_2O(l)$$

Or:

The overall equation below may be written instead of the two equations above.

$$2[Al(H_2O)_6]^{3+}(aq) + 3Mg(s) \longrightarrow 2Al(H_2O)_3(OH)_3\ (s) + 3Mg^{2+}\ (aq)+3H_2(g)$$

4. Explain why aluminium carbonate does not exist.

Most metal carbonates are insoluble and are therefore prepared by precipitation. The preparation of aluminium carbonate would involve mixing aqueous solutions of a soluble aluminium salt with an aqueous solution of a soluble metal carbonate. However, aqueous solutions of aluminium salts contain hydrated aluminium ions which undergo hydrolysis to form hydrogen/hydroxonium ions which make the solution acidic.

The hydrogen/hydroxonium ions would then react with the carbonate ions liberating carbon dioxide and precipitation of insoluble aluminium hydroxide instead of aluminium carbonate.

$$2Al^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O\ (l) \longrightarrow 2Al(OH)_3(s) + 2CO_2(g)$$

Or

$$2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \longrightarrow 2[Al(H_2O)_3(OH)3]\ (s)+3CO_2(g)+3H_2O(l)$$

a) The halides of aluminium

These include aluminium fluoride AlF_3, aluminium chloride $AlCl_3$, aluminium bromide $AlBr_3$ and aluminium iodide AlI_3

The anhydrous halides are prepared by passing the dry halogen gas (for fluorine and chlorine) or vapour (for bromine and iodine) over the heated metal. This reaction is known as direct synthesis.

$$2Al(s) + 3X_2\ (g) \longrightarrow 2AlX_3(s)$$

Where X = F, Cl, Br, and I

For example

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

$$2Al(s) + 3Br_2\ (g) \longrightarrow 2AlBr_3(s)$$

Aluminium fluoride is predominantly ionic while the rest of the halides of aluminium are predominantly covalent. The ionic character hence melting point of the aluminium halides decreases and are in the order;

AlF_3> $AlCl_3$> $AlBr_3$> AlI_3

Explanation

The radius of the halide ions increases from the fluoride ion to the iodide ion. Thus the ability of the halide ions to be polarised by the aluminium cation increases from the fluoride to the iodide ion, this results into an increase in covalent character (or decrease in ionic character) from aluminium fluoride to aluminium iodide, this also accounts for the decrease in melting points of the halides.

The structure and properties of anhydrous $AlCl_3$, $AlBr_3$ AlI_3 are very similar, but different from that of AlF_3. For instance, they are covalent solids that dimerise in the gaseous state and readily hydrolysed by water forming aluminium hydroxide and the corresponding hydrogen halides (hydrogen chloride, hydrogen bromide and hydrogen iodide) which fume in moist air.

$$AlCl_3(s) + 3H_2O(l) \xrightarrow{\qquad\qquad} Al(OH)_3(s) + 3HCl(g)$$

$$AlBr_3(s) + 3H_2O(l) \xrightarrow{\qquad\qquad} Al(OH)_3(s) + 3HBr(g)$$

$$AlCl_3(s) + 3H_2O(l) \xrightarrow{\qquad\qquad} Al(OH)_3(s) + 3HCl(g)$$

Revision questions

Explain why aluminium fluoride is ionic while aluminium chloride is covalent.

The fluoride ion has a smaller radius than the chloride ion. The valency electrons of the fluoride ion are strongly attracted by the nucleus. Therefore the fluoride ion is weakly polarized by the aluminium cation, so aluminium fluoride is ionic.

The chloride ion has a bigger ionic radius compared to the fluoride ion. Also, the valency electrons of the chloride are weakly attracted by the nucleus thus the chloride ion is strongly polarized by the aluminium cation. This makes aluminium chloride covalent.

Briefly describe how hydrated aluminium chloride ($AlCl_3.6H_2O$) can be prepared

Aluminium is reacted with warm concentrated hydrochloric acid. The resultant solution is heated to the point of crystallization and cooled to form crystals of hydrated aluminium chloride. The crystals are filtered, washed with a little cold distilled water and dried by pressing them between filter paper.

$$2Al(s) + 6HCl(aq) \xrightarrow{\qquad\qquad} 2AlCl_3(aq) + 3H_2(g)$$

State what would be observed when hydrated aluminium chloride is strongly heated and write equation for the reaction that takes place.

Observation:

White fumes are given off and white crystals which turn to a white powder are formed.

$$\mathbf{AlCl_3.6H_2O(s) \longrightarrow Al_2O_3(s) + 6HCl(g) + 9H_2O(g)}$$

Explain what would be observed when sodium carbonate solution is added to a concentrated solution of aluminium chloride.

Observation:

A white precipitate is formed with effervescence of a colourless gas which forms a white precipitate with calcium hydroxide solution.

Explanation:

Aluminium chloride hydrolyses in aqueous solution forming an acidic solution containing hydroxonium/hydrogen ions

$$\mathbf{[Al\ (H_2O)_6]3+(aq) + 3H2O(l) \longrightarrow Al(H_2O)_3.3OH(s) + 3H_3O+(aq)}$$

Or

$$\mathbf{Al^{3+}(aq) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3H^+(aq)}$$

The hydroxonium/hydrogen ions formed react with carbonate ions in sodium carbonate solution to form carbon dioxide gas and insoluble aluminium hydroxide as a white precipitate.

$$\mathbf{2H_3O^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + 3H_2O(l)}$$

Or

$$\mathbf{2H^+(aq) + CO_3^{2-}(aq) \longrightarrow CO_2(g) + H_2O(l)}$$

Overall equations of reactions

$$\mathbf{2[Al(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \longrightarrow 2Al(H_2O)_3.3OH(s) + 3CO_2\ (g) + 3H_2O(l)}$$

Or

$$\mathbf{2Al^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(l) \longrightarrow 2Al(OH)_3(s) + 3CO_2(g)}$$

Aluminium hydroxide

It is a white precipitate formed when ammonia solution/aqueous ammonia or a sodium hydroxide solution is added to a solution containing aluminium ions.

$Al^{3+}(aq) + 3^{-}OH(aq) \longrightarrow Al(OH)_3(s)$

Aluminium hydroxide is amphoteric in nature
It reacts with mineral dilute acids to form aluminium salts and water

$Al(OH)_3(s) + 3H^{+}(aq) \longrightarrow Al^{3+}(aq) + H_2O(l)$

It also reacts with alkalis (sodium hydroxide and potassium hydroxide solutions) to form a sodium/potassium aluminate.

$Al(OH)_3(s) + {}^{-}OH(aq) \longrightarrow AlO_2^{-}(aq) + 2H_2O(l)$

Or

$Al(OH)_3(s) + {}^{-}OH(aq) \longrightarrow [Al(OH)_4]^{-}(aq)$

Or

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

Revision questions

State what would be observed when dilute sodium hydroxide solution is added drop-wise until in excess to aluminium sulphate solution.

Observation
A white precipitate dissolves in excess to form a colourless solution

Explain the observation in (a) above.
Aluminium ions in aluminium sulphate solution react with hydroxide ions in alkali to form insoluble aluminium hydroxide as a white precipitate.

$Al^{3+}(aq) + 3^{-}OH(aq) \longrightarrow Al(OH)_3(s)$

Aluminium hydroxide formed is amphoteric hence reacts with hydroxide ions in the excess alkali to form soluble aluminate ions (a complex) which are colourless.

$Al(OH)_3(s) + {}^{-}OH(aq) \longrightarrow AlO_2\text{-}(aq) + 2H_2O(l)$

Or

$Al(OH)_3(s) + {}^{-}OH(aq) \longrightarrow [Al(OH)_4]\text{-}(aq)$

Or

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

Aluminium Sulphate

This is manufactured by reacting aluminium hydroxide or aluminium oxide with hot concentrated sulphuric acid.

$$2Al(OH)_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO4)_3(aq) + 6H_2O(l)$$

Or

$$Al_2O_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$$

It crystallizes from water with 18 molecules of water of crystallization i.e $Al_2(SO_4)_3.10H_2O$

Qualitative analysis of aluminium ions Al^{3+}in solution

Reagent: Sodium hydroxide solution (or aqueous sodium hydroxide)

Procedure

To a solution containing Al^{3+} ions, added sodium hydroxide solution drop-wise until in excess.

Observation:

A white precipitate soluble in excess forming a colourless solution

First

$$Al^{3+}(aq) + 3^-OH(aq) \longrightarrow Al(OH)_3(s)$$

Then

$$Al(OH)_3(s) + {}^-OH(aq) \longrightarrow AlO_2^-(aq) + 2H_2O(l)$$

Or

$$Al(OH)_3(s) + {}^-OH(aq) \longrightarrow [Al(OH)_4]^-(aq)$$

Reagent: Ammonia solution (or aqueous ammonia or ammonium hydroxide solution)

Procedure

To a solution containing Al^{3+} ions, add ammonia solution drop-wise until in excess.

Observation:

A white precipitate insoluble in excess.

$$Al^{3+}(aq) + 3^-OH(aq) \longrightarrow Al(OH)_3(s)$$

Reagent: Litmus solution

Procedure

To a solution containing Al^{3+} ions, add 1-2 drops of litmus solution followed by dilute hydrochloric acid and then ammonia solution until it is just alkaline.

Observation:

A blue lake forms. This confirms presence of Al^{3+} ion

Reagent: Alizarin solution

Procedure

To a solution containing Al^{3+} ions is alizarin solution followed solution followed by ammonia solution until just alkaline.

Observation:

A pink lake forms. This also confirms presence of Al^{3+} ion

Reagent: Aluminon reagent

Procedure

To a solution containing Al^{3+} ions is added dilute hydrochloric acid followed by ammonium ethanoate then aluminon reagent.

Observation:

A red precipitate is formed. This also confirms presence of Al^{3+} ion

GROUP(IV) ELEMENTS

GROUP(VII) ELEMENTS

These are elements in the P block of the periodic table, they include

- Fluorine, F_2
- Chlorine, Cl_2
- Bromine, Br_2
- Iodine, I_2

They are all electronegative non-metals and electronegativity reduces down the group.

The electronic configuration of fluorine and chlorine are given below;

^{9}F, E.C= $1S^22S^22P^5$

^{17}Cl, E.C = $1S^22S^22P^63S^23P^5$

From the above, it can be concluded that the elements in group(VII) have a general outermost electronic configuration of **nS^2nP^5.**

They all form ions with a single negative charge, i.e. **X^-** **(**X= F, Cl, Br, I**)**

They all exist as simple diatomic molecules of formulae **X_2**, this is because each atom forms one covalent bond.

The molecules are held by weak Van der Waal's forces of attraction whose strength and magnitude increases with increase in molecular weight due to increased polarization.

F_2 *is a yellow gas*

Cl_2 *is a greenish-yellow gas*

Br_2 *is a red liquid*

I_2 *is a black solid*

Moving down the group, the physical states change from gas through liquid to solid, this is because the strength and magnitude of Van der Waal's forces of attraction increase down the group leading to increase in boiling and melting points.

Question 1

Explain why chlorine is a gas while iodine is a solid at room temperature.

Trends in the group

a) Electronegativity

Trend

Electronegativity decreases down the group.

Explanation

Down the group, nuclear charge increases due to addition of protons to the nucleus from one element to the next.

Similarly, screening effect increases due to addition of a full inner energy level of electrons.

The increase in screening effect outweighs the increase in nuclear charge, therefore the effective nuclear attraction for incoming electrons decreases hence the decrease in electronegativity.

b) Electron affinity

Electron affinity is the energy(enthalpy) change which occurs when an electron is added to a gaseous atom to form a mononegatively or uninegatively charged gaseous ion.

Equation

$$X(g) + e \longrightarrow X^{-}(g) + \text{Energy}$$

OR

It is the energy change which occurs when one mole of electrons is added to one mole of gaseous atoms to form one mole of uninegatively or mononegatively charged gaseous ions.

Equation

$$X(g) + e \longrightarrow X\text{-}(g) + \text{Energy}$$

The table below shows different electron affinities for group(VII) elements

Element	Electron affinity ($KJMol^{-1}$)
F	-328
Cl	-349
Br	-325
I	-295

Table G7.0, electron affinity of group(VII) elements

Trend

Generally, electron affinity decreases down the group, however, the electron affinity of fluorine is abnormally lower than expected.

Explanation

Down the group, nuclear charge increases due to addition of protons to the nucleus from one element to the next.

Similarly, screening effect increases due to addition of a full inner energy level of electrons.

The increase in screening effect outweighs the increase in nuclear charge; therefore the effective nuclear attraction for incoming electrons decreases thus a decrease in electron affinity.

Fluorine is a small atom with a high electron density in the outermost energy level so these electrons tend to repel the incoming electrons(reduce nuclear attraction for incoming electrons) leading to very low energy given out thus low electron affinity.

Question

Explain why the electron affinity of fluorine is lower than that of chlorine.

c) Bond dissociation energy (BDE)

This is the energy given out when one mole of a covalent bond of a gaseous compound is broken to free gaseous atoms.

The table below shows the bond dissociation energies for group(VII) elements.

Element	**Bond dissociation energy (KJMol^{-1})**
F	**+158**
Cl	**+243**
Br	**+193**
I	**+151**

Table G7.1, bond dissociation energy of group(VII) elements

Trend

Generally, the halogen-halogen bond dissociation energy decreases down the group, although the F-F bond dissociation energy is lower than expected.

Explanation

Down the group, nuclear charge increases due to addition of protons to the nucleus from one element to the next.

Similarly, screening effect increases due to addition of a full inner energy level of electrons.

The increase in screening effect outweighs the increase in nuclear charge; therefore the effective nuclear attraction for incoming electrons decreases; therefore the atomic radius increases and hence the halogen-halogen covalent bonds become longer and weaker. Also the overlap of atomic orbitals increases down the group, consequently; bond dissociation energy reduces.

For fluorine, the F-F bond dissociation energy is lower because of its small atomic radius so when the two fluorine atoms are bonded together, the non-bonding electrons of each atom repel each atom. Also the nuclei of the two atoms repel each other since they are too close, thus the bond dissociation energy is lower than expected.

Question

Use the following thermochemical data to determine the lattice energy of copper(II) chloride.

Enthalpy of formation of copper(II) chloride = -220KJMol^{-1}

Enthalpy of sublimation of copper = + 338.3 KJMol^{-1}

First ionization energy of copper = + 745 KJMol^{-1}

Second ionization energy of copper = +1958 KJMol^{-1}

Electron affinity of chlorine = -364 KJMol^{-1}

BDE of chlorine = +121 KJMol^{-1}

d) Oxidizing power

It is defined as the ability to accept electrons.

It is measured in terms of electrode potentials, the more positive(less negative) the electrode potential, the greater the oxidizing power and the more negative(less positive) it is, the greater the reducing power.

The table below shows the electrode potentials for group(VII) elements.

System	**Electrode potential (V)**
F_2(g)/F^-(aq)	**+3.07**
Cl_2(g)/Cl^-(aq)	**+1.36**
Br_2(g)/Br^-(aq)	**+1.06**
I_2(g)/I^-(aq)	**+0.54**

Table G7.2, electrode potential for group(VII) elements

Standard electrode potentials are dependent on the following factors;

- Heat of atomization
- Electron affinity
- Hydration energy

Trend

Oxidizing power decreases (becomes less positive) down the group

Explanation

Down the group, heat of atomization, electron affinity and hydration energy decrease, however, electron affinity and hydration energy decrease much more rapidly than heat of atomization hence electrode potentials become less positive.

It follows that therefore a halogen of lower atomic number can oxidise the ions of another halogen with a higher atomic number.